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BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



**EFFECT OF THE DIELECTRIC CONSTANT OF THE
MEDIUM ON THE MICELLIZATION PROPERTIES OF AN
IONIC SURFACTANT IN THE PRESENCE OF
ELECTROLYTE**

MASTER OF SCIENCE

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BOLU, DECEMBER 25

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ABSTRACT

EFFECT OF THE DIELECTRIC CONSTANT OF THE MEDIUM ON THE MICELLIZATION PROPERTIES OF AN IONIC SURFACTANT IN THE PRESENCE OF ELECTROLYTE

MASTER THESIS

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Micellization properties of cationic dodecyltrimethylammonium bromide (DTMABr) surfactant were studied in the absence and presence of some electrolytes in polar organic solvents/water mixtures. The selected electrolytes were LiBr, NaBr, KBr, RbBr, and CsBr, whose cations prefer to be located in the intermicellar region (Gouy-Chapman or diffuse layer), and KF and KCl, whose anions tend to be bound to the micelle surfaces in the Stern layer. While some of those ions exhibit kosmotropic behaviour, others have chaotropic behaviour. The effect of the dielectric constant of the bulk solution was also investigated by varying the polar organic solvents ethylene glycol (EG) and formamide (FA) concentrations in the solutions. The micellization parameters (micellization Gibbs energy, ΔG_{mic} , degree of counterion from micelle, α , and degree of counterion binding to micelle, β) were evaluated from electrical conductivity measurements. Zeta potential measurements were performed to find some valuable information about the change in thickness of the layers around the micelles. The average micelle diameters were determined from Small-angle X-ray scattering measurements. All results indicated that both the specific interactions between ionic species and the dielectric constant of the medium have crucial effects on the micellization properties of surfactants.

KEYWORDS: Surfactant, Micellization, Kosmotropic ion, Dielectric constant, Conductivity

ÖZET

**ELEKTROLİT VARLIĞINDA İYONİK BİR SÜRFAKTANIN
MİSELLEŞME ÖZELLİKLERİ ÜZERİNE ORTAMIN
DİELEKTRİK SABİTİNİN ETKİSİ
YÜKSEK LİSANS TEZİ
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Katyonik dodesiltrimetilamonyum bromür (DTMABr) sürfaktanının miselleşme özellikleri, polar organik çözücüler/su karışımlarında bazı elektrolitlerin varlığında ve yokluğunda çalışılmıştır. Seçilen elektrolitler, katyonları miseller arası bölgede (Gouy-Chapman veya difüz tabaka) yerleşmeyi tercih eden LiBr, NaBr, KBr, RbBr ve CsBr ile anyonları Stern tabakasında misel yüzeylerine bağlanma eğiliminde olan KF ve KCl'dir. Bu iyonların bazıları kozmotropik davranış sergilerken, diğerleri kaotropik davranışa sahiptir. Yığın çözeltinin dielektrik sabitinin etkisi, çözeltilerdeki polar organik çözücüler etilen glikol (EG) ve formamit (FA) konsantrasyonlarını değiştirerek de araştırılmıştır. Miselleşme parametreleri (miselleşme Gibbs enerjisi, ΔG_{mic} , karşıt iyon miselden ayrışma derecesi, α , ve karşıt iyon misele bağlanma derecesi, β), elektriksel iletkenlik ölçümlerinden belirlendi. Zeta potansiyel ölçümleri, miseller etrafındaki katmanların kalınlığındaki değişim hakkında bazı değerli bilgiler elde etmek için yapıldı. Ortalama misel çapları, küçük açılı X-ışını saçılımı ölçümlerinden belirlendi. Tüm sonuçlar, hem iyonik türler arasındaki spesifik etkileşimlerin hem de ortamın dielektrik sabitinin, sürfaktanların miselleşme özellikleri üzerinde önemli etkilere sahip olduğunu gösterdi.

ANAHTAR KELİMELELER: Sürfaktan, Miselleşme, Kozmotropik iyon, Dielektrik sabiti, İletkenlik

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LIST OF ABBREVIATIONS AND SYMBOLS

CMC	: Critical Micelle Concentration
X_{CMC}	: Mole fraction of a surfactant at cmc
κ	: Specific conductivity
ΔG[°]_{mic}	: Standard Gibbs Free Energy of Micellization
ΔH[°]_{mic}	: Standard Enthalpy of Micellization
ε	: Dielectric constant
ζ	: Zeta Potential
EDL	: Electrical Double Layer
SAXS	: Small-angle X-ray Scattering (SAXS)
λ	: Wavelength
d	: Distance between particles, layers, or planes
SD	: Standard deviation
β	: Degree of counterion binding to micelle
α	: Degree of ionization from micelle
R	: Ideal gas constant (8.3145 J K ⁻¹ mol ⁻¹)
I	: Relative scattering intensity
q	: Scattering vector
DTMABr	: Dodecyltrimethylammonium bromide
SDS	: Sodium dodecyl sulfate
FA	: Formamide
EG	: Ethylene Glycol
KF	: Potassium Fluoride
KCl	: Potassium Chloride
KBr	: Potassium Bromide
LiBr	: Lithium Bromide
NaBr	: Sodium Bromide
RbBr	: Rubidium Bromide
CsBr	: Cesium Bromide

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1.INTRODUCTION

1.1 Background on Surfactants and Micellization

Surfactants, or surface-active agents, are amphiphilic molecules consisting of a hydrophilic head that attracts water and a hydrophobic tail that repels water, Figure 1.1. Owing to this dual attraction, surfactants possess a distinctive capability to diminish surface and interfacial tension between disparate phases, such as oil and water. This feature renders them indispensable elements in several applications, such as detergents, emulsifiers, medicines, cosmetics, and increased oil recovery procedures (Rosen & Kunjappu, 2012).

Surfactants have exceptional self-assembly behavior in aqueous liquids. When surfactant concentration above a specified threshold, so-called the critical micelle concentration (CMC), the molecules autonomously arrange into aggregates known as micelles. In these formations, the hydrophobic tails cluster internally to evade water interaction, while the hydrophilic heads orient outward, engaging with the surrounding aquatic environment. This self-organization minimizes the free energy of the system and signals a thermodynamically advantageous process (Myers, 2020).

