

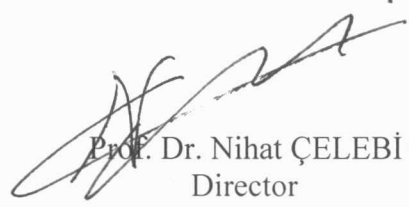
MICELLIZATION THERMODYNAMICS OF SOME AMPHIPHILIC
ENANTIOMERS AND THEIR RACEMIC MIXTURES

by
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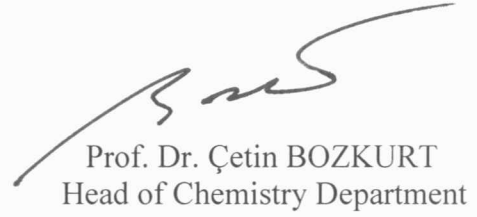
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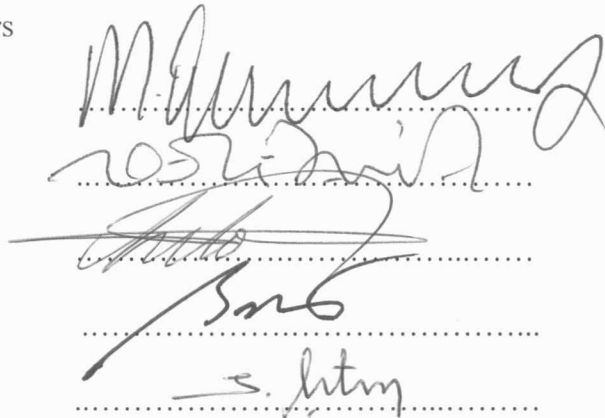
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ABSTRACT

MICELLIZATION THERMODYNAMICS OF SOME AMPHIPHILIC ENANTIOMERS AND THEIR RACEMIC MIXTURES

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This thesis deals with the micellization process of the aqueous solutions of amphiphilic enantiomers (AEs) and their racemates as hydrogenated and partially fluorinated esters of alanine and serine, which are L/DL-alaninehydrochloride dodecylester (L/DL-ADDE), L/DL-serinehydrochloride dodecylester (L/DL-SDDE), L/DL-alaninehydrochloride *1H,1H,2H,2H*-perfluorooctylester (L/DL-APFOE) and L/DL-serine hydrochloride *1H,1H,2H,2H*-perfluorooctylester (L/DL-SPFOE). The thermodynamic, surface, volumetric and the structural properties of all these systems in pre-micellar and post-micellar regions have been investigated via electrical conductivity, surface tension, density, dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements.

Krafft temperatures (T_K) and critical micelle concentrations (cmc) of all systems were determined from the electrical conductivity measurements. The cmc

values of partially fluorinated, DL/L-APFOE and DL/L-SPFOE, amphiphiles were found to be markedly higher than those of the hydrogenated ones, DL/L-ADDE and DL/L-SDDE. In addition, remarkable differences in the *cmc* values of the chiral and racemic partially fluorinated amphiphiles were observed where the amphiphiles with serine head groups had larger *cmcs* compared to that of alanine. The obtained standard Gibbs free energy change of micellization (ΔG_{mic}°) showed that the micellization process was energetically favored. The calculated standard enthalpy (ΔH_{mic}°) and entropy (ΔS_{mic}°) changes of micellization showed that micellization process was entropy-controlled at low temperatures and enthalpy-controlled at high temperatures for all systems.

It was observed that the *cmc* values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE obtained from the surface tension measurements were smaller than those of conductivity measurements. For all systems, the *cmc* values of racemic mixtures and L-enantiomers were almost the same within the error limits. It was observed that maximum surface excess concentration (Γ_{max}) values decreased and minimum area per head group of the molecule at the air-water interface (A_{min}) values increased with the increase in the temperature. However, there was no significant difference in the Γ_{max} and A_{min} values of enantiomeric and racemic forms of the esters. It was observed that the partially fluorinated esters reduced the surface tension more than hydrogenated esters. Furthermore, the standard Gibbs free energy change of adsorption (ΔG_{ad}°) indicated that the adsorption of our systems at the air/water interface was spontaneous. Besides, it was found that the standard enthalpy change of adsorption (ΔH_{ad}°) was positive for hydrogenated dodecyl ester while it was

negative for partially fluorinated octyl esters. The calculated standard entropy change of adsorption (ΔS_{ad}°) was found to be more positive than the ΔS_{mic}° for all of the systems.

From the density measurements, it was observed that both partial specific volumes of monomer ($\tilde{v}_m$) and micelles ($\tilde{v}_{mic}$), apparent molal volume of monomer at infinite dilution (V_{ϕ}^o) and apparent molal volume of micelle (V_{ϕ}^{mic}) values increased with the temperature. In addition, it was also found that the values of $\tilde{v}_{mic}$ and V_{ϕ}^{mic} were significantly higher than those of $\tilde{v}_m$ and V_{ϕ}^o values for each temperature. Furthermore, variations of volume change upon micellization (ΔV_{ϕ}^{mic}) with temperature exhibited considerably different behavior for the hydrogenated systems as compared to the fluorinated systems.

Finally, from DLS and SEM investigations, it was found that all the hydrodynamic radii (R_h) of the racemic mixtures and the L-enantiomers were almost the same. In addition, we observed that the R_h values of SPFOE and APFOE systems were markedly higher than ADDE and SDDE systems. The SEM images indicated that the micelles of our systems were nearly spherical in shape.

Keywords: Amphiphilic molecules, chiral effect, critical micelle concentration, thermodynamics of micellization and adsorption, electrical conductivity, surface tension, density, DLS.

ÖZET

BAZI AMFİFİLİK ENANSİYOMERLERİN VE RASEMİK KARIŞIMLARININ MİSELLEŞME TERMODİNAMİĞİ

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Bu tez, hidrojenlenmiş ve kısmi florlanmış alanin ve serin esterlerin amfifilik enansiyomerleri ve onların rasemik karışımlarının sulu ortamda miselleşme süreçlerini ele almaktadır. Bu esterler sırasıyla L/DL-alaninhidroklorür dodesilester (L/DL-ADDE), L/DL-serinhidroklorür dodesilester (L/DL-SDDE), L/DL-alaninhidroklorür *1H,1H,2H,2H*-perfloro-oktilester (L/DL-APFOE) ve L/DL-serinhidroklorür *1H,1H,2H,2H*-perfloro-oktilesterdir (L/DL-SPFOE). Bu sistemlerin miselleşme öncesi ve miselleşme sonrası için, termodinamik, yüzeysel, hacimsel ve yapısal özellikleri elektriksel iletkenlik, yüzey gerilimi, yoğunluk, dinamik ışık saçılması (DLS) ve taramalı elektron mikroskopi (SEM) yöntemleri kullanılarak araştırılmıştır.

Tüm sistemler için Krafft sıcaklığı (T_K) ve kritik misel derişimi (cmc) elektriksel iletkenlik ölçümlerinden belirlenmiştir. DL/L-APFOE ve DL/L-SPFOE'in cmc

değerlerinin DL/L-ADDE ve DL/L-SDDE'inkinden önemli derecede büyük olduğu bulunmuştur. Buna ek olarak, kısmi flüorlanmış kiral (L-enansiyomer) ve rasemik amfifilik moleküllerin *cmc* değerleri arasında dikkat çekici farklılıkların ve serin baş grubuna sahip amfifilik moleküllerin *cmc* 'lerinin alanine kıyasla daha büyük olduğu gözlemlendi. Elde edilen standart miselleşme Gibbs serbest enerji değişimleri (ΔG_{mic}^o), tüm sistemler için miselleşmenin tercih edildiğini göstermiştir. Sistemlerin standart miselleşme entalpi (ΔH_{mic}^o) ve entropi (ΔS_{mic}^o) değişimleri miselleşme sürecinin düşük sıcaklıklarda entropi, yüksek sıcaklıklarda ise entalpi kontrollü olarak gerçekleştiğini göstermiştir.

DL/L-ADDE, DL/L-SDDE, DL/L-APFOE ve DL/L-SPFOE sistemleri için yüzey gerilimi ölçümlerinden elde edilen *cmc* değerlerinin iletkenlik ölçümlerinden elde edilen değerlere göre daha düşük olduğu gözlemlenmiştir. Tüm sistemler için, rasemik karışım ve L-enansiyomerlerin *cmc* 'lerinin hata sınırları içinde hemen hemen aynı olduğu bulunmuştur. Sıcaklık artışıyla amfifilik moleküllerin maximum yüzey fazlası derişiminin (Γ_{max}) azaldığı, hava/su ara yüzeyinde molekülün baş grubunun kapladığı yüzey alanın (A_{min}) ise arttığı gözlemlenmiştir. Ayrıca, rasemik karışım ve L-enansiyomerlerin Γ_{max} ve A_{min} değerlerinde belirgin bir fark yoktur. Bununla birlikte, kısmi olarak flüorlanmış olan esterlerin yüzey gerilimini karbonzinciri hidrojenlenmiş esterlere göre daha fazla düşürdüğü bulunmuştur. Tüm bunlara ek olarak, tüm esterler için standart adsorpsiyon Gibbs serbest enerji değişimi (ΔG_{ad}^o) hava/su ara yüzeyinde adsorpsiyonun kendiliğinden olduğunu göstermiştir. Ayrıca, kısmi flüorlu oktil esterler için standart adsorpsiyon entalpi değişimi (ΔH_{ad}^o) negatif

iken hidrojenli dodesil esterlerin ΔH_{ad}^o değerlerinin pozitif olduğu bulunmuştur.

Hesaplanan standart adsorpsiyon entropi değişimlerinin (ΔS_{ad}^o), tüm sistemler için ΔS_{mic}^o değerlerinden daha pozitif olduğu bulunmuştur.

Yoğunluk ölçümlerinden, monomerin ve miselin kısmi özgül hacimlerinin ($\tilde{v}_m$ ve $\tilde{v}_{mic}$), sonsuz seyreltik çözeltide monomerin görünen molal haciminin (V_{ϕ}^o) ve miselin görünen molal haciminin (V_{ϕ}^{mic}) sıcaklıkla arttığı gözlenmiştir. Tüm bunlara ek olarak, her bir sıcaklıkta $\tilde{v}_{mic}$ ve V_{ϕ}^{mic} değerlerinin, $\tilde{v}_m$ ve V_{ϕ}^o değerlerinden önemli ölçüde yüksek olduğu bulunmuştur. Ayrıca, hidrojenli sistemlerin miselleşme kaynaklı hacimsel değişim (ΔV_{ϕ}^{mic}) değerleri florlu sistemler ile karşılaştırıldığında sıcaklığa bağlı olarak farklı bir davranış sergilemektedir.

Son olarak, DLS ve SEM ölçümlerinden misellerin hidrodinamik yarıçaplarının (R_h) rasemik ve L-enansiyomerleri için hemen hemen aynı olduğu bulunmuştur. Buna ek olarak, SPFOE ve APFOE'nin R_h değerlerinin ADDE ve SDDE'kinden önemli derecede yüksek olduğu gözlenmiştir. SEM görüntüleri misellerin yaklaşık olarak küresel şeklinde olduğunu göstermiştir.

Anahtar Kelimeler: Amfifilik moleküller, kiral etkisi, kritik misel derişimi, miselleşme ve adsorpsiyon termodinamiği, elektriksel iletkenlik, yüzey gerilimi, yoğunluk, dinamik ışık saçılması.

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CHAPTER 1

INTRODUCTION

A unique class of chemical compounds that contain both a polar or hydrophilic head group and a non-polar or hydrophobic tail are called amphiphilic molecules. The term, amphiphilic molecule, is synonymous with the terms, surfactants, surface-active agents, tensides, or, in the very old literature, paraffin-chain salts [1,2]. Soaps and detergents are also amphiphilic molecules. In terms of industrial applications and scientific interest, amphiphilic molecules have a great importance in our daily life. In many areas such as foods, pharmaceuticals, personal care and laundry products, petroleum industry, mineral ores, fuel additives and lubricants, paints, coatings and adhesives as well as biological processes amphiphilic molecules perform significant role [1-9]. Such important roles are related to their ability to adsorb at interfaces in an oriented direction and to form self-assembly structures (micelles) in which the hydrophobic tail of the surfactant forms the core of the micelle, while the hydrophilic head is located at the micelle-water interface [5,8]. Since the time of McBain who first found the unusual behavior of the aqueous solution of fatty acid salts [9,10], the micelle formation or micellization of amphiphilic molecules in water has been extensively studied to get information about the solution, surface and structural properties [2,5,11-29].

The narrow concentration range at which monomers start to form micelle is called the critical micelle concentration (*cmc*) [1,2,4,5,6,11,29-38]. The term *cmc* is also called very often critical aggregation concentration, *cac* [24,28,39]. The *cmc* is the most important parameter for amphiphilic molecules because of their industrial usefulness and biological activity as well as other interesting amphiphilic features like solute-solvent and solute-solute interactions [1,4,10,11,26,]. Experimentally, the *cmc* is determined from the break point in the plot of a physical property of the solution as a function of concentration in which a sudden change is observed [1,2,5,11,13,15,16,18,22,24,28-30,32,35,36]. A great variety of methods have been used to determine the *cmc*. The most preferred methods are electrical conductivity, surface tension, dynamic light scattering, density, dye solubilization and fluorescence [2,5,11-16,18-30,33-42].

The micelles are of various types, shapes and sizes related to the molecular structure of the amphiphilic molecules as well as concentration, temperature, pH, electrolyte, [36,38,43-46]. At low concentrations, slightly above the *cmc*, the micelles are considered to be spherical in shape [32]. As the concentration increases, the structure of the micelle changes from spherical to cylindrical- or disc-like to lamellar i.e. ordered lyotropic liquid crystalline phases are formed. Since the smallest unit in these liquid crystals is the micelle, this type of liquid crystals is appropriately called “micellar lyotropic liquid crystals”.

One of the most common micellar lyotropic liquid crystalline (*llc*) phases is the micellar nematic. In general, micellar nematic (*N*) phases consist of cylindrical- or

disc-like micelles and have orientational order but no positional order. They are recognized easily by their microscopic textures, threaded or schlieren textures, under a polarizing light microscope [47-49]. However, micellar chiral nematic (N^*) phases are different from the N phases e.g. the micelles in these systems are arranged to form a helical superstructure, which manifests itself as fingerprint texture. A chiral nematic phase can be directly obtained either by an amphiphilic enantiomer (AE) [50-52] or addition of a suitable chiral dopant to a nematic phase [53-55]. The most important parameter for a chiral amphiphile or chiral dopant in the N^* phases is the helical twisting power (htp), which is a quantitative measure for the phase chirality.

It is known that the AEs form chiral nematic phases, whereas their racemates form nematic phases. In our recent investigation [56], the novel AEs as esters of alanine and serine with a partially fluorinated octyl chain, L-alaninehydrochloride 1H,1H,2H,2H-perfluorooctylester (L-APFOE) and L-serinehydrochloride 1H,1H,2H,2H-perfluorooctylester (L-SPFOE), formed intrinsic N^* phases with water only. They exhibited high htp values which were compared with their hydrogenated counterparts, L-alaninehydrochloride dodecylester (L-ADDE) and L-serinehydrochloride dodecylester (L-SDDE), that possess dodecyl hydrocarbon chain with the same head groups; for example, the htp of L-APFOE is $157.8 \mu\text{m}^{-1}$ whereas that of the L-ADDE is $4.0 \mu\text{m}^{-1}$.

This htp result has motivated us to trace the influence of the chirality in the isotropic micellar solutions. So, the aim of this thesis is (i) to determine the cmc s of

the amphiphilic enantiomers and their racemates, (ii) to compare the *cmcs* of the partially fluorinated amphiphiles with their hydrogenated counterparts, and (iii) to study the structural properties above the *cmcs* of these amphiphilic solutions. The point (i) is controversial in the literature [24], then small differences between the *cmc* values of the enantiomers and their racemates were regarded as important by some authors but other authors consider these differences to be within the experimental error [13,24,57-60].

For the purpose of this thesis the racemic/enantiomeric pairs, DL-ADDE/L-ADDE, DL-SDDE/L-SDDE, DL-APFOE/L-APFOE and DL-SPFOE/L-SPFOE, were chosen. The *cmcs* of these amphiphilic molecules were determined by electrical conductivity, surface tension and density measurements. The hydrodynamic radii and the shape of the micelles above the *cmc* were determined by dynamic light scattering (DLS) and scanning electron microscopy (SEM).

CHAPTER 2

THEORETICAL BACKGROUND

The main goal of this chapter is to give a brief description about amphiphilic molecules and their aqueous solutions, i.e. adsorption, micellization and volumetric properties.

2.1. General features of amphiphilic molecules

Soaps, detergents, lipids and proteins are amphiphilic molecules. These types of molecules contain two parts with different properties, a polar or hydrophilic (water-loving) head and a non-polar or hydrophobic (water-hating) tail. They can be found in a wide range of chemical structures. The hydrophobic tail of amphiphiles can be a flexible hydrocarbon chain or a stiff fluorocarbon chain while the hydrophilic head can be ionic or uncharged. Moreover, one or two tails can bind to one hydrophilic head, and these tails can be branched. In general, one common way to classify the amphiphiles is to look at the nature of hydrophilic head group, whether it is anionic, cationic, nonionic or zwitterionic (amphoteric), Figure 2.1.

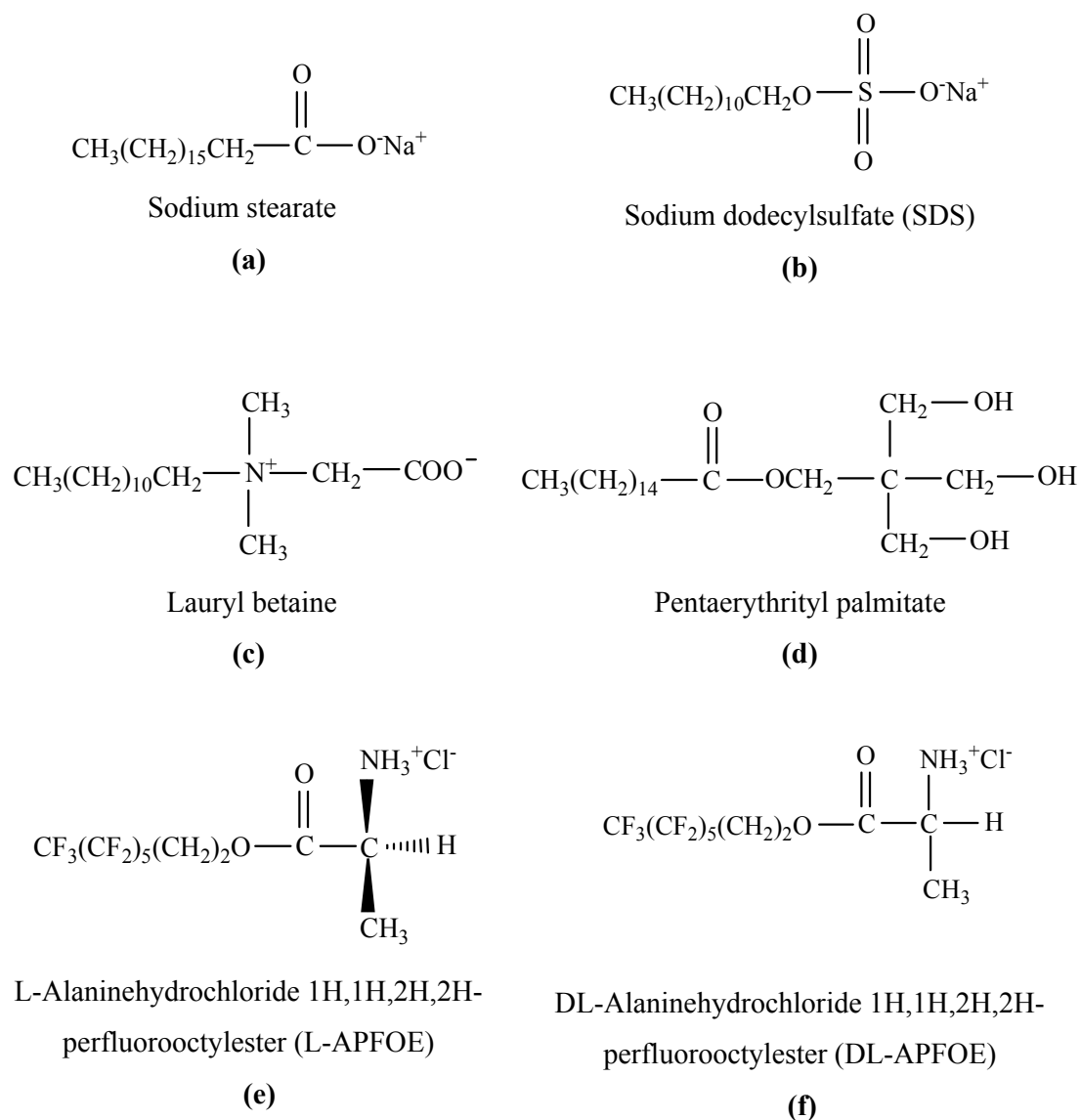


Figure 2.1 Examples for amphiphilic molecules. **(a)** Anionic soap, **(b)** anionic detergent, **(c)** zwitterionic, **(d)** nonionic, **(e)** cationic chiral and **(f)** cationic racemic amphiphilic molecules.

2.2. Micellization of amphiphilic molecules in aqueous solutions

When amphiphilic molecules are dissolved in water, hydrophobic parts distort the hydrogen-bonded structure of water molecules and increase the free energy of

the system. Therefore, amphiphilic molecules adsorb at the air/water interface with their hydrophobic parts oriented toward the air to avoid contact with the water molecules while their hydrophilic groups are in the water and so free energy of the system is minimized. As a consequence of this adsorption, a decrease in the surface tension of water is observed. If the concentration of amphiphilic molecules is increased gradually, the surface concentration reaches a maximum level and there are no more a vacant area for the monomers, single amphiphilic molecules, i.e. the surface of water is covered completely. This result in aggregate formation of the amphiphilic molecules into structures called micelles, where the hydrophobic tails of the molecules are protected from contact with water in order to reduce the free energy of the system. Typically, aqueous solutions of amphiphilic molecules have a dynamic equilibrium between the monomers, which adsorbed at the air/water interface and in the water, and micelles at a given temperature, pressure and concentration, Figure 2.2.

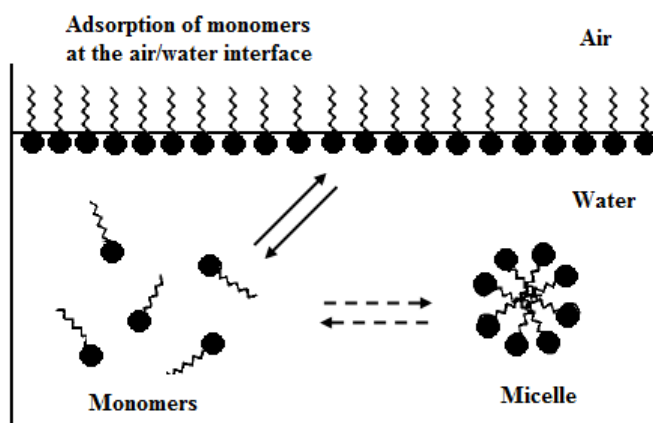


Figure 2.2 Schematic representation of the amphiphilic molecules adsorbed at the air/water interface and in the water, and micelle [2,11].

Even though the kinetic energy of the molecules and repulsive forces (or steric effects) between the head groups oppose the micelle formation, van der Waals and hydrophobic forces override them. Thus, the driving force for micelle formation or micellization, which is an entropically-driven process, arises from the hydrophobic effect.

The narrow concentration range at which monomers start to form micelle is called the critical micelle concentration (*cmc*) [1,2,4,5,6,11,29-38]. The *cmc* is a characteristic of the particular amphiphiles and can be determined from the break point in the plot of a physical property of the solution as a function of concentration [2,5,11,16,18,28,29,32,36]. Since the most of the physical property of the amphiphilic solutions show sudden change at *cmc* as it is illustrated in Figure 2.3, a large number of methods such as electrical conductivity, surface tension, dynamic light scattering, density, dye solubilization and fluorescence have been used to determine the *cmc* [2,5,11-16,18-30,33-42].

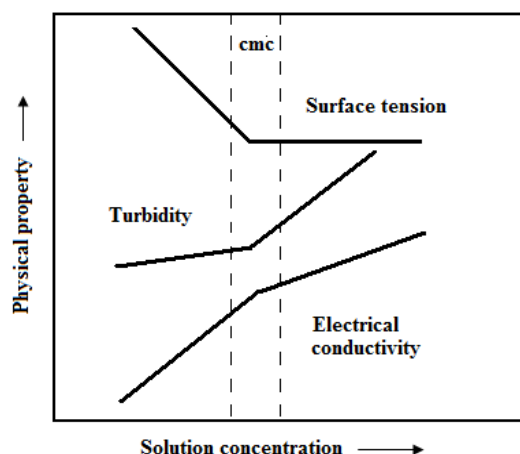


Figure 2.3 Variation in physical properties of amphiphilic solutions below and above the *cmc*.

The concept, Krafft temperature (T_K), where the solubility of amphiphiles rises sharply, is important in studying ionic amphiphiles in aqueous solution [2,11,44,61-65]. At temperatures below the T_K , solubility of monomers is relatively low, i.e. insoluble; however, at the T_K their solubility is equal to the *cmc* and above this temperature, the total solubility increases markedly because of the formation of micelles. Since all self-assembled structures are concentration-dependent, there can be no aggregation if the temperature is too low. Generally, the T_K depends upon the hydrophobic chain length of the amphiphiles as well as the type and valence of counter-ions. The T_K of ionic amphiphiles is generally determined from the abrupt change in a graph of electrical conductivity or solubility against the temperature [2,11,27,44,62-66].

The value of the *cmc*, in aqueous medium, depends on a number of parameters. Among these are structure of amphiphilic molecules, presence of added electrolyte and temperature [2,5,11,32]. In general, the *cmc* decreases as the number of carbon atoms in the hydrophobic tail increases. Perfluorinated amphiphiles have lower *cmc* than the hydrogenated ones. Interestingly, partial fluorination may increase the *cmc* which is the result of unfavorable interactions between the hydrocarbon and fluorocarbon groups. From the point of hydrophilic head group, the *cmc* of ionic amphiphiles is much higher than nonionic's containing equivalent hydrophobic tail. The effect of added electrolyte on the *cmc* is very pronounced for anionic and cationic than for zwitterionic and nonionic amphiphiles. For ionic amphiphiles, the reduction in the *cmc* is due to the decrease in electrical repulsion between the ionic head groups in the micelle. The effect of temperature on the *cmc* is rather complex

for ionic amphiphiles. The *cmc* of most ionic surfactants initially decreases, and then increases as the temperature increases [26,33,36,37,61,67-77]. This phenomenon is related to the hydration of both the hydrophilic head and the hydrophobic tail. The hydration of the hydrophilic group, which favors micellization, decreases as the temperature increases. Furthermore, an increase in temperature also causes distortion of the structured water surrounding the hydrophobic group, which opposes micellization.

In micellization process, there is a dynamic exchange of the monomers in and out of the micelles. However, the number of monomers incorporated in a micelle is usually relatively constant. This number is called average aggregation number (N_{agg}) of the micelle, and there are generally two main factors, hydrophobic effect and repulsive forces between the head groups, that act on it. As mentioned before, the aggregation of amphiphilic molecules in water is primarily due to the hydrophobic effect that drives the hydrophobic tails out of contact with water. Therefore, in order to minimize the hydrophobic tail-water interaction a minimum number of monomers have to associate with each other. On the other hand, the existence of the repulsive forces between the head groups, which oppose the micelle formation, keep the micelles from growing in size to large aggregates and limit the number of monomers in the micelle. In general, at low surfactant concentration, N_{agg} varies from 10 to 100 for the most ionic micelles. The N_{agg} can be determined from the small-angle neutron scattering (SANS) [44], static light scattering (SLS) [19] and fluorescence [20] measurements.

In order to quantify the micelle shape and thus to predict the structure which will be formed by a given amphiphilic molecule, a dimensionless parameter, packing parameter or shape factor, has been proposed by Israelachvili et al. [78,79]. The packing parameter (P) is a measure of the tendency of an amphiphilic molecule to form aggregates of different shape. Generally, it depends strongly on the structure of the amphiphilic molecule. The volume occupied by the hydrophobic tail in the spherical micelle core (V_h), the maximum extended length of the hydrocarbon chain ($l_{\max}$) and the minimum head group area of the hydrophilic group at the micelle-solution interface ($A_{\min}$) are needed to calculate the $P \left(\frac{V_h}{A_{\min} l_{\max}} \right)$, Figure 2.4.

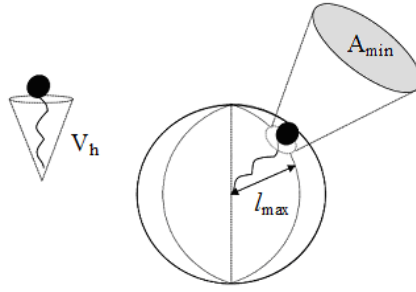


Figure 2.4 Schematic representations of the V_h , $l_{\max}$, and $A_{\min}$ of an amphiphilic molecule.

According to Tanford [8,80] V_h is calculated from

$$V_h = (27.4 + 26.9 n_c) m \quad (\text{\AA}^3) \quad (2.1)$$

where n_c represents the number of carbon atoms embedded in the core of micelle, which is the total number of carbon atoms in the hydrocarbon chain or one $-\text{CH}_2-$ less, and m is the number of hydrocarbon chains. $27.4 \text{ \AA}^3$ and $26.9 \text{ \AA}^3$ are the volumes of the $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively. The $l_{\max}$ [8,80] can be

obtained from the equation,

$$l_{\max} = 1.5 + 1.265 n_c \quad (\text{\AA}) \quad (2.2)$$

where 1.265 Å is one-half the distance of 2.53 Å between alternate carbon atoms of the maximum extended chain, and 1.5 Å is the sum of one-half the van der Waals radius of the terminal –CH₃ group (2.1 Å) and one-half the bond length to the first atom not contained within the hydrophobic core (≈ 0.6 Å). The typical values of P and their corresponding micelle structures in aqueous medium are given as follows [5,11,79,81].

Value of Packing parameter	Structure of the micelle
$0 < \frac{V_h}{A_{\min} l_{\max}} < \frac{1}{3}$	Spherical micelles
$\frac{1}{3} < \frac{V_h}{A_{\min} l_{\max}} < \frac{1}{2}$	Cylindrical micelles
$\frac{1}{2} < \frac{V_h}{A_{\min} l_{\max}} < 1$	Vesicles, disc-like or lamellar
$\frac{V_h}{A_{\min} l_{\max}} > 1$	Inverted (reversed) micelles in non-polar medium

Table 2.1 The table of correlation between the packing parameter (P) and micelle structures.

For spherical micelle with radius R_{mic} , the aggregation number N_{agg} can be expressed as

$$N_{agg} = \frac{4\pi R_{mic}^2}{A_{\min}} = \frac{4\pi R_{mic}^3}{3V_h} \quad (2.3)$$

After simplifying the equation, we obtain the following

$$\frac{V_h}{A_{\min} R_{mic}} = \frac{1}{3} \quad (2.4)$$

Since micelle radius R_{mic} cannot exceed the maximum extended length of the hydrocarbon chain $l_{\max}$, so we find that packing parameter $\frac{V_h}{A_{\min} R_{mic}}$ is less than or equal to $\frac{1}{3}$ for a spherical micelle [78].

In general, for a concentration ranging from the *cmc* to at least ten times the *cmc*, micelles are considered to be spherical [82]. Changes in structure and concentration of amphiphiles, temperature, and ionic strength of solution may cause change in the aggregation number, size and shape of the micelles. So, the changes are observed from spherical to cylindrical- or disc-like to lamellar, i.e. ordered lyotropic liquid crystalline phases may form, depending on the amphiphile structure and physical or chemical conditions, Figure 2.5 [2,6,11,65].

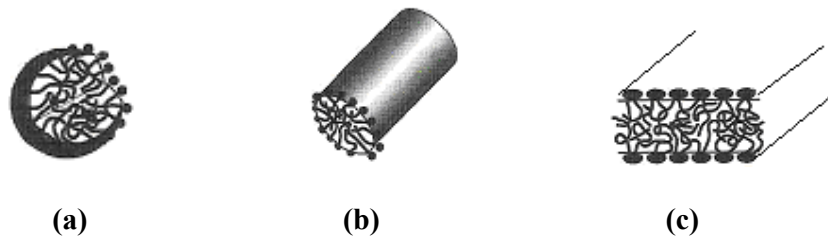


Figure 2.5 Schematic representations of (a) spherical, (b) cylindrical and (c) lamellar micelles.

2.3. Thermodynamic models of micellization

There are two fundamentally different theoretical models that have been widely used in the interpretation of micelle formation. These are mass-action [83] and pseudo-phase [84] separation models, in which classical thermodynamic approaches are used. Neither of these models is perfect, but both models can explain certain aspects of micellization. Although both of them are used by the workers regardless of the type of surfactants in the literature [5,17,36,38,46,66,85], the available experimental evidence seems to be in agreement with the first one [17,31,69,86].

2.3.1 Pseudo-phase separation model

The pseudo-phase separation (PS) model is based on the assumption that the monomers exist in the solution up to the *cmc* and the micellization occurs thereafter as a distinct phase separation from the solution. In the PS model, the *cmc* is regarded as the maximum solubility of the monomers, and there are two well-defined phases, micellar phase and the aqueous phase beyond the *cmc*. Consequently, surfactant addition above the *cmc* only affects the micelle concentration, but not the monomer concentration. The main disadvantage is that the model is applicable only above the *cmc* and therefore no information is available regarding the monomer state. Therefore, the PS model is convenient for long hydrocarbon chain surfactants having a relatively lower *cmc* or a higher aggregation number.

2.3.2 Mass-action model

The mass-action (MA) model assumes that there is dissociation–association equilibrium between monomers and micelles containing a fixed number of ionic surfactant monomers.



where n is the number of surfactant molecules (S) associating to form the micelle (i.e. the aggregation number), m is the number of bound counter-ions (C) and α is the degree of ionization of the surfactant in the micelle, respectively. The MA model includes parameters to account for monomer–monomer and micelle–micelle interactions that may occur. Besides, it takes into account the fraction of counter-ions bound to the micelle and is much better suited for modeling ionic surfactants. The MA model is applicable to short and medium hydrocarbon chain surfactants having a relatively higher *cmc* or lower aggregation number.

2.4. Thermodynamics of micellization

For a given surfactant, information on the thermodynamic parameters of micellization, which is the differences between the thermodynamic parameters of surfactant in the monomeric state and in the micellar state in the solution, can be obtained from the temperature dependence of the *cmc* and degree of ionization of the surfactant in the micelle (α). In general, conductivity method has been extensively used for determination of *cmc* and α [5,16,26,27,30,35,37,41,44,77]. A plot of the conductivity (κ) of an ionic surfactant versus its concentration in the aqueous solution is linear, with a break at the *cmc*, above which the slope of the plot

again becomes linear, Figure 2.6. The break in the plot is due to the binding of some of the counter-ions of the ionic surfactant to the micelle.

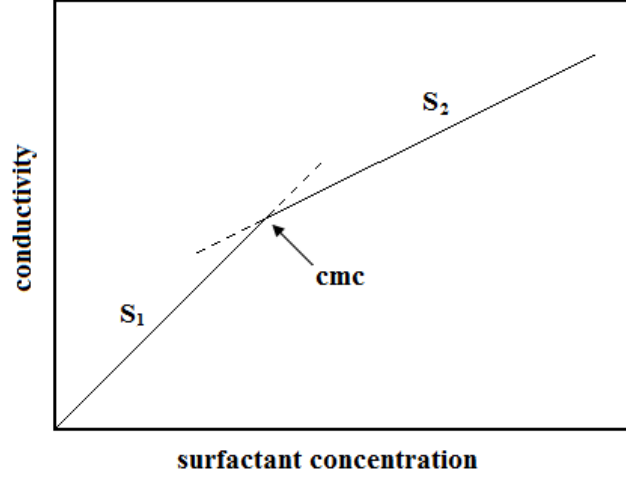


Figure 2.6 Plot of conductivity (κ) versus surfactant concentration, indicating change in slopes before (S_1) and after (S_2) the cmc .

The ratio of slopes before and after the cmc plot gives usually an estimate value of α as proposed by Evans [30],

$$\alpha = \frac{S_2}{S_1} \quad (2.6)$$

The α has the value within $0 \leq \alpha \leq 1$. In addition to this, the degree of binding of the counter-ion to the micelle (β), for an ionic surfactant, is $(1 - \alpha)$.

In accordance with both models, the standard Gibbs free energy of micellization (ΔG_{mic}°) for ionic surfactants can be calculated from the relation:

$$\Delta G_{mic}^\circ = (2 - \alpha)RT \ln X_{cmc} \quad (2.7)$$

where X_{cmc} is the *cmc* value expressed in terms of mole fraction [46,66,87,88].

Since,

$$\Delta G_{mic}^{\circ} = \Delta H_{mic}^{\circ} - T\Delta S_{mic}^{\circ} \quad (2.8)$$

knowledge of the temperature dependence of the *cmc* and α helps in calculating the standard enthalpy of micellization (ΔH_{mic}°) from the Gibbs-Helmholtz relation [66]:

$$\frac{\partial(\Delta G_{mic}^{\circ} / T)}{\partial T} = -\frac{\Delta H_{mic}^{\circ}}{T^2} \quad (2.9)$$

Hence, if the ΔH_{mic}° is assumed to be constant in the temperature range studied, it can be calculated from the equation:

$$\Delta H_{mic}^{\circ} = -(2 - \alpha)RT^2 \left(\frac{\partial \ln X_{cmc}}{\partial T} \right) \quad (2.10)$$

Here, the partial derivative of X_{cmc} depending on temperature is taken because micellization or the *cmc* is affected by various factors including surfactant (hydrophobic volume, chain length, and head group area), temperature, pressure, ionic strength, pH [36,38,43-46]. The term $\left(\frac{\partial \ln X_{cmc}}{\partial T} \right)$ is calculated by fitting the $\ln X_{cmc}$ versus temperature data to a suitable equation. Finally, the corresponding standard entropy change (ΔS_{mic}°) of micellization is determined by the general equation given below [36,38,46,66,85]:

$$\Delta S_{mic}^{\circ} = \frac{(\Delta H_{mic}^{\circ} - \Delta G_{mic}^{\circ})}{T} \quad (2.11)$$

The standard free energy of micellization, ΔG_{mic}° , indicates that micelle formation is spontaneous ($\Delta G_{mic}^{\circ} < 0$) or not ($\Delta G_{mic}^{\circ} > 0$). Additionally, the standard enthalpy of

micellization, ΔH_{mic}° , gives information of the solubility of the surfactant molecule in solvent, i.e. if ΔH_{mic}° has negative value ($\Delta H_{mic}^{\circ} < 0$) the solution gets hotter and if ΔH_{mic}° has positive value ($\Delta H_{mic}^{\circ} > 0$) the solution gets colder. The standard entropy ΔS_{mic}° indicates whether the system becomes more ordered ($\Delta S_{mic}^{\circ} < 0$) or more random ($\Delta S_{mic}^{\circ} > 0$).

2.5. Adsorption of amphiphilic molecules at air/water interface

Amphiphilic molecules adsorb at the air/water interface with their hydrophobic tail away from the water and their hydrophilic groups in a solution. A consequence of that some of the water molecules at the interface will be replaced by amphiphilic molecules (surfactants). Since the interaction forces between water molecules decrease, adsorption of surfactants at the interface causes a reduction in the surface tension of the solution. The adsorption process is commonly characterized by the adsorption isotherm, which gives information on the maximum total amount of surfactant that can be adsorbed on the surface (Γ_{max}) and the affinity of the surfactant towards the surface. The most commonly used adsorption isotherm for dilute surfactant solutions (1×10^{-2} M or less) is the Gibbs equation [5,44,66,89-92],

$$\Gamma_{max} = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_{T,P} \quad (2.12)$$

where γ is the surface tension in N.m^{-1} , C is the concentration of the surfactant solution, T is absolute temperature in Kelvin, R is the ideal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$), and n is the ionic species, respectively. For 1:1 ionic surfactants in the absence of any other solutes, n is equal to 2. Then, the Γ_{max} can be used to

calculate the minimum area per head group of the molecule at the air/water interface (A_{min}) in $\text{\AA}^2$ using the relation,

$$A_{min} = \frac{10^{16}}{N_A \Gamma_{max}} \quad (2.13)$$

where N_A is the Avogadro's number and the Γ_{max} is in mol.cm^{-2} .

For a surfactant solution, the surface tension decreases with increasing concentration until micelles form, i.e., up to the *cmc*. Thereafter, any additional molecule added to the solution does not increase the monomer concentration, since only the surfactant monomers adsorb at the air/water interface, the surface tension remains constant. Figure 2.7 shows a typical γ – $\ln C$ plot for a surfactant solution.

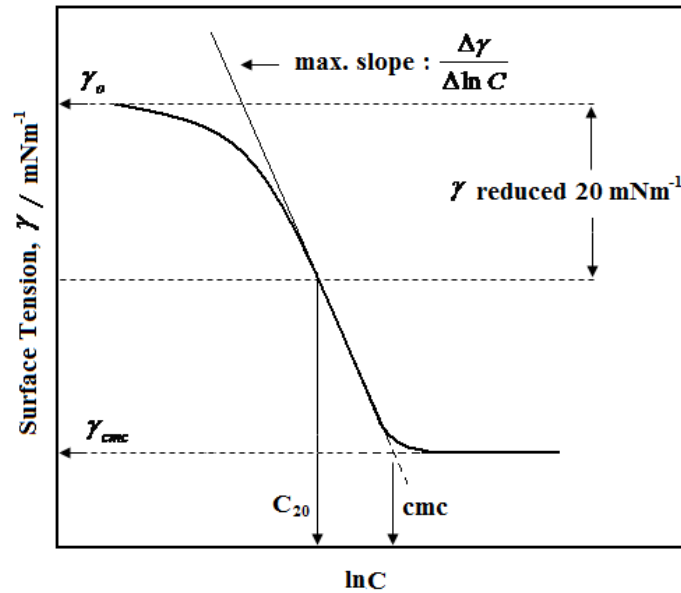


Figure 2.7 A plot of surface tension (γ) versus $\ln C$ for evaluation of the Γ_{max} , A_{min} ,

cmc , γ_{cmc} , π_{cmc} and C_{20} .

The break point in the γ versus $\ln C$ (or $\log C$) curve is indicative of the *cmc*. Besides, the various surface phenomena, the effectiveness of surface tension reduction (γ_{cmc}), surface pressure at *cmc* (π_{cmc}), and the efficiency of surface tension reduction (pC_{20}) of the surfactant systems can be determined from the γ - $\ln C$ plot as it is shown in the Figure 2.7. The effectiveness of the surfactant, which is given by the value of the surface tension at the *cmc*, is generally discussed by the γ_{cmc} . It is obtained directly from the intersection point of the γ at the *cmc*, which is the maximum lowering of surface tension. Then, to find the π_{cmc} and γ_{cmc} value of the solution is subtracted from the surface tension of the solvent, pure water (γ_o), as shown in the equation below [5,15,18,21,28,40,44,64]:

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \quad (2.14)$$

The efficiency of a surfactant, (C_{20}), is the concentration of surfactant required to produce a 20 m.Nm⁻¹ reduction in γ . When the γ has been reduced by 20 mNm⁻¹, the value of the Γ is close to its maximum value, i.e. the Γ_{max} has been reached, and most surfactant molecules are lying slightly tilted to the interface. At this point the surfactant concentration is close to the minimum concentration needed to produce maximum adsorption at the interface. In the literature, the efficiency is generally expressed as pC_{20} ($-\log C_{20} = pC_{20}$) rather than concentration, the C_{20} itself [5,18,40,93].

2.6. Thermodynamics of adsorption

The standard thermodynamic parameters of adsorption, Gibbs free energy (ΔG_{ad}°), enthalpy (ΔH_{ad}°) and entropy (ΔS_{ad}°) can be easily calculated from surface tension data in the vicinity of the *cmc* using the equations 2.15 – 2.18 [5,16,17,26,33,35,37, 41,44,65,76,77],

$$\Delta G_{ad}^\circ = \Delta G_{mic}^\circ - \pi_{cmc} / \Gamma_{\max} \quad (2.15)$$

$$\Delta G_{ad}^\circ = \Delta H_{ad}^\circ - T \Delta S_{ad}^\circ \quad (2.16)$$

$$\frac{d(\Delta G_{ad}^\circ)}{dT} = -\Delta S_{ad}^\circ \quad (2.17)$$

$$\frac{\partial(\Delta G_{ad}^\circ/T)}{\partial T} = -\frac{\Delta H_{ad}^\circ}{T^2} \quad (2.18)$$

if the ΔH_{ad}° and ΔS_{ad}° are constant over the temperature range investigated.

The standard free energy change upon adsorption tells us whether adsorption is spontaneous ($\Delta G_{ad}^\circ < 0$) or not and the magnitude of the driving force. The standard enthalpy change upon adsorption indicates whether bond making ($\Delta H_{ad}^\circ < 0$) or bond breaking ($\Delta H_{ad}^\circ > 0$) predominates in the adsorption process. The standard entropy indicates whether the system becomes more structured ($\Delta S_{ad}^\circ < 0$) or more random ($\Delta S_{ad}^\circ > 0$).

2.7. Volumetric properties of micellar solutions

As mentioned before, aqueous solutions of surfactants exhibit unusual physicochemical properties associated with the ordering of water molecules around the surfactant, as they distort water structure and therefore increase the free energy of the system. The free energy of the solution can be reduced by the aggregation of the surfactants into micelle. Aggregation of the surfactants into micelles is related to a change of the apparent molal and the partial specific volumes. Since plots of density as a function of surfactant concentration display a discontinuity when structural changes occur in the solution, density measurements are powerful methods to determine these volumetric parameters, which are related to this aggregation. These are partial specific volumes of monomer ($\tilde{v}_m$) and micelle ($\tilde{v}_{mic}$), apparent molal volume of monomer (V_ϕ^o), apparent molal volume of micelle (V_ϕ^{mic}), and volume change upon micellization (ΔV_ϕ^{mic}) [38,45,85,87,90,94,95] of the amphiphilic molecules.