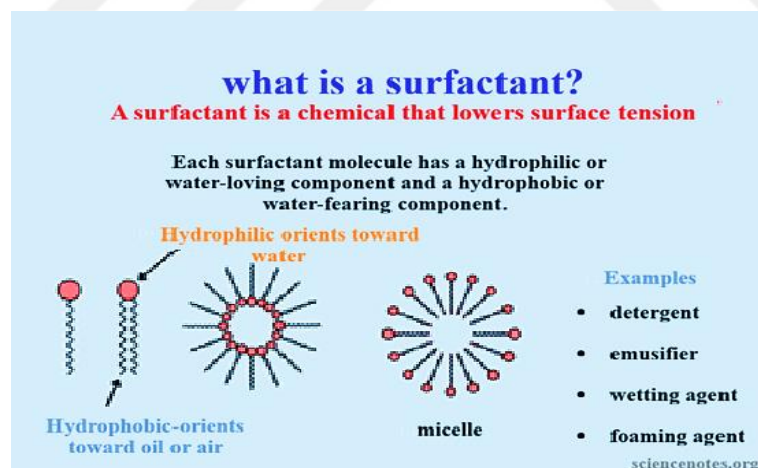


Figure 1.1. Surfactant definition and examples.

Micellization is regulated by various factors, including the nature of the surfactant (ionic or nonionic), temperature, ionic strength, pH, and the dielectric constant of the medium. Ionic surfactants, such as potassium laurate, are highly sensitive to the presence of electrolytes. Electrolytes can screen electrostatic repulsions between charged head groups, thus decrease CMC and stabilize micelle formation. Conversely, in solvents with lower dielectric constants, the

electrostatic interactions become stronger, potentially inhibiting micellization unless counterions or cosolvents are present (Mukerjee & Mysels, 1971).

The thermodynamics of micellization is commonly defined by metrics such as the Gibbs free energy change ($\Delta G^{\circ}_{\text{mic}}$), enthalpy ($\Delta H^{\circ}_{\text{mic}}$), and entropy ($\Delta S^{\circ}_{\text{mic}}$). A negative Gibbs free energy reflects the spontaneous nature of micelle formation. While the process is primarily entropy-driven due to the release of structured water molecules surrounding hydrophobic chains, enthalpic contributions also become substantial in systems containing electrostatic or hydrogen bonding interactions (Attwood, 2012).

1.2 Factors Influencing Micellization

Micellization is a complex physicochemical process driven by various inherent and external factors. Understanding these characteristics is critical for managing surfactant behavior in different applications, including medicine delivery, cosmetics, detergency, and nanotechnology. Below are the most significant factors that affect micelle development.

1.2.1 Nature and Type of Surfactant

The chemical structure of a surfactant plays a vital role in micellization. Surfactants may be ionic (anionic or cationic), nonionic, zwitterionic, or amphoteric. Ionic surfactants, such as sodium dodecyl sulfate (SDS), are more sensitive to the ionic environment of the medium due to electrostatic repulsions between charged head groups. Nonionic surfactants, on the other hand, are often less sensitive to electrolytes and temperature but may show substantial dependency on hydrogen bonding relationships (Rosen & Kunjappu, 2012).

1.2.2 Surfactant Concentration

Micelles begin to form only when the surfactant concentration exceeds a specific threshold called the **Critical Micelle Concentration (CMC)**. Below this concentration, surfactants exist primarily as monomers. Once the CMC is reached, the free energy of the system is minimized by the aggregation of surfactant molecules into micelles (Myers, 2020).

1.2.3 Temperature

Temperature substantially affects the CMC and the stability of micelles. For nonionic surfactants, raising temperature usually reduces hydration of the head groups and lowers the CMC. In contrast, for ionic surfactants, CMC may initially decrease with temperature but then rise due to rupture of hydration shells or higher kinetic energy (Attwood 2012; Wiseman et al., 1989).

1.2.4 Electrolyte Presence

In solutions containing ionic surfactants, electrolytes such as NaCl can screen the electrostatic repulsion between oppositely charged head groups. This leads to a decrease in the CMC and an increase in micelle stability. Higher ionic strength facilitates micellization, especially in low dielectric media (Mukerjee & Mysels, 1971).

1.2.5 Dielectric Constant of the Medium

The polarity of the solvent, indicated by its dielectric constant, is a key parameter. In polar liquids like water (with a high dielectric constant), ionic surfactants dissociate rapidly and produce micelles readily. However, in less polar solvents (low dielectric constant), electrostatic interactions between head groups are higher, making micellization less favorable unless counterions or co-solvents are introduced (Rosen & Kunjappu, 2012; Bhattarai, 2015).

1.2.6 PH of the Medium

For surfactants having ionizable groups (e.g., carboxylic acids or amines), the pH of the medium impacts the degree of ionization and consequently the CMC. At severe pH values, surfactant solubility and micellization behavior can change substantially.

1.2.7 Hydrophobic Chain Length

Longer hydrocarbon chains typically decrease the CMC due to enhanced hydrophobic interactions among surfactant tails. However, very long chains may result in solubility issues or formation of more complex aggregates like vesicles or bilayers.

Factors Affecting Micellization

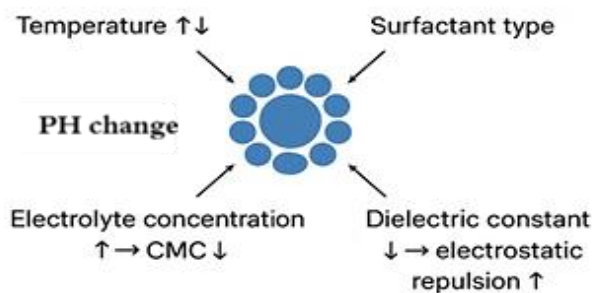


Figure 1.2. Factors Affecting Micellization, (arrows indicate trends: ↑ means increase, ↓ means decrease, and → shows a cause–effect relation. increasing electrolyte concentration decreases the CMC, while decreasing the dielectric constant increases electrostatic repulsion (Mukerjee & Mysels, 1971).)

Figure 1.2. shows the main factors influencing the micellization process, including temperature, surfactant type, electrolyte concentration, pH, and dielectric constant of the medium (Mukerjee & Mysels 1971).

1.3 Role of Dielectric Constant in Micelle Formation

The dielectric constant (ϵ) of a solvent is a fundamental physical parameter that represents its capacity to minimize electrostatic interactions between charged species. In the context of micellization, this parameter plays a vital role, particularly for ionic surfactants, where strong repulsive forces between charged head groups must be neutralized to facilitate aggregation into micelles.

In high dielectric media like water ($\epsilon = 78$ at 25°C), electrostatic interactions are greatly screened, allowing the charged head groups of ionic surfactants to stay relatively stable in solutions. This screening enhances the production of micelles at relatively low concentrations, resulting in reduced critical micelle concentrations (CMC) and more thermodynamically favorable micellization (Myers, 2020; Mukerjee & Mysels, 1971).

Conversely, in low dielectric media, such as alcohol, ethylene glycol, electrostatic interactions are not as effectively shielded, Figure 1.3. As a result, the repulsion between similarly charged head groups becomes more prominent, which might raise the CMC, diminish micellization tendency, or even prohibit micelle

formation completely unless electrolytes are given to neutralize these effects (Florence & Attwood, 2015).

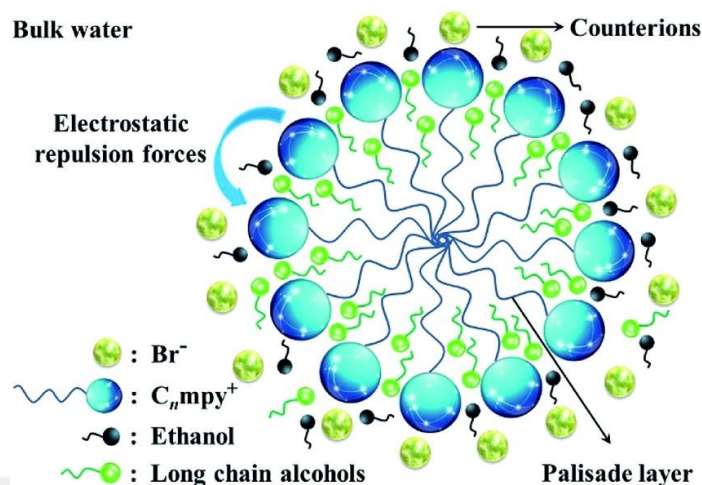


Figure 1.3. Schematic of ionic micelle and counterion screening effects in solvents of varying dielectric constants (adapted from Fu et al., 2019).

Moreover, the dielectric constant affects not only the energetics of micellization but also the micellar morphology. In liquids with intermediate polarity, surfactants may form cylindrical or vesicular structures instead of traditional spherical micelles. This shift depends on the balance between hydrophobic contacts (which favor aggregation) and electrostatic repulsion (which resists aggregation) (Florence & Attwood, 2015).

Studies have also revealed that combining solvents of different dielectric constants helps fine-tune micellization behavior. For example, mixing water with formamide or ethylene glycol affects the overall dielectric environment, allowing researchers to explore how tiny alterations in polarity affect micelle formation, size, and thermodynamics (Rosen & Kunjappu, 2012).

Overall, the dielectric constant is a key environmental factor in micellization studies. Its manipulation provides a useful technique to study and manage the self-assembly of surfactants, particularly in non-aqueous environments or when designing surfactant-based systems for pharmaceutical or industrial uses.

1.4 Effect of Electrolytes on Micellization Behavior

Electrolytes greatly influence the micellization behavior of ionic surfactants, principally by modifying the electrostatic interactions between the charged head groups. When ions (such as NaCl, KBr, or CaCl₂) are put into a surfactant solution, they reduce the repulsive forces between similarly charged surfactant molecules, so decreasing the critical micelle concentration (CMC) and encouraging micelle formation (Reziqat, 2018).

The reason behind this resides in the electrolyte's ability to introduce counterions that collect near the charged surfactant head groups. These counterions diminish the effective surface charge density, which decreases the repulsion among head groups and allows the hydrophobic tails to combine more easily into micelles (Myers, 2020).

The extent of this effect depends on several factors:

a) Type of Electrolyte: Multivalent ions (e.g., Ca²⁺, Mg²⁺) are more successful than monovalent ions (e.g., Na⁺, K⁺) in decreasing the CMC, due to their better charge-screening capabilities. This results in more compact micelles with lower aggregation numbers (Florence & Attwood, 2015; Huibers & Jacobs, 1998; Rosen & Kunjappu, 2012).

b) Electrolyte Concentration: As electrolyte concentration increases, the screening effect becomes more intense. However, at a certain concentration, micellar development may occur, leading to the formation of bigger or even non-spherical aggregates such rod-like micelles or lamellar structures (Rosen & Kunjappu, 2012).

c) Nature of the Surfactant: The influence of electrolytes is more substantial for ionic surfactants compared to nonionic ones, which do not possess charged head groups and hence exhibit less sensitivity to ionic strength. However, in mixed solutions, even nonionic surfactants may exhibit variations in micellization behavior due to indirect effects from additional salts (Mukerjee & Mysels, 1971; Naskar et al., 2013).

Electrolytes also influence micellar thermodynamics by reducing the Gibbs free energy of micellization, so making the process more favorable. Additionally, in low dielectric liquids, where electrostatic repulsions are stronger,

the presence of electrolytes becomes critical in enabling micelle formation in the first place (Florence & Attwood, 2015).

Understanding the role of electrolytes is critical for applications in formulations, such as medicines, detergents, and emulsions, where precise control over micellar characteristics is necessary.

1.5 Physicochemical Properties of DTMABr

Dodecyl trimethylammonium bromide (DTMABr) is a cationic surfactant belonging to the family of quaternary ammonium compounds. It has the chemical formula $C_{12}H_{25}N(CH_3)_3Br$ and consists of a hydrophobic alkyl chain (dodecyl, $C_{12}H_{25}$) connected to a hydrophilic quaternary ammonium head group ($-N^+(CH_3)_3$), with bromide (Br^-) as the counterion, Figure 1.4. Its structure facilitates significant surface activity, making it commonly employed in micellization and interfacial investigations.