The partial specific volume of monomer and micelles are determined from gradients of linear portions of plots of solution density (d) versus concentration below (C_1) and above (C_2) the *cmc* using the following equation [12,38,87,90], Figure 2.8:

$$d = d_o + (1 - \tilde{v}_m d_o)C_1 + (1 - \tilde{v}_{mic} d_o)C_2 \quad (2.19)$$

where d_o is the density of solvent, the $\tilde{v}_m$ and $\tilde{v}_{mic}$ are the partial specific volumes of monomer and micelles in $\text{cm}^3 \cdot \text{g}^{-1}$, and C_1 and C_2 are the concentration of solutions below and above the *cmc* in $\text{g} \cdot \text{cm}^{-3}$, respectively.

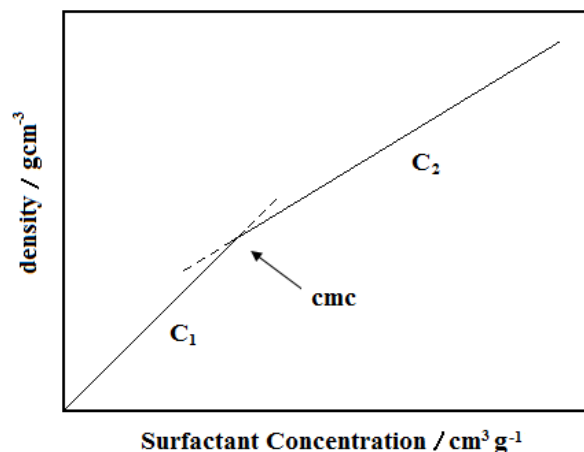


Figure 2.8 A plot of density (d) versus surfactant concentration graph.

In consideration of Equation 2.19 and Figure 2.8, at concentrations below the cmc , the partial specific volume is that of the surfactant monomer and at concentrations above the cmc , virtually all surfactants added to the solution form micelles, and the slope therefore gives the partial specific volume of micelle.

Determination of the apparent molal volume (V_ϕ) of a surfactant monomer in a solution provides important information regarding monomer-monomer and monomer-solvent interactions in the solution. Typically the surfactant volume obtained at infinite dilution is interpreted in terms of the monomer-solvent interactions. As the surfactant concentration is increased, variations in the apparent molal volume reflect the effect of the monomer-monomer interactions. At the cmc an abrupt increase in the apparent molal volume is usually observed. It is associated with the decreased hydrophobic hydration of the monomers and their self-assembly to form a micelle. The magnitude of this transition can be used to assess the packing efficiency within the micelle. The apparent molal volume (V_ϕ) of the

aqueous solution of the surfactant is calculated from the following relation by using density measurements [6,38,45,85,87,90,94,95]:

$$V_{\phi} = \frac{M}{d} - \frac{10^3(d - d_o)}{m d d_o} \quad (2.20)$$

where M is the molecular weight of the surfactant and m is the molality of the solution in mol.kg^{-1} . The data in the pre-micellar region and post-micellar region are extrapolated to the V_{ϕ} to find the apparent molal volume of monomer, V_{ϕ}^o , and the micelle, V_{ϕ}^{mic} , respectively, Figure 2.9.

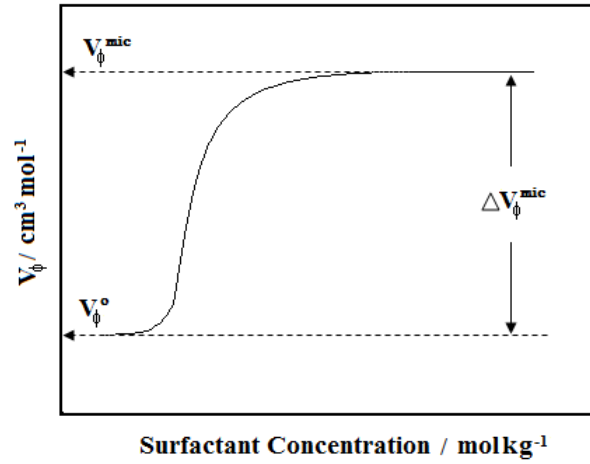


Figure 2.9 A representative plot of apparent molal volume (V_{ϕ}) versus surfactant concentration graph.

The corresponding micellization volume (ΔV_{ϕ}^{mic}), which gives information regarding the monomer packing within the micelle, can be obtained as the difference between the estimated the V_{ϕ}^o and V_{ϕ}^{mic} [96]:

$$\Delta V_{\phi}^{mic} = V_{\phi}^{mic} - V_{\phi}^o \quad (2.21)$$

CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1. Electrical conductivity

The electrical conductance or conductivity of a solution is directly measured by conductivity meter that consists of a conductivity cell and a meter. The conductivity cell consists of two electrodes (platinum plates) rigidly held at a constant distance from each other and are connected by cables to the meter. The meter consists of a Wheatstone bridge circuit as shown in the Figure 3.1.

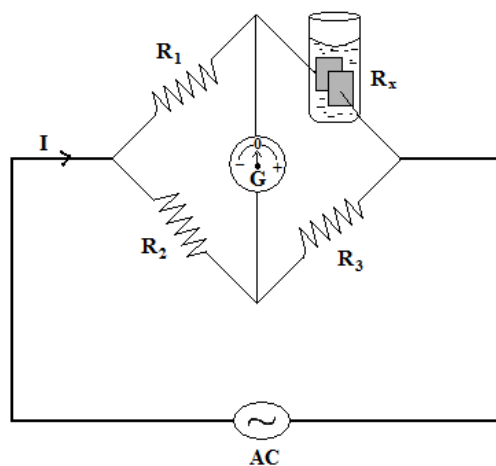


Figure 3.1 Schematic representation of circuit diagram for a Wheatstone bridge.

The source of electric current (I) in the meter applies a potential to the plates and the meter measures the electrical resistance of the solution in terms of

known resistances R_1 , R_2 and R_3 while there is no current in the galvanometer (G). Some conductivity meters read resistance (ohm, Ω) while others read in units of conductance (Siemens, $S = \Omega^{-1}$).

Since the charge on ions in a solution enables the conductance of electrical current, the conductivity of the solution is proportional to its ion concentration. The transition from surfactant monomers to micelles, i.e. at the cmc, involves a dramatic change in the size of the mobile charged species, and this effect will show itself in the resistance of the solution. This phenomenon can be monitored by conductance measurements, where the conductance (L) is defined as reciprocal of the resistance, R . The actual conductance of the solution is obtained by subtracting the conductance of solvent from the measured conductance of the solution:

$$L = L_{\text{measured}} - L_{\text{solvent}} \quad (3.1)$$

The L is related to the conductivity (κ) according to the following equation:

$$\kappa = L K \quad (3.2)$$

where K is the cell constant which is determined by using a reference solution and, for this purpose, KCl solutions are almost used. The unit of conductivity is $S.m^{-1}$.

3.2. Surface tension

The molecules of a liquid attract each other. The interactions of a molecule in the interior of the liquid are balanced by an equal attractive force in all directions. However, at the surface, the molecule is partially surrounded by other molecules, as a consequence of that it is pulled toward molecules in the interior of the liquid, Figure 3.2.

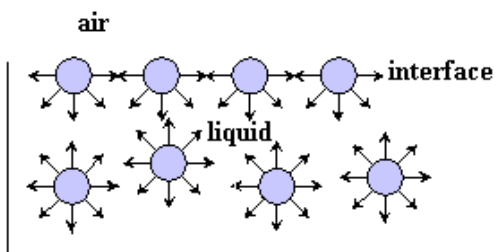


Figure 3.2 Forces acting on a molecule at the air/liquid interface and in the interior of the liquid.

Due to the attraction of the surface molecules into the interior of the liquid, a tension at the surface of the liquid takes place which is called surface tension. So, the molecules at the surface of the liquid have potential energies greater than those of similar molecules in the interior of the liquid. Surface tension or surface free energy per unit area can be understood as the minimum amount of work required to equal this difference in potential energy by bringing sufficient molecules to the surface from the interior and increase the surface area of a liquid by unit area (J.m^{-2}). Hence, surface tension is the force (N) acting at right angles to any line of unit length (m) on the surface, and is expressed with units of (N.m^{-1}).

Surface tension is one of the most commonly measured properties of surfactant solutions. There are many measurements techniques such as capillary rise, Wilhelmy plate, du Noüy ring and drop weight in the study of surfaces of the surfactant solutions. In the du Noüy ring tensiometer that has been used in this thesis, a thin platinum wire ring is firstly held above the interface, secondly it is inserted below the interface and then it is pulled up through the interface, Figures 3.3(a)-(c). The force required per unit length to detach the ring from interface

is measured by a balance as the surface tension (γ).

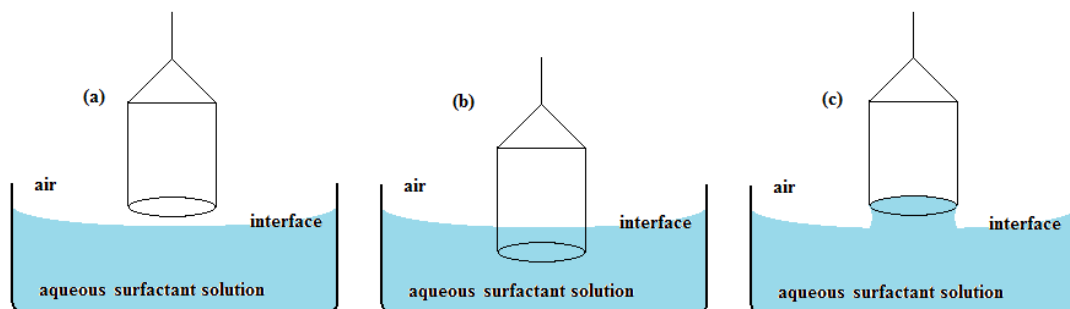


Figure 3.3 Schematic representation of measurement of surface tension by a ring tensiometer. Du Noüy ring is **(a)** above, **(b)** below and **(c)** at the interface of the solution.

3.3. Density

Density is the property of a sample which is given by the ratio of its mass to its volume ($\text{g}\cdot\text{cm}^{-3}$). This property can be determined using several measuring instruments, such as pycnometers and oscillation-type density meters. The latter is the most preferred instrument because of its simplicity and response time, and needed small volume of sample. An oscillation-type density meter consists of an oscillator formed by a U-shaped glass tube filled with the sample, a platinum thermometer provides a high accuracy of temperature control and an electrical component that provide a signal transmission of the period for the processor unit Figure 3.4.

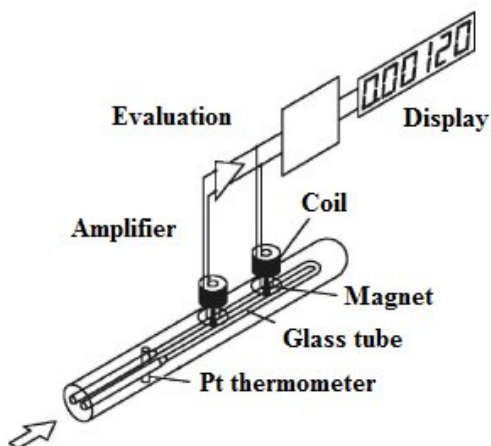


Figure 3.4 Schematic representation of an oscillation-type density meter.

The magnet, which is placed in a coil that has an oscillating frequency in it as in the Figure 3.4, causes the U-tube to oscillate. The frequency of the oscillating current is varied until the resonance frequency of the U-tube is found. The processor unit of density meter converts the oscillation frequency into the measured density using a polynomial calibration equation. Since the volume of the sample inside the tube is constant, the oscillation frequency of the filled U-tube is related to its mass, i.e. the oscillation frequency is therefore a function of the sample density. During the measuring process, the density meter also determines the temperature and applies a viscosity correction for the density calculation.

3.4. Dynamic light scattering (DLS)

When small enough particles are present in a solution the incident light, which is usually polarized monochromatic light, is scattered (i.e. particle diameter $\ll$ wavelength). Light scattering has been used for decades to determine particle sizes.

Dynamic light scattering (DLS), also referred to as quasi-elastic light scattering or photon correlation spectroscopy, is a very important experimental technique for the study of the size of micelles in surfactant solutions [11,19,24,39,65]. In a DLS experiment, the time-dependent fluctuations of the scattered light intensities due to the Brownian motion of the particles are measured by a photon correlator at a fixed scattering angle (usually at 90°), Figure 3.5.

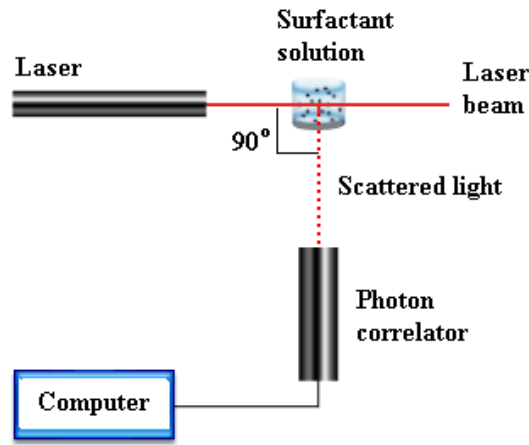


Figure 3.5 Schematic diagram of a conventional 90° DLS instrument.

As particles diffuse due to the Brownian motion, the scattered light undergoes interference effects, and the scattered intensity fluctuates randomly with time. The small particles diffuse or fluctuate faster than the larger ones. These intensity fluctuations allow for the determination of the diffusion coefficient (D), which is closely linked to the particle size by the Stokes-Einstein relationship [11,39,97]:

$$R_h = \frac{k_B T}{6 \pi \eta D} \quad (3.3)$$

where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent at the same temperature, and R_h is the hydrodynamic radius of

the particles (micelles).

3.5. Scanning Electron Microscopy (SEM)

The particle shape and size can be easily monitored by scanning electron microscopy (SEM). The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. The SEM produces a largely magnified image by using electrons instead of light to form an image. Figure 3.6 shows a schematic representation of a scanning electron microscope.

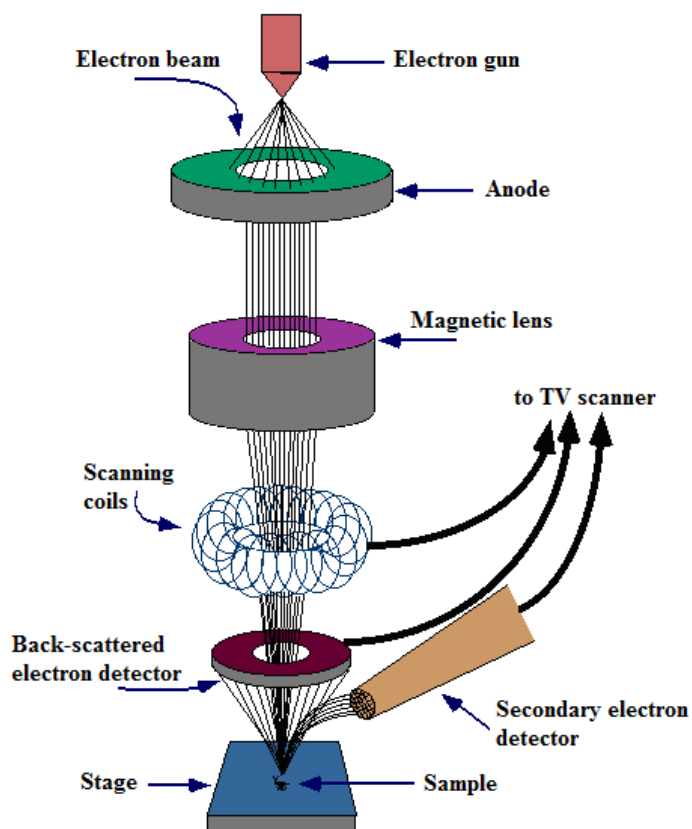


Figure 3.6 Schematic representation of a scanning electron microscope.

The electron gun, which is at the top of the microscope, produces a beam of electrons. Then, this electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and x-rays are scattered from the sample. The scattered x-rays and electrons are collected by detector, which converts them into a signal. Then, the signals are sent to a screen similar to a television screen, thus images are produced.

CHAPTER 4

EXPERIMENTAL

4.1. Materials

The chemicals, DL-alanine, L-alanine, DL-serine, L-serine, n-dodecanol and sodium chloride (NaCl), were purchased from Merck of high purity (>99%). *1H,1H,2H,2H*-perfluoro-1-octanol(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol) was purchased from Alfa Aesar of 97% purity. Sulfuric acid (H₂SO₄), which was used to produce hydrochloric acid (HCl) vapor, was purchased from Riedel-de Haën. Sodium dodecyl sulfate (NaDDS) was purchased from Sigma of 99% purity and recrystallized from ethanol before use. The used common solvents, ethyl acetate, ethanol, diethyl ether were of high purity (99%).

4.2. Synthesis of dodecyl and *1H,1H,2H,2H*-perfluoro octyl esters of alanine and serine

The AEs and their racemates as esters of alanine and serine were synthesized using the n-dodecanol and partially fluorinated *1H,1H,2H,2H*-perfluoro-1-octanol according to the procedure reported by Acımiş et al. [50,56]. Figure 4.1 represents the esterification of the amino acids, alanine and serine, with the n-dodecanol and partially fluorinated *1H,1H,2H,2H*-perfluoro-1-octanol. It was noted that the mole ratio of alanine or serine to alcohol was 1:7 in the reaction.

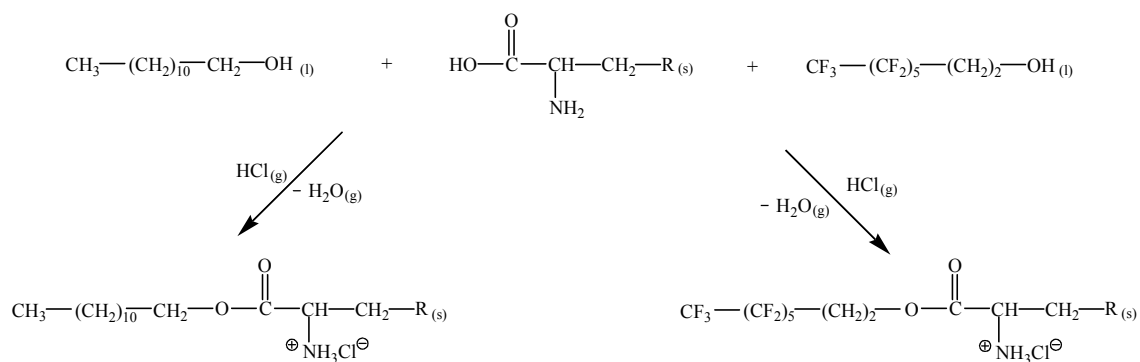


Figure 4.1 The reaction routes for the synthesis of investigated esters. R = H and OH for alanine and serine, respectively.

The structures, abbreviations and nomenclatures of the amphiphilic molecules under study are illustrated in Figure 4.2.

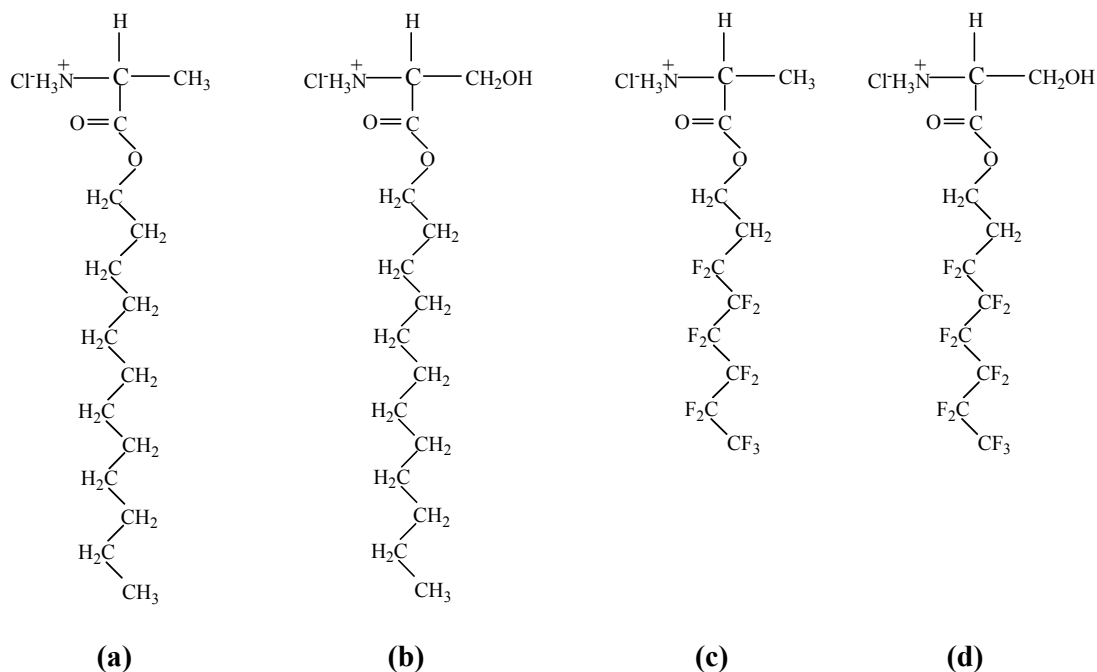


Figure 4.2 The molecular structures of **(a)** L/DL-alaninehydrochloride dodecylester (L/DL-ADDE), **(b)** L/DL-serinehydrochloride dodecylester (L/DL-SDDE), **(c)** L/DL-alaninehydrochloride *1H,1H,2H,2H*-perfluorooctylester (L/DL-APFOE) and **(d)** L/DL-serine hydrochloride *1H,1H,2H,2H*-perfluorooctylester (L/DL-SPFOE).

DL-ADDE, L-ADDE, DL-SDDE, L-SDDE, DL-APFOE and L-APFOE were recrystallized at least 3 times from ethyl acetate. However, DL-SPFOE and L-SPFOE were recrystallized at least 3 times from ether-ethyl alcohol (4:1). The purity of compounds was checked by using elemental analysis and melting point measurements; Table 4.1(a) and (b).

Elemental Analysis						
	Calculated			Found		
	C%	H%	N%	C%	H%	N%
DL-ADDE	61.31	10.98	4.77	61.15	10.92	4.80
L-ADDE				61.29	10.98	4.77
DL-SDDE	58.14	10.41	4.52	57.30	10.10	4.63
L-SDDE				57.17	10.25	4.58
DL-APFOE	28.01	2.35	2.97	28.37	2.55	2.99
L-APFOE				28.59	2.63	3.02
DL-SPFOE	27.09	2.27	2.87	27.20	2.49	3.11
L-SPFOE				27.51	2.69	2.91

(a)

Melting point / °C				
	ADDE	SDDE	APFOE	SPFOE
DL-	77	70	77	141 dec.
L-	105	91	84	128 dec.

(b)

Table 4.1 The values of **(a)** elemental analysis and **(b)** melting point of the investigated amphiphilic molecules.

4.3. Preparation of aqueous solutions of dodecyl and 1H,1H,2H,2H-perfluorooctyl esters of alanine and serine

The aqueous isotropic solutions were prepared by weighing appropriate amounts of esters and water. The mixtures were homogenized by using centrifuge or magnetic stirrer. Each solution was left at room temperature at least 2 h before conductivity, surface tension and density measurements (24 h before DLS measurements). The water used for the preparation of solutions was distilled over a fractionating column of approximately 125 cm height. The conductance of distilled water was $\leq 2.0 \pm 0.5$ μS at 25 °C, indicating a high purity.

4.4. Methods

4.4.1. Electrical conductivity measurements

All conductivity measurements were carried out with Cyberscan PC 510 digital conductivity meter using a conductivity cell having a cell constant of 1.03 cm^{-1} , which was determined from KCl solutions of known concentrations. This instrument has a sensitivity of 0.01 μS .

The Krafft temperature (T_K) was determined by conductivity method. For this purpose, clear aqueous 1 percent solutions of AEs and their racemates, L/DL-ADDE, L/DL-SDDE, L/DL-APFOE, and L/DL-SPFOE, were prepared at room temperature. DL-ADDE and DL-SPFOE were placed in a refrigerator at c.a. 5 °C, whereas L-ADDE, L/DL-SDDE, L/DL-APFOE and L-SPFOE had to be frozen and then left to melt slowly at about 0 °C at least 24 h until precipitate of the

hydrated surfactants crystals appeared. Thereafter, the temperature of the precipitated solutions was gradually raised using thermostated bath of accuracy of ± 0.1 °C. The conductance of the solutions was measured under constant stirring every 10 min at each temperature. The T_K was taken as the temperature where the conductance versus temperature plot showed an abrupt change in the slope. This temperature was the same as that required to dissolve the hydrated surfactant crystals completely, i.e. the point of complete clarification. The reproducibility in T_K measurements was ± 0.1 °C.

The *cmc* and the thermodynamic parameters of micellization, mentioned in section 2.4, for the surfactants above were determined from conductivity measurements. The conductance of different aqueous surfactant solutions, which were obtained by addition of definite volume of stock solution ($50.00 \text{ mmol.kg}^{-1}$) into the conductivity cell containing known amount of distilled water, were measured in a thermostated bath (± 0.1 °C). The measurements were done at temperature range from 15 °C to 35 °C at 5 °C intervals. Before starting the experiment, the system was equilibrated at each temperature at least 15 min. After each addition, solutions were vigorously stirred and waited for 5 min to reach thermal equilibrium even though it reaches a steady value in 2 min, and then the conductivity was measured. At least two independent runs on each solution were made for the conductivity measurements. In order to determine the real conductance of the surfactant solutions, the conductance of distilled water was subtracted from that of the surfactants solutions. Then, the conductivity (κ) of the surfactant solutions was calculated by the equations (3.1) and (3.2).

4.4.2. Surface tension measurements

Surface tension measurements as a function of concentration of the aqueous surfactants solutions were performed using a du Noüy ring digital tensiometer (KSV Sigma 702, Finland) equipped with a thermostated vessel holder. This instrument is computer controlled so that it possible to make several measurements on the same solution automatically by lowering and rising the vessel that contains the solution. The temperatures, 15 °C, 25 °C and 35 °C, were controlled within ± 0.01 °C by the thermostated bath. The solution placed in the tensiometer was gently stirred by magnetic stirrer and allowed to stand thermal equilibrium at each temperature at least 30 min before starting the experiment. The du Noüy ring was thoroughly cleaned using distilled water, ethanol and acetone, and dried before each measurement. A series of three measurements were made on each solution after the thermal equilibrium was reached. The concentration change was made by adding appropriate volumes of the stock solution (50.00 mmol.kg⁻¹) to the distilled water in the vessel. The surface tension data were averages of at least two independent runs. The tensiometer was calibrated and checked by measuring the surface tension of the distilled water. The precision of the surface tension measurements given by the manufacturer is ± 0.01 m.Nm⁻¹.

4.4.3. Density measurements

The densities of the solutions were carried out by using an Anton Paar DMA 5000 density meter. All solutions were allowed to stand 10 min before each measurement. The measurements were recorded as a function of concentration in

the temperature range of 15 °C - 35 °C at 5 °C intervals. Each density value was determined from the average of at least two independent measurements. The density meter was calibrated using air and water. The precision of the density and temperature measurements is given by the manufacturer to be as $\pm 0.000001 \text{ g.cm}^{-3}$ and $\pm 0.001 \text{ }^{\circ}\text{C}$, respectively.

4.4.4. Dynamic light scattering (DLS) measurements

DLS measurements were performed at $25 \pm 0.2 \text{ }^{\circ}\text{C}$ with scattering angle of 90° using an ALV/CGS-3 compact goniometer system (Malvern, UK). He-Ne laser operating at $\lambda = 632.8 \text{ nm}$ was used as a light source (output power of 22 mW). In order to avoid dust, all solutions were filtered through $0.20 \text{ }\mu\text{m}$ pore size NY filter (Sartorius, Germany) prior to measurements. The measurements were taken in 5-10 min after the solutions were introduced into the DLS optical system to equilibrate them at the temperature bath. The diffusion coefficients (D) were analyzed by the ALV-Fit & Plot Software provided by the manufacturer to obtain R_h .

4.4.5. Scanning Electron Microscopy (SEM) measurements

The structures of surfactant aggregates were observed with scanning electron microscopy (SEM) method. A drop of the solution was placed onto a SEM holder and allowed to dry in air for 1 day at room temperature. After drying the samples were imaged with a JEOL 6390-LV scanning electron microscope at room temperature under an accelerating voltage of 20 kV for x1000 and x2000 magnifications.

CHAPTER 5

RESULTS AND DISCUSSION

5.1. Determination of the Krafft temperatures

Although most of surfactants have a substantial solubility in water, their solubilities can change significantly with temperature, nature of head group and counter-ion, hydrophobic tail length and addition of salt. In general, surfactants display a dramatic temperature-dependent solubility. At low temperature, the solubility of the ionic surfactants is quite limited until the temperature reaches some critical point, i.e. the Krafft Temperature (T_K) [2,11,44,61-65]. The solubility of the surfactants shows a strong increase at T_K due to the micelle formation [84,98]. Below the T_K , the solubility of the surfactant is too low for micellization, i.e. monomers only exist in equilibrium with the hydrated surfactant crystals, and above the T_K , micelles are formed providing much greater surfactant solubility. As a result, T_K is a most important parameter of ionic surfactants. A high value of this parameter makes these surfactants inconvenient for research or applications at room temperature.

In general, the T_K of a given surfactant is determined to choose appropriate temperature range for investigation of its micellar properties. It is usually obtained from the conductivity, solubility, spectroscopy and differential scanning calorimetry

(DSC) measurements [2,5,63,64,99,100]. In this study, the T_K values were obtained by conductivity measurements that have been commonly used method in the literature [2,5,11,27,62-66]. The conductance of the aqueous solutions of amphiphilic enantiomers (AEs) and their racemates as hydrogenated and partially fluorinated esters of alanine and serine, which are L/DL-alaninehydrochloride dodecylester (L/DL-ADDE), L/DL-serinehydrochloride dodecylester (L/DL-SDDE), L/DL-alaninehydrochloride *1H,1H,2H,2H*-perfluoro-octylester (L/DL-APFOE) and L/DL-serine hydrochloride *1H,1H,2H,2H*-perfluoro-octylester (L/DL-SPFOE), were measured as a function of temperature, respectively. The conductivity (κ) of the solutions was calculated from the equations (3.1) and (3.2). The variations of the κ with the temperature ($\kappa - t$ curves) are given in Figure 5.1.

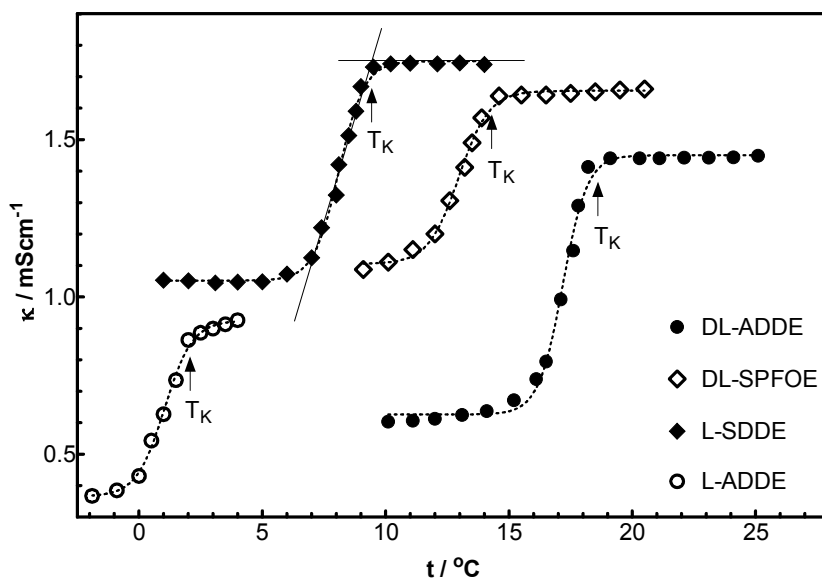


Figure 5.1 Temperature dependence of conductivity (κ) of systems containing 1% wt/wt of DL-ADDE, DL-SPFOE, L-SDDE and L-ADDE. The arrows indicate the T_K and the complete dissolution of the surfactants. The dotted lines are only drawn to guide the eye. The solid line is used to determine the T_K .

The κ - t curves show that the κ increases rapidly with raising the temperature due to dissolution of the hydrated surfactant crystal until the T_K is reached. Then, the κ increases very slowly due to the increase in ionic mobility with the temperature.

The values of T_K were determined from the intercept of the two straight lines, Figure 5.1, drawn through the data above and below the T_K . It should be noted that this point usually coincided with the temperature of full clarification of the system. The T_K values of aqueous solutions of DL-ADDE, DL-SPFOE, L-SDDE and L-ADDE could be determined, however, the T_K values of DL-SDDE, DL-APFOE, L-APFOE and L-SPFOE systems could not, because they were below 0 °C, i.e. they gave no precipitate although they kept at 0 °C. Table 5.1 lists the all T_K values determined as described above.

$T_K \pm 0.1 / ^\circ\text{C}$			
DL-ADDE	18.5	DL-APFOE	< 0
L-ADDE	2.1	L-APFOE	< 0
DL-SDDE	< 0	DL-SPFOE	14.3
L-SDDE	9.3	L-SPFOE	< 0

Table 5.1 The T_K values of DL-ADDE, L-ADDE, DL-SDDE, L-SDDE, DL-APFOE, L-APFOE, DL-SPFOE and L-SPFOE.

Since the T_K of a surfactant is related to its solubility, a decrease in the T_K represents an increase in the solubility of the surfactant. According to the obtained results, the T_K is below 0 °C for DL-SDDE, DL-APFOE, L-APFOE and L-SPFOE

that may indicates their high solubility in the water.

If we look at the T_K values in terms of chirality, in ADDE and SPFOE systems, the T_K of the racemic (DL-) forms was higher than that of the enantiomeric (L-) forms, whereas in the SDDE system it was just the contrary. However, for APFOE system the T_K of both the DL-form and the L-form were below 0 °C. Ohta et al. [100] studied chiral effect of N-hexadecanoyl amino acid surfactant with different amino acid residue, L/DL-alanine, L/DL-valine, L/DL-leucine and L/DL-phenylalanine, on the T_K . They found that the T_K of DL-forms of alanine and phenylalanine surfactants were higher than that of the L-forms. On the other hand, an opposite situation was observed for L/DL-valine, L/DL-leucine systems. They explained these results in terms of hetero-chiral (D-L) and homo-chiral (L-L) interactions. In alanine and phenylalanine systems, D-L interactions promoted the molecular packing in the solid state, whereas in valine and leucine systems L-L interactions undertook this task. Furthermore, Sjöbom et al. [101] found identical the T_K values for racemic and R-form of 2-methyl-decanoate. They interpreted this result as molecular packing which was nearly same for both systems. According to our T_K values, we suggest that the hetero-chiral (D-L) interactions in ADDE and SPFOE systems and the homo-chiral (L-L) interactions in SDDE system are dominant. Nevertheless, we can not say clearly what kind of interaction in APFOE system is dominant, and then the T_K values of L- and DL-forms are below zero.

5.2. Determination of the critical micelle concentrations of sodium dodecyl sulfate

Preparatory to our experiments, the critical micelle concentration (cmc) of aqueous solution of sodium dodecyl sulfate (NaDDS) was determined in order to check the accuracy of the used methods, electrical conductivity, surface tension and density. NaDDS is an anionic surfactant, and it has been generally used for this purpose by many authors [102-104]. Figures 5.2(a)-(c) represent the results of electrical conductivity (κ), surface tension (γ) and density (d) measurements of NaDDS at 25°C, respectively.

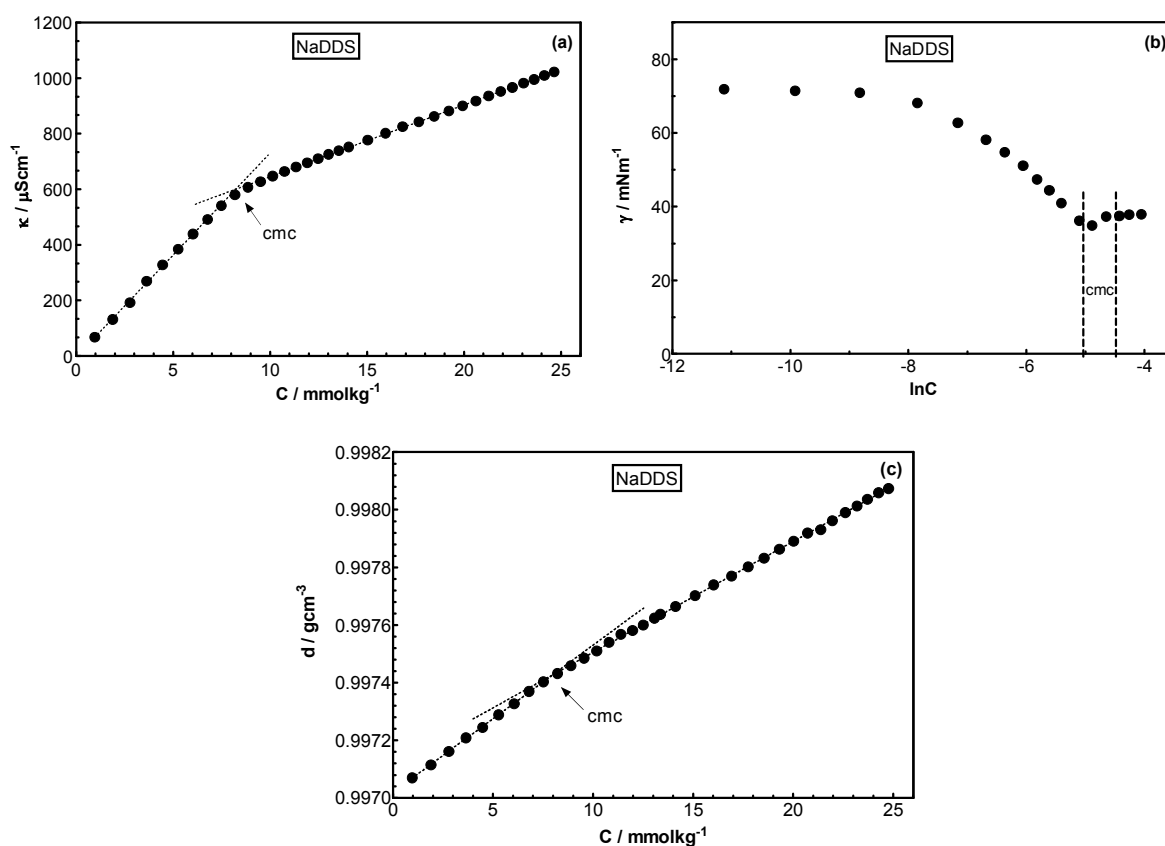


Figure 5.2 (a) Conductivity (b) surface tension and (c) density data of NaDDS at 25 °C. The arrow indicates the cmc . The dotted line is a guide to the eye.

It is generally observed that there are two linear regions with different slopes, as in Figure 5.2(a) and (c), corresponding to the pre-micellar and post-micellar regions, respectively and where the break point is defined as the *cmc*. However, in Figure 5.2(b), a small minimum was observed due to the some impurities. Thus, the *cmc* value was determined by taking the first derivative of the surface tension data in which the maximum peak value corresponded to the *cmc*. It has been found that the obtained the *cmc* values of NaDDS are in good agreement with the literature [103-106], Table 5.2.

<i>cmc</i> / mmol.kg ⁻¹			
Conductivity	Surface tension	Density	
8.059	8.136	8.110	This work
8.3	—	—	Ref [104,105]
8.0	—	—	Ref [103]
—	8.30	—	Ref [106]

Table 5.2 The *cmc* of NaDDS determined by conductivity, surface tension and density at 25 °C.

5.3. Determination of the critical micelle concentrations

In general, the determination of the *cmc* can be made by use of every measurable physical property. In this study, the *cmc* of the DL/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE systems in the water were determined by electrical conductivity, surface tension and density measurements at 15, 20, 25, 30 and 35 °C.

5.3.1. Electrical conductivity measurements

The *cmc* values were evaluated from break points of the plots of the κ versus total surfactant concentration (*C*) for each system at five different temperatures (in the 15 °C – 35 °C temperature range at 5 °C intervals), Figures 5.3(a)-(h) and Table 5.3.

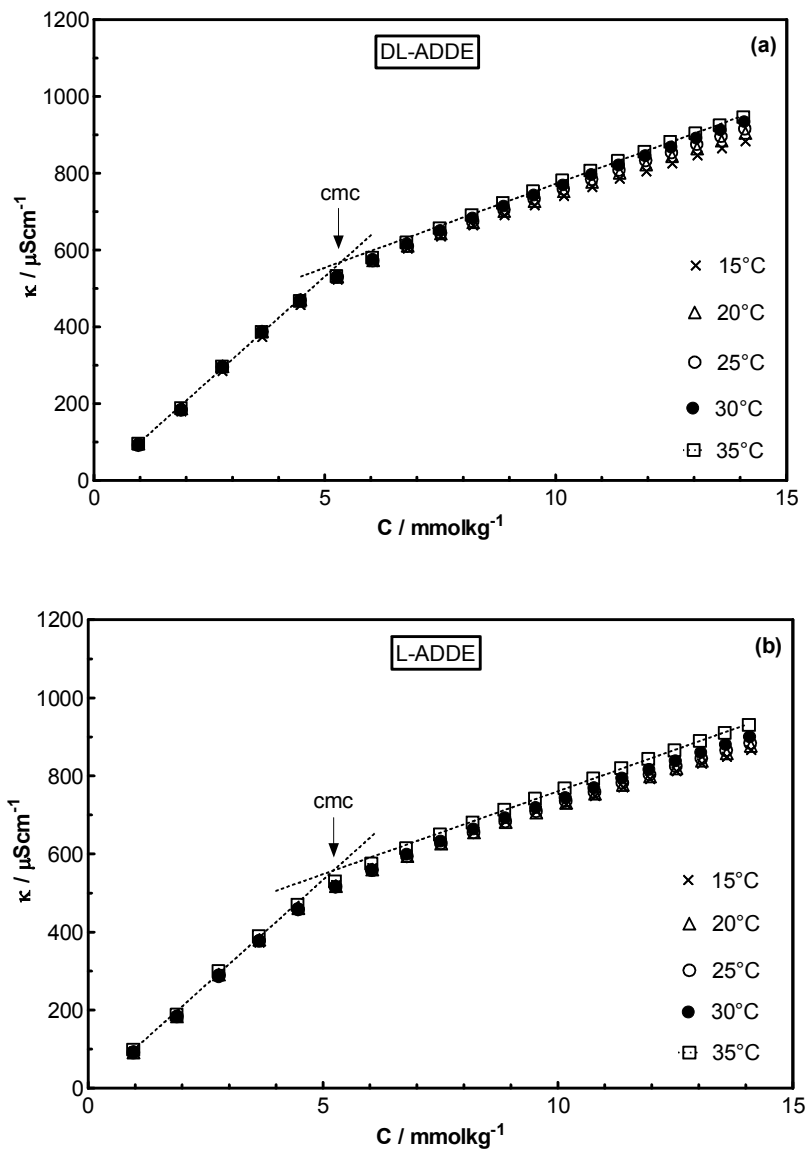


Figure 5.3 Variation of the κ of aqueous solutions with the concentration of (a) DL-ADDE and (b) L-ADDE systems at different temperatures. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

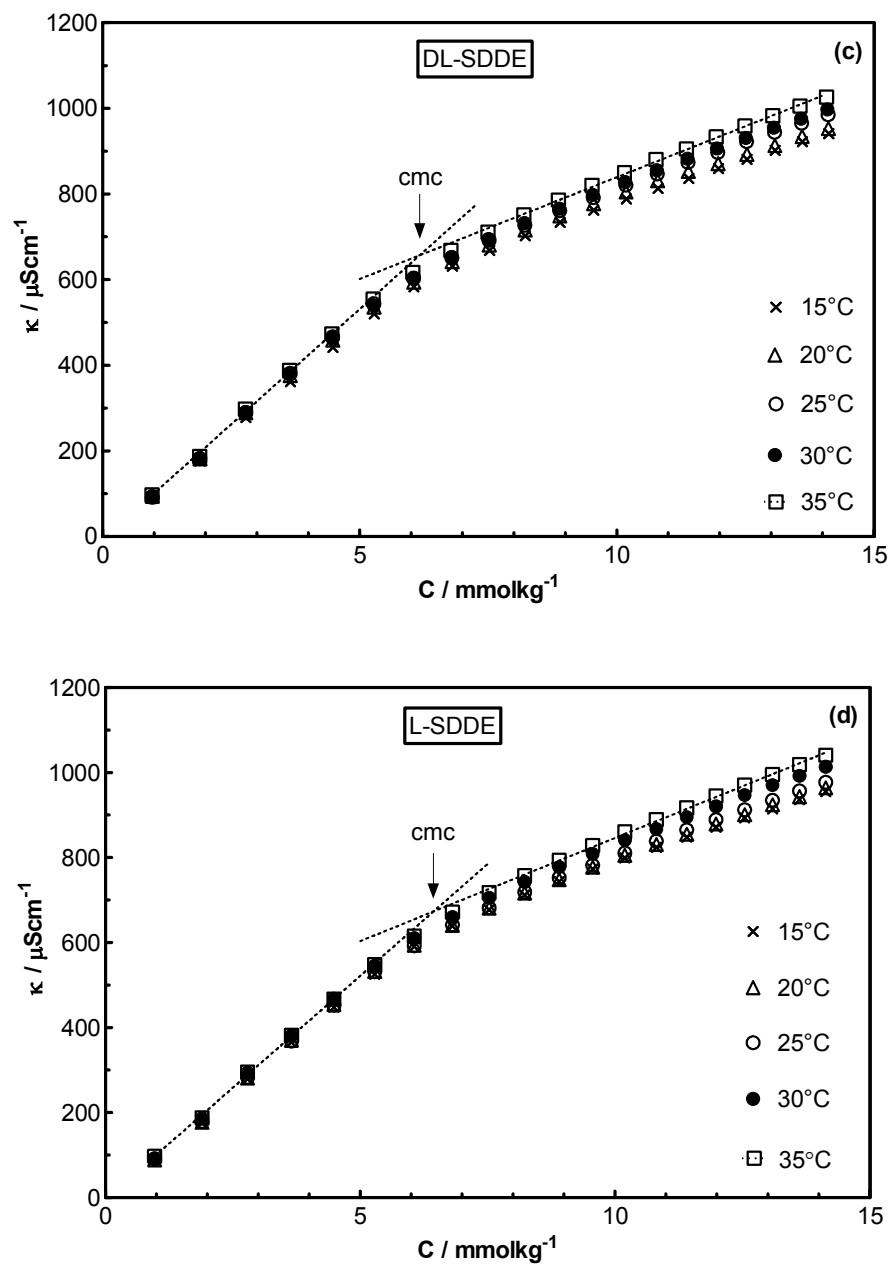


Figure 5.3 Variation of the κ of aqueous solutions with the concentration of (c) DL-SDDE and (d) L-SDDE systems at different temperatures. The arrow indicates the cmc . The dotted line is drawn as a guide to the eye.