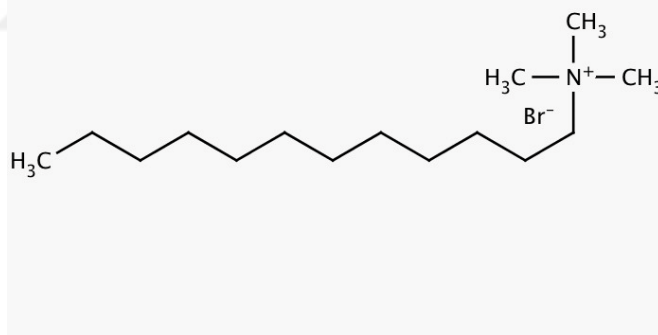


Figure 1.4. Dodecyltrimethylammonium bromide (DTMABr) structure.

a) Micellization Behavior

In water, DTMABr forms spherical micelles at relatively low CMC values (~ 15 mM at $25^\circ C$), thanks to the strong hydrophobic effect and effective electrostatic screening by water molecules (Myers, 2020). The presence of the Br^- counterion facilitates micellization by neutralizing the repulsive forces between adjacent positive head groups.

In mixed solvents or low dielectric media, such as formamide or ethylene glycol, the micellization of DTMABr becomes more sensitive to the environment.

The lower dielectric constant of these media increases head group repulsion, thus raising the CMC, unless countered by added electrolytes (Rosen & Kunjappu, 2012).

b) Thermodynamic and Structural Characteristics

Thermodynamic analyses indicate that micelle production by DTMABr is an entropy-driven phenomenon, mostly attributed to the liberation of structured water molecules from the hydrophobic tails during. The morphology of micelles and their aggregation number can fluctuate according to solvent polarity, ionic strength, and temperature (Mukerjee & Mysels, 1971). Moreover, the bromide ion occupies a unique position in the micelle's interfacial area, often penetrating closer to the surfactant headgroup than other counterions (such as Cl^-), potentially affecting micellar stability and dynamics (Rosen & Kunjappu, 2012).

c) Applications

DTMABr is commonly utilized in colloid and interface science, template synthesis of nanomaterials, emulsification, and electrochemical applications. Its evident micellization behavior and well-defined structure make it a model surfactant in academic and industry research.

1.6 Physicochemical Properties of Selected Solvents (Water, Ethylene Glycol, Formamide)

The selection of solvents in micellization investigations is critical since their physicochemical qualities directly influence surfactant aggregation behavior. In this context, water (H_2O), ethylene glycol (EG), and formamide (FA) were chosen due to their varied dielectric constants, viscosities, hydrogen bonding ability, and polarity, Table 1.1. Each of these elements impacts micelle production and surfactant-solvent interactions in various ways, as explained below:

- **Dielectric constant:** Water has a moderately high dielectric constant, making it particularly effective for screening electrostatic repulsions between charged surfactant head groups, thereby facilitating micellization (Rosen & Kunjappu, 2012).

EG, having a lower dielectric constant, offers weaker screening, which can hamper micelle formation unless screening is modified by additional electrolytes. FA, interestingly, has an even greater dielectric constant than water, which may accelerate ionic dissociation; however, its behavior is confounded by significant solvent-solute interactions (Marcus, 2002).

- **Viscosity:** Viscosity impacts the mobility and diffusion of surfactant molecules. Water's low viscosity allows rapid micelle production. EG's high viscosity may impede aggregation kinetics. FA gives an intermediate case.

- **Hydrogen Bonding:** All three solvents are capable of hydrogen bonding, which alters hydration shells surrounding surfactant head groups (Reziqat, 2018). Water and FA are excellent hydrogen bond donors and acceptors, supporting structured solvations. EG also forms hydrogen bonds, but its long chain alters the overall dynamics (Reichardt & Welton, 2011).

- **Polarity:** Water is the most polar of the three based on empirical polarity scales, which favors micelle stabilization via solvophobic effects. EG and FA, while slightly less polar, nonetheless maintain sufficient interaction with surfactant head groups, especially in mixed solvent environments (Reichardt & Welton, 2011).

Table 1.1. Comparative properties of water, ethylene glycol (EG), and formamide (FA)

Property	Water (H ₂ O)	Ethylene Glycol (EG)	Formamide (FA)
Dielectric Constant (25°C)	~78.5	~37.7	~109
Viscosity (mPa·s at 25°C)	~0.89	~16.1	~3.3
Hydrogen Bonding Ability	Very High (donor & acceptor)	High (donor & acceptor)	Very High (mainly donor)
Polarity (ET(30) scale)	63.1	56.3	58.8

1.7 Kosmotropic and Chaotropic Ions and Their Influence on Micellization

Kosmotropic ions are small, highly charged ions, such as Li⁺, Mg²⁺, and SO₄²⁻, Figure 1.5. They strongly interact with water molecules, enhancing the water structure (i.e., “structure-makers”). This property stabilizes molecular assemblies like proteins and micelles (Sultana, 2023).

In ionic surfactants, kosmotropic ions tend to form strongly (weakly) bound ion pairs with kosmotropic (chaotropic) surfactant headgroups. This leads to a reduction in critical micelle concentration (CMC) and increases micellar stability. Kosmotropes also support the formation of more ordered mesophases, such as nematic liquid-crystalline phases (Akpinar et al., 2016).

Chaotropic ions are larger ions with low charge density, such as I^- , SCN^- , and Cs^+ , Figure 1.5. They interact weakly with water molecules and disrupt its hydrogen-bonded network (i.e., “structure-breakers”). This leads to increased solubility of nonpolar compounds (Moghaddam, 2017). Chaotropic ions tend to form weaker interactions with surfactant headgroups exhibiting opposite character, i.e. strongly kosmotropic ones. This can increase CMC, destabilize micelles, and result in changes to micellar size and shape. They may also reduce order in structure (Akpinar et al., 2016).

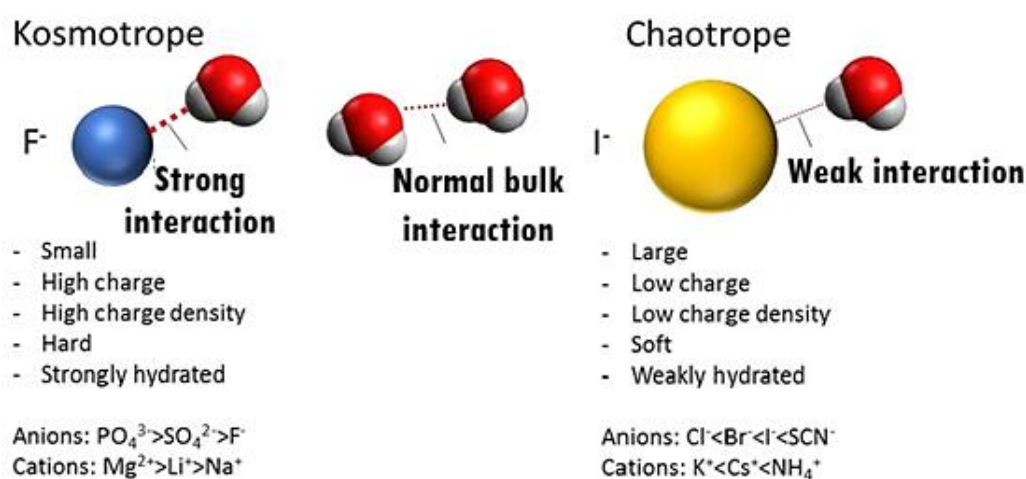


Figure 1.5. Illustration of kosmotropic and chaotropic ions (structure-maker and breaker) interacting strongly and weakly with water molecules, respectively.

Table 1.2. Comparative effects of kosmotropic and chaotropic ions on micellization

Property	Kosmotropic ions	Chaotropic ions
Size	Small	Large
Charge Density	High	Low
Water interaction	Strong (structure-maker)	Weak (structure-breaker)
Effect on CMC	Decreases	Increases
Effect on micelle stability	Stabilizes	Destabilizes
Effect on mesophase	Supports order of structures	Reduces order

Table 1.2. compares some effects of kosmotropic and chaotropic ions on micellization behaviour of surfactants, which were obtained from some experimental results given in literature (Akpınar et al., 2016).

1.8 Zeta Potential in Micellar Solutions

The electrokinetic potential at a particle's sliding or slipping plane in a colloidal dispersion is known as the zeta potential (ζ -potential). It is an important metric of colloidal stability and effectively measures the net charge in the electrical double layer; bigger magnitudes, whether positive or negative, often indicate stronger electrostatic repulsion and more stability (Kaszuba et al., 2010; Kosmulski & Mączka, 2022).

The ζ -potential also indicates the potential of the diffuse electrical double layer surrounding ionic micelles, Figure 1.6. It serves as a quantitative measure of the degree of repulsion between neighboring similarly charged aggregates in solution, and hence, its magnitude gives a direct assessment of colloidal system stability (Naskar et al, 2013; Cassidy & Warr, 1996).

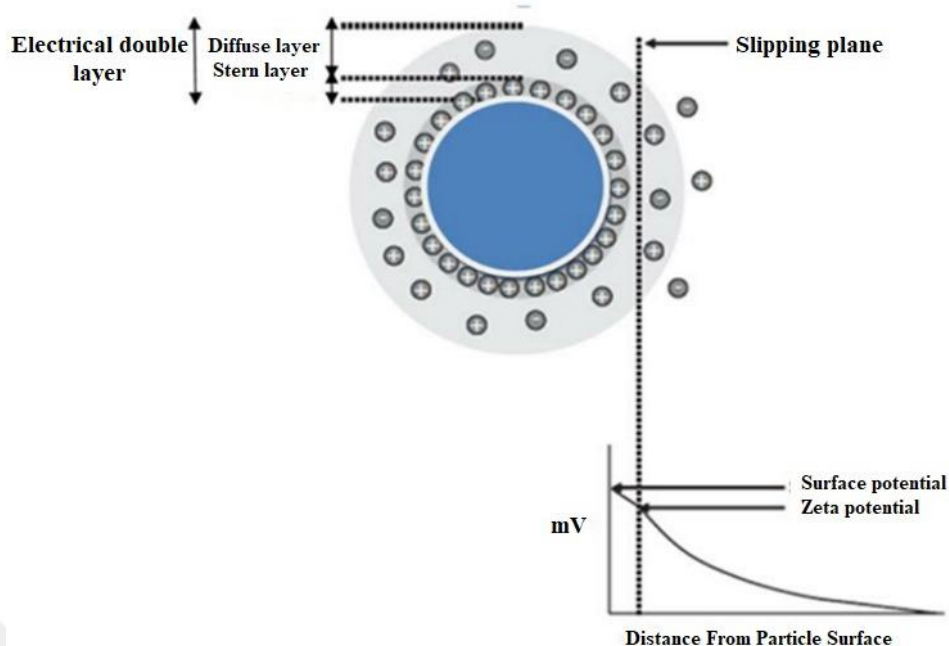


Figure 1.6. Schematic of the electrical double layer including the Stern layer (the layer of condensed counter-ions) and the diffuse part of the double layer

Understanding ζ -potential is particularly crucial in micellar systems, as it determines aggregation behavior, micelle–micelle interactions, and the stability of encapsulated structures, such as in drug delivery systems or nanofluids (Kosmulski & Kalbarczyk, 2023).

The addition of electrolytes modifies zeta potential. Electrolytes (e.g., salts such as NaCl) elevate the ionic strength of the fluid. This compresses the electrical double layer (decreased Debye length), thereby diminishing the size of the zeta potential. Elevated ionic strength mitigates surface charges, hence reducing the repulsion of micelles (Kosmulski & Mączka, 2022). This behavior is consistent with traditional electrochemical theory: an increased presence of counter-ions more efficiently neutralizes surface charges, hence reducing the zeta potential.