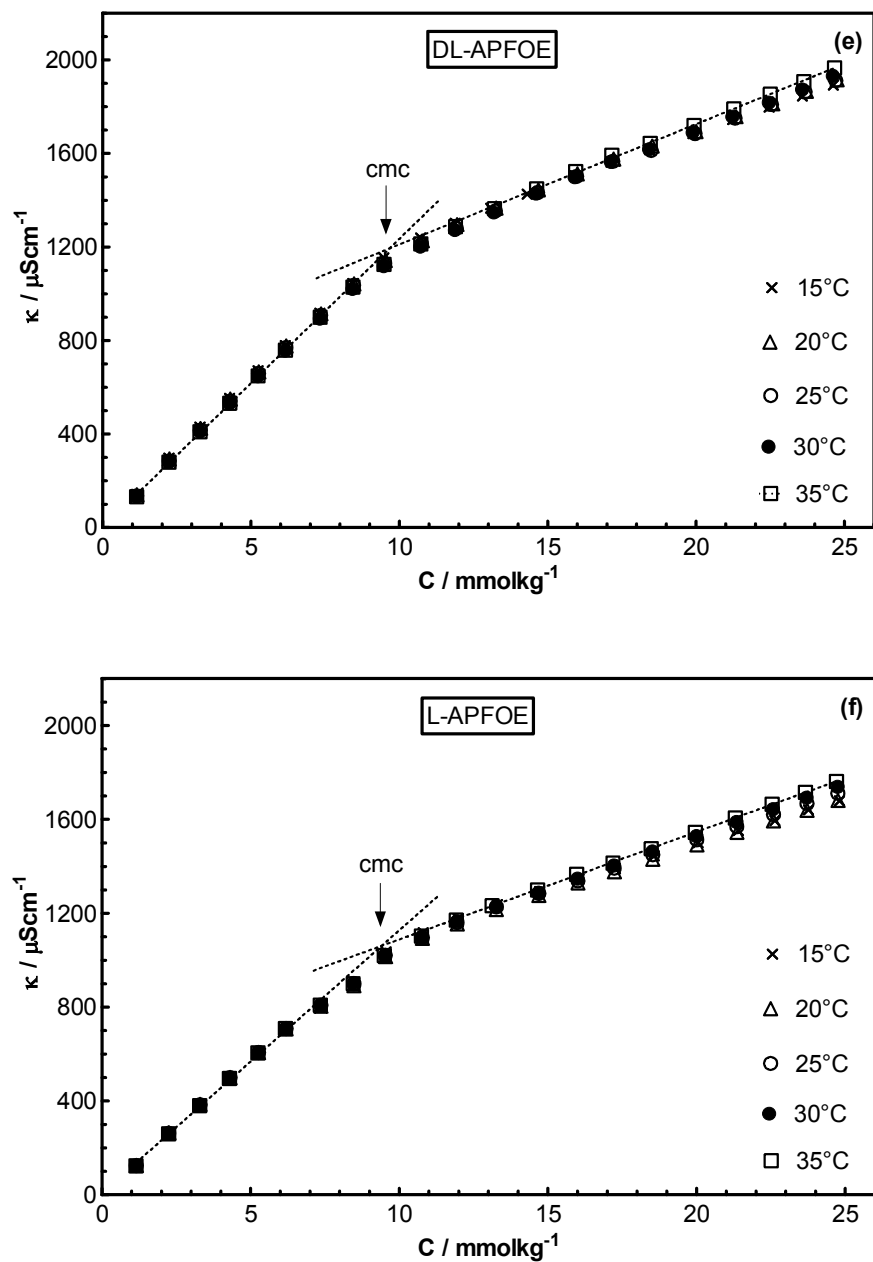


Figure 5.3 Variation of the κ of aqueous solutions with the concentration of (e) DL-APFOE and (f) L-APFOE systems at different temperatures. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

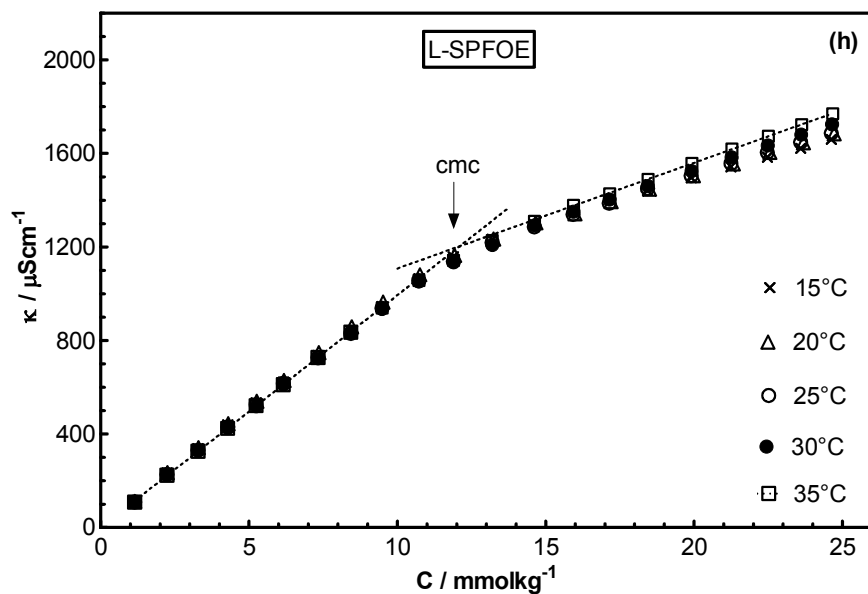
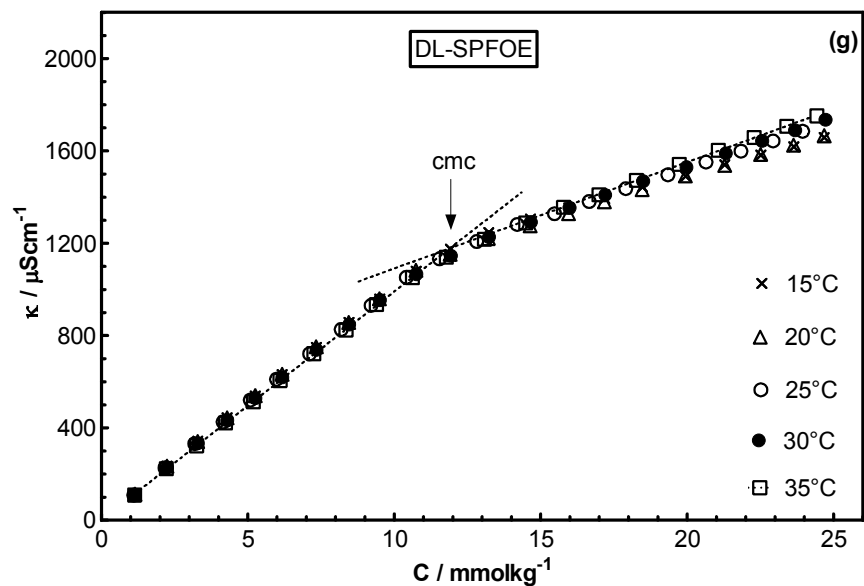


Figure 5.3 Variation of the conductivity of aqueous solutions with the concentration of (g) DL-SPFOE and (h) L-SPFOE at different temperatures. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

t / °C	$cmc \pm 0.05 / \text{mmol.kg}^{-1}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	5.46	5.42	6.38	6.39	9.68	9.42	12.03	12.37
20	5.24	5.17	6.26	6.31	9.56	9.10	11.77	12.11
25	5.20	5.16	6.20	6.29	9.48	9.02	11.68	12.06
30	5.25	5.19	6.23	6.30	9.46	8.94	11.77	12.08
35	5.36	5.27	6.29	6.40	9.46	8.99	11.88	12.18

Table 5.3 The cmc values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE obtained from electrical conductivity measurements at different temperatures. The cmc is given in mmol.kg^{-1} . The average standard deviation in the cmc values was $\pm 0.05 \text{ mmol.kg}^{-1}$.

As seen from Figures 5.3(a)-(h), the conductivity is linearly related to the surfactant concentration, it changes at different rates in the pre-micellar region, below the cmc , and in the post-micellar region, above the cmc . Below the cmc , the conductivity arises from the contributions of the free counter-ion and charged monomers. However, above the cmc , the binding of some of the counter-ions to the micelle causes a reduction in the effective charge on the micelle, and an increase in the size of the micelle. As a result, the ionic mobility of the micelle is lowered compared to monomers, so that a slow increase in the conductivity is observed with respect to that one below the cmc . In order to determine the break points from the graphs, the data points in the pre-micellar and post-micellar regions are fitted to two equations of the form $\kappa = mC + b$, where m and b are fitting parameters. Then, the intersection point of the two straight lines is obtained by solving the equations simultaneously, and taken as the cmc .

The results, Table 5.3, may be discussed along the following lines: (i) effect of chirality, (ii) the effect of the head groups, alanine and serine, and (iii) the effect of the hydrophobic tail, hydrogenated and partially fluorinated hydrocarbon chain.

According to the results that are represented in Table 5.3, the *cmc* values of L-enantiomers for alanine systems, both hydrogenated and partially fluorinated ones, are lower than their racemic mixtures at all temperatures. However, in serine systems, it is just the contrary, i.e. DL-forms have lower *cmc* values than L-isomers. The differences in the *cmc* values of the DL/L-ADDE and DL/L-SDDE system are to be accepted as real even so, we consider the average standard value of $\pm 0.05 \text{ mmol.kg}^{-1}$ for all the *cmc* results. Besides, in the partially fluorinated systems, DL/L-APFOE and DL/L-SPFOE, an analogous behavior to the DL/L-ADDE and DL/L-SDDE systems with respect to the *cmc* values is observed. In these systems there are two important points that need a thorough discussion. The first point is that the *cmc* values of the L-enantiomer, L-APFOE, are strikingly lower than those of the DL-APFOE system at all temperatures whereas the L-SPFOE system shows an interesting opposite behavior. The second point is that the *cmc* values of the DL/L-APFOE and DL/L-SPFOE systems are nearly twice those of the DL/L-ADDE and DL/L-SDDE systems. The first point may be related to the chirality where the *cmc* values for the L-enantiomers (L-ADDE and L-APFOE) are higher than their racemates. In particular, the difference in the *cmc* values of the DL/L-APFOE is enormous, compared to the hydrogenated ones, whereas the SPFOE system exhibits an opposite behavior. Apparently, the chirality indicates an effect which, however, has no direction. This means that the *cmc*s of the L-

enantiomers may be higher or lower than their racemates. As the literature has been scrutinized, it is found that there is limited number of studies related to micellization of racemic and chiral surfactants [13,24,57,58,59,60,100]. Some of these studies show that the *cmc*s of the racemic mixtures are higher than their enantiomers [13,58,59] while the rest of them reports no obvious difference between them [24,57,58,60,100].

In general, the *cmc* increases as the hydrophobicity of the surfactants decrease in aqueous medium [2,5,11]. Here, it is also necessary to compare the partially fluorinated octyl chain, $\text{CF}_3-(\text{CF}_2)_5-(\text{CH}_2)_2-$, with the hydrogenated dodecyl chain, $\text{CH}_3-(\text{CH}_2)_{11}-$. If we look at the *cmc* values of our partially fluorinated and hydrogenated systems, it is seen that the *cmc* values of the formers, DL/L-APFOE and DL/L-SPFOE, are nearly twice the *cmc* values of the DL/L-ADDE and DL/L-SDDE systems at each temperature. According to these results, it is understood that $\text{CF}_3-(\text{CF}_2)_5-(\text{CH}_2)_2-$ group is not exactly counterpart of $\text{CH}_3-(\text{CH}_2)_{11}-$ group. Usually perfluorination of the alkyl chain decreases the *cmc*, however, partial fluorination may increase the *cmc* due to the unfavorable interactions between the hydrocarbon and fluorocarbon groups [2]. It has been reported that a CF_2 group is approximately equivalent to 1.5 (or 1.6) CH_2 group in perfluorinated systems; this has been attributed to the difference in the transferring free energy of $-\text{CF}_2-$ and $-\text{CH}_2-$ from the aqueous environment to the micellar state [61,107,108]. However, interestingly, this rule ($1 \text{ CF}_2 \approx 1.5 \text{ CH}_2$) is not valid for partially fluorinated surfactants [109]. In such a case, a hydrocarbon moiety between a fluorinated tail and the polar head does not contribute fully to the micellization and adsorption

processes. This means that micellization and adsorption processes are controlled by the fluorinated tail length, and the hydrocarbon moiety makes a minor contribution to these processes due to unfavorable interactions between the hydrocarbon and fluorocarbon groups [109]. Our partially fluorinated carbon chain consists of $\text{CF}_3-(\text{CF}_2)_5-(\text{CH}_2)_2-$ groups, and so the high cmc values of the APFOE and SPFOE systems may be explained on the basis of the unfavorable interactions between the $\text{CF}_3-(\text{CF}_2)_5-$ and $-(\text{CH}_2)_2-$ groups in the partially fluorinated carbon chain. Although this explanation may be regarded as a satisfactory answer to the second point, we have to question what are the “unfavorable” interactions? These may be understood as a different driving force for agglomerations, i.e. since the fluorocarbon group is more hydrophobic than the hydrocarbon group, it agglomerates easier compared to the hydrocarbon group, so there are conflicting forces for agglomerations, which require more concentration to balance these forces, and thus the cmc values increase, Table 5.3.

Another result that should be discussed, is that the effect of head group polarity on the *cmc* s. The *cmc* values of surfactants, for both hydrogenated and partially fluorinated systems, with alanine head group ($-\text{CH}_3$) are significantly smaller than those of serine head groups ($-\text{CH}_2\text{OH}$) at each temperature. The reason is that the monomers with serine head group are more polar, i.e. more soluble in water, as compared to alanine head group. So, as it is expected, the *cmc* increases when the head group changes from alanine to serine.

From the Table 5.3, it is seen that, in all cases, the variation of the *cmc* with the temperature is small. A rather shallow minimum appears to occur at around 25 °C for the most of the studied systems. As the temperature is increased, the *cmc* values of our systems firstly decrease to a minimum value, then, the *cmc* increases by further increase in the temperature, Figures 5.4(a)-(d).

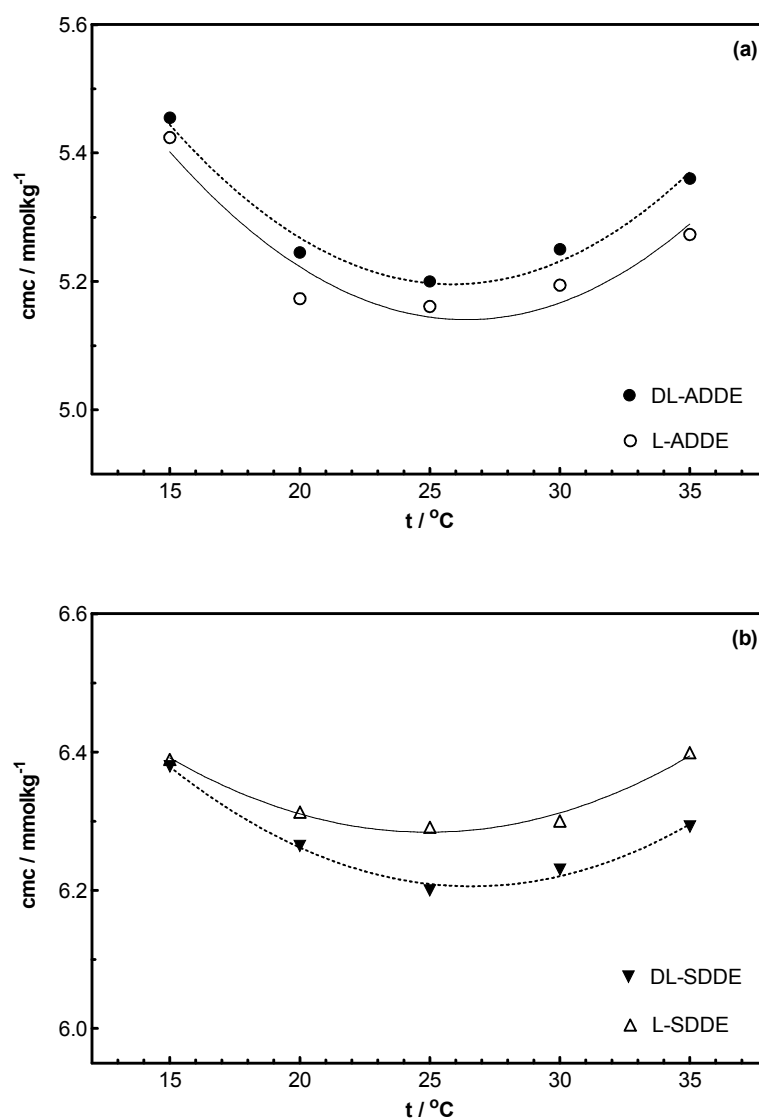


Figure 5.4 Temperature dependence of the *cmc* values of aqueous solutions of (a) DL/L-ADDE and (b) DL/L-SDDE. The dotted line is drawn as a guide to the eye.

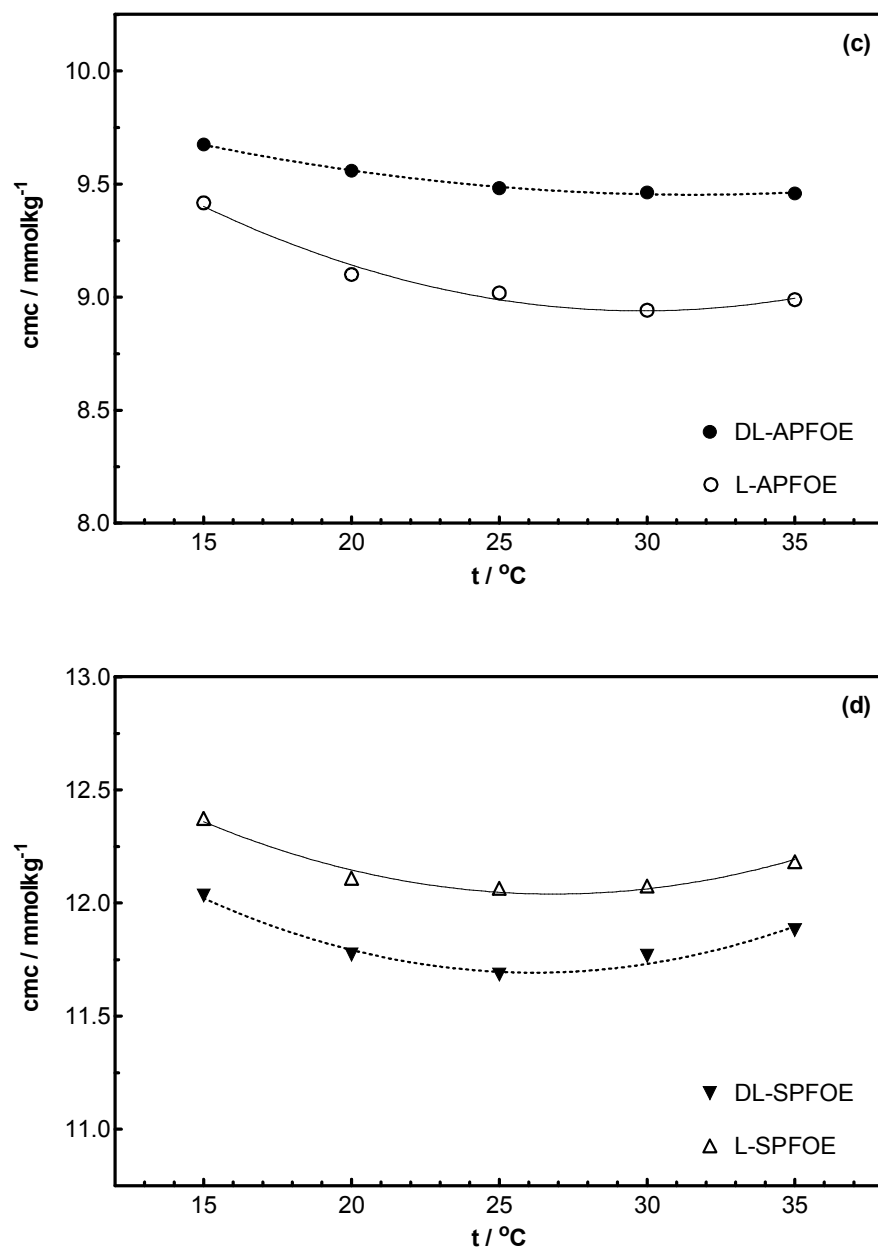


Figure 5.4 Temperature dependence of the *cmc* values of aqueous solutions of (c) DL/L-APFOE and (d) DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

In general, the influence of temperature on micellization is usually weak; however, it is also quite complex. The *cmc* of most ionic surfactants initially decreases, and then increases as the temperature increases [36,37,46,59,67,68,70-75,77]. This behavior can be explained by two opposing effects [5,11,37,110]. These effects are related to (i) the hydration of the head group and (ii) the structured water molecules surrounding the hydrophobic tail. The increase in temperature causes a decrease in hydration of the hydrophilic head group, which favors the micellization. On the other hand, when the surfactant molecules dissolve in water, the hydrophobic tail group distorts the water structure. Therefore, an increase in temperature causes distortion of the structured water molecules surrounding the hydrophobic tail group, which opposes micellization. Consequently, the existence of a minimum *cmc* is thus an outcome of these two opposing effects.

5.3.2. Surface tension measurements

Plots of the surface tension (γ) versus the logarithm of the surfactant concentration ($\ln C$) for DL/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE in water at 15 °C, 25 °C and 35 °C are shown in Figures 5.5(a)-(h), respectively.

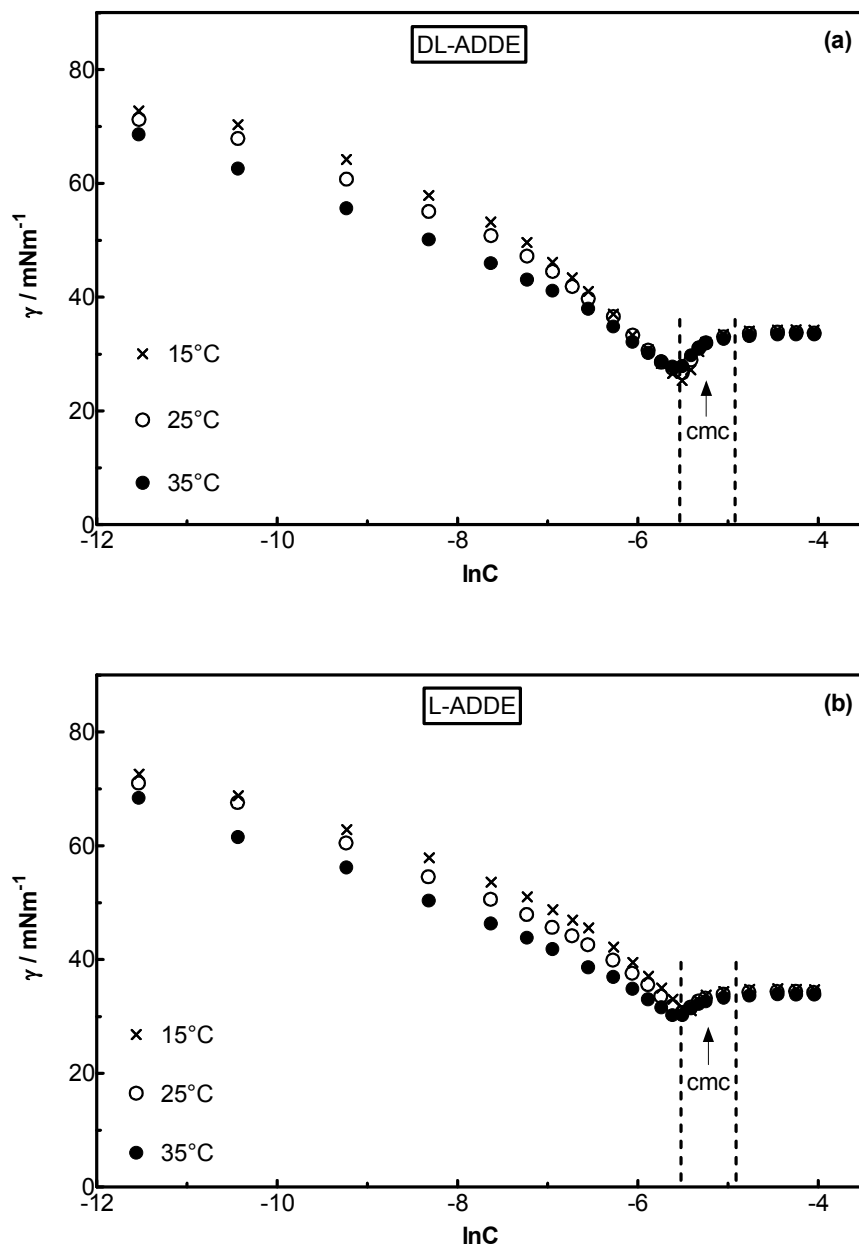


Figure 5.5 Variations of the surface tension (γ) of aqueous solutions of **(a)** DL-ADDE and **(b)** L-ADDE at 15 °C, 25 °C and 35 °C. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

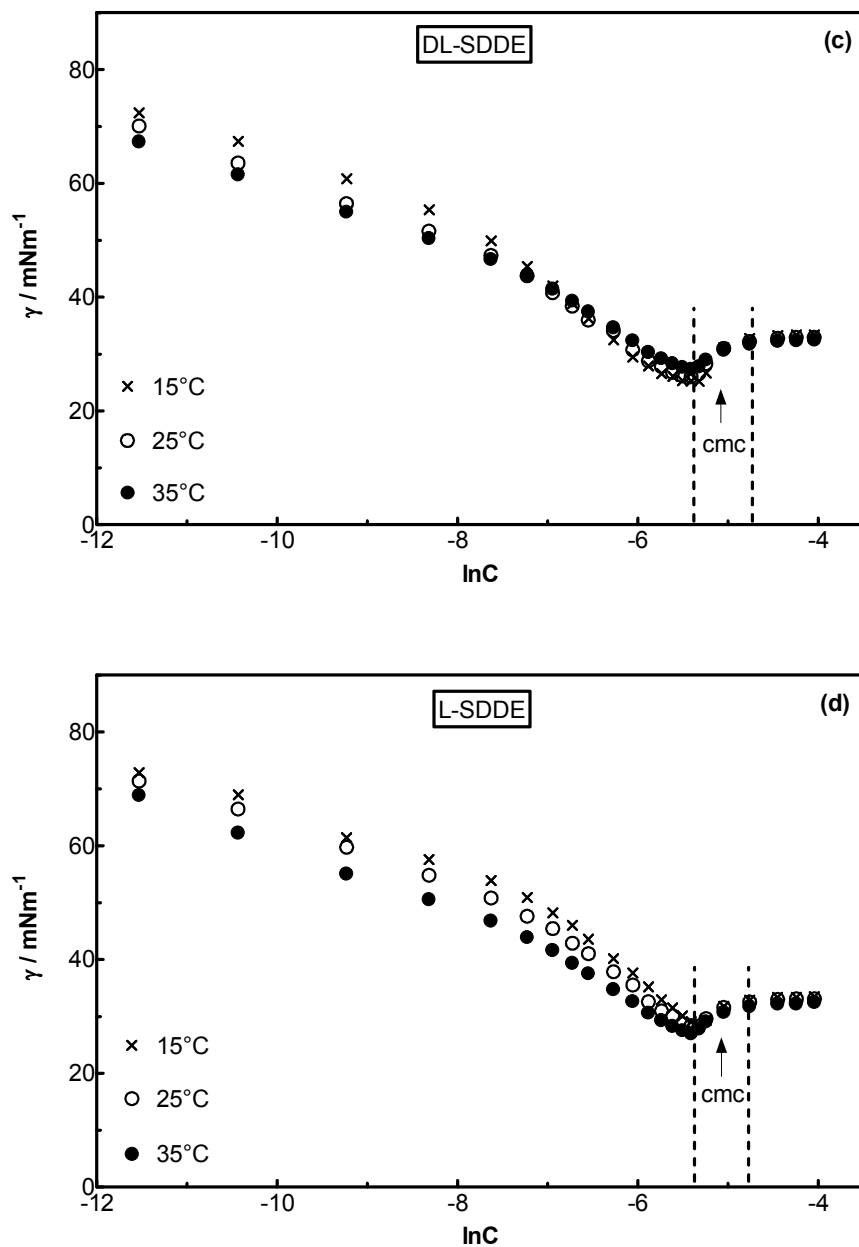


Figure 5.5 Variations of the surface tension (γ) of aqueous solutions of (c) DL-SDDE and (d) L-SDDE at 15 °C, 25 °C and 35 °C. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

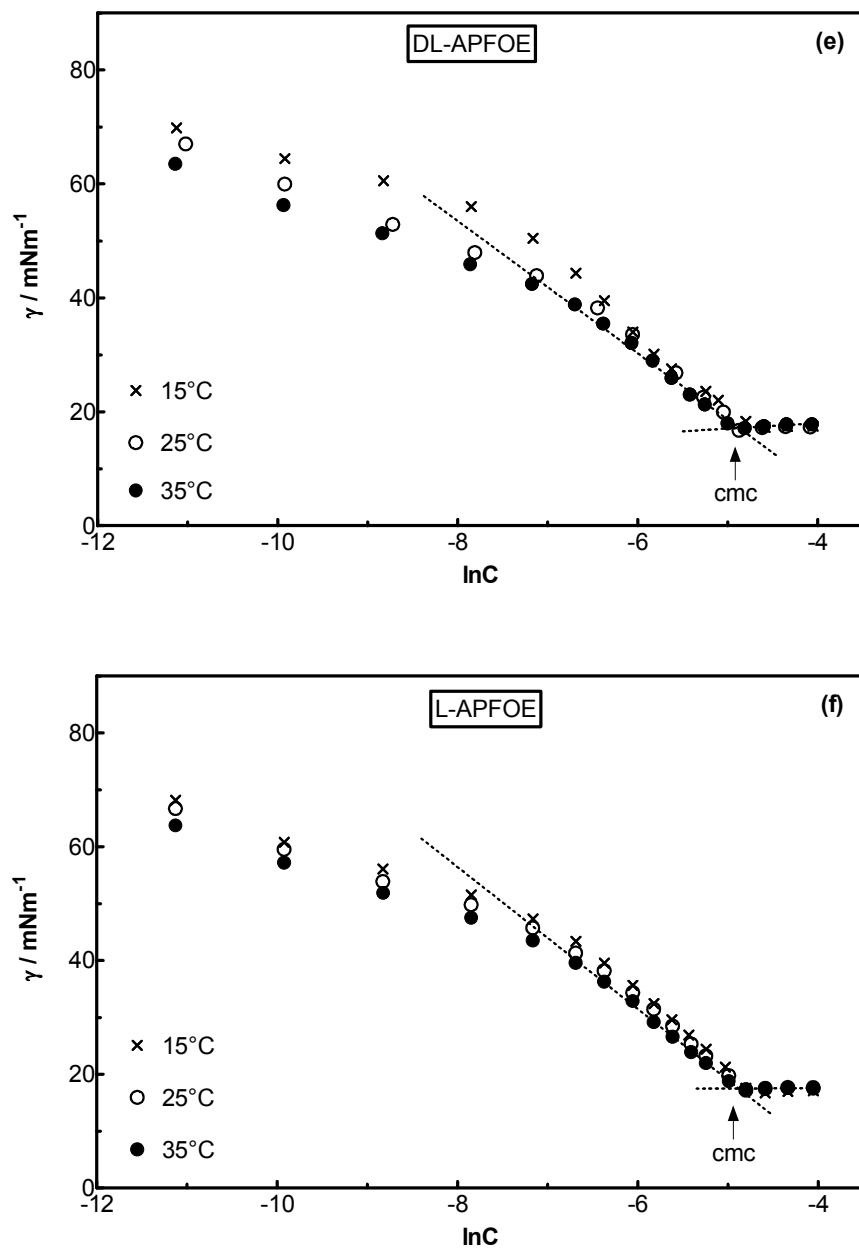


Figure 5.5 Variations of the surface tension (γ) of aqueous solutions of (e) DL-APFOE and (f) L-APFOE at 15 °C, 25 °C and 35 °C. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

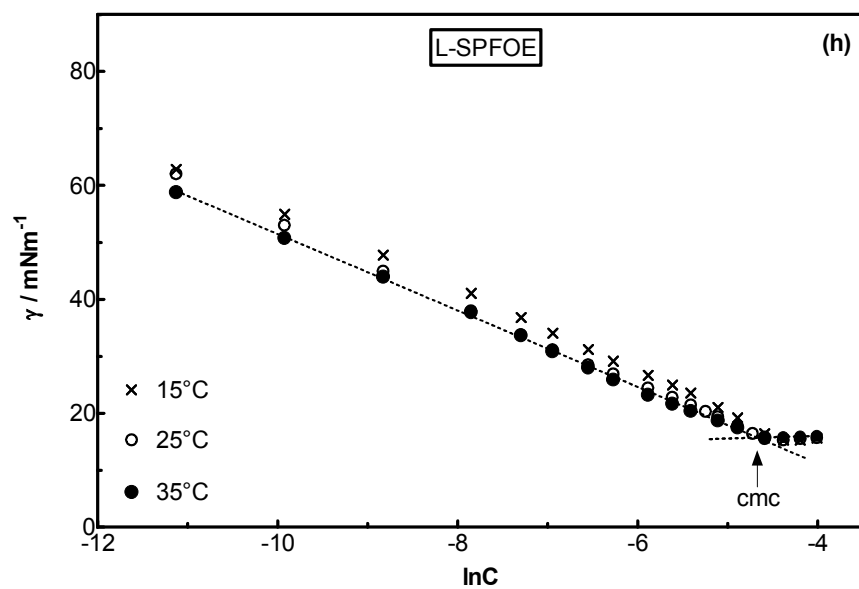
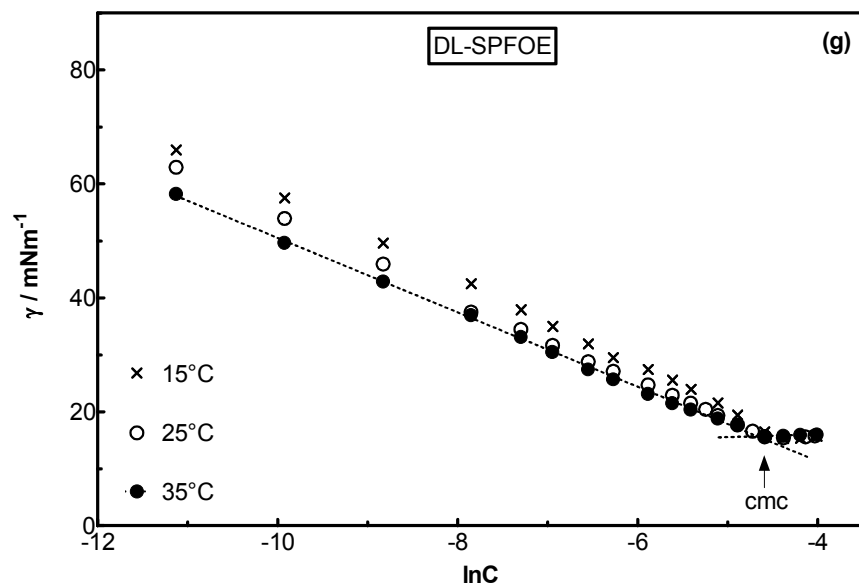


Figure 5.5 Variations of the surface tension (γ) of aqueous solutions of **(g)** DL-SPFOE and **(h)** L-SPFOE at 15 °C, 25 °C and 35 °C. The arrow indicates the *cmc*.

The dotted line is drawn as a guide to the eye.

For all systems, the surface tension gradually decreases with increasing concentrations up to a certain level, i.e. *cmc*, above which a nearly constant value is reached. As well known, the reduction of the surface tension is the result of the adsorption of surfactant monomers at the interface, above the *cmc*, since almost all of the added surfactants are consumed in micelle formation, the surface tension of the solution remains constant. From the plots, it can be recognized that partially fluorinated octyl esters show a clear break with the absence of a minimum at the *cmc*, while the hydrogenated dodecyl esters show a slight minimum, see Figures 5.5(a)-(d). The presence of minimum can be attributed to surface-active impurities in the solution. It is often observed for ionic surfactants that are synthesized from long-chain alcohols that partially hydrolyze in water [11,111]. So, the hydrogenated dodecyl esters probably hydrolyze in a slight amount to dodecanol during the measurements. This minimum disappears, as the impurity, i.e. dodecanol, dissolves in the micelles above the *cmc*.

Figures 5.5(a)-(h) also show that the effect of the temperature on the surface tension for each system is small. In addition to that the partially fluorinated octyl esters noticeably reduce the surface tension much more than the hydrogenated dodecyl esters due to their surface-active fluorocarbon tail. Furthermore, reduction in the surface tension of the surfactants with serine head group is more remarkable than that of alanine. This may be explained by suggesting that the surfactants with more hydrophilic group, polar head, have a high solubility and low surface tension in the water as in the serine systems. Consequently, we can say that the effect of hydrophilic group is also important in the surface tension reduction.

The *cmc* values of the esters were determined from the intersection of the two linear plots, Figures 5.5(a)-(h). The values of *cmc* that are obtained in this way are listed in Table 5.4 as a function of temperature.

<i>cmc</i> ± 0.09 / mmol.kg ⁻¹								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	4.92	4.88	5.38	5.38	8.77	8.83	12.50	12.45
25	4.50	4.50	5.28	5.28	7.77	7.91	9.94	9.89
35	4.46	4.45	5.28	5.10	7.30	7.58	9.35	9.34

Table 5.4 The *cmc* values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE obtained from surface tension measurements at different temperatures. The *cmc* is given in mmol.kg⁻¹. The average standard deviation in the *cmc* values was ± 0.09 mmol.kg⁻¹.

The temperature dependence of the *cmc* values are plotted in Figures 5.6(a)-(d).

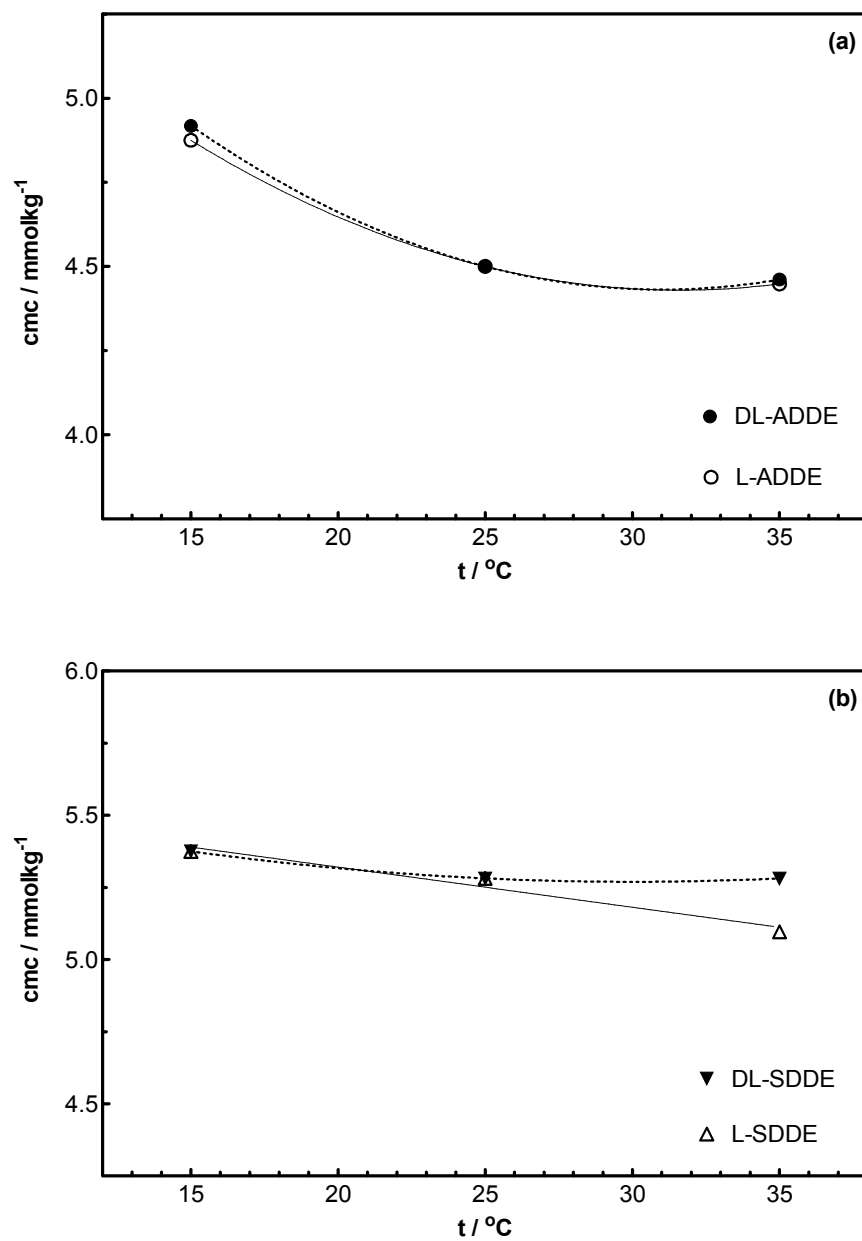


Figure 5.6 Temperature dependence of the cmc values of aqueous solutions of **(a)** DL/L-ADDE and **(b)** DL/L-SDDE. The dotted line is drawn as a guide to the eye.

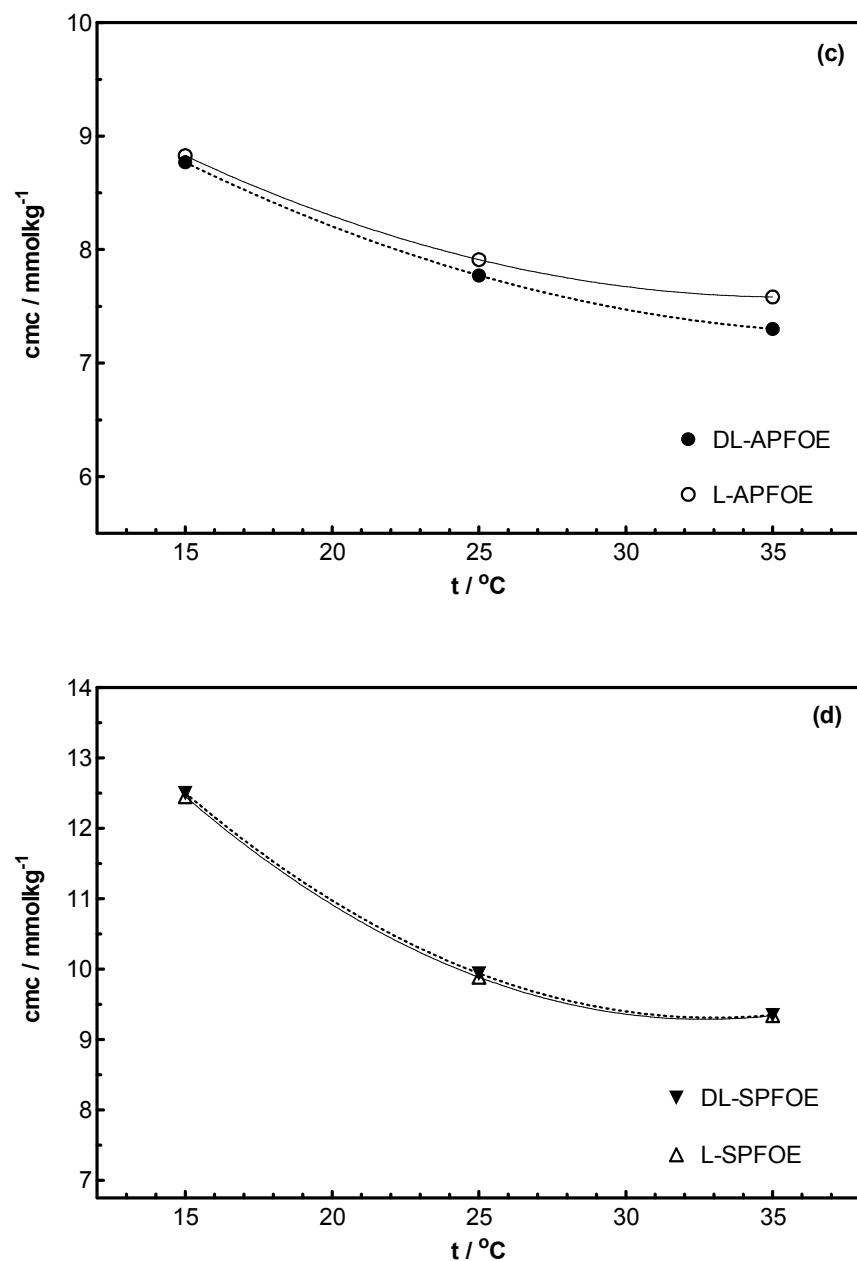


Figure 5.6 Temperature dependence of the cmc values of aqueous solutions of (c) DL/L-APFOE and (d) DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

However, as can be seen in Figures 5.6(a)-(d), the effect of temperature on hydrogenated dodecyl esters is small as compared to the partially fluorinated octyl esters. This is probably due to the temperature dependence of the solubility of octyl esters in water. The *cmc* values of racemic and L-enantiomers are almost the same within the error limits. As it is expected that the *cmc* values of partially fluorinated octyl esters, DL/L-APFOE and DL/L-SPFOE, are greater than hydrogenated dodecyl esters, DL/L-ADDE and DL/L-SDDE. Once again, the effect of hydrophilic head group on the *cmc* values, serine > alanine, can easily be recognized from the Table 5.4.

Finally, it was observed that all the *cmc* values obtained from the surface tension measurements were smaller than those of conductivity measurements. The reason is that the surface tension method is very sensitive to impurities, since it only measures the surface concentration of all surface-active species present in solution and does not detect the presence of micelles in the solution.

5.3.3. Density measurements

The *cmc* values of the hydrogenated dodecyl and partially fluorinated octyl esters were also confirmed by the density measurements. Figures 5.7(a)-(h) show the variations of the density difference (Δd), which is the solution density (d) minus that of water (d_0), with the ester concentrations at different temperatures, respectively.

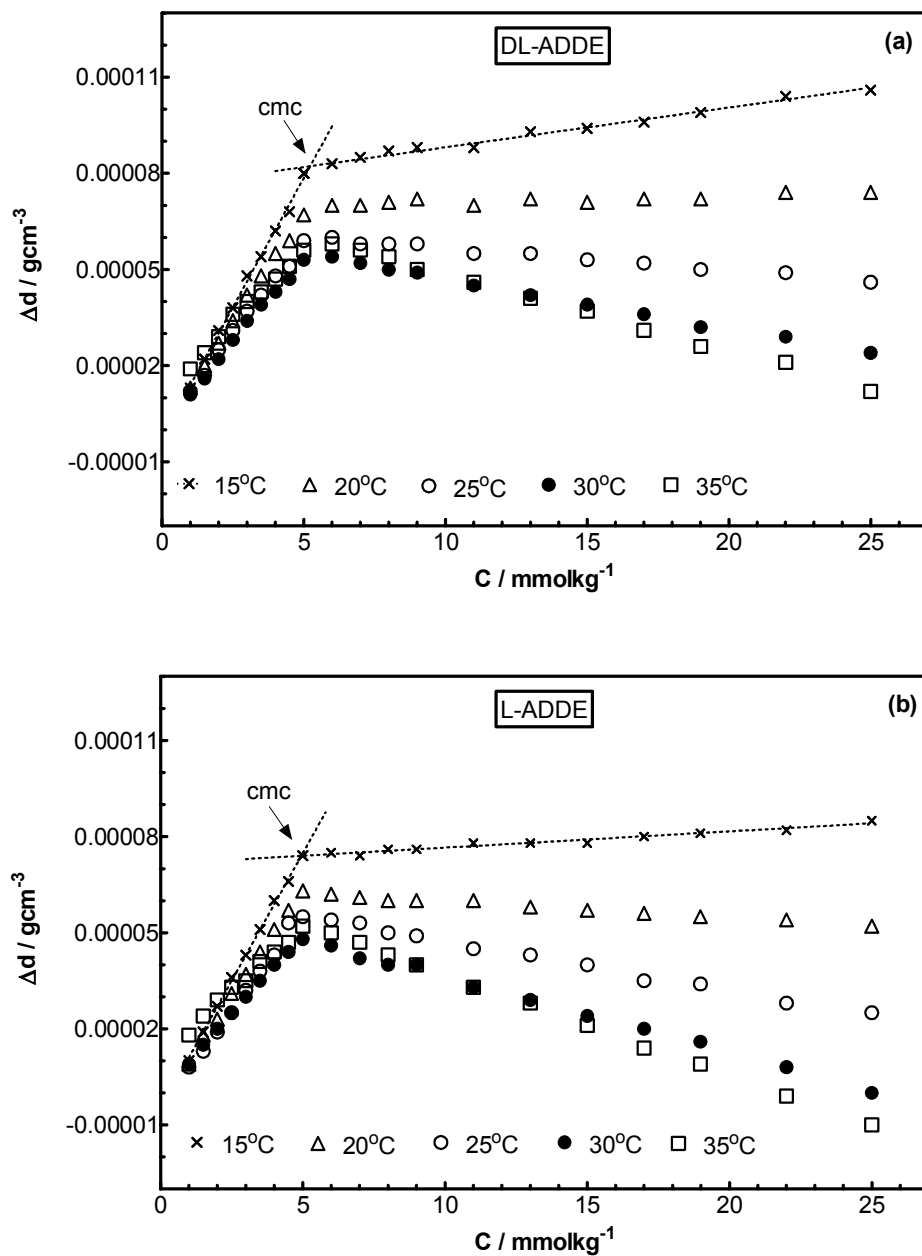


Figure 5.7 Variations of the Δd with the concentration of (a) DL-ADDE and (b) L-ADDE at different temperatures. The arrow indicates the cmc . The dotted line is drawn as a guide to the eye.

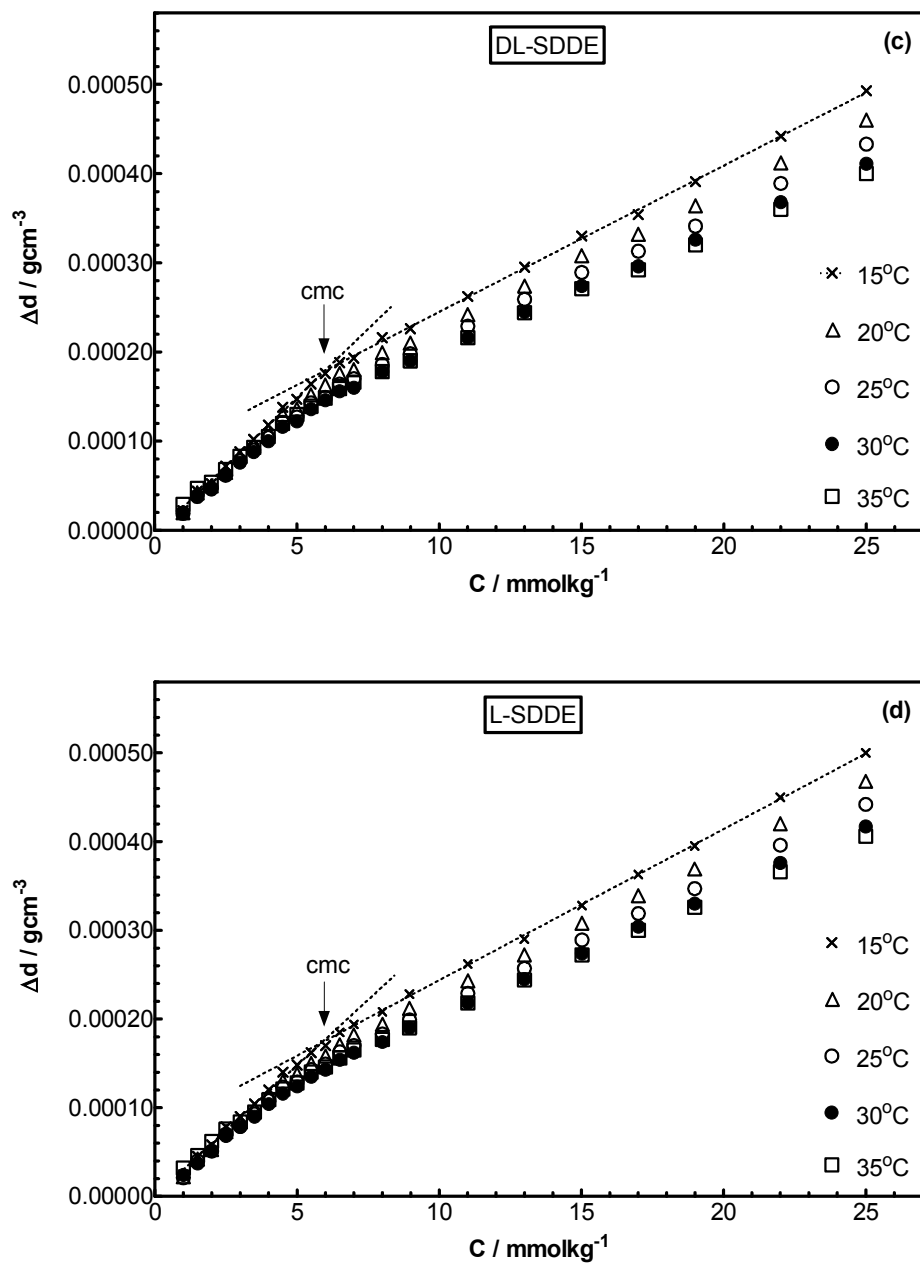


Figure 5.7 Variations of the Δd with the concentration of (c) DL-SDDE and (d) L-SDDE at different temperatures. The arrow indicates the cmc . The dotted line is drawn as a guide to the eye.

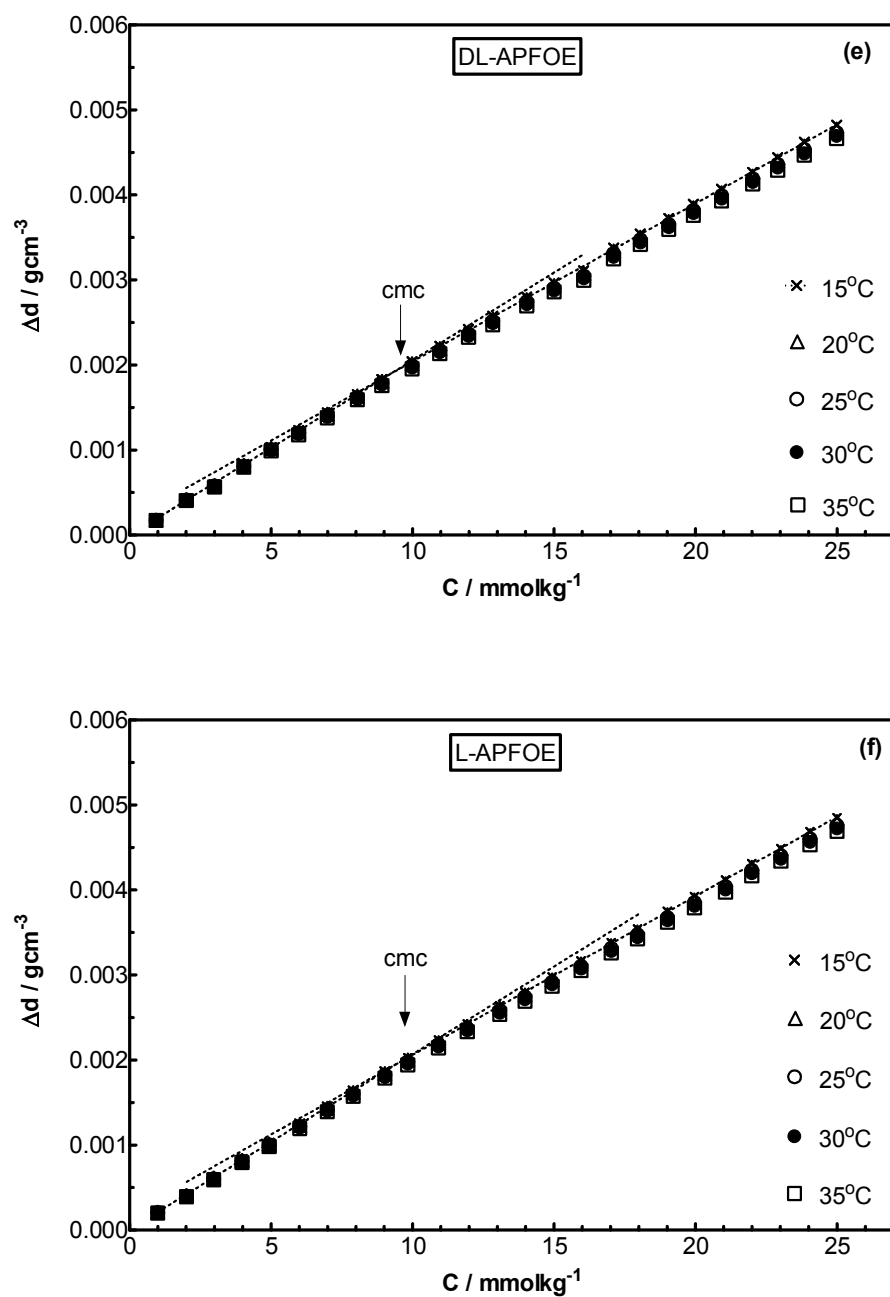


Figure 5.7 Variations of the Δd with the concentration of (e) DL-APFOE and (f) L-APFOE at different temperatures. The arrow indicates the *cmc*. The dotted line is drawn as a guide to the eye.

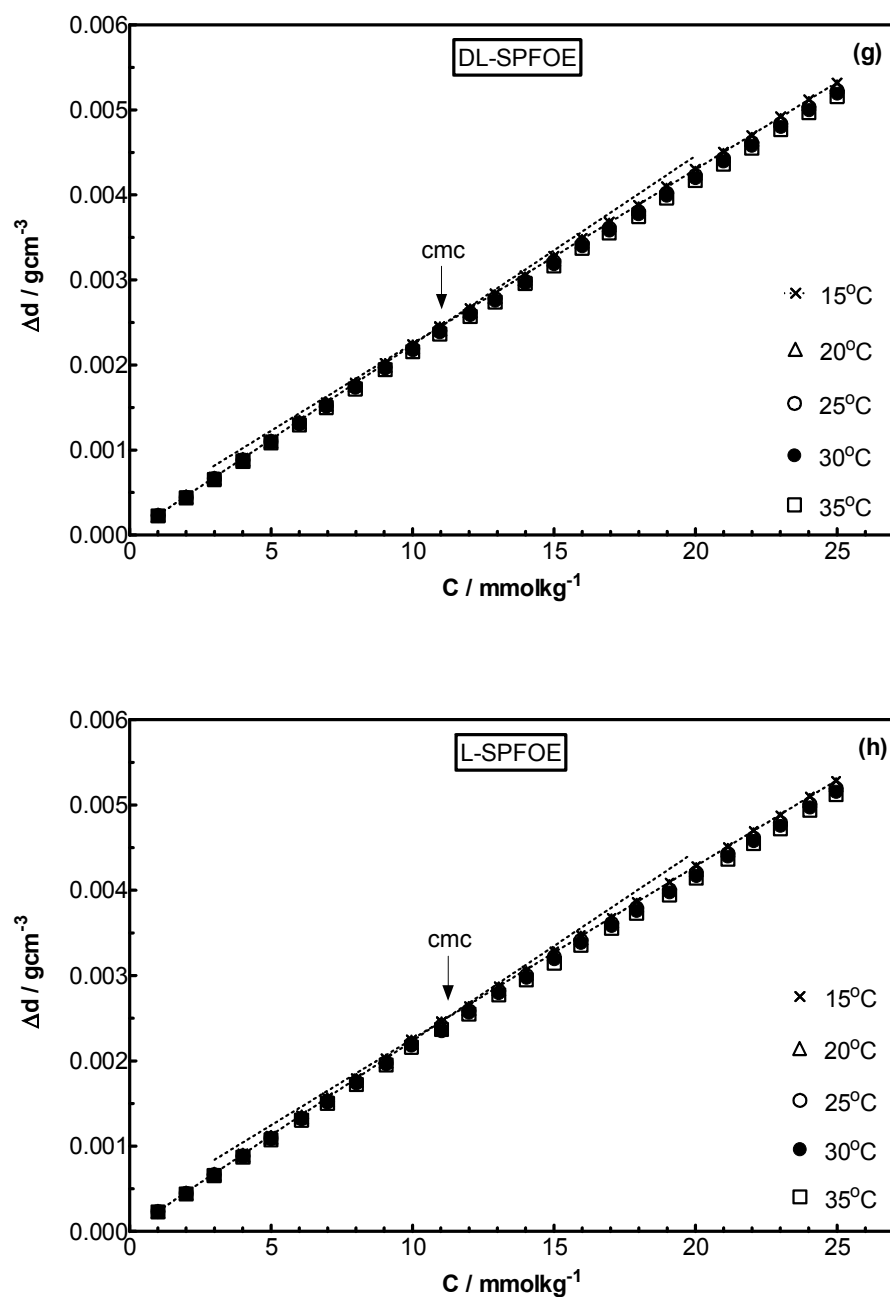


Figure 5.7 Variations of the Δd with the concentration of (g) DL-SPFOE and (h) L-SPFOE at different temperatures. The arrow indicates the cmc . The dotted line is drawn as a guide to the eye.

As seen from Figures 5.7(a)-(h), the density differences or densities, increased with the concentration up to the *cmc*. At *cmc*, an indistinct change was obtained for the partially fluorinated esters, DL/L-APFOE and DL/L-SPFOE, while a clear break was observed for the hydrogenated dodecyl esters, DL/L-ADDE and DL/L-SDDE. This may be result of the bulky fluorocarbon chain. In the literature, it has been also reported that the pre-micellar and the post-micellar region of fluorocarbon surfactants were not distinguishable from the density data [87,38]. Also, it was observed that this behavior was more pronounced as the chain length of the fluorocarbon increased. Above the *cmc*, densities continued to rise linearly with ester concentration with one exception to that, DL/L-ADDE system. That is interestingly enough to be discussed that the density of both the racemic and the enantiomeric of ADDE system decreased as the concentration was increased at and above 20 °C. It is understood that the partial specific molar volume of micelles in the aqueous solutions of DL-ADDE and L-ADDE are relatively high compared to the other studied systems. This is also proved by density differences, ADDE < SDDE < APFOE < SPFOE. Besides, it was recognized that the effect of the temperature on the ADDE systems was more specifically than the others. However, it could be said that serine dodecyl esters, DL/L-SDDE, was slightly affected by the temperature. The partially fluorinated octyl esters are almost temperature-independent.

As mentioned above the density of the all esters has been measured and the data points were fitted well with two straight lines having different slopes to give a break at the *cmc* for each temperature, Figures 5.7(a)-(h). The results are presented in

Table 5.5.

t / °C	<i>cmc</i> ± 0.05 / mmol.kg ⁻¹							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	5.29	4.99	6.02	5.86	9.44	9.55	10.83	11.11
20	5.21	4.89	5.94	5.62	9.24	9.33	10.64	10.99
25	5.14	4.91	5.88	5.47	9.22	9.29	10.58	10.97
30	5.18	4.95	5.92	5.54	9.14	9.15	10.56	10.97
35	5.33	5.07	6.02	5.85	9.21	9.26	10.75	11.05

Table 5.5 The *cmc* values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE obtained from density measurements at different temperatures. The *cmc* is given in mmol.kg⁻¹. The average standard deviation in the *cmc* values was ± 0.05 mmol.kg⁻¹.

From these results, it is inferred that the *cmc* values did not change significantly in the investigated temperature range as obtained from conductivity and surface tension measurements. However, it was observed that the temperature dependence of the *cmc* gave also U-shaped behavior for all the esters as in the conductivity measurements; Figures 5.8(a)-(d).

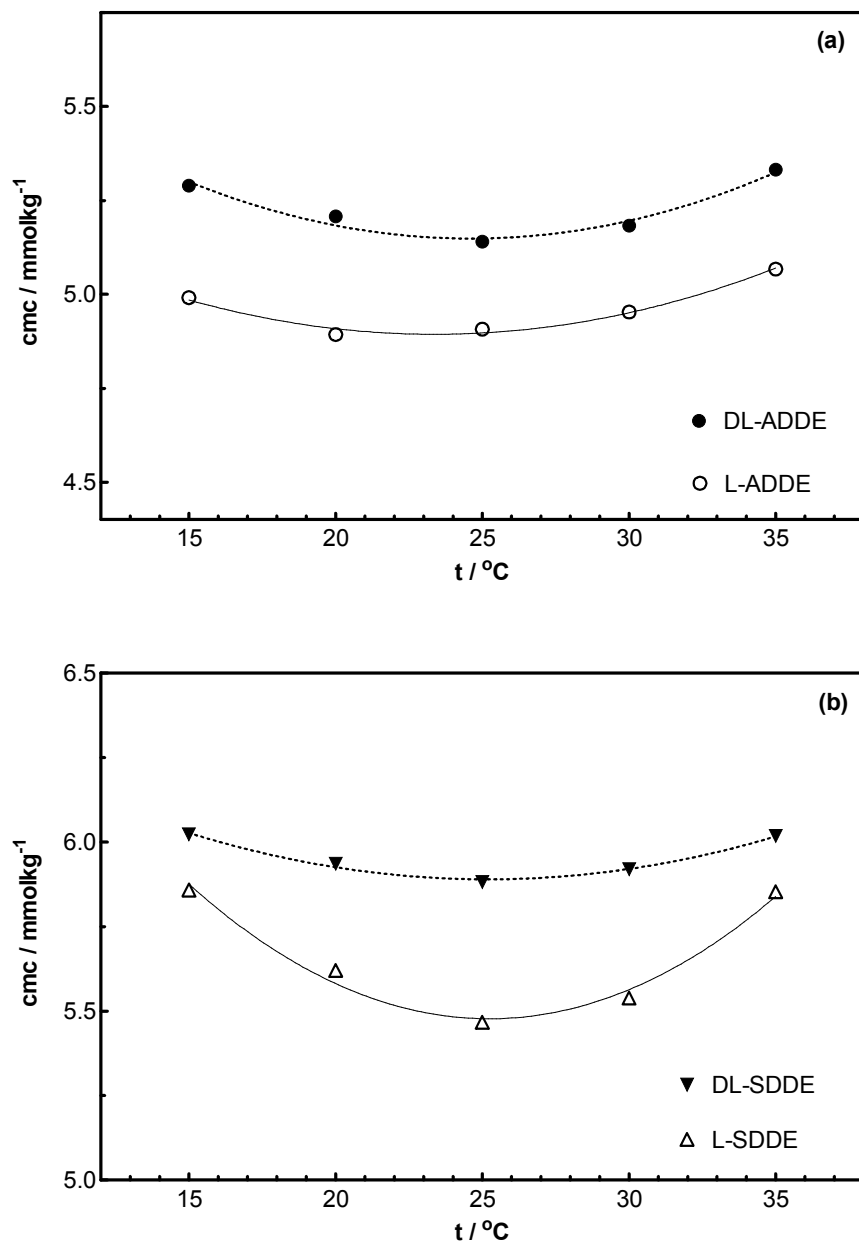


Figure 5.8 Temperature dependence of the *cmc* values of aqueous solutions of (a) DL/L-ADDE and (b) DL/L-SDDE. The dotted line is drawn as a guide to the eye.

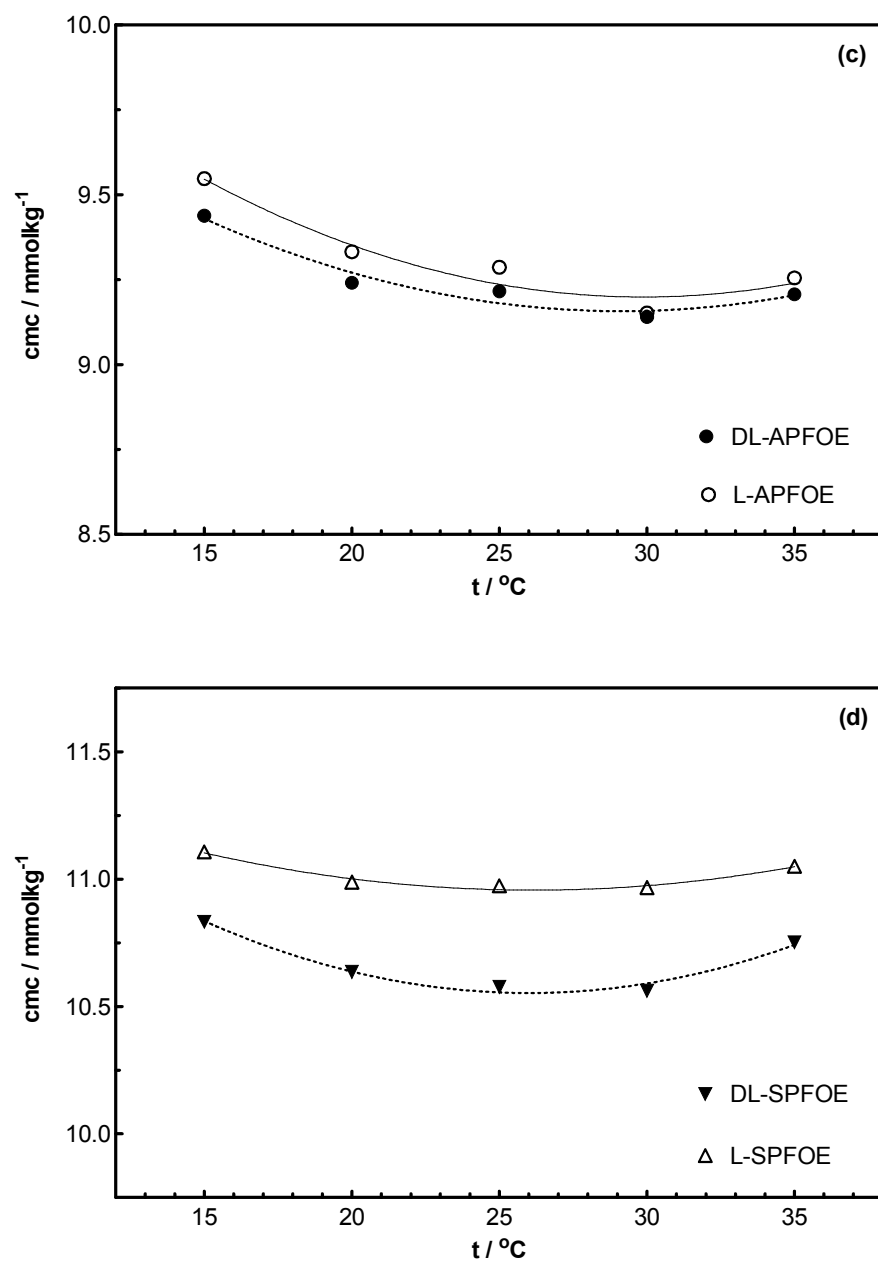


Figure 5.8 Temperature dependence of the *cmc* values of aqueous solutions of **(a)** DL/L-APFOE and **(d)** DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

In conclusion, if the results are compared, we see that the values of the *cmc* of the all esters determined from the conductivity, surface tension and density measurements are somewhat different from each other [14,22,24,26,29,93,104], Table 5.6. Since the three methods monitor micellization process by considering very different properties, this is usual. Furthermore, it is well known that the various methods used for detection of the *cmc* often lead to different numerical estimates, not only because of measurement errors but also because the *cmc* is a range rather than a single pinpointed value [85]. In addition, the measurements are affected by a higher error when working at a low concentration range. For clarity, the *cmc* values obtained by the three different methods at different temperatures are summarized in Table 5.6.

		<i>cmc</i> / mmol.kg ⁻¹					
		Conductivity		Density		Surface tension	
	t / °C	DL	L	DL	L	DL	L
ADDE	15	5.46	5.42	5.29	4.99	4.92	4.88
	20	5.24	5.17	5.21	4.89	–	–
	25	5.20	5.16	5.14	4.91	4.50	4.50
	30	5.25	5.19	5.18	4.95	–	–
	35	5.36	5.27	5.33	5.07	4.46	4.45
	t / °C	DL	L	DL	L	DL	L
SDDE	15	6.38	6.39	6.02	5.86	5.38	5.38
	20	6.26	6.31	5.94	5.62	–	–
	25	6.20	6.29	5.88	5.47	5.28	5.28
	30	6.23	6.30	5.92	5.54	–	–
	35	6.29	6.40	6.02	5.85	5.28	5.10
	t / °C	DL	L	DL	L	DL	L
APFOE	15	9.68	9.42	9.44	9.55	8.77	8.83
	20	9.56	9.10	9.24	9.33	–	–
	25	9.48	9.02	9.22	9.29	7.77	7.91
	30	9.46	8.94	9.14	9.15	–	–
	35	9.46	9.99	9.21	9.26	7.30	7.58
	t / °C	DL	L	DL	L	DL	L
SPFOE	15	12.03	12.37	10.83	11.11	12.50	12.45
	20	11.77	12.11	10.64	10.99	–	–
	25	11.68	12.06	10.58	10.97	9.94	9.89
	30	11.77	12.08	10.56	10.97	–	–
	35	11.88	12.18	10.75	11.05	9.35	9.34

Table 5.6 Comparison of the *cmc* values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE from electrical conductivity, surface tension and density measurements at 15, 20, 25, 30 and 35 °C. The *cmc* is given in mmol.kg⁻¹.

5.4. Determination of the thermodynamic parameters of micellization by conductivity measurements

It is generally known that standard enthalpy change of micellization (ΔH_{mic}°) represents the net changes in intermolecular forces upon micelle formation, while standard entropy change of micellization (ΔS_{mic}°) include changes in the degrees of freedom both solvent and surfactant [16]. However, standard Gibbs free energy change of micellization (ΔG_{mic}°) is the sum of the enthalpic (ΔH_{mic}°) and entropic ($-T\Delta S_{mic}^{\circ}$) contributions, and it gives the valuable information about the spontaneity of the micelle formation [15,16,26,35,36,40].

In the present work, the micellization process of the hydrogenated dodecyl esters, DL/L-ADDE and DL/L-SDDE, and the partially fluorinated octyl esters, DL/L-APFOE and DL/L-SPFOE, in aqueous solutions have been studied for the first time. From these investigations, it has been aimed to understand (i) whether there is any difference between the micellization process of the aqueous solutions of the racemic and the enantiomeric esters or not, and (ii) the influence of hydrophobic tail and hydrophilic head group on the micellization process. Consequently, the thermodynamic parameters, ΔG_{mic}° , ΔH_{mic}° and ΔS_{mic}° , have been investigated which may give insight on the micellization process of our systems.

It is well known that the temperature dependence of the *cmc* of surfactants can be used to estimate the thermodynamic parameters of micellization, which are important to understand the micellization process of the surfactants in a solvent

[15,16,26,35,36,40]. In order to determine the ΔG_{mic}° , ΔH_{mic}° and ΔS_{mic}° , as stated in section 2.4, some values such as the degree of ionization of the surfactant in the micelle (α), the *cmc* value expressed in terms of mole fraction (X_{cmc}) and the variation of the X_{cmc} with temperature $\left(\frac{\partial \ln X_{cmc}}{\partial T}\right)$ should be known. This term has to be determined experimentally in order to calculate the ΔH_{mic}° according to the Equation (2.10).

The approximate values of the α from the micelle, which are calculated from the κ vs. C plot as the ratio of slopes above and below the *cmc* as proposed by Evans [30], are presented in Table 5.7 for all studied systems.

$\alpha \pm 0.01$								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	0.35	0.34	0.40	0.40	0.36	0.34	0.37	0.38
20	0.36	0.36	0.41	0.41	0.37	0.36	0.40	0.40
25	0.38	0.37	0.41	0.42	0.39	0.37	0.42	0.42
30	0.39	0.38	0.43	0.43	0.40	0.39	0.45	0.46
35	0.41	0.39	0.43	0.45	0.42	0.40	0.47	0.48

Table 5.7 The α values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.

The results show that the α values increase with increased temperature for all these esters. Nevertheless, the overall variation of α with temperature is small for

ADDE, SDDE and APFOE, $\Delta\alpha \approx 0.05$, whereas for SPFOE this value appears to be larger, $\Delta\alpha \approx 0.10$. Furthermore, it is also to note that there is no clear difference in the α values of the racemic (DL) and chiral (L) forms of the esters within the error limit at each temperature. Since the α is related to ionization of surfactant head group, it can get higher degree with increasing head group polarity [44]. Table 5.7 shows that, as it is expected, serine esters, SDDE and SPFOE, have a higher α value than those of the alanines, ADDE and APFOE. This result also explains why *cmc* values of serine esters are higher than those of the alanine esters. So, an increase in the α value gives rise to a strong ionic repulsion between the head groups, which oppose the micellization process for serine esters. Finally, the temperature dependencies of the calculated α values for all systems have been given in Figure 5.9 (a) and (b).

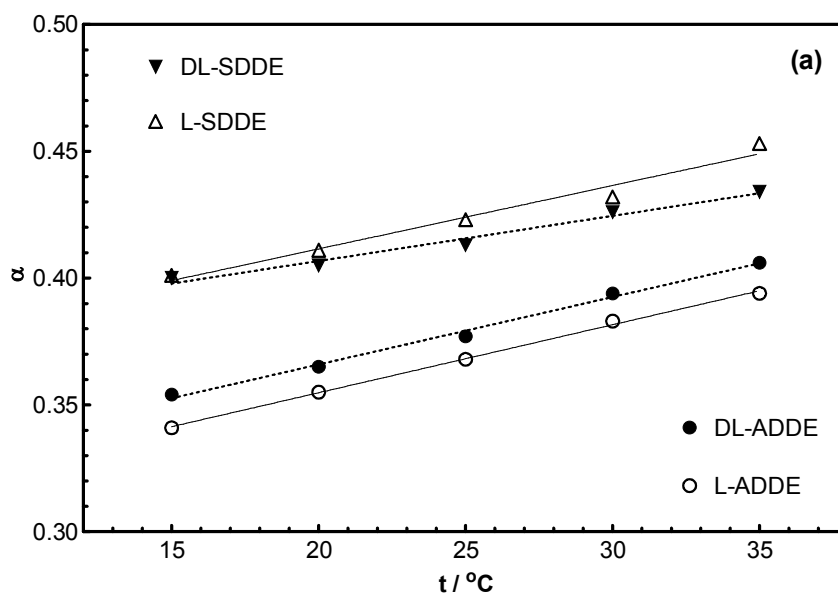


Figure 5.9 (a) Temperature dependence of the α values of aqueous solutions of DL/L-ADDE and DL/L-SDDE. The dotted line is drawn as a guide to the eye.

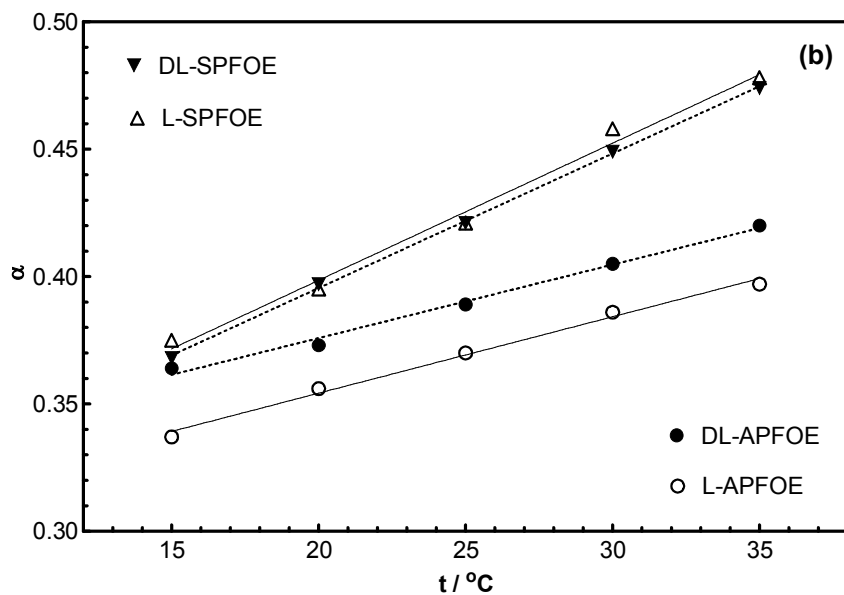


Figure 5.9 (b) Temperature dependence of the α values of aqueous solutions of DL/L-APFOE and DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

The cmc values obtained from the conductivity measurements have been used to determine $\ln X_{cmc}$ of the esters. The $\ln X_{cmc}$ – temperature curves, Figures 5.10(a)-(d), were fitted to the equation of second order polynomial in all cases

$$\ln X_{cmc} = a + bT + cT^2 \quad (5.1)$$

where T is the temperature in Kelvin and a , b and c are the fitting parameters.

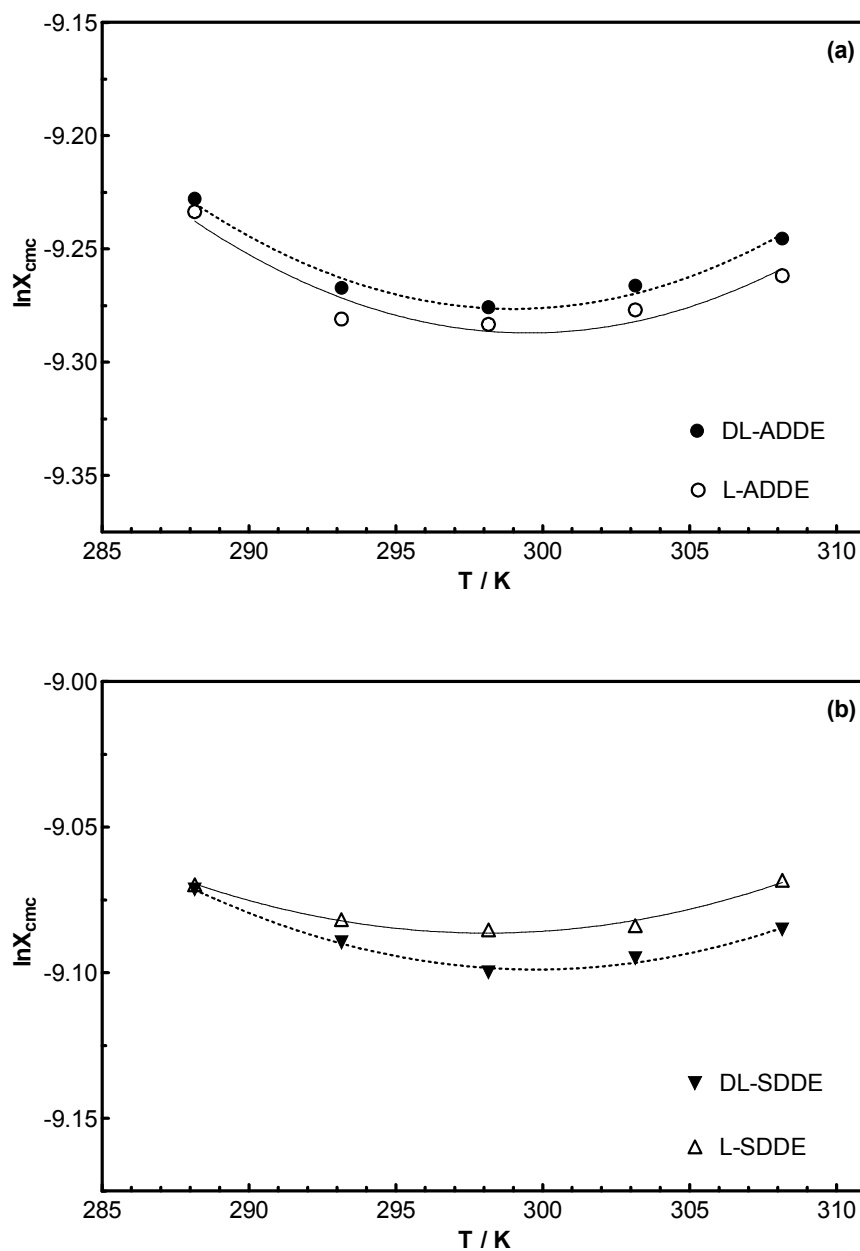


Figure 5.10 Temperature dependence of the $\ln X_{cmc}$ of (a) DL/L-ADDE and (b) DL/L-SDDE. The dotted lines show the fitting of second order polynomial equation.

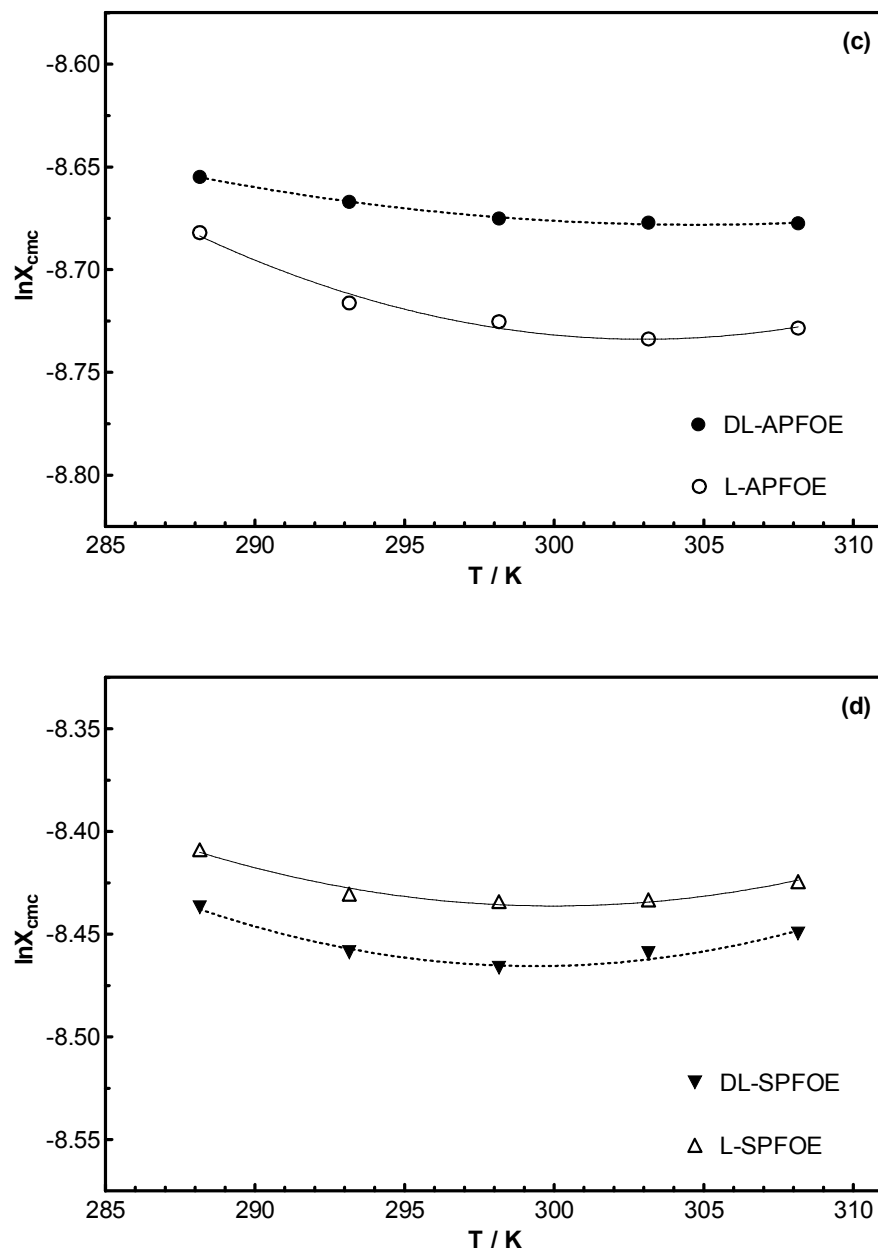


Figure 5.10 Temperature dependence of the $\ln X_{cmc}$ of (c) DL/L-APFOE and (d) DL/L-SPFOE. The dotted lines show the fitting of second order polynomial equation.

The $\left(\frac{\partial \ln X_{cmc}}{\partial T}\right)$ values were determined by taking the derivative of the above equation and using the fitting parameters. This method allows the determination of the ΔG_{mic}° , ΔH_{mic}° and ΔS_{mic}° from the parameters of the polynomial fit and the equations (2.7), (2.10) and (2.11). The numerical values obtained for the ΔG_{mic}° are listed in Table 5.8.

		$\Delta G_{mic}^{\circ} / kJ mol^{-1}$							
t / °C	T / K	ADDE		SDDE		APFOE		SPFOE	
		DL	L	DL	L	DL	L	DL	L
15	288.15	-36.4	-36.7	-34.8	-34.7	-33.9	-34.6	-33.0	-32.7
20	293.15	-36.9	-37.2	-35.3	-35.2	-34.4	-34.9	-33.0	-33.0
25	298.15	-37.3	-37.6	-35.8	-35.5	-34.6	-35.3	-33.1	-33.0
30	303.15	-37.5	-37.8	-36.1	-35.9	-34.9	-35.5	-33.1	-32.8
35	308.15	-37.8	-38.1	-36.4	-35.9	-35.1	-35.8	-33.0	-32.8

Table 5.8 ΔG_{mic}° values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.

The results show that the ΔG_{mic}° values are always negative for all studied esters indicating that the micellization process is thermodynamically favorable, i.e. it is spontaneous. Besides, the observations imply that the ΔG_{mic}° values of the esters vary between -32.7 and -38.1 kJ.mol⁻¹ similar to the most of ionic surfactants [5]. The ΔG_{mic}° values of the ADDE system is more negative than those obtained for the SDDE system indicating more favorable micellization of the ADDE. Similarly, the

ΔG_{mic}° value of the APFOE system is more negative than the SPFOE indicating that the micelle formation is more favorable for the former. In addition, it is seen that all hydrogenated dodecyl ester have more negative ΔG_{mic}° values compared to partially fluorinated octyl esters. These results are all consistent with the behavior of their α and cmc values. We also note that there is no obvious difference between the ΔG_{mic}° values of the DL- and L- forms of the esters. Nevertheless, as can be seen from the Table 5.8, the temperature dependence of the ΔG_{mic}° is weak, Figures 5.11(a) and (b). On the other hand, it has been recognized that the ΔG_{mic}° of the SPFOE system appears to be independent of the temperature [112].

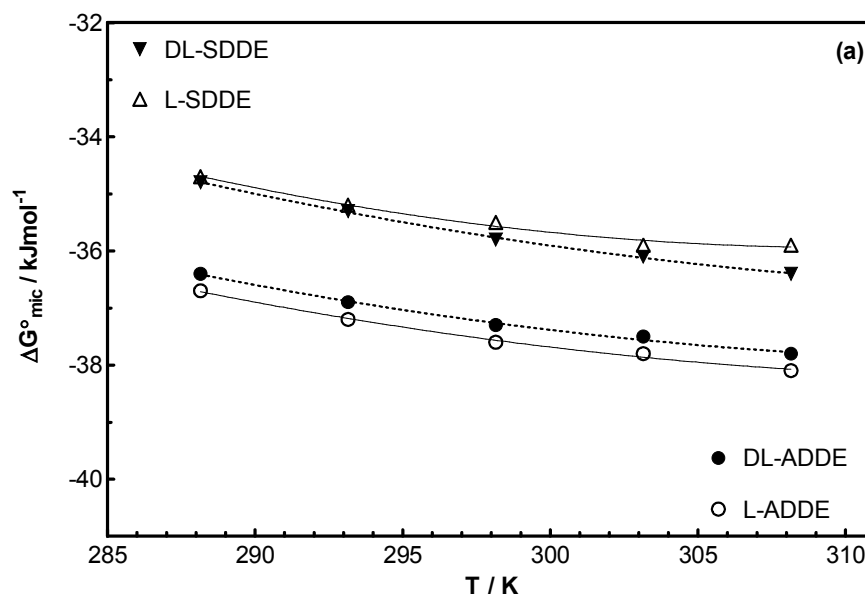


Figure 5.11 (a) Temperature dependence of the ΔG_{mic}° of DL/L-ADDE and DL/L-SDDE. The dotted lines show the fitting of second order polynomial equation.