Specific adsorption may occur depending on the type of ion. For example, in a non-aqueous mixed solvent (50% ethylene glycol), research involving titania nanoparticles showed that Na^+ ions preferentially adsorb at the nanoparticle surface (Kosmulski & Mączka, 2022), which at elevated base concentrations (>1 mM) effectively diminishes the negative ζ -potential. The introduction of powerful electrolytes such as HCl or NaOH can effectively alter both the sign and

magnitude of the ζ -potential in mixed solvents. In 50% EG, HCl or CTMABr generates a positive ζ -potential beyond +70 mV, while NaOH produces a significantly negative ζ -potential below -70 mV (Kosmulski & Kalbarczyk, 2023).

An “overdose” of base (extremely high concentration) may lead to a decline in magnitude of zeta potential due to processes like particular ion binding or saturation (Kosmulski & Kalbarczyk, 2023). This shows that there is an optimal concentration limit for electrolytes to maximize colloidal stability, beyond which instability may occur.

Zeta potential changes in the presence of organic solvents (EG, FA, etc.) in solutions. The addition of organic solvents such as ethylene glycol (EG) or formamide (FA) drastically modifies the dielectric environment of micellar dispersions. The dielectric constant of the medium is a significant element in determining the level of ion dissociation at the micelle surface or particle contact. Water has a high dielectric constant (~ 78.5 at 25°C), which enables effective dissociation of ionic surfactants and electrolytes. In contrast, EG (~ 37 at 25°C) and FA (~ 109 at 25°C , but with distinct hydrogen-bonding characteristics) vary the medium polarity, influencing how ions interact with the micelle surface (Kosmulski & Kalbarczyk, 2023).

Lower dielectric constant environments (e.g., water-EG mixtures) lower the ability of the medium to screen electrostatic interactions, which can lead to higher inter-particle attractions if the surface charges are not entirely dissociated. This, in turn, affects the magnitude and sign of the zeta potential. For instance, in partially aqueous EG solutions, cationic surfactants may yield greater ζ -potentials because the counter-ions are less mobile and less able to neutralize surface charge (Xu et al., 2022).

Moreover, solvent polarity also determines the thickness of the electrical double layer (EDL). In lower dielectric settings, the Debye length is effectively longer per unit ionic strength, but the effective surface charge may be lowered if the solvent creates hydrogen-bonded networks that stabilize ions away from the micelle surface. This combination between dielectric screening and solvent-ion interactions provides a complicated dependence of ζ -potential on solvent composition (Kosmulski & Mączka, 2022).

In addition, solvents like EG and FA can interact directly with the micellar

headgroups or particle surface via hydrogen bonding or dipole interactions, further modifying surface charge distribution. Such solvent–surface interactions may even rise to charge reversal phenomena, where the sign of the ζ -potential changes depending on solvent concentration and type. These effects are most prominent in mixed solvents where EG or FA is present at high ratios (~50%), which can considerably modify the critical micelle concentration (CMC) and alter the micellar aggregation behavior (Kosmulski & Kalbarczyk, 2023).

1.9 Rationale and Objectives of the Study

The degree of electrostatic interactions between the head groups of ionic surfactants and their counterions is largely controlled by the solvent medium's dielectric constant. Changes in the dielectric constant can drastically alter the delicate balance between hydrophobic attraction and electrostatic repulsion that micellization represents (Rosen & Kunjappu, 2012). Weaker electrostatic screening can improve repulsion among cationic head groups (Marcus, 2002). In lower-dielectric solvents like ethylene glycol ($\epsilon = 37.7$), leading to smaller micelles and higher CMC values (Sohrabi et al., 2010). On the other hand, micellization behavior becomes more complex in high-dielectric solvents such as formamide ($\epsilon = 109$) because of strong hydrogen bonds between the solvent and the solute (Reichardt & Welton, 2011).

Electrolytes, which further alter micellization behavior by screening charge and binding counterions, are nearly always present whether they are utilized in mixes or nonaqueous environments (Chen, 2015). The combined effects of electrolyte concentration, kosmotropic/chapotropic properties of electrolyte ions, organic solvent concentration and dielectric constant of the medium on micellization behaviour of DTMABr have not been thoroughly and comprehensively studied for DTMABr, despite a large number of studies on individual components.

By examining the micellization behavior of DTMABr in mixed solvents (water-EG and water-FA) with varying dielectric constants (water, ethylene glycol, and formamide) in the absence and presence of electrolytes, the main aims of the present study are given below:

1.To study the effect of electrolyte ions located in the diffuse or Gouy-Chapman layer on the micellization behaviour of DTMABr at constant dielectric constant of solution.

2.To evaluate the effect of electrolyte ions adsorbed at the micelle surfaces (Stern layer) at constant dielectric constant of solution.

3.To determine the effect of dielectric properties of solution on the micellization behavior of DTMABr by varying the organic solvent concentration in mixed solvent systems at constant electrolyte concentrations.

4.To reveal kosmotropic and chaotropic nature of electrolyte ions on the micellization properties of DTMABr in the absence and presence of EG and FA polar organic solvents.

To realize the aims of the present study, conductivity, zate potential and Small-angle X-ray scattering measurements were performed.

2. MATERIALS AND METHODS

2.1 Materials

Micellization properties of surfactant molecule DTMABr in the absence and presence of organic polar solvents were studied at constant electrolyte concentrations (30.00 mmol/kg). Electrolytes were LiBr, NaBr, KBr, RbBr, CsBr, KF, and KCl. Ethylene glycol and formamide organic solvents were added at total constant solvent concentrations, i.e., some part of water was replaced with those polar solvents at certain mole percent ranging from 2% to 10%. All chemicals were commercially purchased from Merck and Sigma-Aldrich with a purity of >99%. Ultrapure water was obtained from the Millipore Direct-Q3 UV purification system which produces water with a resistivity of 18.2 MΩ.cm at 25°C.

2.2 Methods

2.2.1 Electrical Conductivity

The electrical conductivities of the solutions were measured by a Mettler Toledo S470 SevenExcellence conductivity meter at a constant temperature (25.0°C). The conductivity meter automatically adjusts the cell constant as 0.549231 cm⁻¹. This value of the cell constant was also confirmed with standard KCl solutions. The conductivities of surfactant/electrolyte/water solutions were measured as a function of the surfactant concentration by the successive addition of DTMABr/water stock solutions into 8 g of 30.00 mmol/kg aqueous electrolyte solutions, existing in the conductivity cell, in the absence and presence of organic solvents EG and FA, separately. The experimental set-up is given in Photo 2.1.