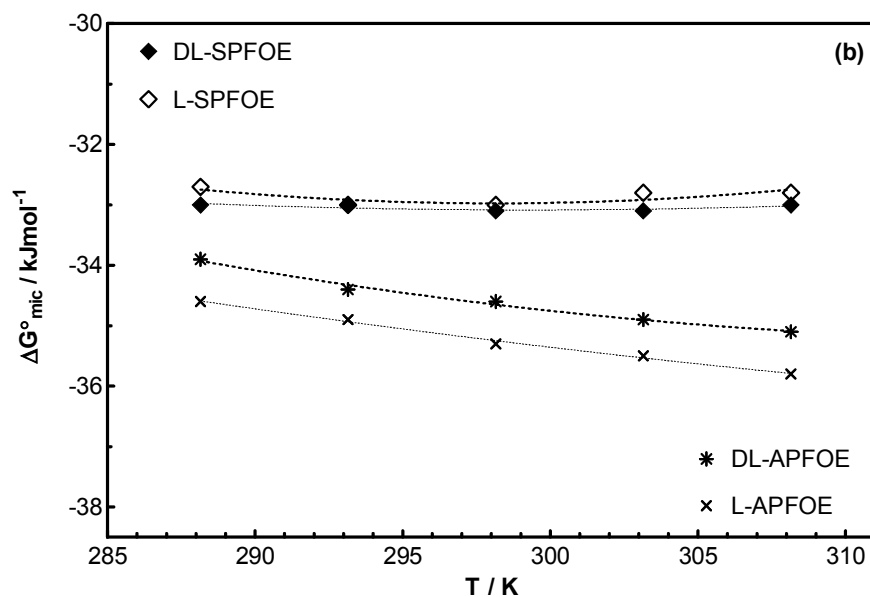


Figure 5.11 (b) Temperature dependence of the ΔG_{mic}° of DL/L-APFOE and DL/L-SPFOE. The dotted lines show the fitting of second order polynomial equation.

The values of the ΔH_{mic}° are given in Table 5.9 and are plotted in Figures 5.12(a) and (b) as a function of temperature, respectively.

t / °C	T / K	$\Delta H_{mic}^{\circ} / kJ mol^{-1}$							
		ADDE		SDDE		APFOE		SPFOE	
		DL	L	DL	L	DL	L	DL	L
15	288.15	9.81	9.93	5.20	3.82	3.14	7.77	5.59	4.91
20	293.15	5.48	5.70	3.04	1.99	2.26	5.28	3.14	2.87
25	298.15	0.89	1.25	0.74	0.04	1.32	2.68	0.61	0.74
30	303.15	-3.93	-3.44	-1.69	-2.01	0.33	-0.06	-2.01	-1.46
35	308.15	-9.00	-8.37	-4.25	-4.15	-0.71	-2.94	-4.72	-3.74

Table 5.9 The ΔH_{mic}° values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.

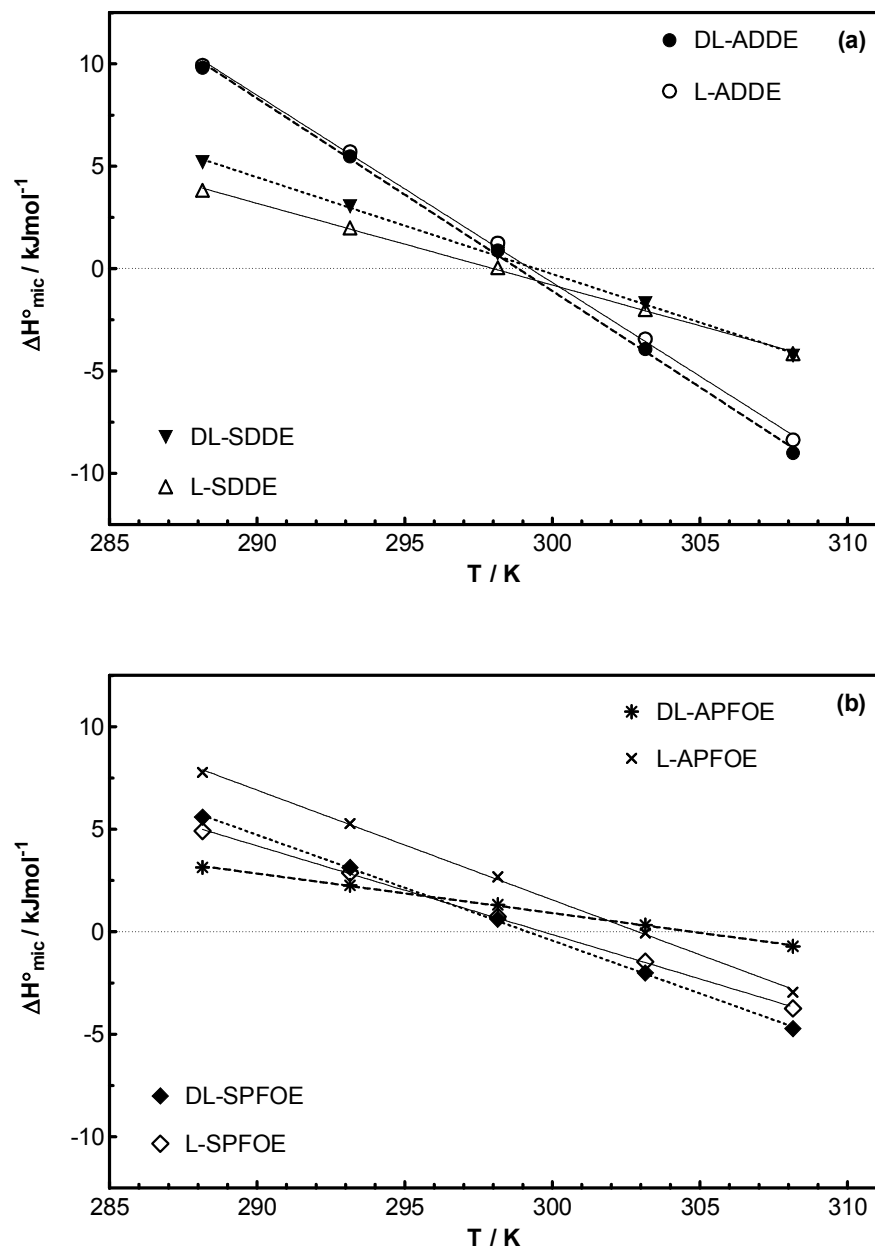


Figure 5.12 Temperature dependence of the ΔH°_{mic} of (a) DL/L-ADDE and DL/L-SDDE, and (b) DL/L-APFOE and DL/L-SPFOE. The dotted lines show the fitting of linear regression equation.

From the Table 5.9 and the Figures 5.12 (a) and (b), it is clear that the ΔH_{mic}° of DL/L-ADDE, DL/L-SDDE and DL/L-SPFOE show a change from positive to negative values close to 299.15 K (26 °C) while this turning point of DL/L-APFOE takes place at about 303.15 K (30 °C). In other words, the micellization process for our systems is endothermic at low temperatures while it is exothermic as the temperature is increased.

The values of the ΔS_{mic}° is given in Table 5.10 and is plotted in Figures 5.13(a) and (b) as a function of the temperature, respectively.

		$\Delta S_{mic}^{\circ} / kJ mol^{-1}$							
T / °C	T / K	ADDE		SDDE		APFOE		SPFOE	
		DL	L	DL	L	DL	L	DL	L
15	288.15	0.160	0.162	0.139	0.134	0.129	0.147	0.134	0.131
20	293.15	0.145	0.146	0.131	0.127	0.125	0.137	0.123	0.122
25	298.15	0.128	0.130	0.123	0.119	0.121	0.127	0.113	0.113
30	303.15	0.111	0.113	0.113	0.112	0.116	0.117	0.102	0.103
35	308.15	0.093	0.096	0.104	0.103	0.112	0.107	0.092	0.094

Table 5.10 The ΔS_{mic}° values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.

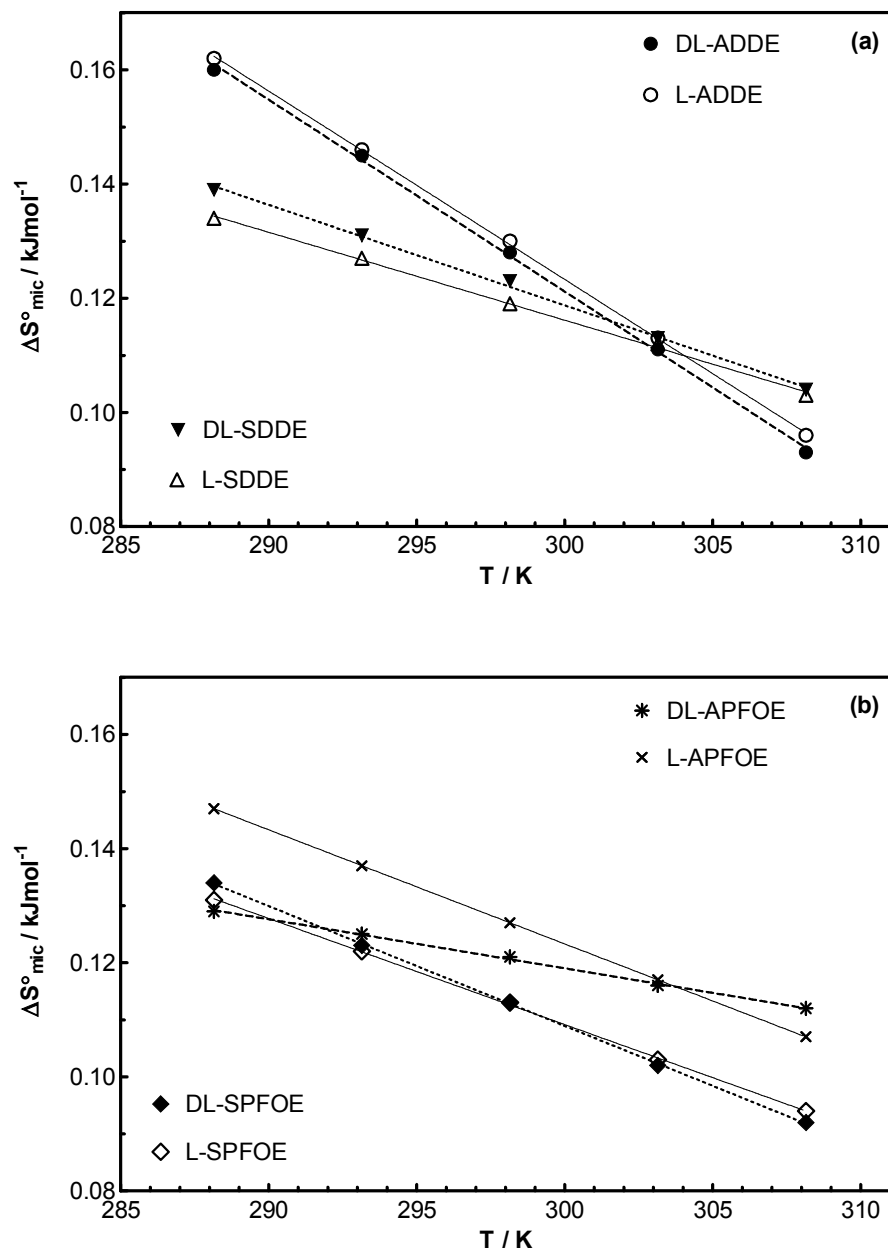


Figure 5.13 Temperature dependence of the ΔS°_{mic} of (a) DL/L-ADDE and DL/L-SDDE, and (b) DL/L-APFOE and DL/L-SPFOE. The dotted lines show the fitting of linear regression equation.

In contrary to the ΔH_{mic}° values, the ΔS_{mic}° of our systems are all positive at the given temperature range. Also, the ΔS_{mic}° values of all systems decrease as the temperature is increased. The results, obtained for both the ΔH_{mic}° and ΔS_{mic}° , indicate that the micellization process is entropy-controlled at low temperatures while it is enthalpy-controlled at high temperatures, which has been generally observed for ionic surfactants [5,16,26,35,36,44,61,113]. The variation in both the ΔH_{mic}° and ΔS_{mic}° values suggests the mutual relationship of the enthalpy/entropy compensation phenomenon [16,26,33,61]. This enthalpy/entropy compensation can be usually explained by the hydrophobic effect [8], which is the main driving force for the micellization process. There are two main contributions for the hydrophobic effect [2]. The first contribution is associated with the structured water molecules, i.e. ordered water molecules, in the vicinity of the surface of the hydrophobic tail [2,4,114]. When hydrophobic tails of free surfactant monomers are surrounded by water, the water molecules form a single layer in which vicinal water molecules have fewer conformations available than “free” water because the vicinal water molecules can not be hydrogen bonded to the hydrophobic tail. In other words, free surfactants monomers increase the degree of the structure in the surrounding water, which leads to negative entropy, Figure 5.14(a). Tanford [8] discussed this behavior in detail to account for the very slight solubility of hydrocarbons in water. Hence the strength or number of effective hydrogen bonds between the vicinal water molecules increase, which gives rise to a negative enthalpy. The second and opposite contribution arises from the large energy required to form a cavity in the water to accommodate the hydrophobic tail of the surfactant monomer, i.e. water has a very high cohesion energy density [2,114].

As the monomers are transferred into micelles, molecular interactions (arising from the tendency of the water molecules to regain their normal tetrahedral structure and the attractive dispersion, hydrophobic, forces between the hydrophobic tails) act cooperatively to remove the hydrophobic tails from the ordered state to the interior of the micelle [4], Figure 5.14(b).

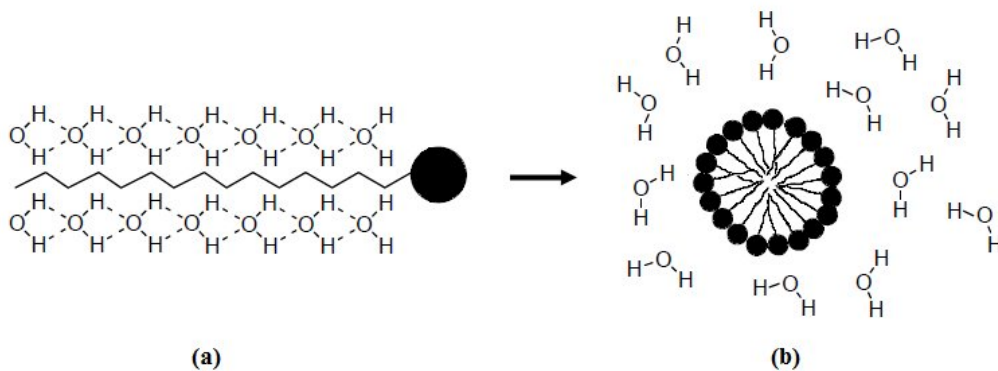


Figure 5.14 **(a)** Highly ordered water molecules and hydrophobic tail of the monomer. **(b)** Free water molecules at the micelle surface and disordered hydrophobic tails in the micelle.

The removal of a free monomer from water to the interior of the micelle at room temperature is always associated with a large increase in entropy and enthalpy, and hence a large negative Gibbs free energy [2,5,43,65,114], see Tables 5.8, 5.9 and 5.10. The increase in entropy and as well as in enthalpy are interpreted in terms of destruction of the ordered water molecules in the vicinity of the surface of the free monomer [43,73], and a large energy is released when the cavity holding the monomer collapses [2,114]. The result is an increase in the degree of freedom of the hydrophobic tail in the micelle core [2,43,114]. The temperature dependence of the entropy and enthalpy of transfer of the surfactant monomer to the interior of the

micelle is entirely determined by the ordered water molecules since the contribution arising from the cavity formation is assumed to be temperature independent [114]. The balance between these two contributions is the cause of minimum in *cmc*, and maximum in adsorption with respect to temperature for ionic surfactants systems [114]. As the temperature is increased, the hydrogen bonds between the water molecules are partially broken down, and consequently, hydrophobic interactions become less significant. So, by increasing the temperature, the enthalpy values become more negative (exothermic) indicating that the micelle formation is favored energetically as well as entropically, Table 5.9. As a result, the calculated ΔH_{mic}° and ΔS_{mic}° have been found to be strongly correlated to each other, Figures 5.15(a) and (b).

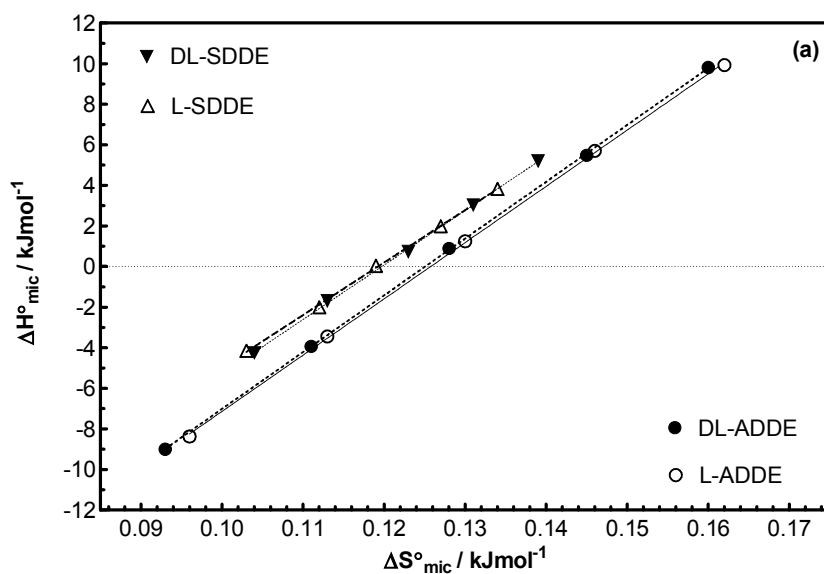


Figure 5.15 (a) The enthalpy/entropy ($\Delta H_{mic}^{\circ} / \Delta S_{mic}^{\circ}$) compensation plot of DL/L-ADDE and DL/L-SDDE. The dotted lines show the fitting of linear regression equation.

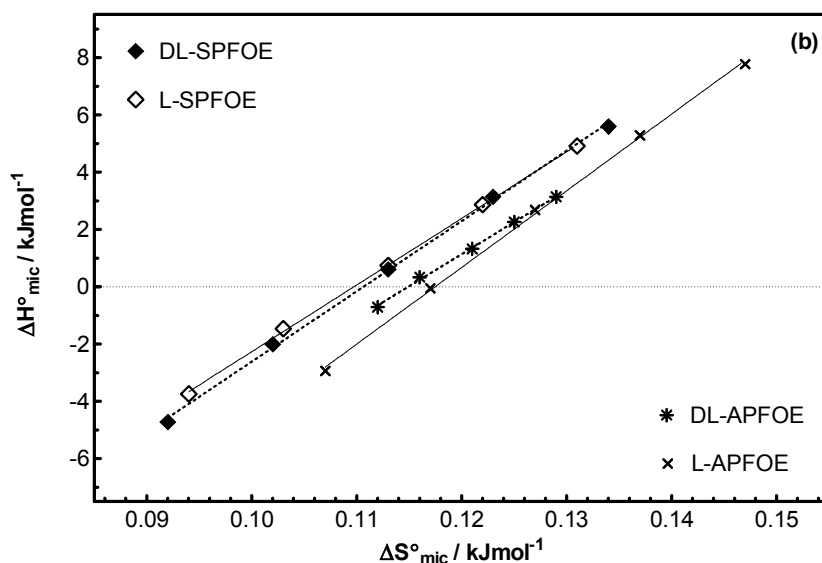


Figure 5.15 (b) The enthalpy/entropy ($\Delta H^{\circ}_{mic} / \Delta S^{\circ}_{mic}$) compensation plot of DL/L-APFOE and DL/L-SPFOE. The dotted lines show the fitting of linear regression equation.

5.5. Determination of the thermodynamic parameters of adsorption by surface tension measurements

Since the surface tension is related to the number of surfactant molecules per unit area adsorbed at the air/water interface, it decreases with increasing surface concentration; see Figures 5.5(a)-(h). As seen from Figures 5.5(a)-(h), for concentrations below but near the cmc , the slope of the curve is essentially constant, indicating that the surface concentration has reached a constant maximum value, i.e. the Γ_{max} . In this range the interface is considered to be saturated with the surfactant, and the continued reduction in the surface tension is due to mainly increased activity of the surfactant in the bulk phase rather than at the interface

[5]. Consequently, the $\Gamma_{\max}$ can be considered to be equal to the actual surface concentration without significant error for the surfactants.

The surface tension measurements can be used to determine the various adsorption parameters at air/water interface. The aqueous solutions of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE have been investigated at three different temperatures ($t = 15, 25$ and 35 °C), Figure 5.5(a)-(h), in order to understand the adsorption process in these systems. The first parameter that has been obtained from the slope of the linear fit of the data below the *cmc* and equation (2.12) is the maximum total amount of surfactant that can be adsorbed on the surface or in other words surface excess concentration ($\Gamma_{\max}$). Then, by using the $\Gamma_{\max}$ values, the minimum area per head group of the molecule at the air/water interface ($A_{\min}$) for our systems has been calculated. The calculated values of the $\Gamma_{\max}$ and $A_{\min}$ are presented in Table 5.11(a) and (b), respectively.

$t / ^\circ\text{C}$	$\Gamma_{\max} / \times 10^{10} \text{ mol cm}^{-2}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	2.87	2.83	2.68	2.68	2.78	2.85	1.53	1.52
25	2.42	2.36	2.20	2.22	2.74	2.72	1.44	1.45
35	1.88	1.83	1.96	2.00	2.44	2.44	1.31	1.31

(a)

Table 5.11 (a) The $\Gamma_{\max}$ values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 25 and 35 °C.

t / °C	$A_{\min} / \pm 1 \text{ \AA}^2$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	58	59	62	62	60	58	109	109
25	69	70	76	75	61	61	116	114
35	88	91	85	83	68	68	127	127

(b)

Table 5.11 (b) The $A_{\min}$ values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 25 and 35 °C.

Table 5.11(a) and (b) indicate an interesting change in the $\Gamma_{\max}$ and $A_{\min}$ of our systems with the temperature. For all systems, it is observed that the $\Gamma_{\max}$ values decrease and the $A_{\min}$ values increase with raising the temperature. This increase in the $A_{\min}$ (or decrease in the $\Gamma_{\max}$) may be due to the increasing the molecular motion at higher temperatures [15,115,116]. If we compare the DL- and L-forms of these systems, it is seen that there is no significant difference in the $\Gamma_{\max}$ and $A_{\min}$ values of enantiomeric and racemic form of the esters. As known, the $A_{\min}$ is related to degree of packing and the orientation of the adsorbed surfactant molecule at the interface [5]. We also note that the $A_{\min}$ values are considerably higher for DL/L-SPFOE system than those for DL/L-APFOE. This effect is presumably brought about by the hydroxyl group (–OH) in the SPFOE system. It may be suggested that the intra- and inter-hydrogen bonding of the hydroxyl group due to the hydration in water increases the head group area, i.e. the $A_{\min}$, at the air/water interface [117]. In dodecyl esters, this effect is not so much pronounced. The values

of the $A_{\min}$ for dodecyl esters, ADDE and SDDE, are close to each other. Consequently, it is inferred that the hydrophobic tail, i.e. the fluorocarbon chain, play an important role in the adsorption process.

Other interesting parameters that obtained from the surface tension measurements are the effectiveness of the surface tension reduction (γ_{cmc}) and the surface pressure at the cmc , (π_{cmc}) and the efficiency of the surface tension reduction (pC_{20}). The γ_{cmc} was obtained from the value of the surface tension at the cmc , Figures 5.5(a)-(h). This value corresponded to the maximum lowering in surface tension. Furthermore, surface pressure at the cmc (π_{cmc}) was calculated from the difference between the surface tension of the pure water (γ_o) and the γ_{cmc} values. However, the efficiency of surfactants (C_{20}) in surface tension reduction was determined from the point at which the surface tension of the pure water decreased by 20 m.Nm⁻¹. As mentioned before, the efficiency is generally expressed as pC_{20} ($-\log C_{20} = pC_{20}$) rather than concentration, the C_{20} itself [5,18,40,93,118-120]. The quantities mentioned above that are regarded as important factors in determining the processes such as foaming, wetting, and emulsification properties of the surfactant [93] are listed in Table 5.12, respectively.

$\gamma_{cmc} \pm 0.5 / mNm^{-1}$								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	30.8	31.9	28.4	29.5	17.2	17.2	15.8	15.8
25	29.3	31.8	28.2	29.6	17.0	17.3	15.5	15.4
35	29.6	31.3	28.8	28.8	17.1	17.5	15.7	15.7

(a)

$\pi_{cmc} \pm 0.5 / mNm^{-1}$								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	42.7	41.5	45.1	44.0	56.3	56.3	57.7	57.7
25	42.7	40.2	43.7	42.4	55.0	54.7	56.5	56.5
35	40.8	39.0	41.6	41.6	53.2	52.9	54.7	54.6

(b)

pC_{20}								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	3.3	3.3	3.5	3.3	3.3	3.6	4.1	4.2
25	3.4	3.4	3.6	3.4	3.7	3.6	4.2	4.2
35	3.6	3.6	3.6	3.6	3.8	3.7	4.4	4.3

(c)

Table 5.12 **(a)** The γ_{cmc} , **(b)** π_{cmc} and **(c)** pC_{20} values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 25 and 35 °C.

As seen from the Table 5.12, the γ_{cmc} of the esters do not vary with the temperature. However, it is recognized that DL- and L-form of dodecyl esters, ADDE and SDDE, show a slight difference, where the γ_{cmc} values of the L-enantiomeric forms of both the ADDE and SDDE have slightly higher than their racemic forms. On the other hand, the γ_{cmc} values of the DL- and L-form of the partially fluorinated octyl esters, SPFOE and APFOE, are nearly same. Besides, their surface tension-concentration graphs, Figures 5.5(e)-(h), do not show any minimum, which indicates that they exhibit a high purity. Moreover, it is interesting to note that the surface tension reduction in the APFOE and SPFOE are almost twice those of the ADDE and SDDE. It has been reported that the fluorocarbon tail lowers the surface tension more readily than their corresponding hydrogenated homologous [29,37,61,108,109,121,122]. Although the APFOE and SPFOE are partially fluorinated surfactants, they exhibit excellent surface activity. As seen from the Table 5.12, they have significantly low γ_{cmc} values that range from approximately 15.4 to 17.5 m.Nm⁻¹ as compared to those of conventional cationic partially fluorinated surfactants [121]. In addition to this, it has been also observed that the head group polarity has an influence on the surface parameters. For instance, serine esters reduce the surface tension more than alanine esters.

It was found that the efficiency of our systems was high among their analogs [5]. A larger value of pC_{20} means that the surfactant is adsorbed more efficiently at the interface [5]. Consequently, it can be said that efficiency of the SPFOE is higher than those of other systems, because it reduces the surface tension more efficiently.

The thermodynamic parameters of adsorption Gibbs free energy (ΔG_{ad}°), enthalpy (ΔH_{ad}°) and entropy (ΔS_{ad}°), were calculated via the equations (2.15) – (2.18) [5,81,118,120], respectively. Table 5.13 shows the values of ΔG_{ad}° , ΔH_{ad}° and ΔS_{ad}° of the studied systems at different temperatures.

t / °C	T / K	$\Delta G_{ad}^{\circ} / kJmol^{-1}$							
		ADDE		SDDE		APFOE		SPFOE	
		DL	L	DL	L	DL	L	DL	L
15	288.15	-51.3	-51.4	-51.6	-51.1	-54.1	-54.4	-70.8	-70.7
25	298.15	-54.9	-54.6	-55.7	-54.6	-54.7	-55.4	-72.4	-71.9
35	308.15	-59.4	-59.5	-57.6	-56.7	-56.9	-57.5	-74.8	-74.5

(a)

t / °C	T / K	$\Delta H_{ad}^{\circ} / kJmol^{-1}$							
		ADDE		SDDE		APFOE		SPFOE	
		DL	L	DL	L	DL	L	DL	L
15	288.15	66.6	64.7	35.1	32.7	-14.0	-9.4	-12.6	-14.8
25	298.15	67.0	65.6	34.0	29.2	-13.3	-8.9	-12.1	-14.1
35	308.15	66.6	64.7	35.1	29.9	-14.0	-9.4	-12.6	-14.7

(b)

	$\Delta S_{ad}^{\circ} / kJmol^{-1}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
	0.41	0.40	0.30	0.28	0.14	0.16	0.20	0.19

(c)

Table 5.13 (a) The ΔG_{ad}° , (b) ΔH_{ad}° and (c) ΔS_{ad}° values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 25 and 35 °C.

The results in Table 5.13 reveal that the ΔG_{ad}° values are all negative and more negative than the ΔG_{mic}° . This indicates that the adsorption of these systems at the air/water interface is also spontaneous. The values of the ΔG_{ad}° of ADDE, SDDE and APFOE are nearly same whereas it is significantly high for SPFOE indicating that the adsorption is more favored than micellization for this system, Table 5.13 and Figure 5.16.

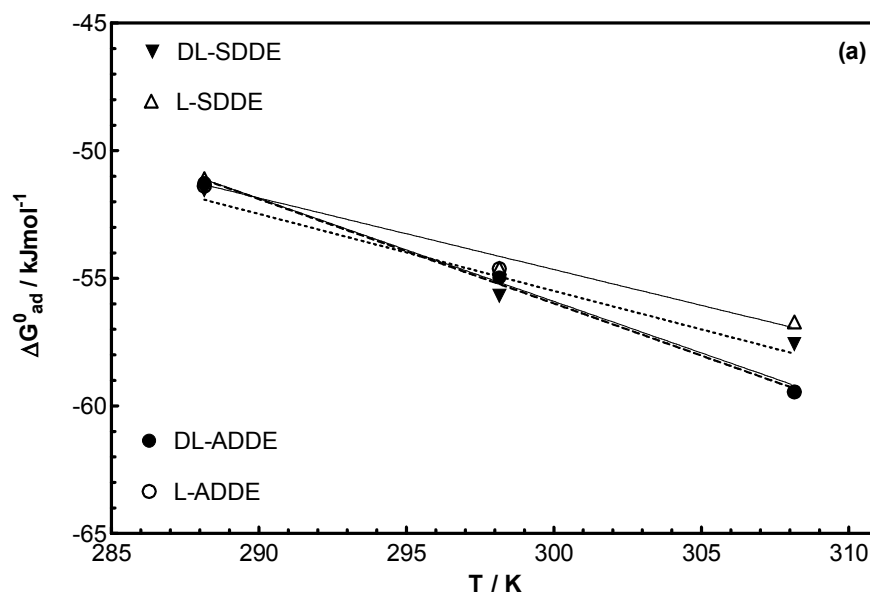


Figure 5.16 (a) The variation of the ΔG_{ad}° with temperature for DL/L-ADDE and DL/L-SDDE. The dotted lines show the fitting of linear regression equation

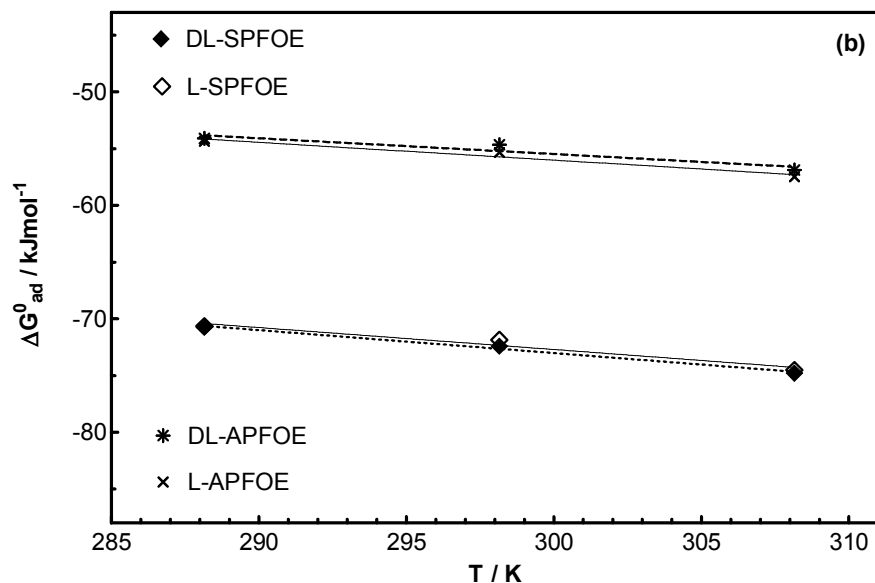


Figure 5.16 (b) The variation of the ΔG_{ad}° with temperature for DL/L-APFOE and DL/L-SPFOE. The dotted lines show the fitting of linear regression equation.

Another interesting feature is that the values of ΔH_{ad}° are positive for hydrogenated dodecyl ester while it is negative for partially fluorinated octyl esters. It appears that the hydrogen bonds between the water and the oxygen of the head group in the surfactant are favored during the adsorption process, which leads to positive ΔH_{ad}° . This process, however, appears to be not favored in the fluorinated surfactants which leads to negative values of the ΔH_{ad}° .

The calculated ΔS_{ad}° values are positive and greater than the values of the ΔS_{mic}° for the same surfactants. This result probably reflects that the hydrophobic tails are distributed at the air/water interface more randomly than in the interior of the micelle.

5.6. Determination of the volumetric properties of the micellar solutions by density measurements

It is generally observed that density as a function of surfactant concentration generally displays a discontinuity due to the micelle formation [41,95,123,124]; see Figures 5.7(a)-(h). However, in the literature molal properties are generally used to monitor structural changes, i.e. micelle formation, rather than density itself. These properties give more substantive information about the concentration dependence of self-aggregation. One of the molal properties that can be determined from the density measurements is the partial specific volume. In the present work, the partial specific volume of monomer ($\tilde{v}_m$) and micelles ($\tilde{v}_{mic}$) were determined from gradients of linear portions of plots of solution density (d) versus concentration and the equation 2.19, respectively.

The obtained results are summarized in Table 5.14(a)-(c) and their temperature dependencies are given in Figures 5.17 and 5.18. From these results, it was observed that the partial specific volumes, both $\tilde{v}_m$ and $\tilde{v}_{mic}$, increased with the temperature. The values of $\tilde{v}_{mic}$ were significantly higher than those of $\tilde{v}_m$ for each temperature.

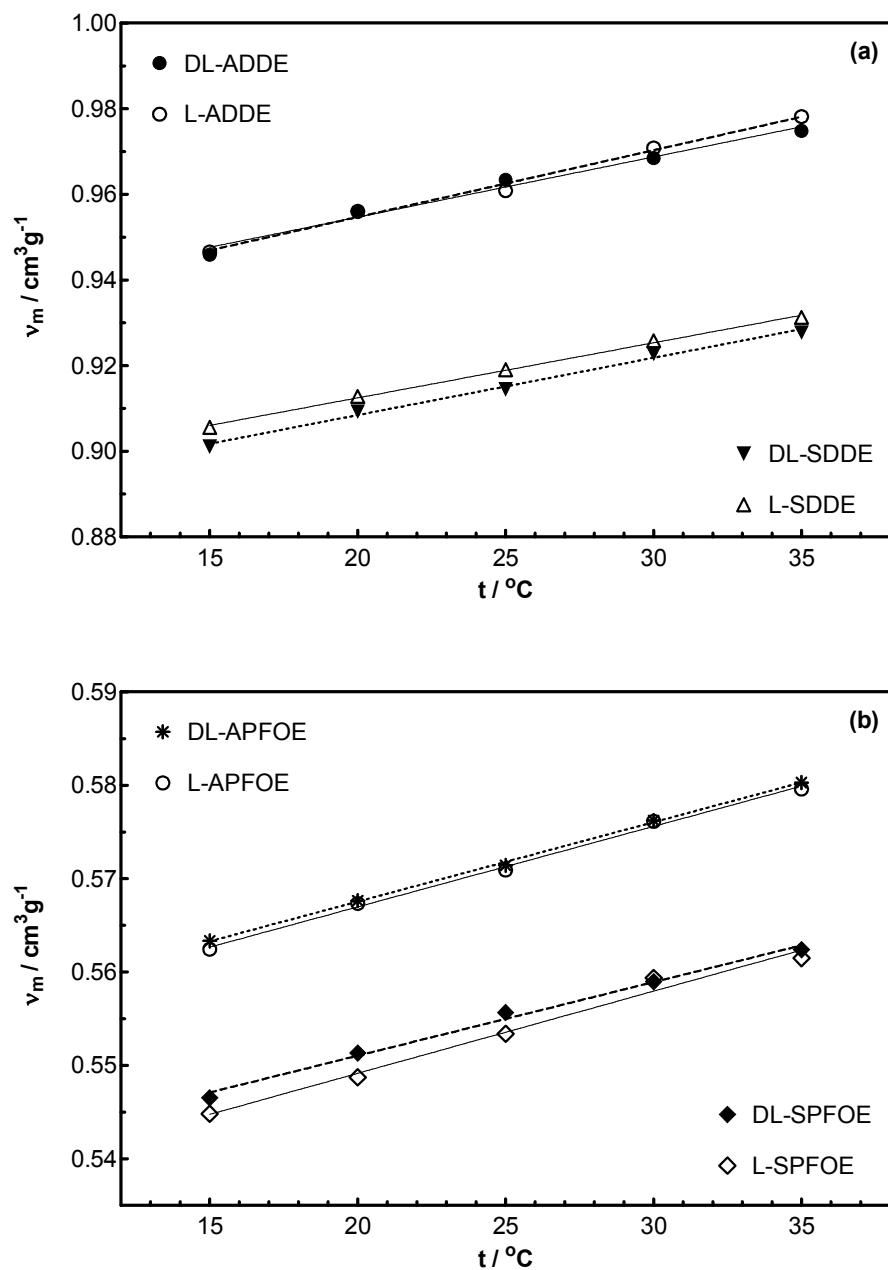
t / °C	$\tilde{v}_m / \text{cm}^3 \text{g}^{-1}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	0.9459	0.9466	0.9011	0.9056	0.5633	0.5624	0.5465	0.5448
20	0.9559	0.9560	0.9093	0.9128	0.5676	0.5673	0.5513	0.5487
25	0.9634	0.9609	0.9145	0.9191	0.5714	0.5709	0.5557	0.5534
30	0.9685	0.9709	0.9228	0.9258	0.5762	0.5761	0.5590	0.5594
35	0.9748	0.9782	0.9278	0.9312	0.5803	0.5796	0.5624	0.5615

(a)

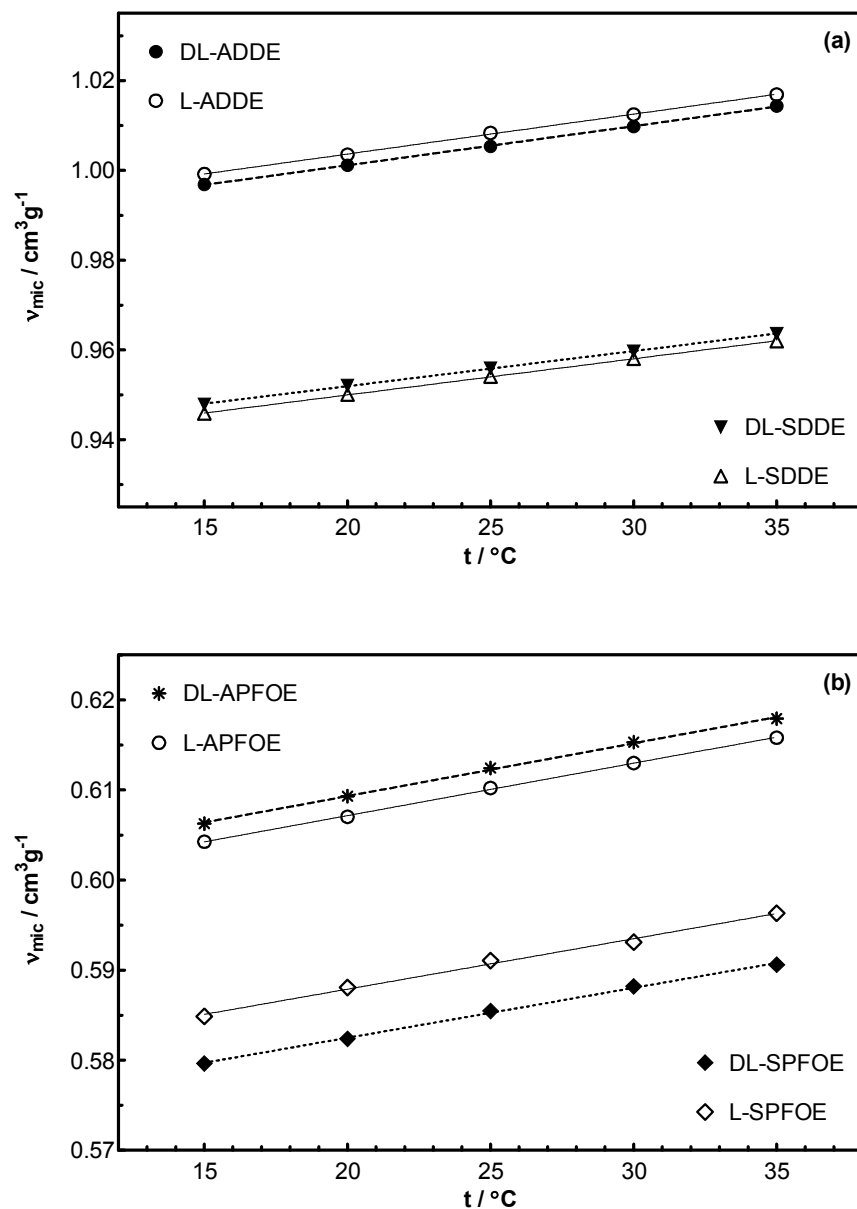
t / °C	$\tilde{v}_{mic} / \text{cm}^3 \text{g}^{-1}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	0.9968	0.9991	0.9478	0.9458	0.6063	0.6043	0.5796	0.5848
20	1.0011	1.0035	0.9520	0.9500	0.6093	0.6070	0.5824	0.5881
25	1.0053	1.0083	0.9559	0.9540	0.6124	0.6102	0.5855	0.5911
30	1.0098	1.0124	0.9597	0.9581	0.6153	0.6130	0.5882	0.5931
35	1.0143	1.0169	0.9636	0.9620	0.6179	0.6158	0.5906	0.5963

(b)

Table 5.14 The **(a)** $\tilde{v}_m$ and **(b)** $\tilde{v}_{mic}$ values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.



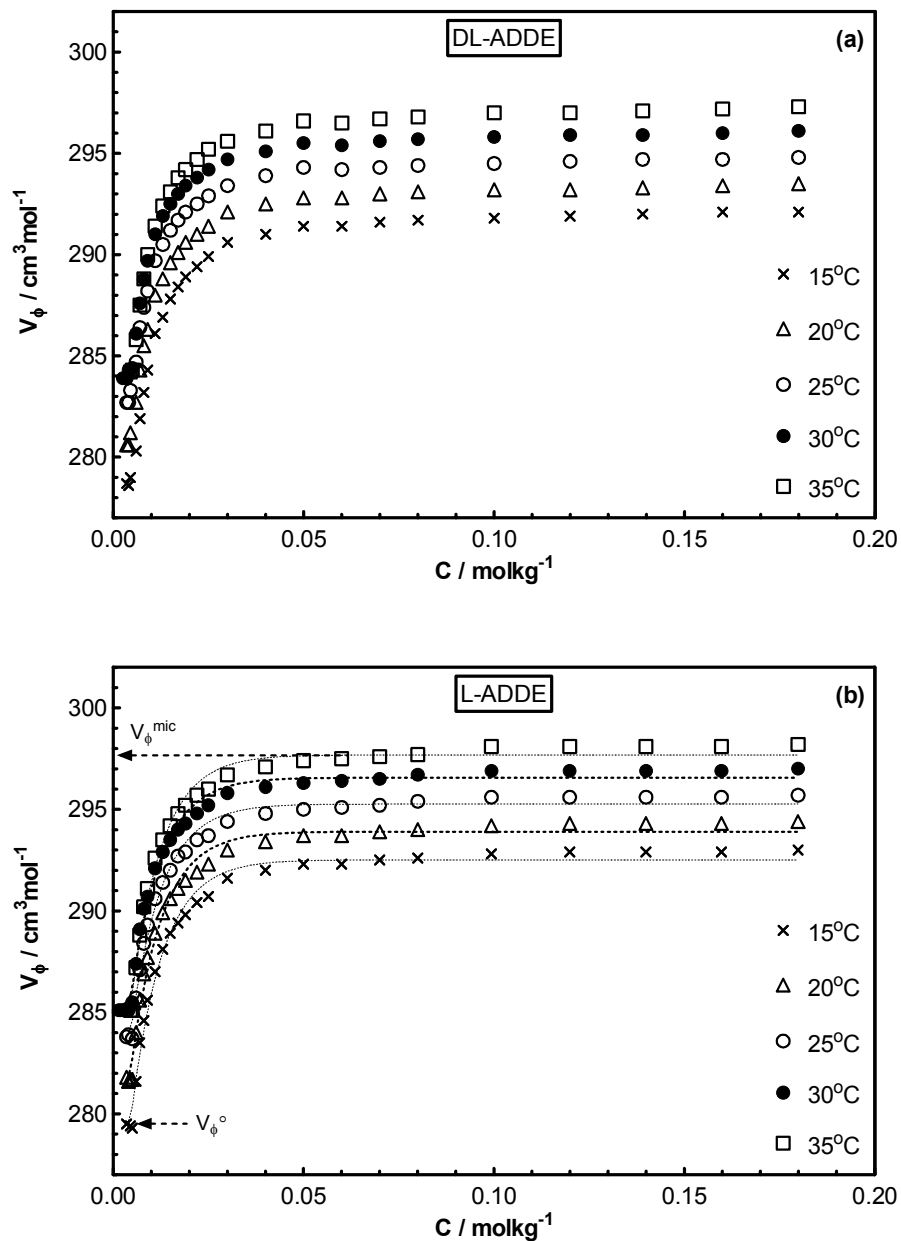
Figures 5.17 Temperature dependence of the $\tilde{v}_m$ of aqueous solutions of **(a)** DL/L-ADDE and DL/L-SDDE **(b)** DL/L-APFOE and DL/L-SPFOE.



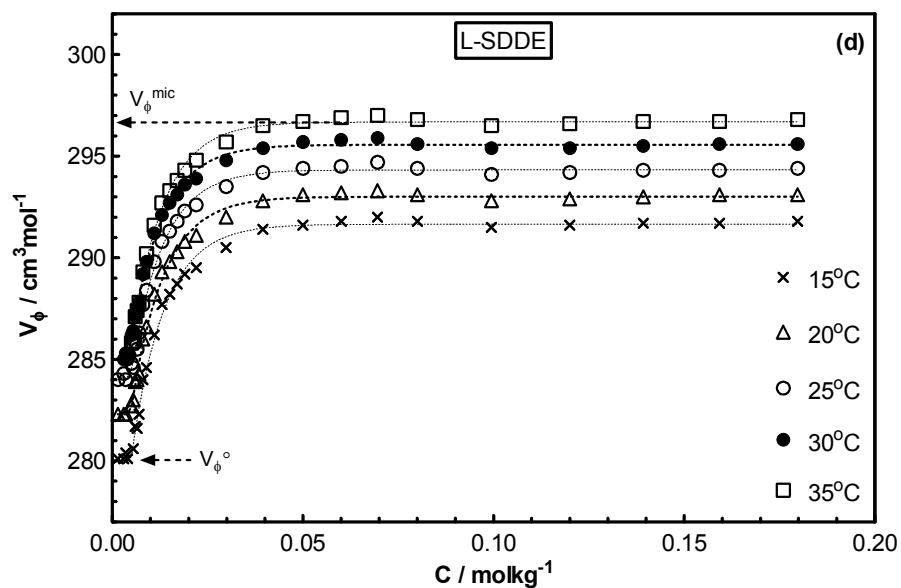
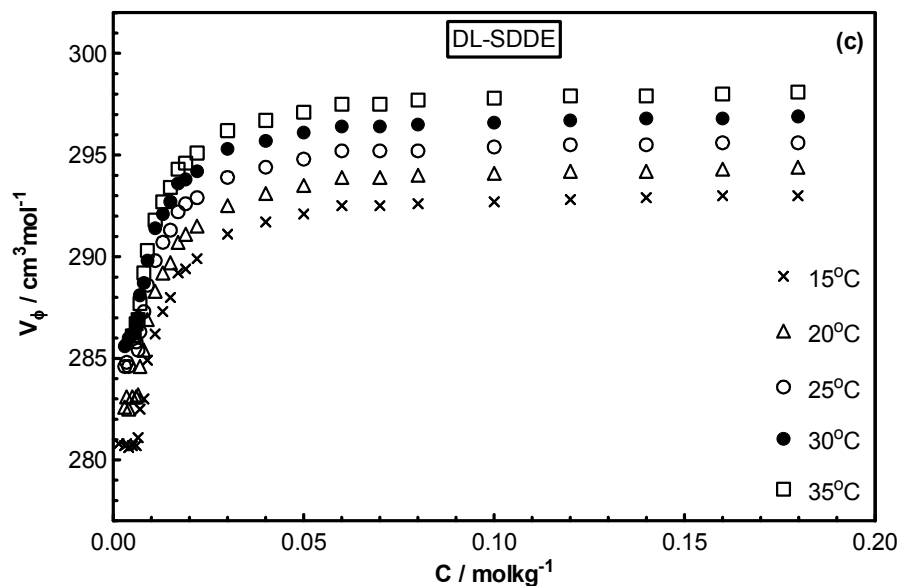
Figures 5.18 Temperature dependence of the $\tilde{v}_{mic}$ of aqueous solutions of **(a)** DL/L-ADDE and DL/L-SDDE **(b)** DL/L-APFOE and DL/L-SPFOE.

Furthermore, the apparent molal volumes (V_ϕ) of the surfactants in water were calculated by inserting the densities of the solution and water into the equation (2.20) at the investigated temperatures. The concentration and temperature

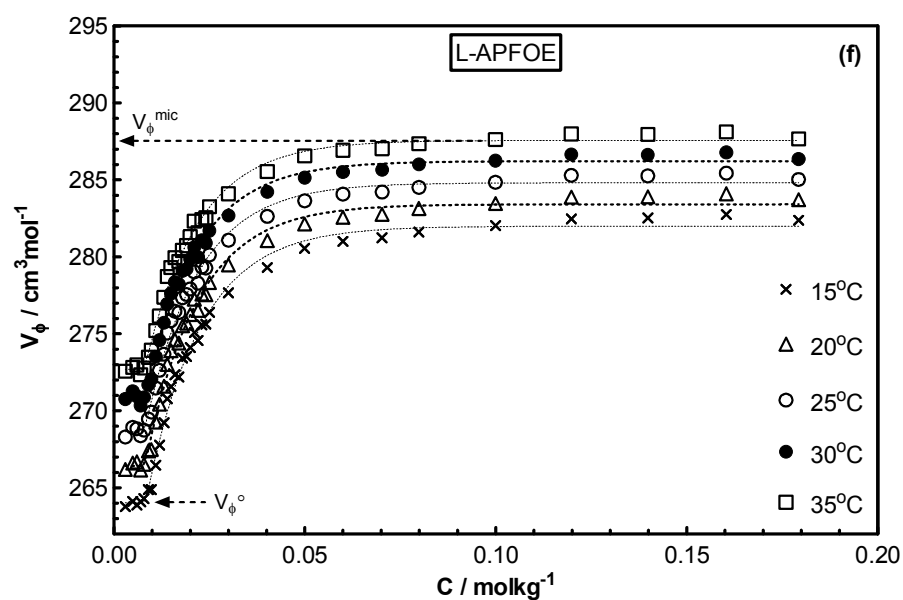
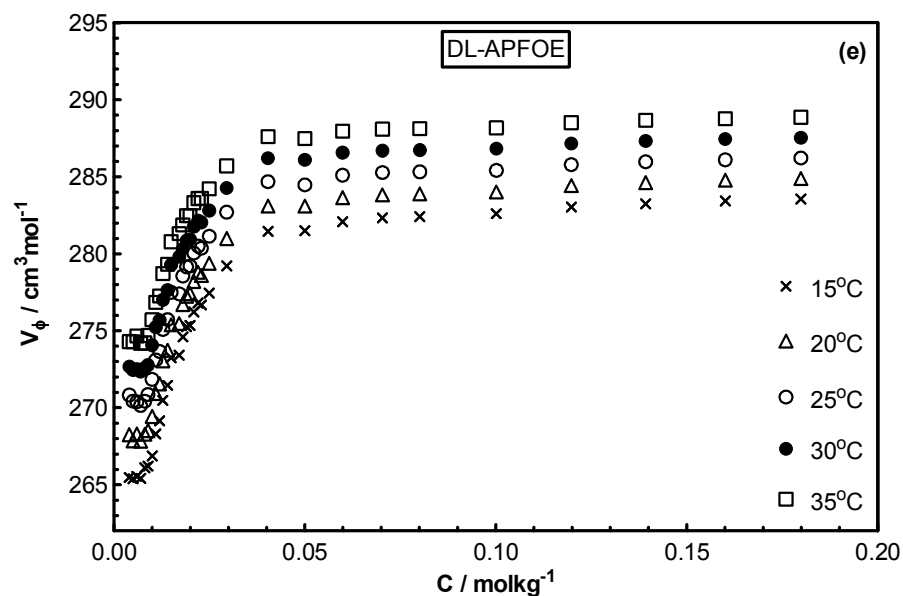
dependence of the V_ϕ values of all esters are given in Figures 5.19(a)-(h).



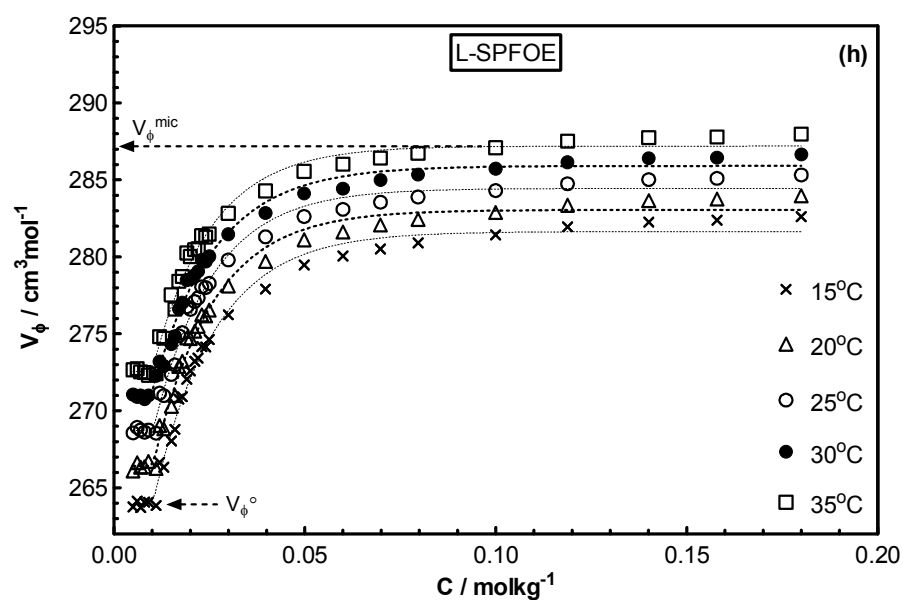
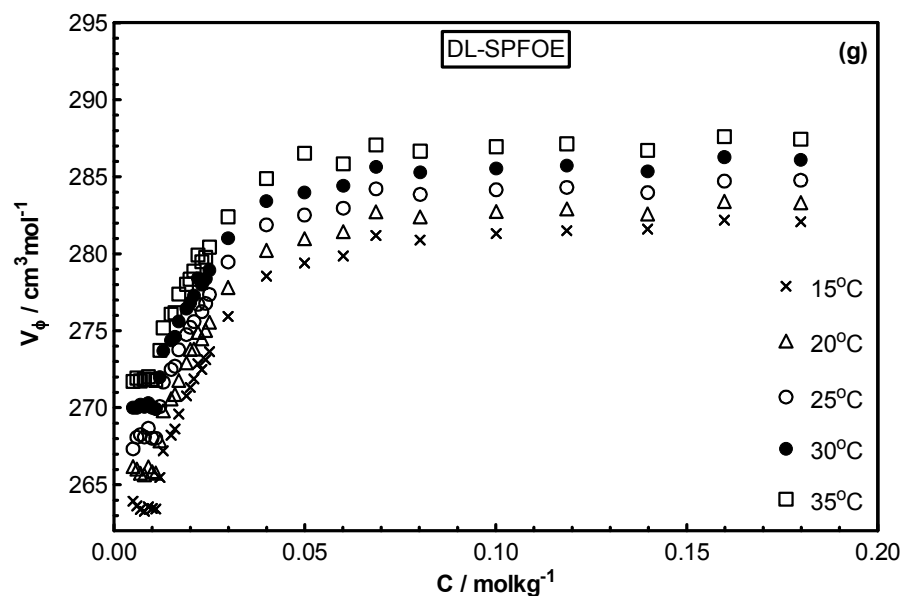
Figures 5.19 Variation of the V_ϕ with the concentration of (a) DL-ADDE and (b) L-ADDE at different temperatures. The arrows indicates the V_ϕ^{o} and V_ϕ^{mic} . The dotted line is drawn as a guide to the eye.



Figures 5.19 Variation of the V_ϕ with the concentration of (c) DL-SDDE and (d) L-SDDE at different temperatures. The arrows indicates the V_ϕ^o and V_ϕ^{mic} . The dotted line is drawn as a guide to the eye.



Figures 5.19 Variation of the V_ϕ with the concentration of (e) DL-APFOE and (f) L-APFOE at different temperatures. The arrows indicates the V_ϕ^o and V_ϕ^{mic} . The dotted line is drawn as a guide to the eye.



Figures 5.19 Variation of the V_ϕ of aqueous solutions with the concentration of **(g)** DL-SPFOE and **(h)** L-SPFOE at different temperatures. The arrows indicates the V_ϕ^o and V_ϕ^{mic} . The dotted line is drawn as a guide to the eye.

The data in the pre-micellar region and post-micellar region were extrapolated to the V_ϕ to find the apparent molal volume of monomers (V_ϕ^o) and micelle (V_ϕ^{mic}), respectively, see Figure 2.9 and Figures 5.19(a)-(h). The plots of the V_ϕ were typical of that displayed by all surfactant solutions [41,61,95,123,125].

As seen from Figures 5.19(a)-(h), the first inflection point in which a transition occurs corresponds to the *cmc*. It is also recognized that the apparent molal volumes of surfactants become independent of the concentration in the post-micellar region. In this region, the V_ϕ values have almost reached a constant value, which corresponds to the V_ϕ^{mic} value. This means that micelles with relatively constant structures are produced by increasing the concentration. The V_ϕ^o and V_ϕ^{mic} shown in Tables 5.15(a) and (b) were calculated using values from a best curve fit of the experimental V_ϕ data. Additionally, the change in the molal volumes of the studied systems upon micellization (ΔV_ϕ^{mic}) were also obtained from the V_ϕ^o and V_ϕ^{mic} by using the equation (2.21), Table 5.15(c).

t / °C	$V_\phi^o \pm 0.5 / \text{cm}^3 \text{mol}^{-1}$							
	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	278.7	279.5	280.7	280.2	265.6	264.0	263.5	263.9
20	280.6	281.7	282.8	282.3	268.1	266.4	265.9	266.4
25	282.7	283.9	284.7	284.1	270.4	268.6	268.1	268.7
30	284.0	285.1	285.8	285.1	272.5	270.8	270.1	270.9
35	284.2	285.1	286.1	285.8	274.3	272.7	271.8	272.5

(a)

$V_{\phi}^{mic} \pm 0.5 / cm^3 mol^{-1}$								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	291.7	292.5	292.6	291.7	282.9	282.0	281.6	281.6
20	293.0	293.9	293.9	293.0	284.3	283.4	282.9	283.0
25	294.4	295.3	295.3	294.3	285.6	284.8	284.4	284.4
30	295.7	296.6	296.5	295.6	287.0	286.2	285.8	285.9
35	296.8	297.7	297.6	296.7	288.4	287.6	287.2	287.2

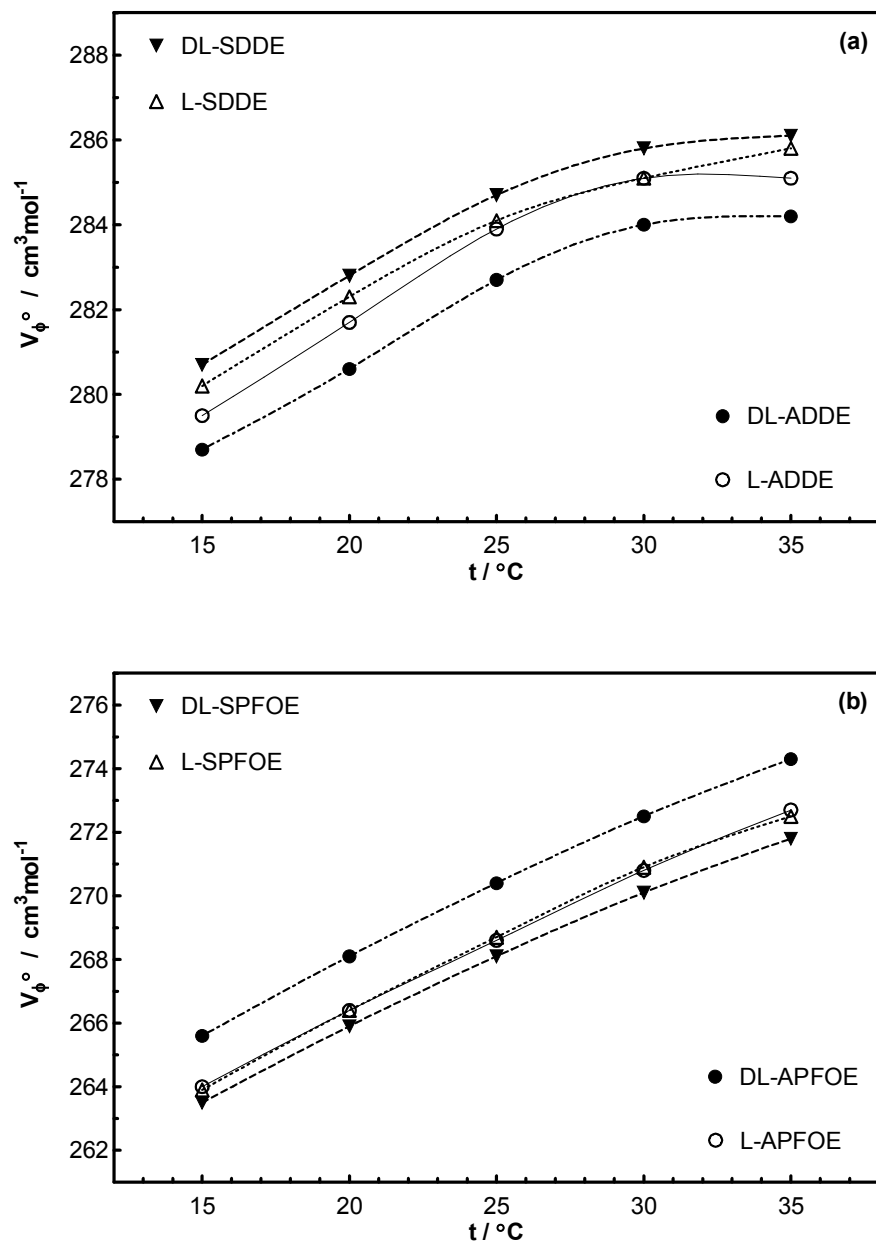
(b)

$\Delta V_{\phi}^{mic} \pm 0.5 / cm^3 mol^{-1}$								
t / °C	ADDE		SDDE		APFOE		SPFOE	
	DL	L	DL	L	DL	L	DL	L
15	13.0	13.0	11.9	11.5	17.3	18.0	18.1	17.7
20	12.4	12.2	11.1	10.7	16.2	17.0	17.0	16.6
25	11.7	11.4	10.6	10.2	15.2	16.2	16.3	15.7
30	11.7	11.5	10.7	10.5	14.6	15.4	15.7	15.0
35	12.6	12.6	11.5	10.9	14.1	14.9	15.4	14.7

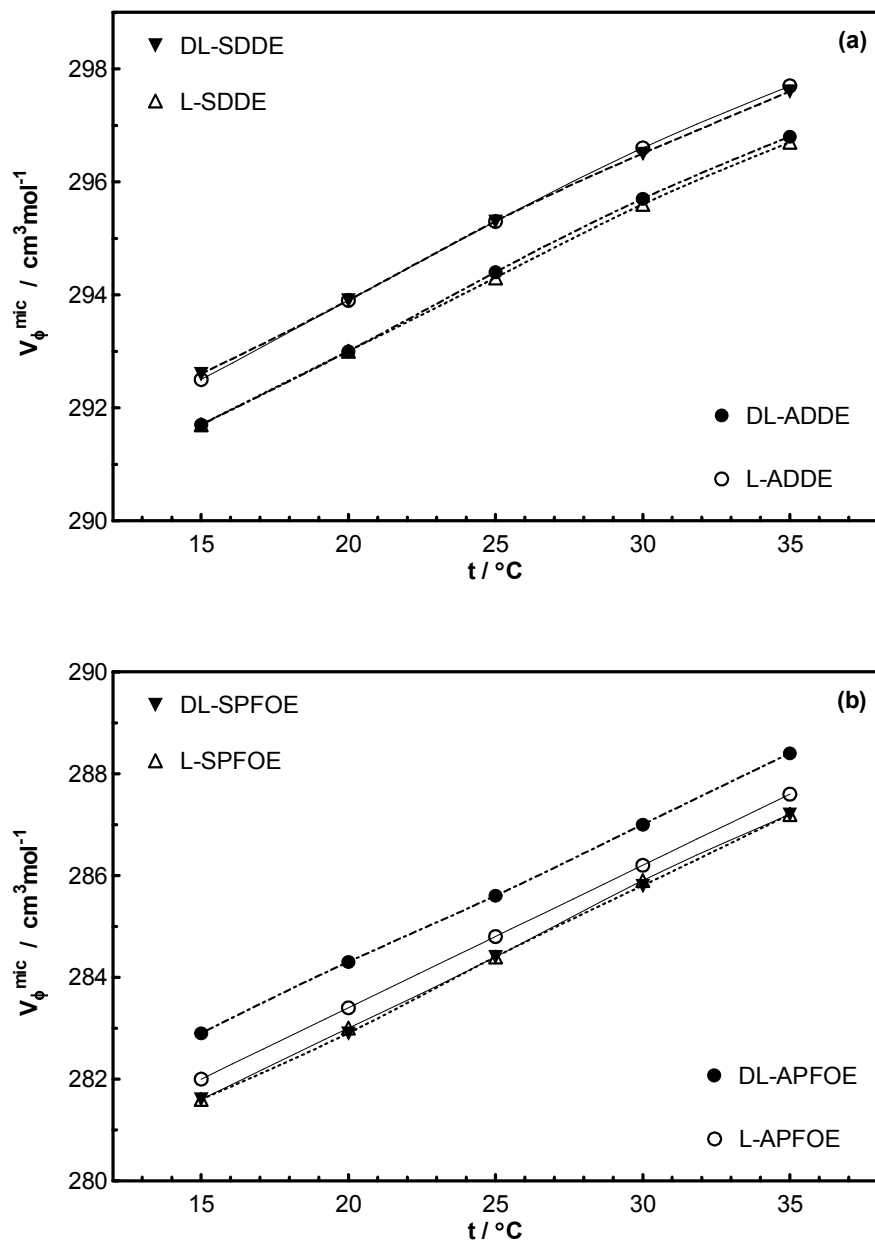
(c)

Table 5.15 The (a) V_{ϕ}^o , (b) V_{ϕ}^{mic} and (c) ΔV_{ϕ}^{mic} values of DL/L-ADDE, DL/L-SDDE, DL/L-APFOE, DL/L-SPFOE at 15, 20, 25, 30 and 35 °C.

Table 5.15 indicates that the V_{ϕ}^{mic} values of the studied systems are larger than those of the V_{ϕ}^o values in the investigated temperature range. In addition, all the V_{ϕ}^o and the V_{ϕ}^{mic} values increase gradually when the temperature is increased, Figure 5.20 and Figure 5.21.



Figures 5.20 Temperature dependence of the V_{ϕ}^o of aqueous solutions of **(a)** DL/L-ADDE and DL/L-SDDE **(b)** DL/L-APFOE and DL/L-SPFOE. The dotted line is drawn as a guide to the eye.



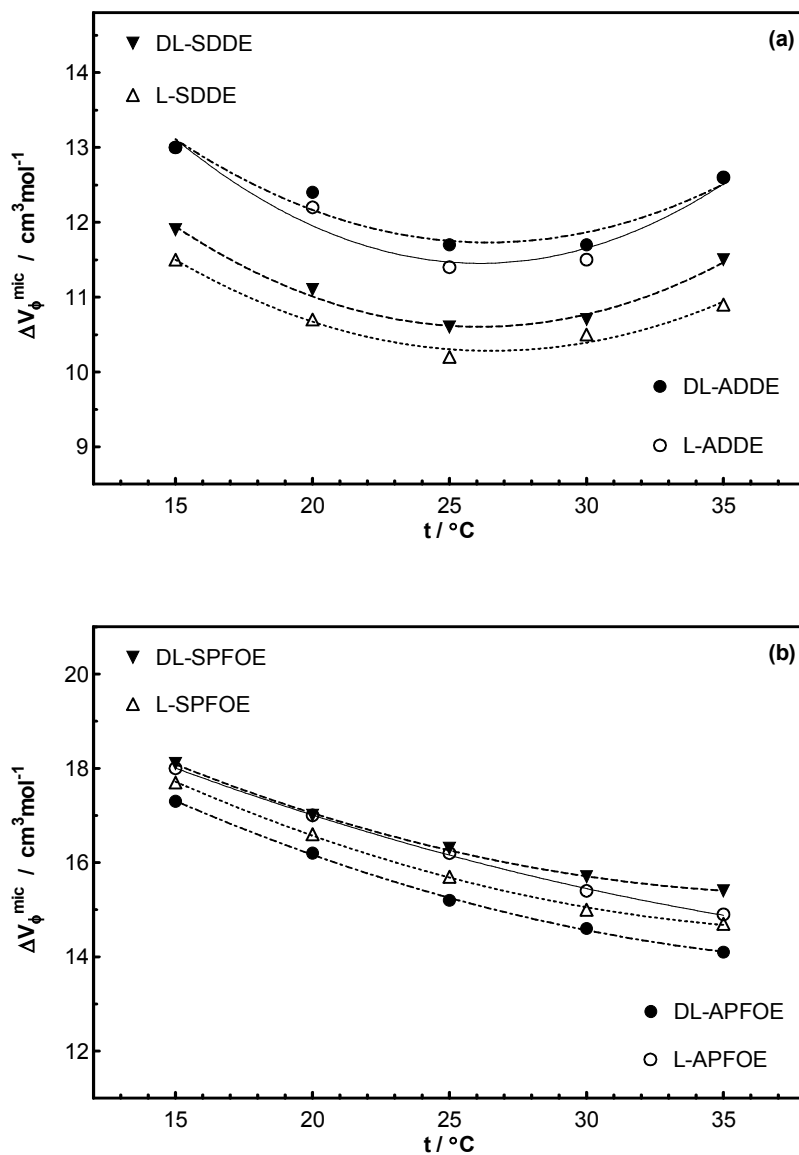
Figures 5.21 Temperature dependence of the V_{ϕ}^{mic} of aqueous solutions of **(a)** DL/L-ADDE and DL/L-SDDE **(b)** DL/L-APFOE and DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

According to the literature [41,123], the increase in the V_ϕ for monomeric surfactant is usually attributed to the reducing of the negative contribution to the V_ϕ^o from hydrophobic hydration and electrostriction. In the case of micellized surfactant, the increase in the V_ϕ^{mic} with the temperature is probably associated with increased dehydration on micellization. In addition to that the positive contribution to the V_ϕ^{mic} from the thermal expansion of the micelles should also be considered. The volume of the ionic groups at the micelle surface will also increase with the temperature [123].

These results indicate that the hydrophobic tail is a dominant factor in affecting the apparent molal volumes whereas the head groups play a minor role. The V_ϕ^o and V_ϕ^{mic} values of partially fluorinated octyl esters, DL/L-APFOE and DL/L-SPFOE, are smaller than those of the hydrogenated dodecyl esters, DL/L-ADDE and DL/L-SDDE. This is probably due to the randomly coiled conformations of the hydrocarbon chains, which occupy a large volume compared to the fluorocarbon chain.

Furthermore, variations of the ΔV_ϕ^{mic} with the temperature exhibited interesting behavior for the studied systems. It was observed that the ΔV_ϕ^{mic} decreased firstly with the temperature, then it showed a small increase as the temperature increased for the hydrogenated dodecyl esters, DL/L-ADDE and DL/L-SDDE, Figure 5.22(a). Besides, there was a deviation from linearity for the partially fluorinated systems, DL/L-APFOE and DL/L-SPFOE, Figure 5.22(b). It was also recognized that the

obtained results for the ΔV_{ϕ}^{mic} are consistent with the *cmc* results. As a result, one can say that the surfactant molecules in the micelles had a quite different environment than those in the monomeric state.



Figures 5.22 Temperature dependence of the ΔV_{ϕ}^{mic} of aqueous solutions of **(a)** DL/L-ADDE and DL/L-SDDE **(b)** DL/L-APFOE and DL/L-SPFOE. The dotted line is drawn as a guide to the eye.

If the V_{ϕ}^o , V_{ϕ}^{mic} and ΔV_{ϕ}^{mic} values for all systems are compared, it is observed that there are some differences between the racemic mixtures and the L-enantiomeric forms of the systems. But, these differences are considered to be in the range of experimental error.

5.7. Determination of the hydrodynamic radii of the micellar solutions by dynamic light scattering measurements

In this thesis, dynamic light scattering measurements (DLS) [19,21,24,27,28,38, 39,97,120] were used to obtain further information about the dimensions of the micelles of the studied systems, DL/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE, in the form of hydrodynamic radii (R_h). The R_h values of the aqueous solutions of the esters were obtained in the presence of NaCl (0.05m, 0.10 m, 0.20 m and 0.3 m) and at different *cmc* values, i.e. 2 *cmc*, 5 *cmc*, 10 *cmc*, 20 *cmc* and 50 *cmc*. For the investigated solutions, the intensity-weighted size distributions of the R_h showed single peak indicating that the micelle solutions were rather monodisperse. The measurements, which were taken without salt, did not give a uniform distribution of the formed aggregates, i.e. the spectrum of the DLS consisted of few bands corresponding to different aggregates in equilibrium, Figure 5.23(a)-(d).

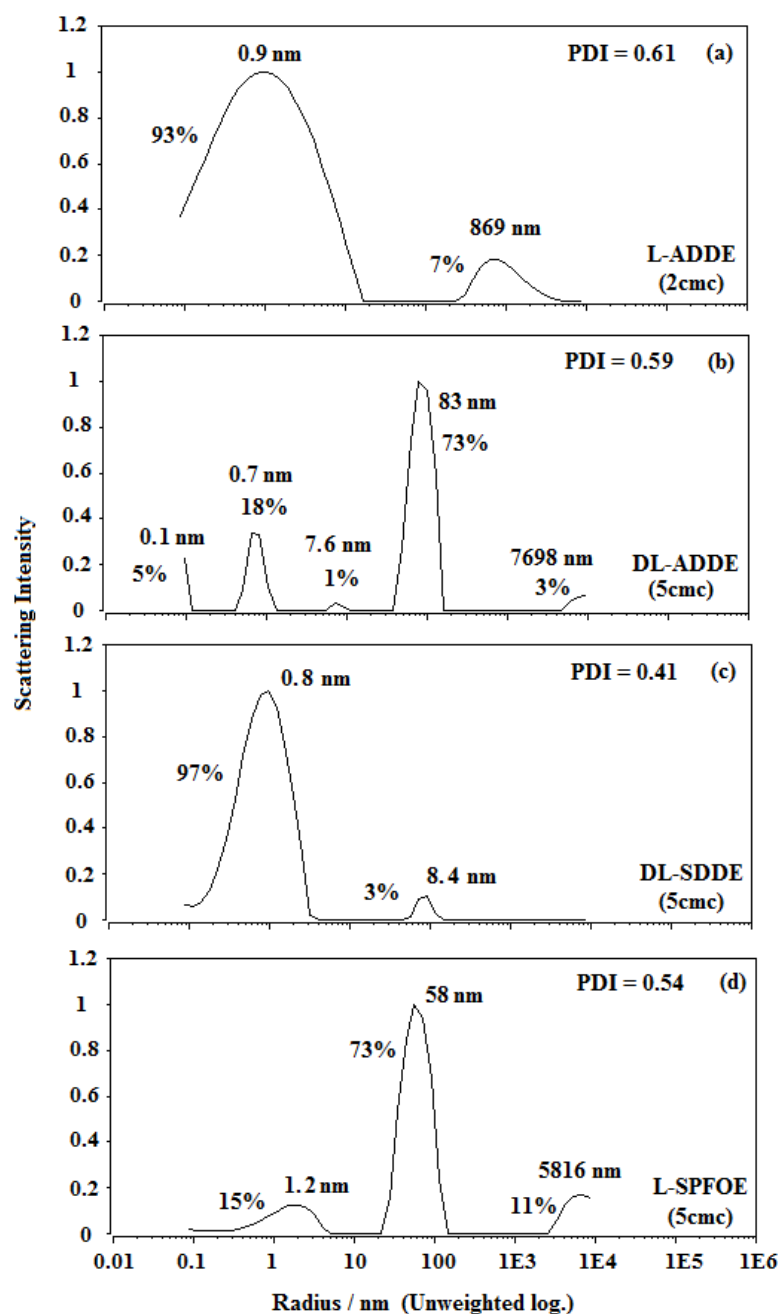


Figure 5.23 The intensity-weighted size distribution of the R_h of the micellar solutions of **(a)** L-ADDE, **(b)** DL-ADDE, **(c)** DL-SDDE and **(d)** L-SPFOE at different *cmc* concentrations without any salt at 25 °C. PDI is polydispersity index, which is a measure of uniform distribution of the shape of the micelles in the solution.

Therefore, DLS measurements were performed with different salt concentrations. The intensity-weighted size distributions of the R_h for the studied systems are given in Figures 5.24-5.51.

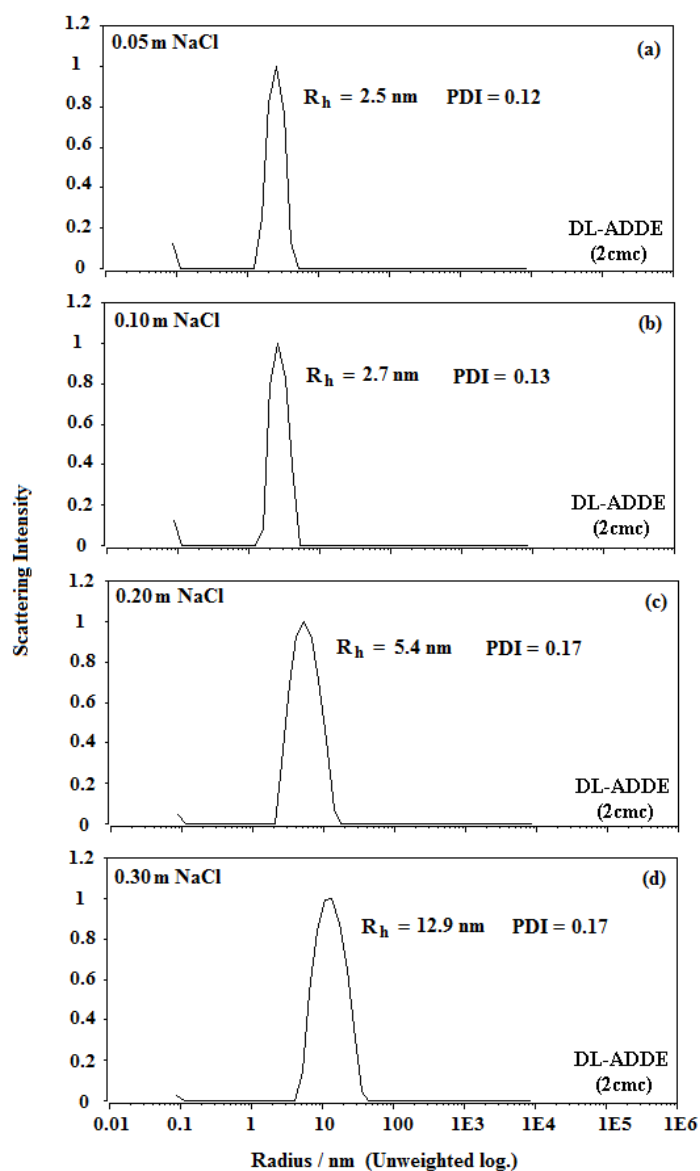


Figure 5.24 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-ADDE (2cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

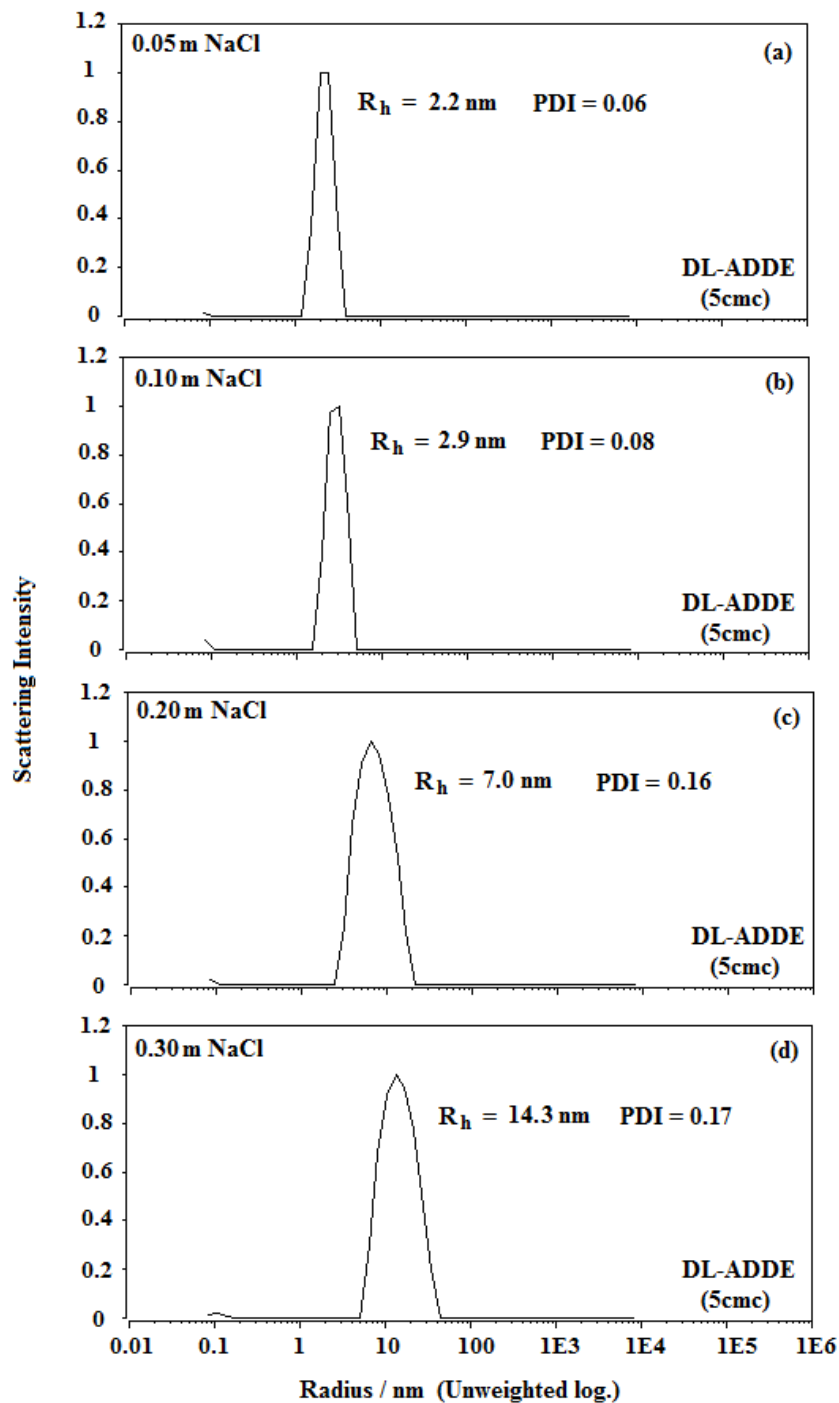


Figure 5.25 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-ADDE (5cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

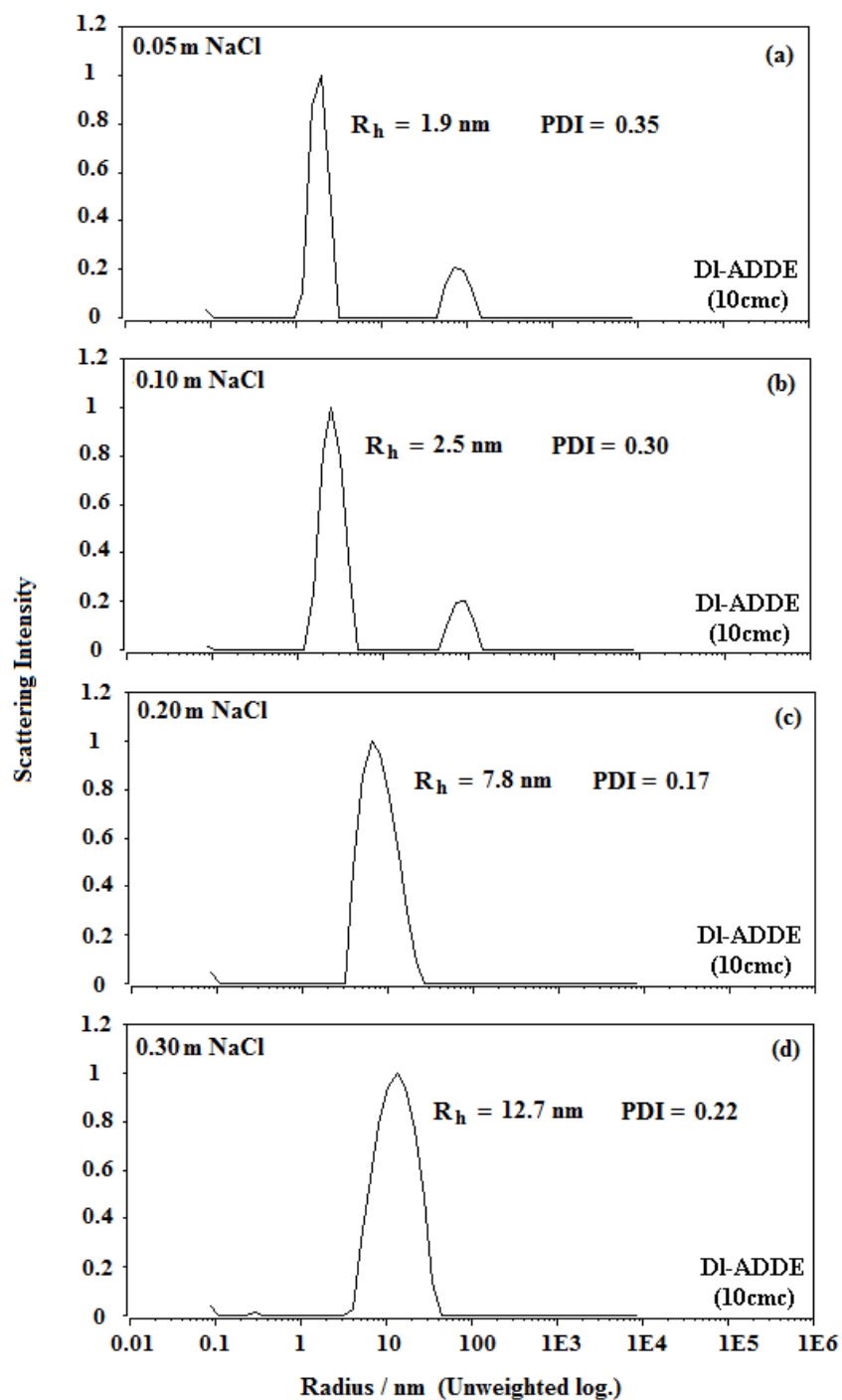


Figure 5.26 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-ADDE (10 cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

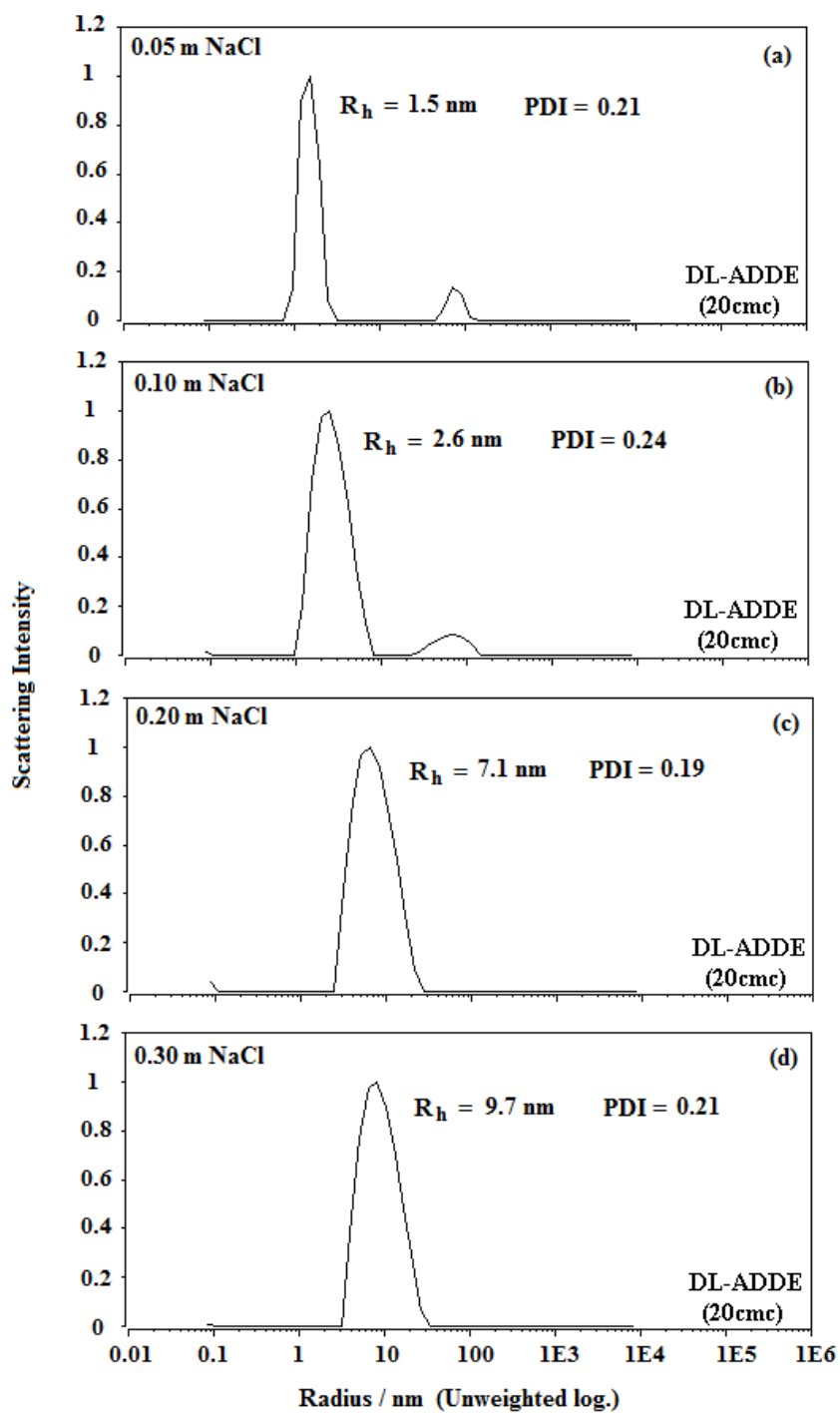


Figure 5.27 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-ADDE (20cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

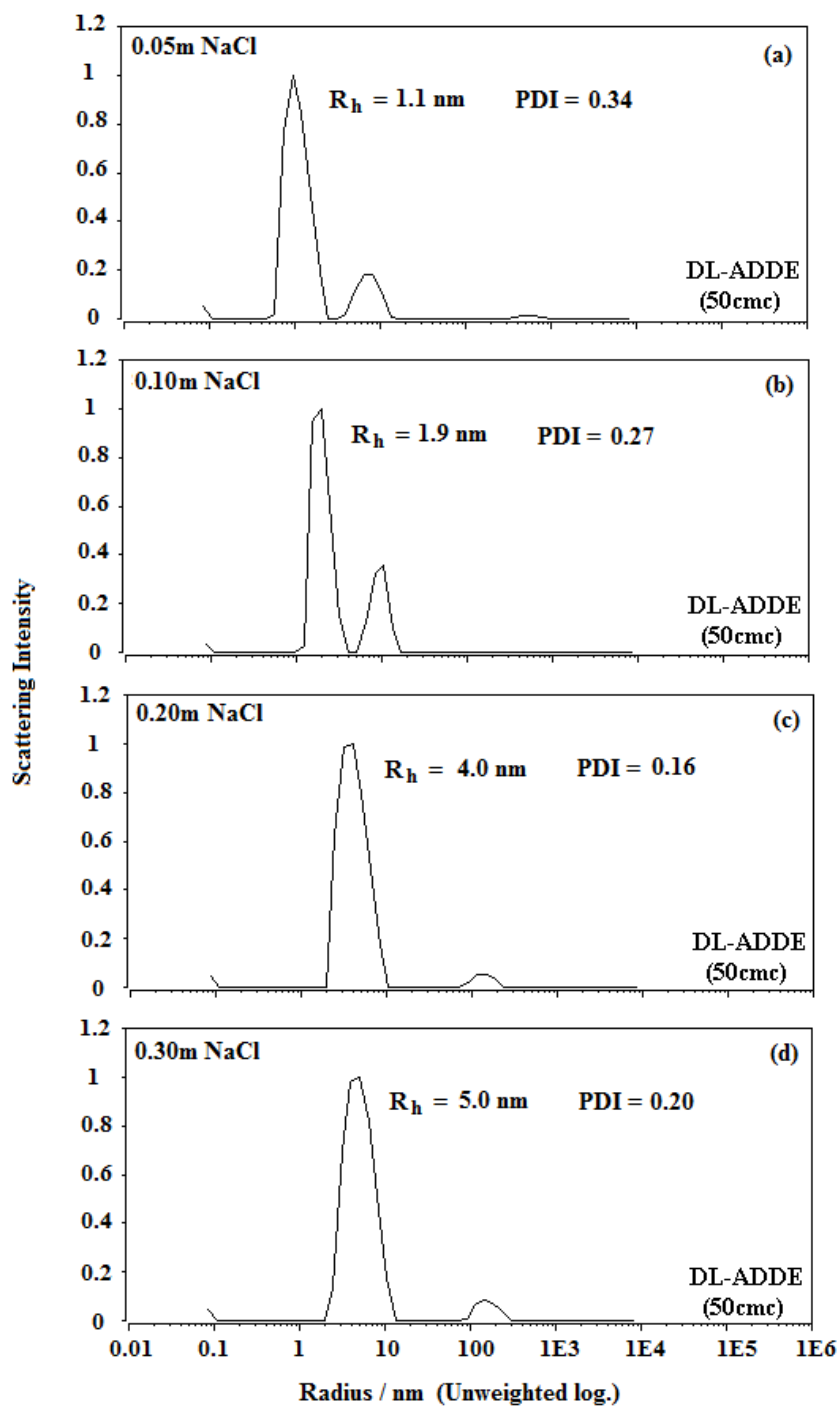


Figure 5.28 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-ADDE (50 cmc) at different NaCl concentrations (a) 0.05 m, (b) 0.10 m, (c) 0.20 m and (d) 0.30 m and at 25 °C.