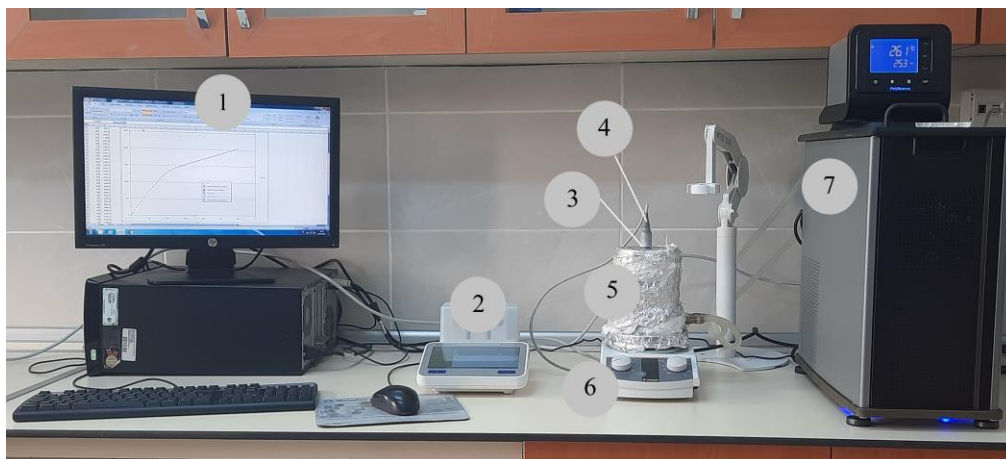


Photo 2.1. The experimental set-up for electrical conductivity measurements of surfactant solutions

1: computer; 2: conductivity meter; 3: glass conductivity cell; 4: probe placed in the conductivity cell; 5: sample holder for conductivity cell; 6: magnetic stirrer; 7: water-circulating bath (Polyscience, USA).

2.2.2 Zeta Potential Measurements

Zeta potential measurements were performed at 25.0°C. Micellar solutions were prepared as follows: First, about totally 100 g of binary EG-water and FA-water solvent mixtures were prepared in 10% mole percent, separately. Then, for all 7 different electrolytes, DTMABr/electrolyte/EG-water and DTMABr/electrolyte/FA-water solutions were prepared by using EG-water and FA-water binary solvents, separately. The concentrations of both DTMABr and electrolytes were chosen as 30.0 mmol/kg. After well-homogenized solutions were obtained by applying vortex and centrifuging occasionally, some parts of these solutions were transferred into a fluorescence quartz cell and univette cuvette was placed in it (Photo 2.2). Finally, the quartz cell with univette cuvette was placed in Anton Paar Litesizer 500 (Photo 2.3). Kalliope analysis software was used for zeta potential measurements.

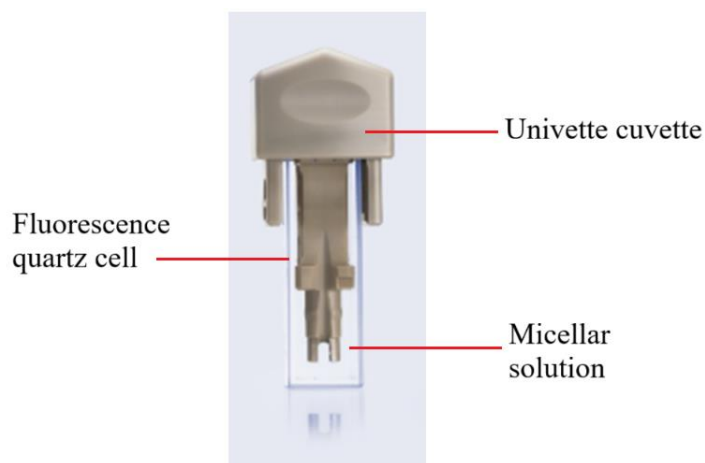


Photo 2.2. Univette is a high-quality reusable cuvette designed for zeta potential and particle size measurements on the Anton Paar Litesizer™ 500.

Univette cuvette was chosen because it is suitable for solutions with high conductivities, used in this Thesis's studies.

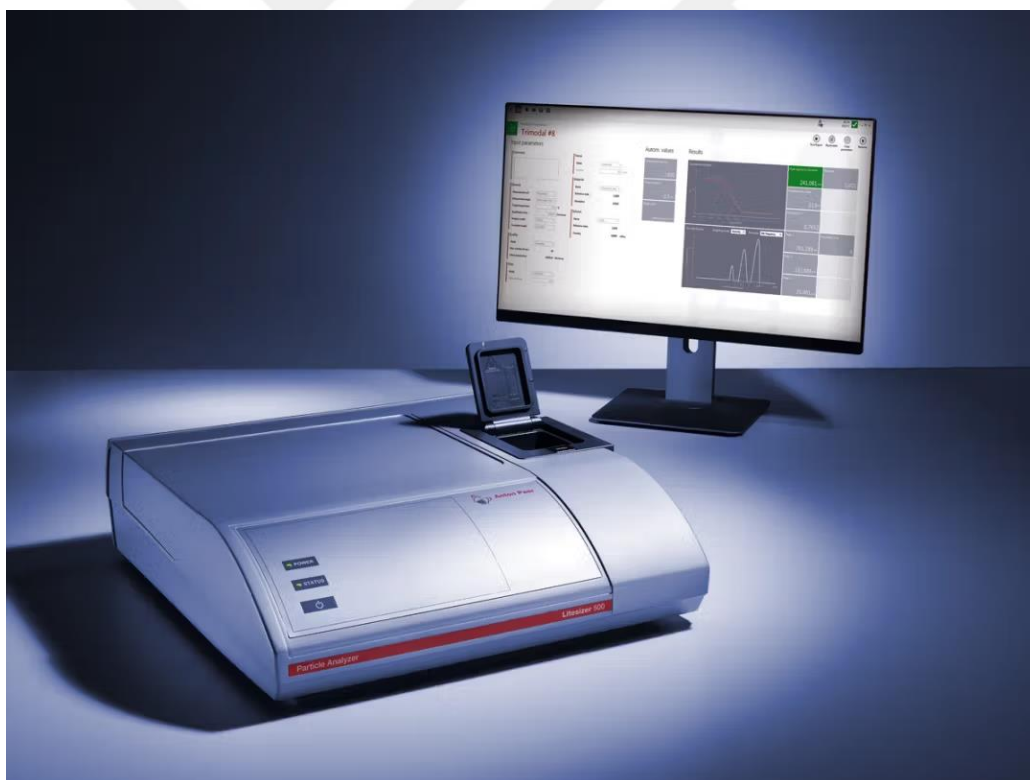


Photo 2.3. Anton Paar Litesizer 500 with Kalliope analysis software.