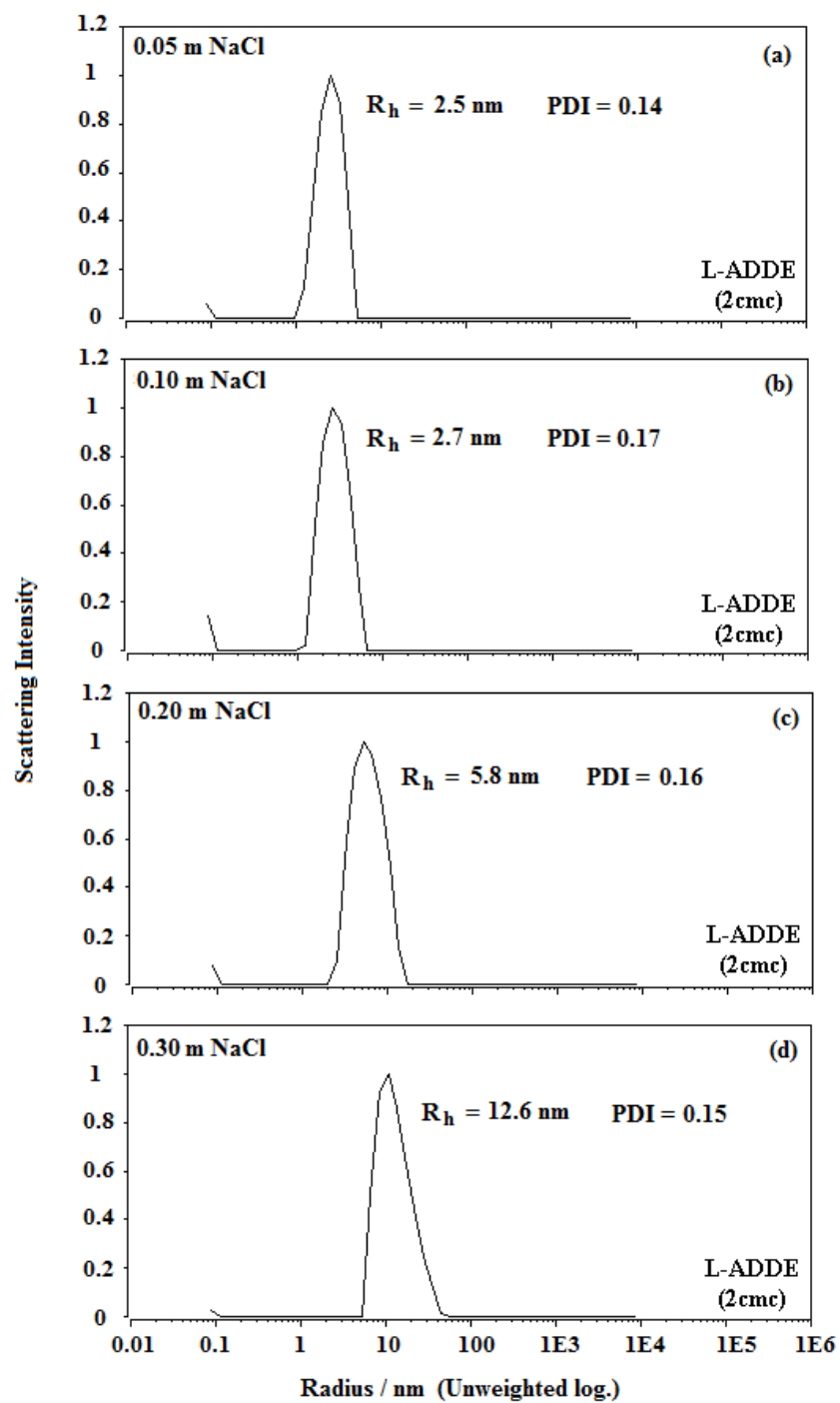


Figure 5.29 The intensity-weighted size distribution of the R_h of the micellar solutions of L-ADDE (2cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

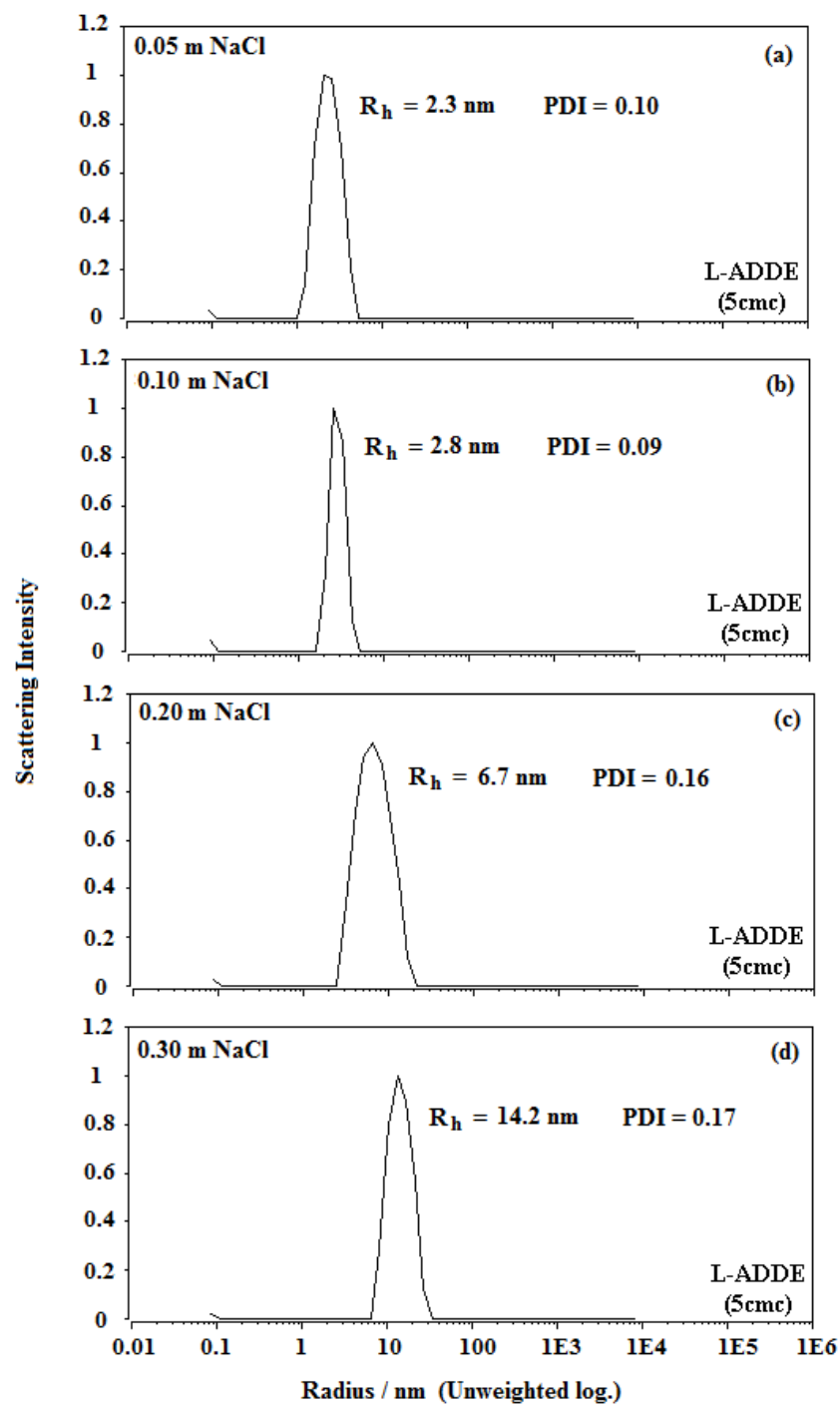


Figure 5.30 The intensity-weighted size distribution of the R_h of the micellar solutions of L-ADDE (5cmc) at different NaCl concentrations (a) 0.05 m, (b) 0.10 m, (c) 0.20 m and (d) 0.30 m and at 25 °C.

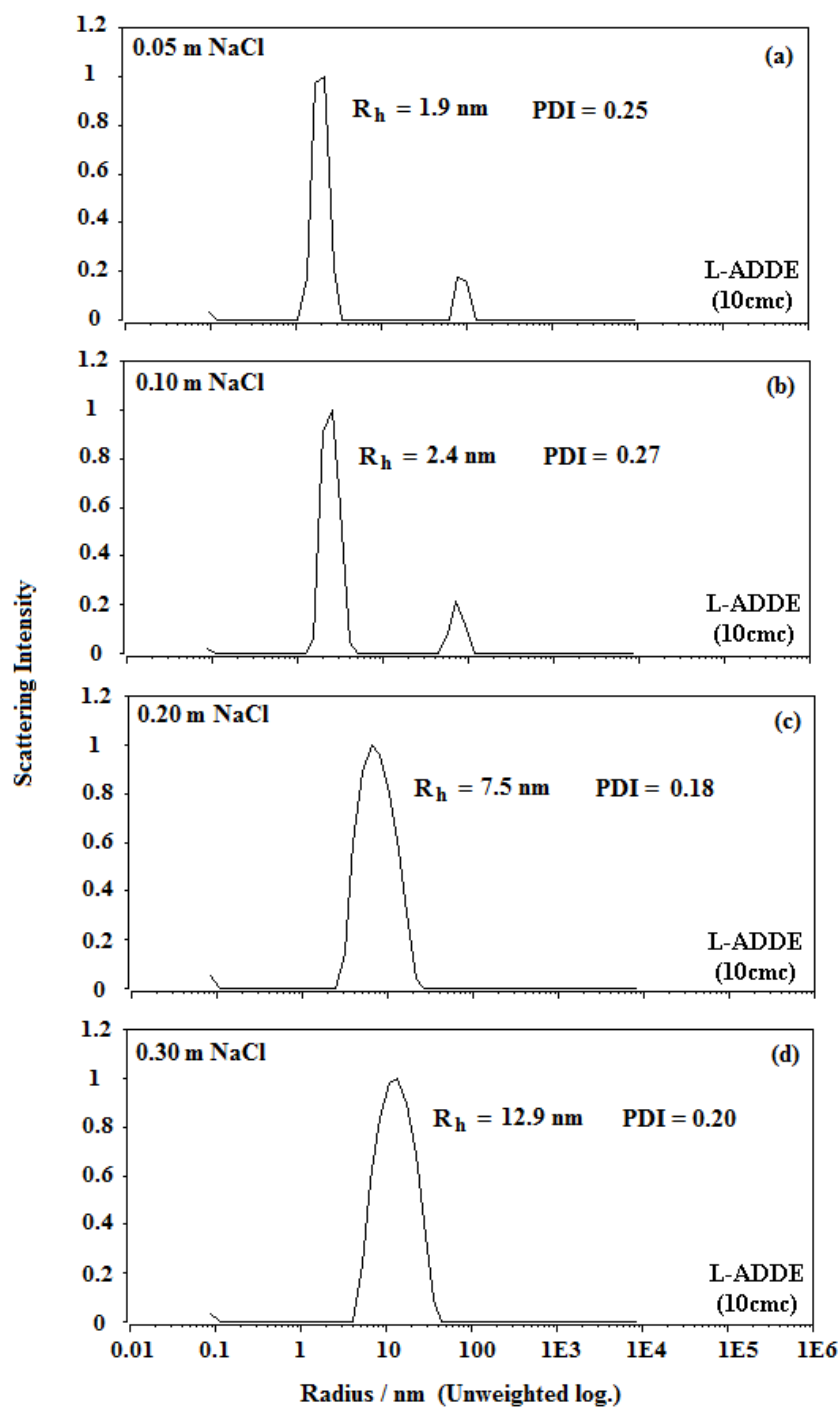


Figure 5.31 The intensity-weighted size distribution of the R_h of the micellar solutions of L-ADDE (10cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

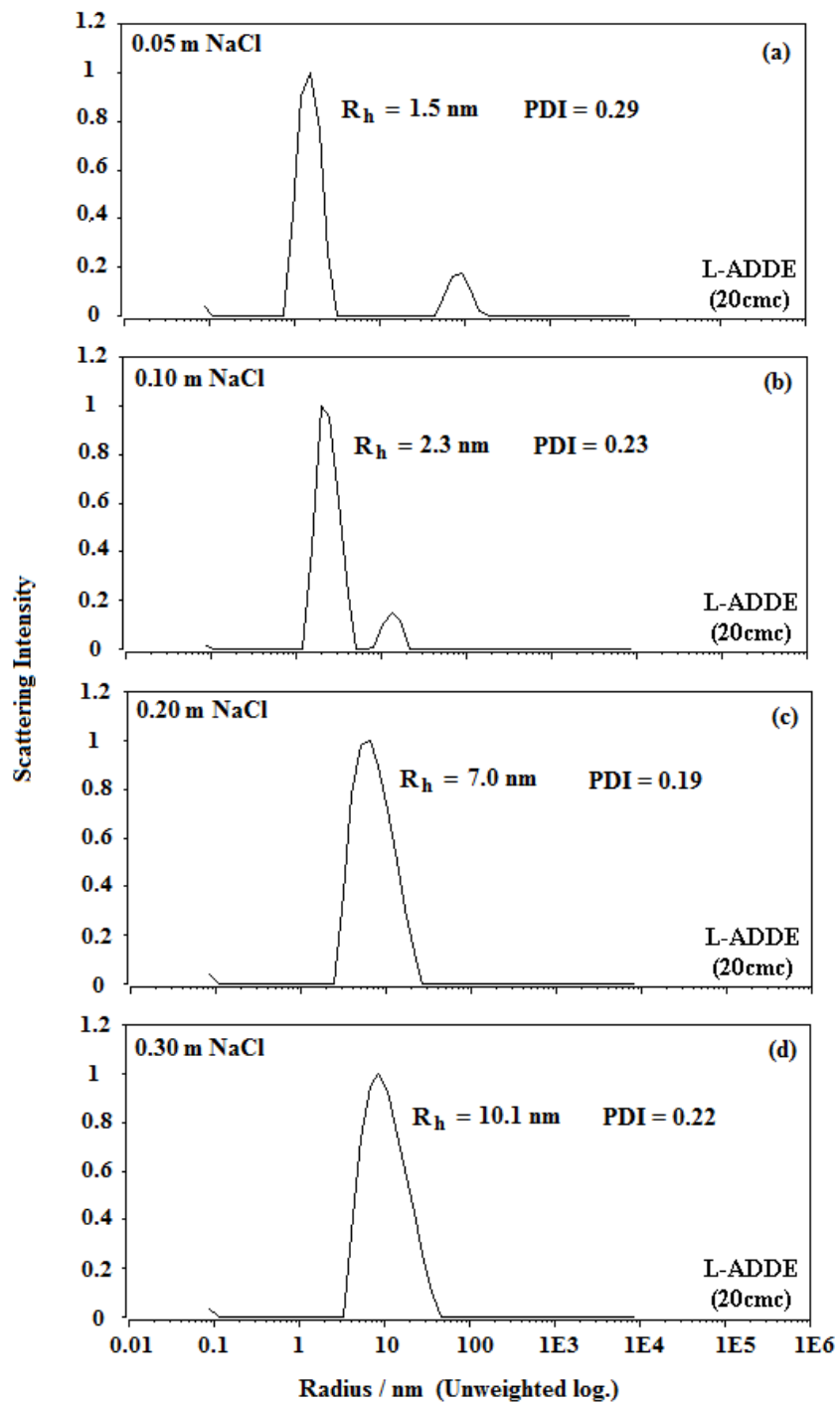


Figure 5.32 The intensity-weighted size distribution of the R_h of the micellar solutions of L-ADDE (20cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

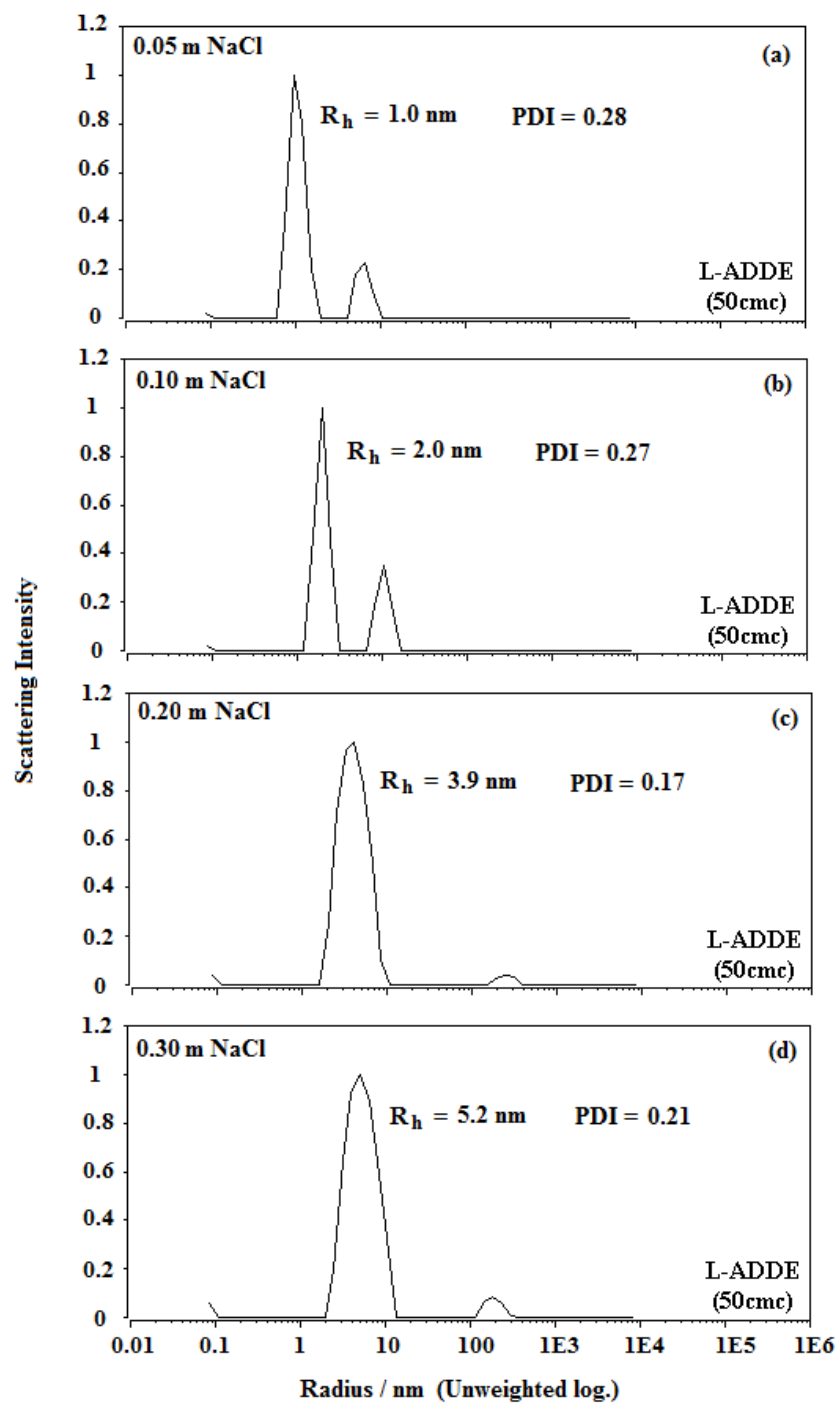


Figure 5.33 The intensity-weighted size distribution of the R_h of the micellar solutions of L-ADDE (50cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

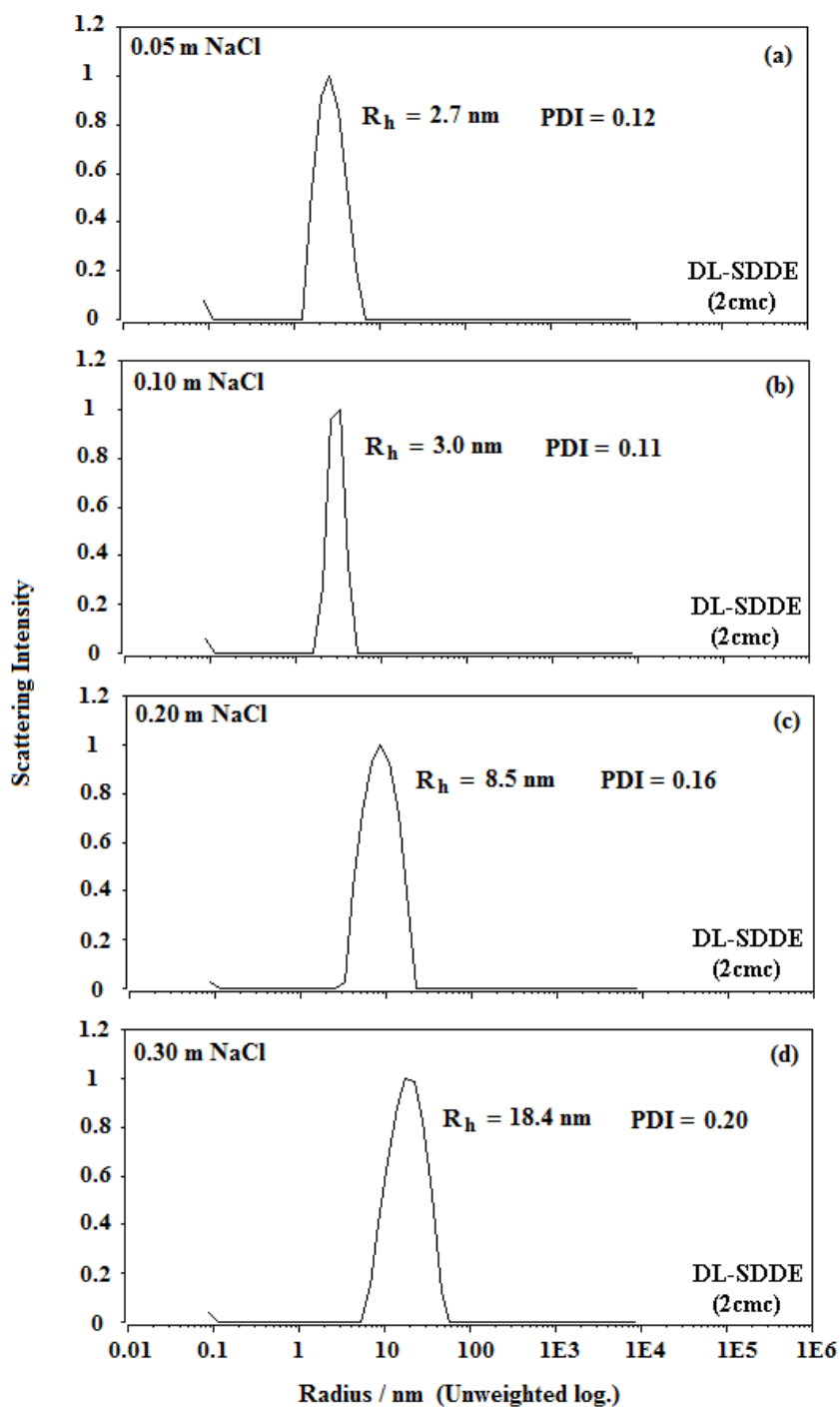


Figure 5.34 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-SDDE (2cmc) at different NaCl concentrations (a) 0.05m, (b) 0.10m, (c) 0.20m and (d) 0.30m and at 25 °C.

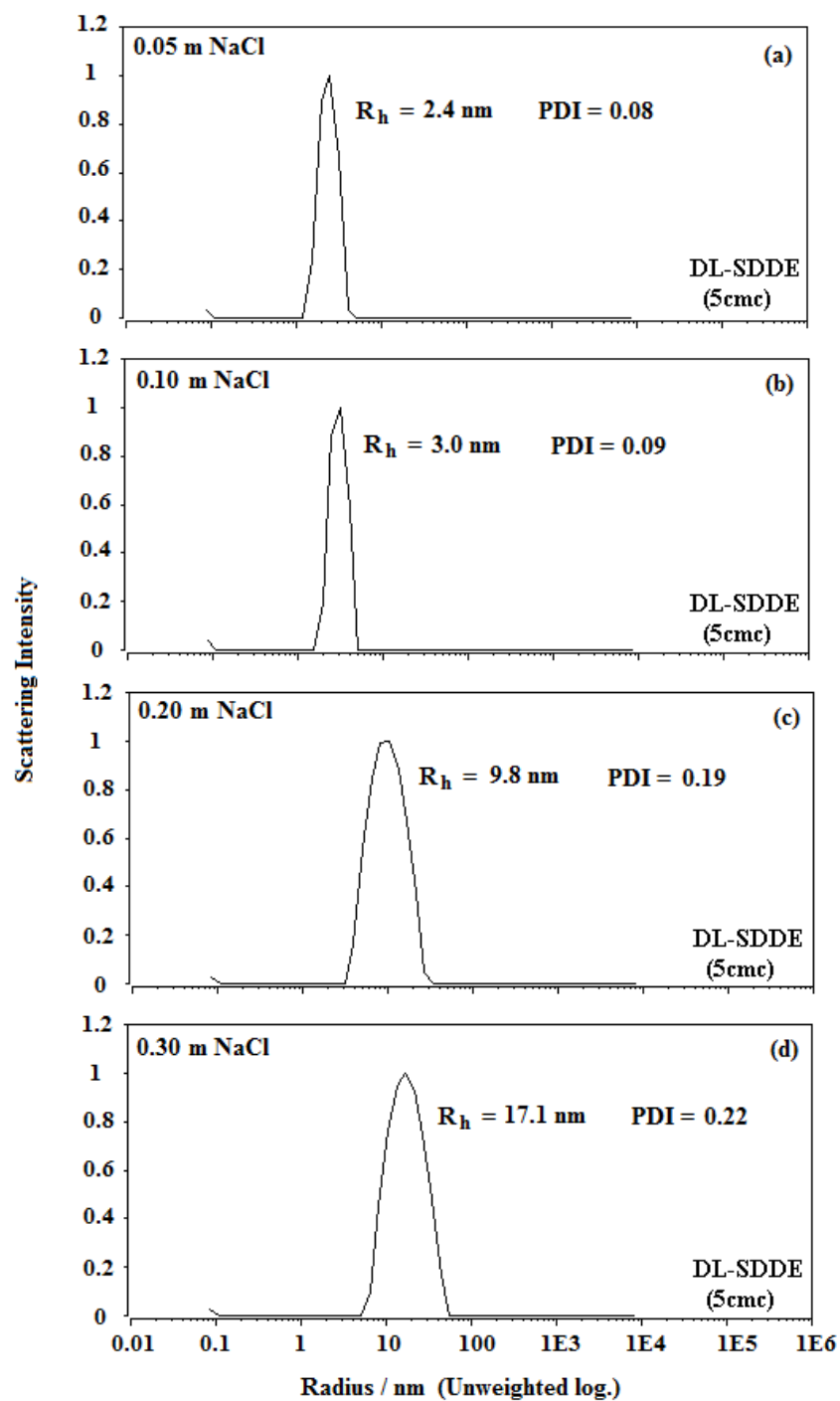


Figure 5.35 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-SDDE (5cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

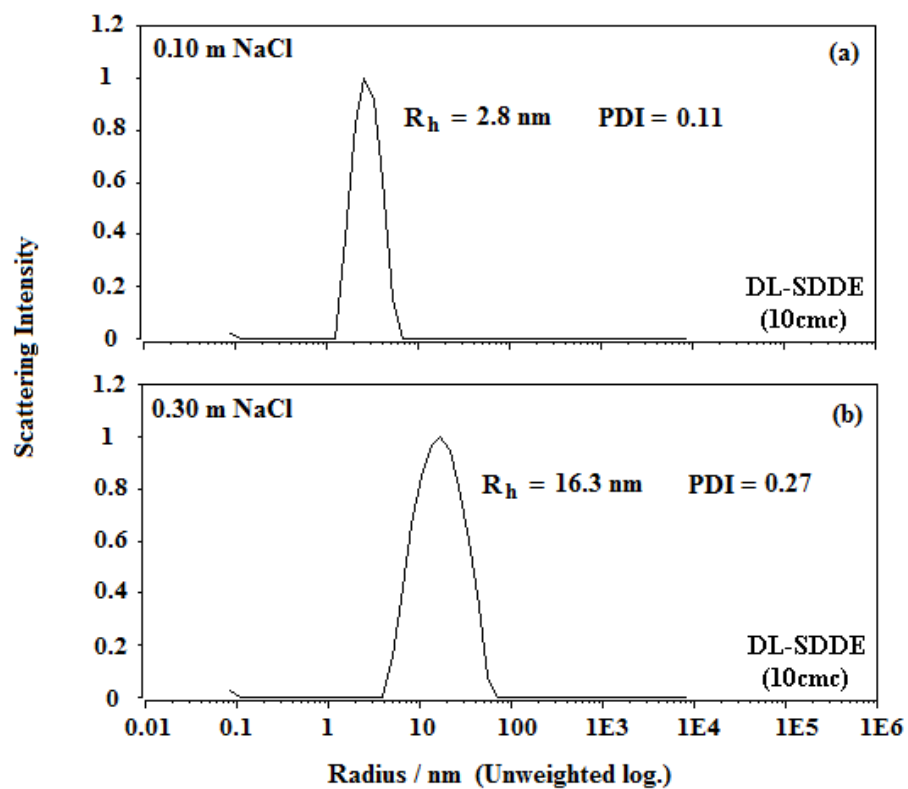


Figure 5.36 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-SDDE (10 cmc) at different NaCl concentrations **(a)** 0.10 m and **(b)** 0.30 m at 25 °C.

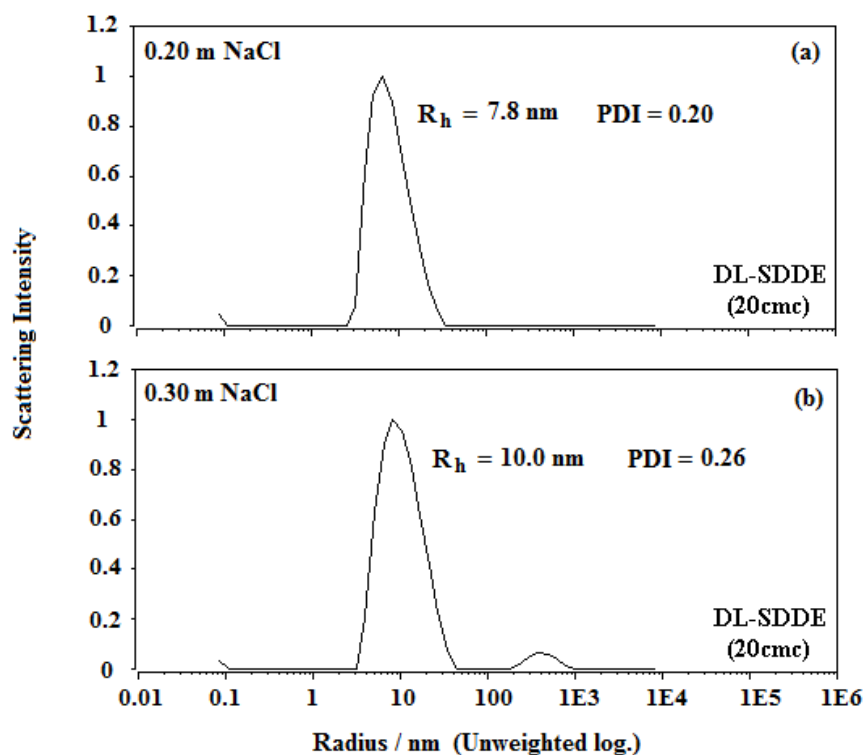


Figure 5.37 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-SDDE (20 cmc) at different NaCl concentrations (a) 0.20 m and (b) 0.30 m at 25 °C.

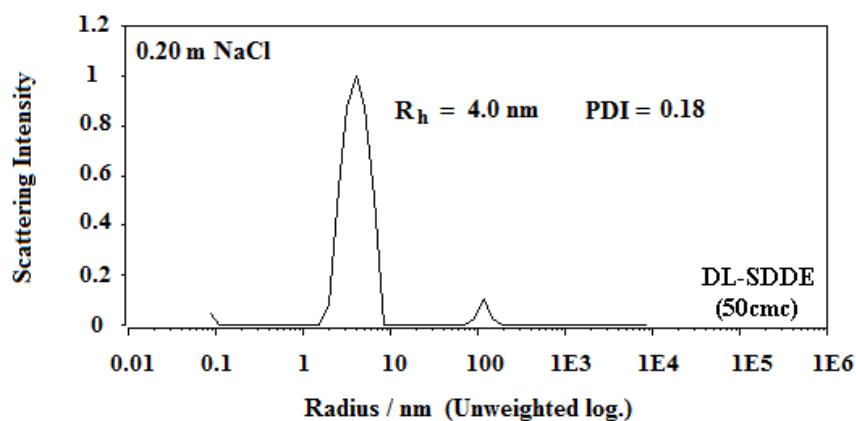


Figure 5.38 The intensity-weighted size distribution of the R_h of the micellar solution of DL-SDDE (50 cmc) at 0.20 m NaCl and at 25 °C.

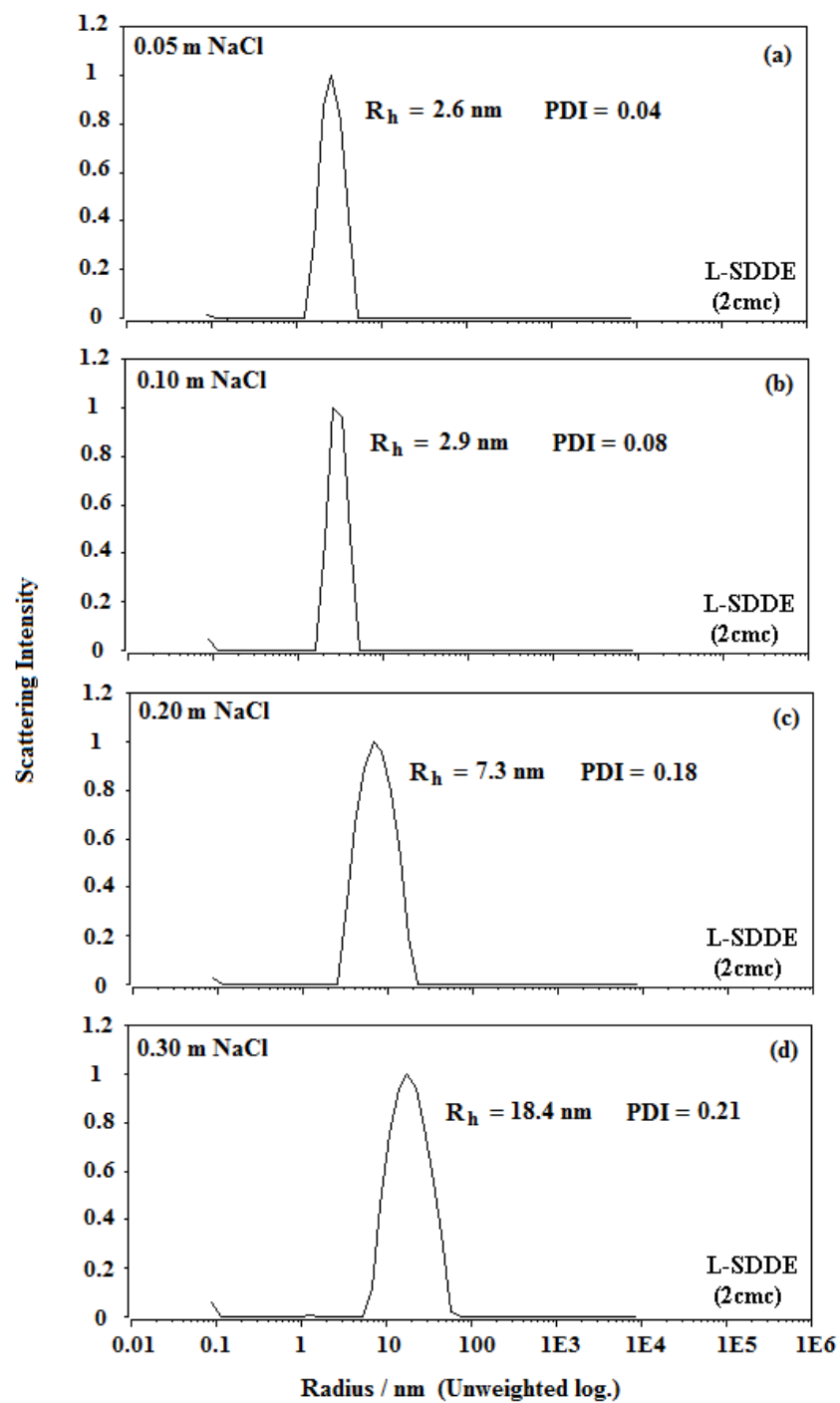


Figure 5.39 The intensity-weighted size distribution of the R_h of the micellar solutions of L-SDDE (2 cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

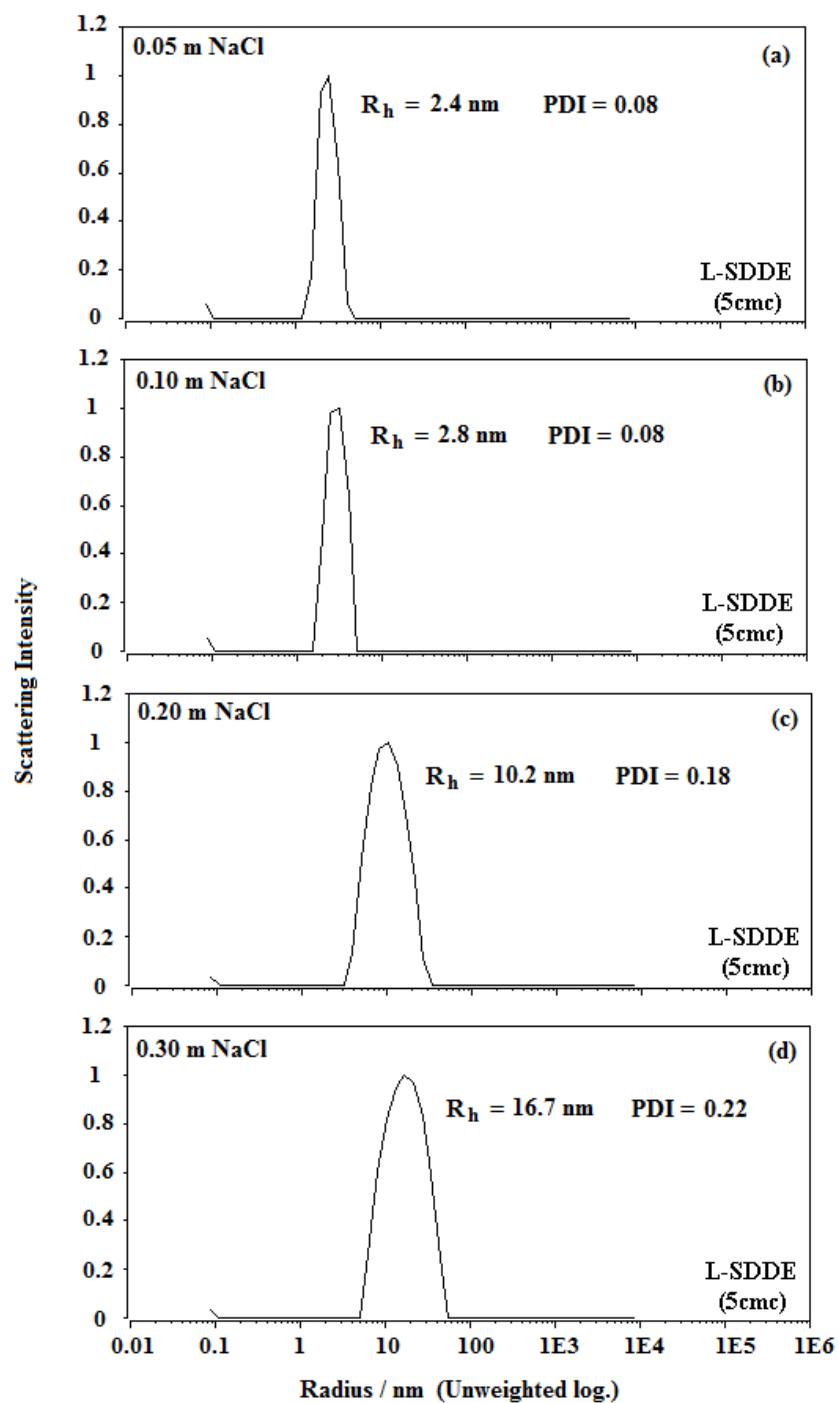


Figure 5.40 The intensity-weighted size distribution of the R_h of the micellar solutions of L-SDDE (5cmc) at different NaCl concentrations **(a)** 0.05 m, **(b)** 0.10 m, **(c)** 0.20 m and **(d)** 0.30 m and at 25 °C.

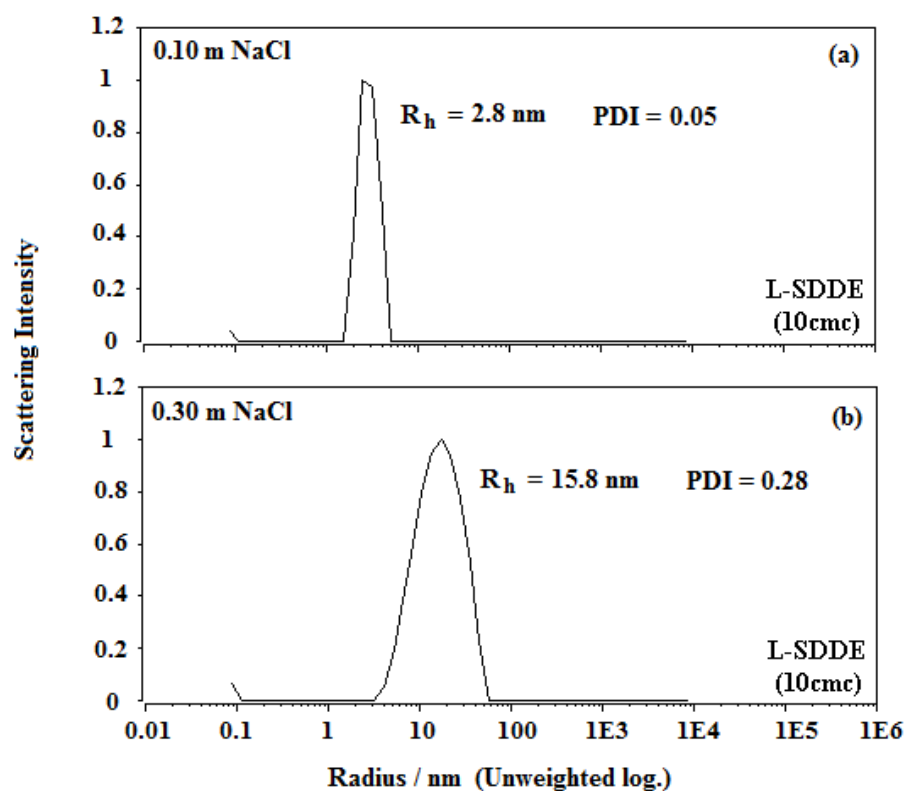


Figure 5.41 The intensity-weighted size distribution of the R_h of the micellar solutions of L-SDDE (10 cmc) at different NaCl concentrations **(a)** 0.10 m and **(b)** 0.30 m and at 25 °C.

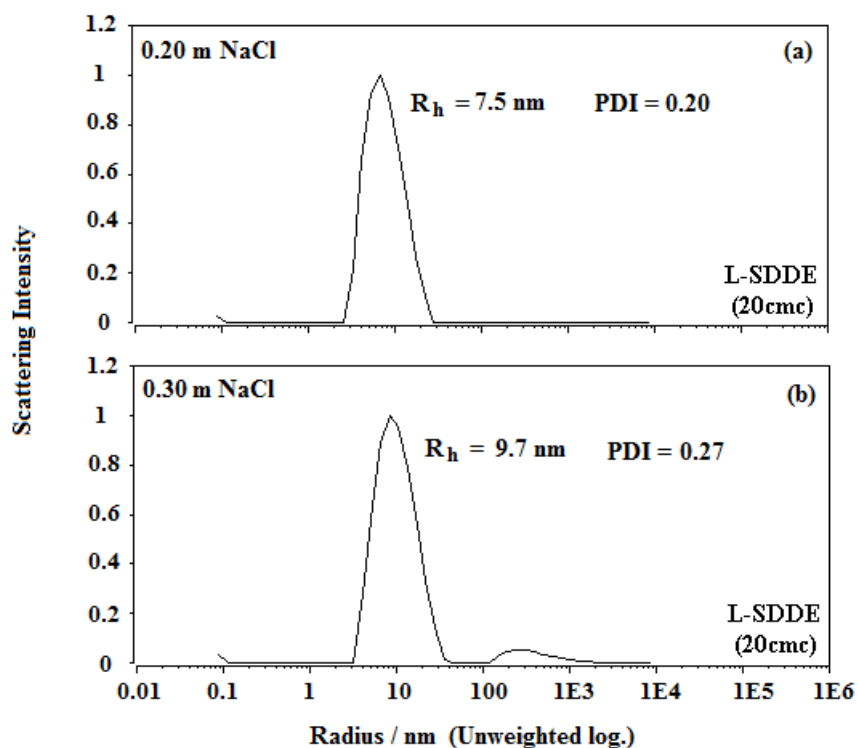


Figure 5.42 The intensity-weighted size distribution of the R_h of the micellar solutions of L-SDDE (20 cmc) at different NaCl concentrations (a) 0.10 m and (b) 0.30 m and at 25 °C.

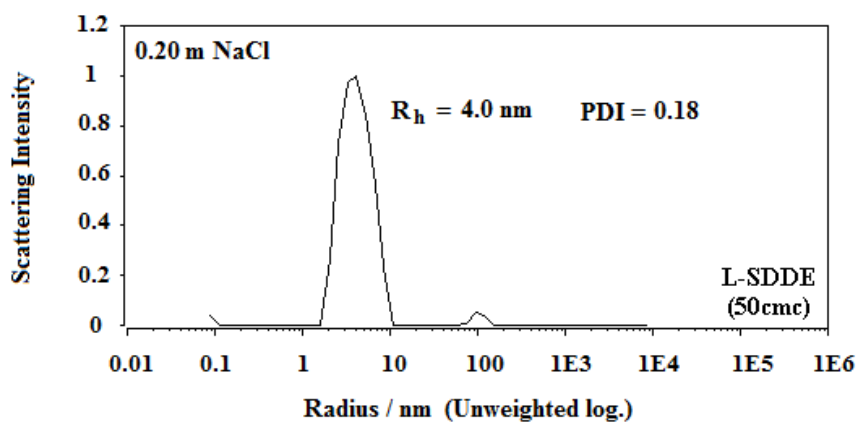


Figure 5.43 The intensity-weighted size distribution of the R_h of the micellar solution of L-SDDE (50 cmc) at 0.20 m NaCl and at 25 °C.

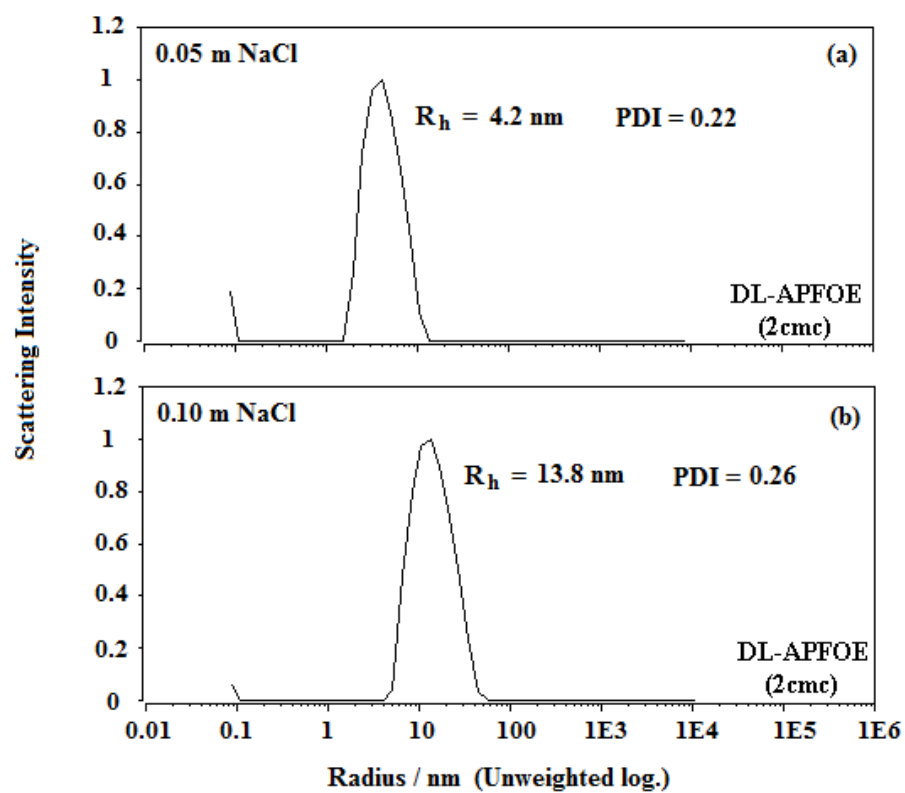


Figure 5.44 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-APFOE (2cmc) at different NaCl concentrations (a) 0.05 m and (b) 0.10 m and at 25 °C.

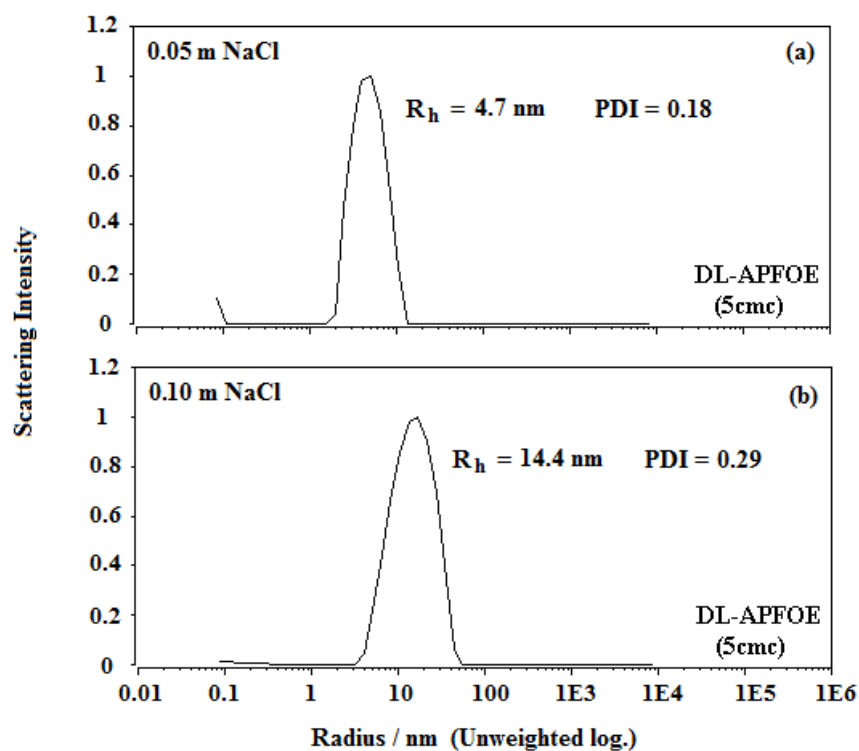


Figure 5.45 The intensity-weighted size distribution of the R_h of the micellar solutions of DL-APFOE (5cmc) at different NaCl concentrations (a) 0.05 m and (b) 0.10 m and at 25 °C.

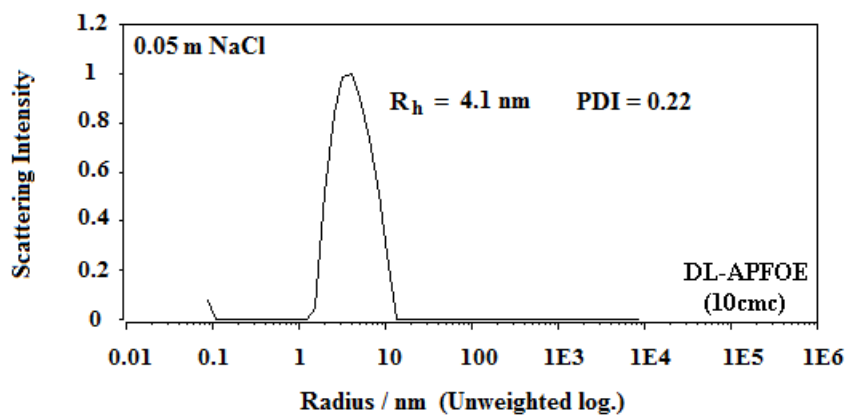


Figure 5.46 The intensity-weighted size distribution of the R_h of the micellar solution of DL-APFOE (10cmc) at 0.05 m NaCl and at 25 °C.

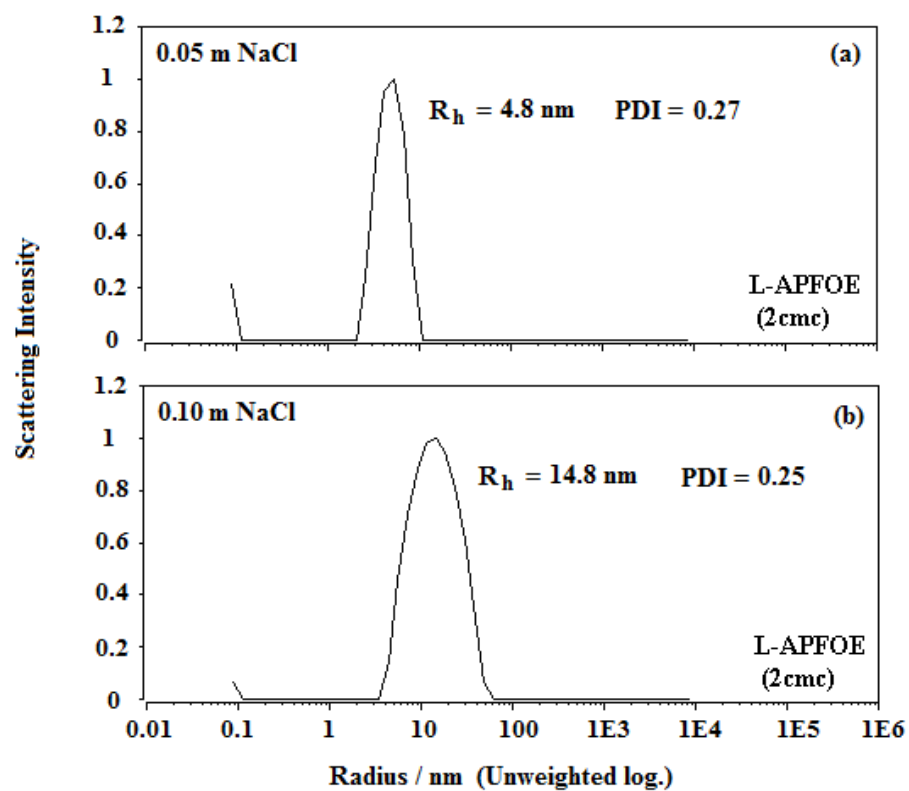


Figure 5.47 The intensity-weighted size distribution of the R_h of the micellar solutions of L-APFOE (2cmc) at different NaCl concentrations **(a)** 0.05 m and **(b)** 0.10 m and at 25 °C.

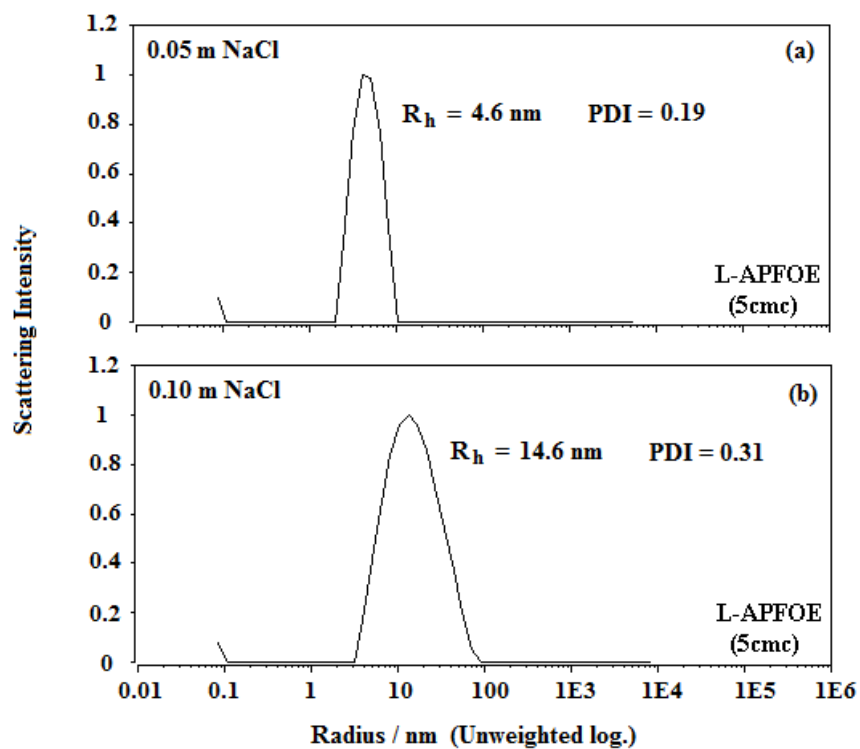


Figure 5.48 The intensity-weighted size distribution of the R_h of the micellar solutions of L-APFOE (5cmc) at different NaCl concentrations **(a)** 0.05 m and **(b)** 0.10 m and at 25 °C.

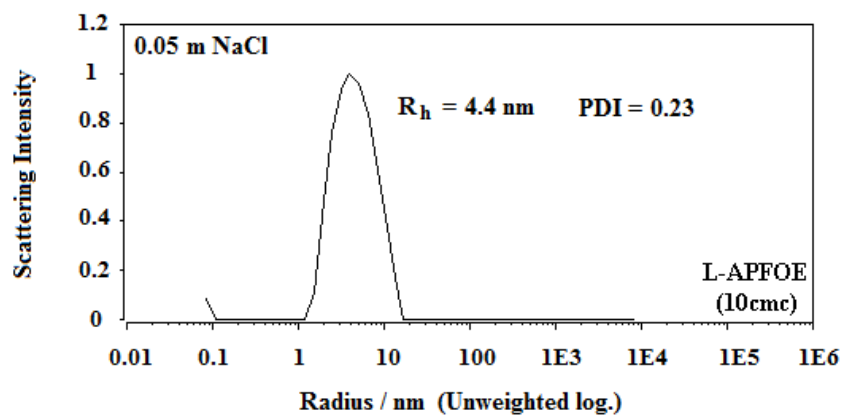


Figure 5.49 The intensity-weighted size distribution of the R_h of the micellar solution of L-APFOE (10cmc) at 0.05 m NaCl and at 25 °C.

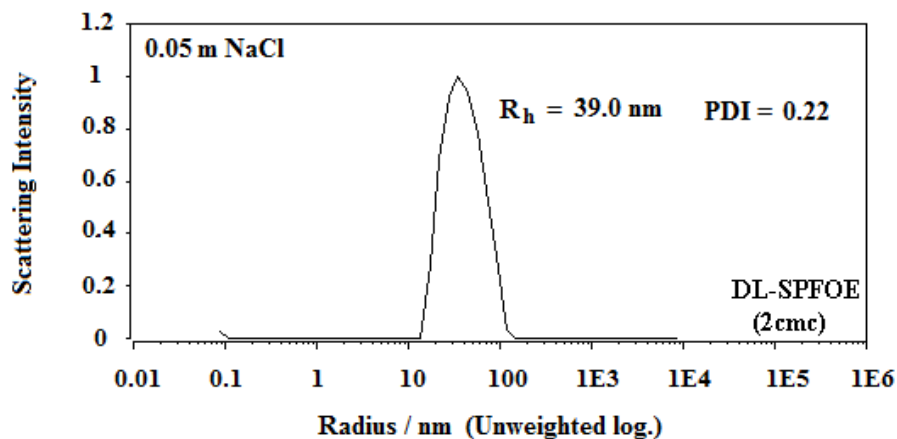


Figure 5.50 The intensity-weighted size distribution of the R_h of the micellar solution of DL-SPFOE (2 *cmc*) at 0.05 m NaCl and at 25 °C.

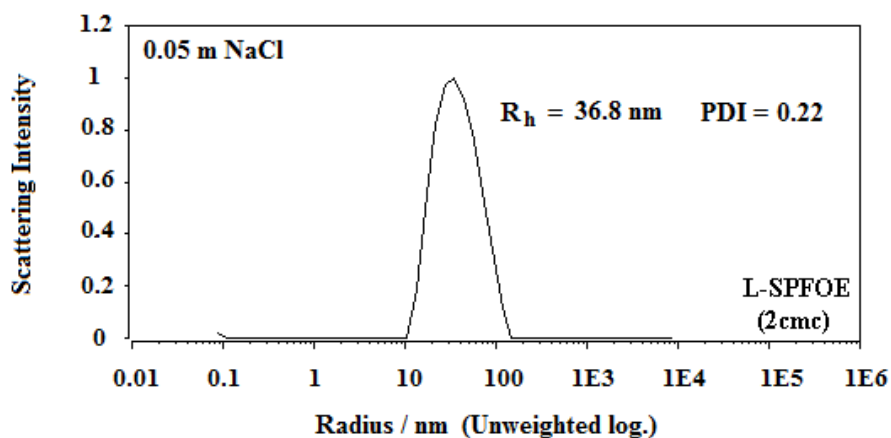


Figure 5.51 The intensity-weighted size distribution of the R_h of the micellar solution of L-SPFOE (2 *cmc*) at 0.05 m NaCl and at 25 °C.

The R_h values of the micelles, in the presence of NaCl for all surfactants, obtained from the above graphs are summarized in Tables 5.16 and 5.17.

$R_h \pm 0.3 / nm$ (PDI) at 2 cmc								
NaCl / m	DL-ADDE		L-ADDE		DL-SDDE		L-SDDE	
0.05	2.5	(0.12)	2.5	(0.14)	2.7	(0.12)	2.6	(0.04)
0.10	2.7	(0.13)	2.7	(0.17)	3.0	(0.11)	2.9	(0.08)
0.20	5.4	(0.17)	5.8	(0.16)	8.5	(0.16)	7.3	(0.18)
0.30	12.9	(0.17)	12.6	(0.15)	18.1	(0.20)	18.4	(0.21)

NaCl / m	DL-APFOE		L-APFOE		DL-SPFOE		L-SPFOE	
0.05	4.2	(0.22)	4.8	(0.27)	39.0	(0.22)	36.8	(0.22)
0.10	13.8	(0.26)	14.8	(0.25)	–		–	

(a)

$R_h \pm 0.3 / nm$ (PDI) at 5 cmc								
NaCl / m	DL-ADDE		L-ADDE		DL-SDDE		L-SDDE	
0.05	2.2	(0.04)	2.3	(0.10)	2.4	(0.08)	2.4	(0.08)
0.10	2.9	(0.08)	2.8	(0.09)	3.0	(0.09)	2.8	(0.08)
0.20	7.0	(0.16)	6.7	(0.16)	9.8	(0.19)	10.2	(0.18)
0.30	14.3	(0.17)	14.2	(0.17)	17.1	(0.22)	16.7	(0.22)

NaCl / m	DL-APFOE		L-APFOE		DL-SPFOE		L-SPFOE	
0.05	4.7	(0.18)	4.6	(0.19)	–		–	
0.10	14.4	(0.29)	14.6	(0.31)	–		–	

(b)

Table 5.16 The results of the DLS measurements for aqueous solutions of D/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE at (a) 2 cmc and (b) 5 cmc, and different NaCl concentrations. All measurements were performed at 25 °C. The number given in parenthesis is the polydispersity index (PDI).

$R_h \pm 0.3 / nm$ (PDI) at 10 cmc						
NaCl / m	DL-ADDE		L-ADDE		DL-SDDE	L-SDDE
0.05	1.9	(0.35)	1.9	(0.25)	—	—
0.10	2.5	(0.30)	2.4	(0.27)	2.8 (0.11)	2.8 (0.05)
0.20	7.8	(0.16)	7.5	(0.18)	—	—
0.30	12.7	(0.22)	12.9	(0.20)	16.3 (0.27)	15.8 (0.28)

NaCl / m	DL-APFOE		L-APFOE		DL-SPFOE	L-SPFOE
0.05	4.1	(0.22)	4.4	(0.23)	—	—

(a)

$R_h \pm 0.3 / nm$ (PDI) at 20 cmc						
NaCl / m	DL-ADDE		L-ADDE		DL-SDDE	L-SDDE
0.05	1.5	(0.21)	1.5	(0.29)	—	—
0.10	2.6	(0.24)	2.3	(0.23)	—	—
0.20	7.1	(0.19)	7.0	(0.19)	7.8 (0.20)	7.5 (0.20)
0.30	9.7	(0.21)	10.1	(0.22)	10.0 (0.26)	9.7 (0.27)

(b)

$R_h \pm 0.3 / nm$ (PDI) at 50 cmc						
NaCl / m	DL-ADDE		L-ADDE		DL-SDDE	L-SDDE
0.05	1.1	(0.34)	1.0	(0.28)	—	—
0.10	1.9	(0.27)	2.0	(0.27)	—	—
0.20	4.0	(0.16)	3.9	(0.17)	4.0 (0.18)	4.0 (0.18)
0.30	5.0	(0.20)	5.2	(0.21)	—	—

(c)

Table 5.17 The results of the DLS measurements for aqueous solutions of D/L-ADDE, DL/L-SDDE, DL/L-APFOE and DL/L-SPFOE at (a) 10 cmc, (b) 20 cmc and (c) 50 cmc, and different NaCl concentrations, and at 25 °C. The number given in parenthesis is the polydispersity index (PDI).

As seen from the Tables 5.16 and 5.17, R_h of DL/L-APFOE and DL/L-SPFOE systems could not be measured at high salt and *cmc* concentrations because much dispersed populations of aggregates are formed. But, all of the hydrogenated esters, DL/L-ADDE and DL/L-SDDE, could be measured at each *cmc* and the salt concentrations. The R_h values of DL/L-SDDE at different *cmc*s and salt concentrations were only taken for the comparison purposes.

As the results are examined one can recognize that all the R_h values of the racemic mixtures and the L-enantiomers are almost the same, Tables 5.16 and 5.17. This means that there is no appreciable difference in the R_h between the DL- and L-forms of the micelles. Consequently, it can be said that DLS could not differentiate between chiral and achiral micelles in the range of experimental error. In addition, the polydispersity index (PDI) of our systems lies in the range of 0.04-0.35. The PDI is an indication of the distribution of the shape of the micelles in the solution. When the PDI value is smaller than 0.05 then there is a uniform distribution of the micelle shape in the solution, i.e. micelles are monodisperse. However, when the PDI values lie between 0.05 and 0.10 and bigger than 0.10, the distribution of the micelle shapes are called near-monodisperse and polydisperse, respectively [126].

On the other hand, it is worth to note that the micelles grow with increasing salt concentrations for all systems, Table 5.16. This is a general result due to the increase in the ionic strength in the micellar solutions [19,27,39]. When the ionic strength, i.e. salt concentration, is increased, counter-ion per micelle increases as well. The increase in the counter-ion binding in the micelle gives rise to

weak electrostatic repulsion between the ionic head groups, so the micelles grow in size. The R_h values of the systems, at low salt concentrations, are small indicating that small spherical micelles exist in the solution. Then, the R_h of the micelles increase as the salt concentration is increased showing that very large aggregates occur in the solution, i.e. vesicle or rod-like micelles. Especially, the R_h values of DL/L-SPFOE systems are very high, i.e. 36.8-39.0 nm at $2cmc$ and 0.05 m NaCl. This probably arises from vesicle formation in the solution which has been generally observed for the fluorinated surfactants [108,121]. As known that in vesicles, there is an aqueous phase in the interior, and so encapsulation of water-soluble compounds is an important characteristic of vesicles [28], Figure 5.52. This important property of vesicles can be used in drug delivery system [108,121].

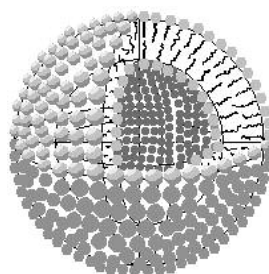


Figure 5.52 A schematic representation of a vesicle structure.

It is also recognized that the head group and the hydrophobic tail on the R_h have a significant role on the hydrogenated and partially fluorinated systems. In the hydrogenated systems, ADDE and SDDE, the differences in the R_h are observed at low cmc s ($2cmc$ / $5cmc$ / $10cmc$) and high salt concentrations (0.2 m-0.3 m NaCl), Table 5.16, Figures 5.53 and 5.54. At these concentrations, the R_h values of

the ADDE are always smaller than that of the SDDE. In addition, for the partially fluorinated systems, APFOE and SPFOE, it is also observed that the R_h values of the APFOE are markedly smaller than that of the SPFOE (at 2 *cmc* and at 0.05 m NaCl), Table 5.16. As we have discussed before that serine head group is more polar and more hydrated than alanine head group, e.g. the *cmc* and α of serine esters are always higher than that of alanine esters.

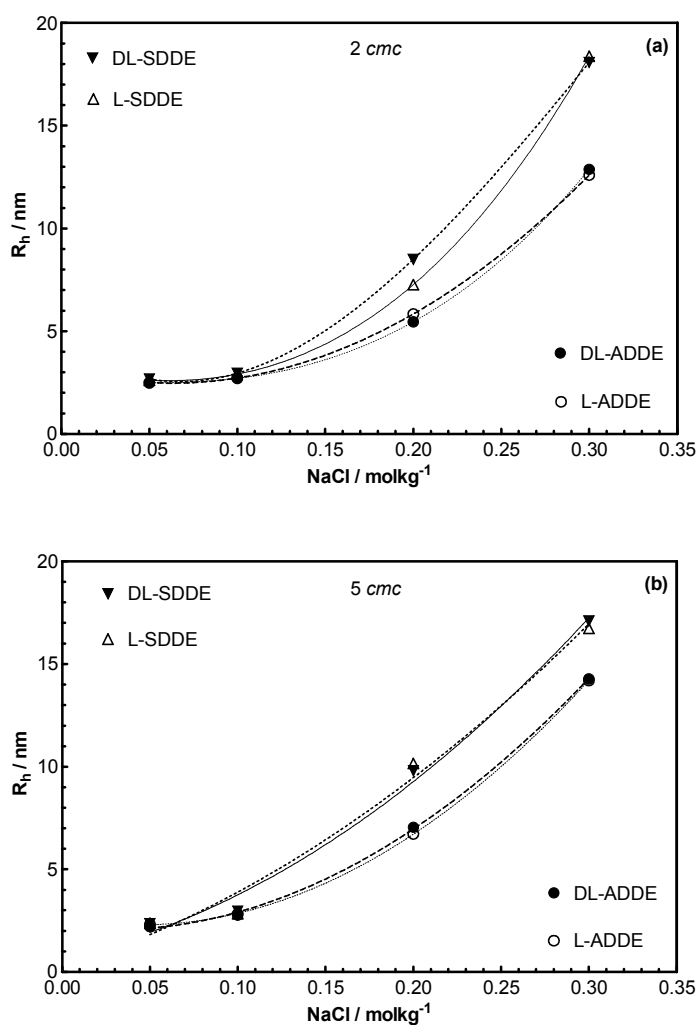


Figure 5.53 Variation of the R_h with the NaCl concentration for aqueous solutions of DL/L-ADDE and DL/L-SDDE at (a) 2 *cmc* and (b) 5 *cmc*, and at 25°C.

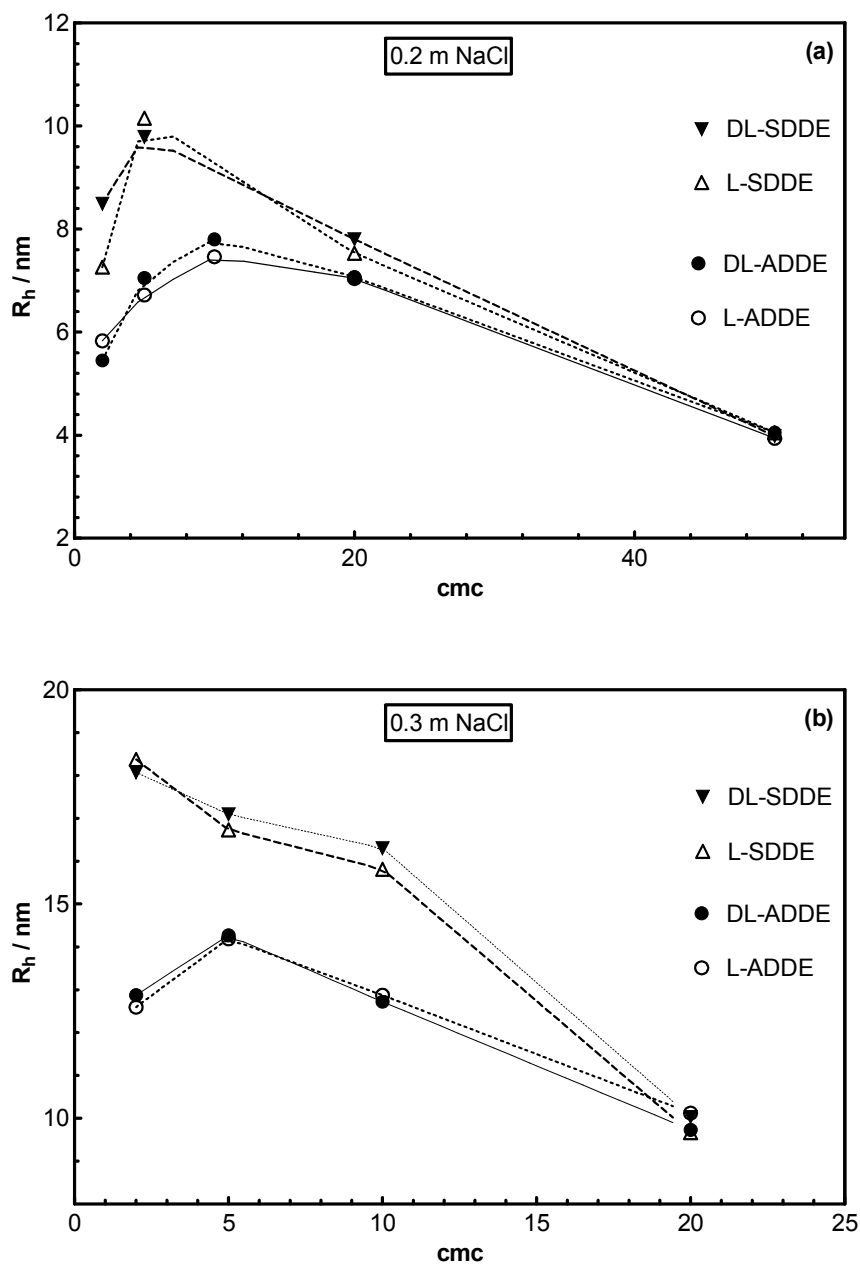


Figure 5.54 Variation of the R_h with concentration of DL/L-ADDE and DL/L-SDDE at **(a)** 0.2 m and **(b)** 0.3 m NaCl concentrations, and at 25°C.

Another interesting feature is that the R_h values of DL/L-ADDE and DL/L-SDDE systems decrease as the concentrations are increased, Figure 5.55 and 5.56. This means that small micelles are formed, i.e. they become more compact, as the concentration of the esters increases.

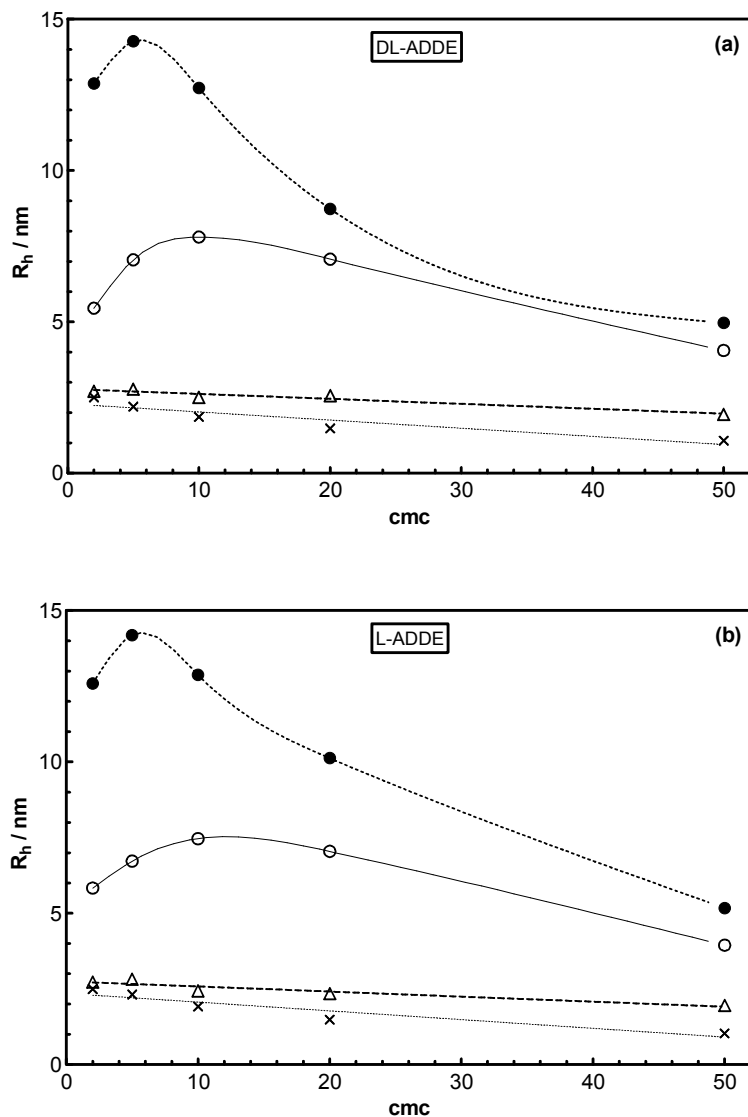


Figure 5.55 Effect of the surfactant concentration on the R_h of (a) DL-ADDE and (b) L-ADDE at selected NaCl concentrations, $\times=0.05$ m, $\Delta=0.10$ m, $\circ=0.20$ m, $\bullet=0.30$ m, and at 25°C.

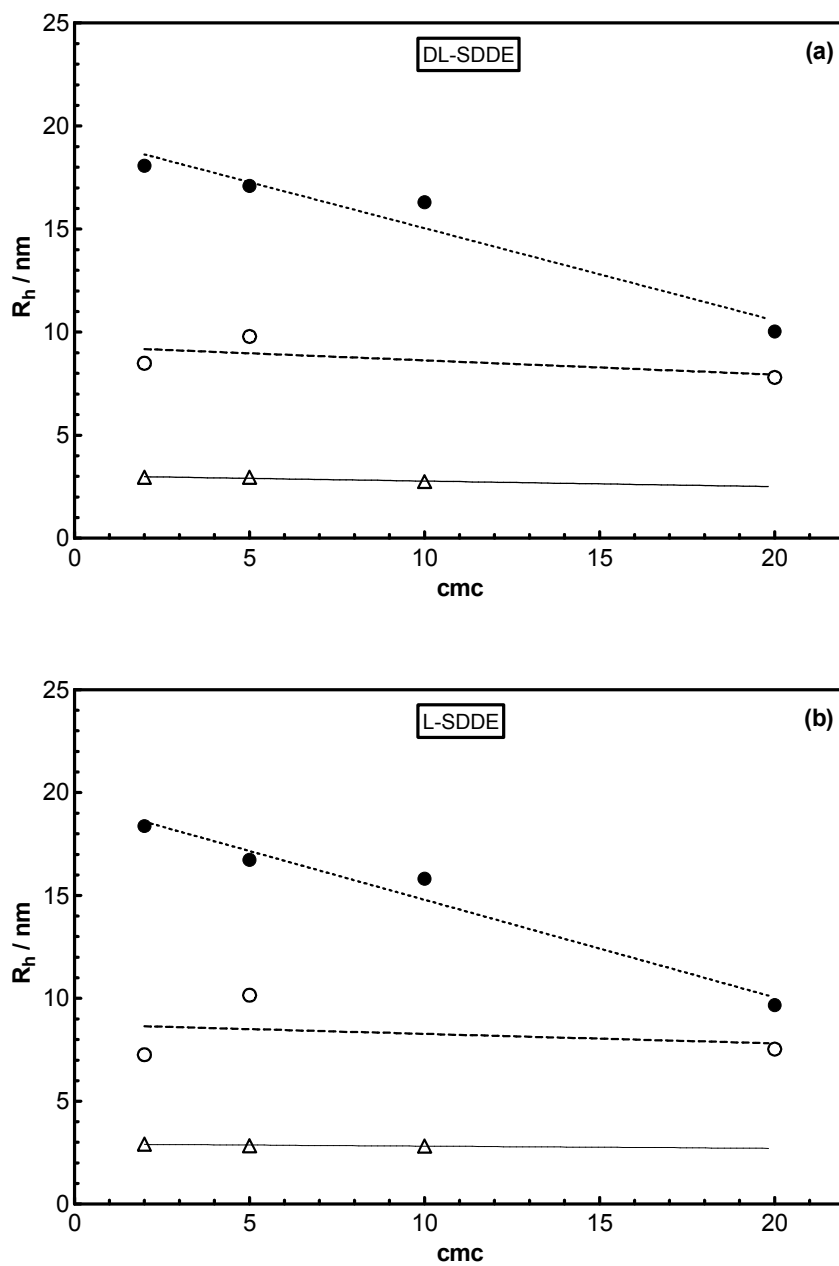


Figure 5.56 Effect of the surfactant concentration on the R_h of (a) DL-SDDE and (b) L-SDDE at selected NaCl concentrations, $\Delta = 0.10$ m, $\circ = 0.20$ m and $\bullet = 0.30$ m, and at 25°C.

5.8. Determination of the structure of the micelles by scanning electron microscopy measurements

Although the DLS measurements give valuable information about the micelle size; however, it is not adequate to extract the shape of the formed aggregates. In order to determine the shape of the formed aggregates, transmission electron microscopy (TEM) measurements are required. These measurements are planned to be done in due course. However, we have made an attempt to measure scanning electron microscopy (SEM) of our some samples. As the SEM samples are prepared, since they are left to dry on a SEM holder, the aggregates coalesce to large aggregates giving unexpected large structure of the formed aggregates, Figures 5.57(a) and (b). For instance, they are approximately hundred times larger than the expected aggregate size for our systems. Nevertheless, these results are regarded as useful because they indicate that the formed aggregates of our systems are nearly spherical in shape.

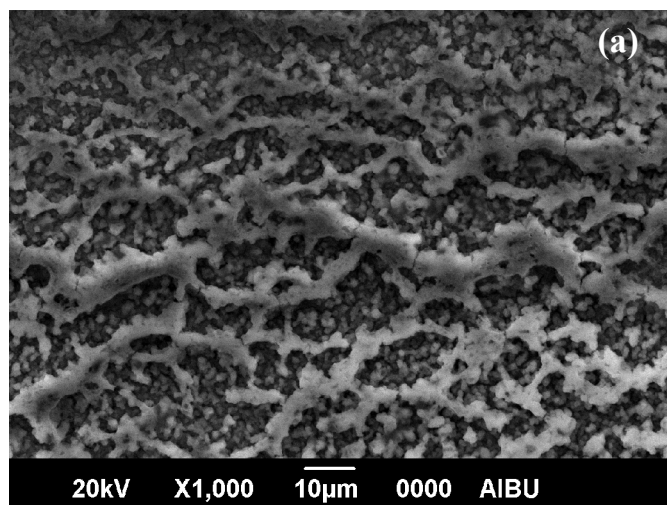


Figure 5.57 The SEM images of (a) L-SPFOE at 2 *cmc* and 0.05 m NaCl.

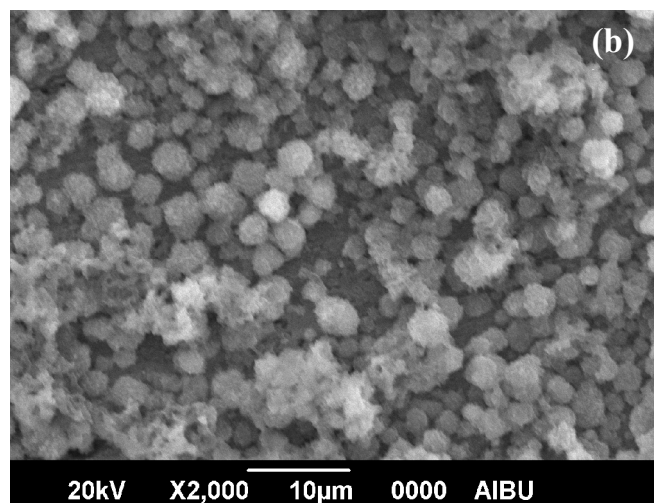


Figure 5.57 The SEM images of **(b)** L-SDDE at 2 *cmc* and 0.05 m NaCl.

As seen from Figure 5.57 (a) and (b), the micelles, in aqueous solutions of L-SPFOE and L-SDDE, coalesce to large aggregates during the drying process in the SEM holder. However, the DLS measurements gave much smaller aggregate sizes than those of the SEM technique then the DLS method is generally applied to liquid solutions.

CHAPTER 6

CONCLUSIONS

In this thesis, Krafft temperatures (T_K s), critical micelle concentrations (cmc s), micellization, adsorption, volumetric and structural properties of aqueous solutions of four enantiomeric/racemic pairs obtained from dodecylesters and partially fluorinated octylesters of alanine and serine were determined by means of electrical conductivity, surface tension, density, dynamic light scattering (DLS) and scanning electron microscopy (SEM) measurements.

The parameters obtained from these measurements were interpreted in the manner of racemic/enantiomeric pairs, fluorinated/hydrogenated hydrophobic tail, and alanine/serine head groups. The results can be summarized as follows:

(i) The T_K values of the all esters were below the room temperature, even below zero for DL/L-APFOE, L-SPFOE and DL-SDDE. Due to the very low Krafft temperatures, these amphiphiles may be used in many practical applications.

(ii) It was seen that there were some differences between the cmc values of the racemic and enantiomeric amphiphiles depending on the measurement techniques. It was recognized that the chiral effect on the cmc s of partially fluorinated

amphiphiles was more striking than that of hydrogenated ones.

(iii) On the other hand, it was found that the *cmc* values of partially fluorinated systems, APFOE and SPFOE, were nearly twice those of hydrogenated systems, ADDE and SDDE. So, it is inferred that the DL/L-ADDE and DL/L-SDDE exhibit considerably better micelle-forming ability at lower concentrations as compared to DL/L-APFOE and DL/L-SPFOE. From these observations, it was discovered that the APFOE and SPFOE systems were not actually counterparts of the ADDE and SDDE systems. Because, there were unfavorable interactions between the $\text{CF}_3\text{-(CF}_2)_5\text{-}$ and $\text{-(CH}_2)_2\text{-}$ groups in the partially fluorinated carbon chain. Thus, it gave rise to increase in the *cmc*.

(iv) In addition, it was found that the *cmc* values of esters increased when the head group changed from alanine to serine. This arises from the polarity of the head groups, i.e. the serine head are more soluble in water as compared to the alanine head.

(v) The temperature dependence of the studied esters was found to be similar to most of the ionic surfactants. The *cmcs* of the esters firstly decreased to a minimum value as the temperature increased, then, the *cmcs* increased by further increased temperature. This showed that the hydration of hydrophilic heads and the hydrophobic tails of the esters decreased with the temperature.

(vi) The standard Gibbs free energy changes of micellization (ΔG_{mic}^o) values of

all the esters showed that the micellization process was thermodynamically favored. Besides, it was observed that the ΔG_{mic}^o of the ADDE and SDDE systems were more negative than those of the APFOE and SPFOE systems. This indicated that the micellization process was more preferred in the formers. These results were all consistent with the $cmcs$. When the temperature dependence of the micellization process was examined, it was seen that the micellization process was entropy-controlled at low temperatures but enthalpy-controlled at high temperatures for all systems.

(vii) The partially fluorinated esters, DL/L-APFOE and DL/L-SPFOE were strongly adsorbed and oriented at the air/water interface indicating the effectiveness in lowering the surface tension of water as compared to DL/L-ADDE and DL/L-SDDE. Thermodynamic parameters of micellization and adsorption provided a further confirmation that the all of the studied esters prefer adsorption to micellization.

(viii) The volumetric properties of the esters were found to be dependent on the hydrophobic tails of the esters. Therefore, all the V_{ϕ}^o and V_{ϕ}^{mic} values of DL/L-APFOE and DL/L-SPFOE were smaller than those of DL/L-ADDE and DL/L-SDDE. This phenomenon was assumed to arise from the randomly coiled conformations of the hydrocarbon chains, which occupy a large volume compared to the fluorocarbon chain.

(viii) The aggregates of the esters, formed in the aqueous solutions, could be assigned a spherical as suggested by the SEM method. Furthermore, it was found that the aggregation of the esters in solution is significantly affected by their hydrophobic tails and head groups. For instance, the hydrogenated esters at 2 *cmc* in the presence of 0.05 m NaCl form micelles with a hydrodynamic radius (R_H) of approximately 2.5 nm. However, the hydrodynamic radii of the DL/L-SPFOE aggregates were much larger than the hydrogenated ones. The hydrodynamic radii of the partially fluorinated esters, DL/L-APFOE and DL/L-SPFOE, at 2 *cmc* in the presence of 0.05 m NaCl were 4.2 nm and 36.8 nm, respectively. Moreover, the hydrodynamic radius of SPFOE system may be indicative for vesicle structure. This property of DL/L-SPFOE system, if any, may be used for drug delivery processes.

Finally, it is planned to perform transmission electron microscopy (TEM) measurements in order to obtain more information about structure of the studied systems. Since the cationic surfactants generally show antimicrobial activity [14], it is also planned to investigate their biological activities, toxicities and biodegradabilities, which are important for scientific and industrial applications.

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Publications

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2. “Kiral yüzey etkin ve racemiklerinin miselleşme termodinamiği”, 21. Ulusal Kimya Kongresi, Malatya, Türkiye, Ağustos (2007).
3. “Determination of micellar properties of enantiomeric/racemic dodecylesters and dodecylamides of alanine in aqueous medium”, 23rd. European Colloid and Interface Society, Antalya, Türkiye, September (2009).
4. “Karbon zinciri florlu DL- ve L-alanin esterlerin nematik ve kiral fazlarının x-ışını saçılması yöntemi ile incelenmesi”, 24. Ulusal Kimya Kongresi, Zonguldak, Türkiye, Haziran (2010).
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Project activity

1. “Fluorokarbonlu moleküllerin kiral nematik fazları üzerine bir araştırma”, A.İ.B.U. Research Foundation, Grant No: 2002.03.03.127 (Researcher)
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