2.2.3 Small-angle X-ray Scattering

Some structural parameters of the micellar solutions were evaluated from SAXS. The samples were placed into cylindrical reusable borosilicate capillaries of 1.5 mm diameter, made from Mark-tubes (Hilgenberg, Germany). The capillaries were placed in a temperature-controlled sample holder of ± 0.2 °C precision.

A Xeuss 2.0 laboratory-based system (Xenocs, France) was used for SAXS measurements. The monochromatic and collimated incident X-ray beam had a square cross-section of 0.7 mm side in the sample's position. The wavelength of the X-ray beam was $\lambda = 1.5419$ Å. The sample-to-detector distance was 936 mm. The images of the X-ray scattering patterns (e.g., photo 2.4) were measured by a Pilatus 300K detector (Dectris, Switzerland).

Frame integration were applied to the images, which resulted in curves of relative scattering intensity, I , as a function of the modulus of the scattering vector, $q = (4\pi/\lambda) \sin\theta$, where 2θ is the scattering angle. Data treatment was applied to each sample curve in two steps: First, normalization of I by the measurement time, by the incident X-ray beam intensity, and by the sample transmittance; right after, background and electronic noise curves subtractions from the normalized sample curve. The background was a measurement of a water sample. After data treatment, the samples curves were analyzed by peak fitting using the software Fityk. Some solutions were chosen for SAXS measurements, whose compositions were given in Table 2.1.

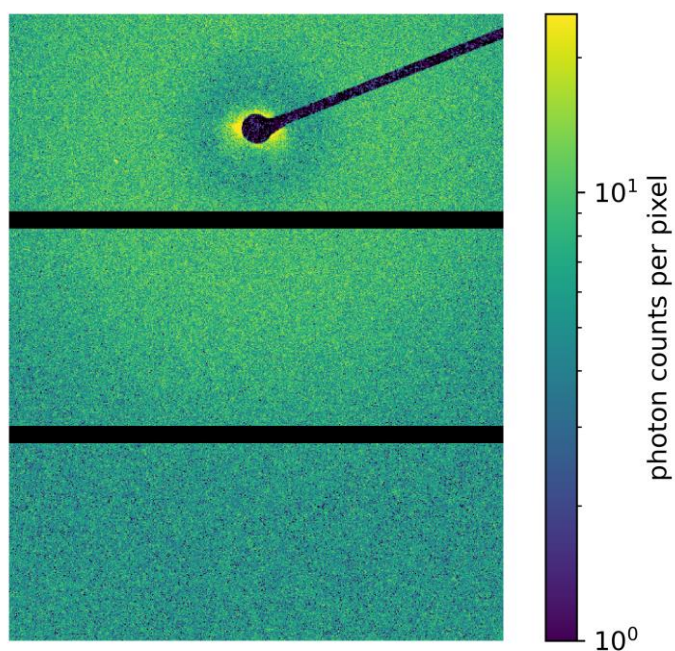


Photo 2.4. A representative 2D isotropic X-ray scattering pattern obtained from solution s5. Similar patterns were obtained for other solutions given in Table 2.1.

Table 2.1. Solutions used in SAXS measurements. Polar solvents are in percent mole fraction.

Solvent	Solution	Electrolyte	$C_{\text{DTMABr}}/\text{mmol kg}^{-1}$	$C_{\text{electrolyte}}/\text{mmol kg}^{-1}$
water	s1	---	100	0
	s2	KBr	100	30
	s3	NaBr	100	30
	s4	KF	100	30
10% EG	s5	---	100	0
	s6	KBr	100	30
	s7	NaBr	100	30
	s8	KF	100	30
10% FA	s9	---	100	0
	s10	KBr	100	30
	s11	NaBr	100	30
	s12	KF	100	30

3.RESULTS

In this part of the thesis, we present (a) electrical conductivity, (b) zeta potential, and (c) SAXS results of micellar solutions. Their analyses were discussed in the “Discussion” part in details.

3.1 Results of Electrical Conductivity Measurements

Table 3.1. includes the conductivity values (κ) of DTMABr/LiBr/water micellar solutions as functions of surfactant concentration. For other micellar solutions, similar results were obtained which are graphically given in Figures 3.1.-3.77. In κ versus surfactant concentration graphs, two different regions are obtained, pre-micellar and post-micellar regions. In both regions, the dependence of κ on surfactant concentration, in general, gives linear curves. The reliability or accuracy of κ -surfactant concentration measurements can be evaluated from the linearity of these two curves. As it is known, the regression (R^2) of the curves gives us information about fitting of experimental data to the equation of the selected curve, i.e., in our case, to the linear curve equation $y=mx+b$, where y , m , x and b parameters are κ , slope (S), DTMABr concentration, and y -intercept values, respectively. For the best fitting, R^2 is 1, and the closer to 1, the higher the reliability or accuracy of the data. In Tables 3.2-3.17, the slopes of the linear curves obtained from the pre-micellar and post-micellar regions, and their R^2 values are given. The R^2 values are between 0.9972-1.0000, mostly >0.9998 , thus the experimental data exhibit highly reliable with high accuracy.

The results were divided into two parts: results of the effects of the organic solvents on the micellization properties of the surfactant in the presence of electrolyte ions which prefer to be located (a) in the intermicellar region (or Gouy-Chapman or diffuse layer) and (b) at the micelle surfaces (Stern layer). The concentrations of each electrolyte were kept constant (30.0 mmol/kg). The mole percents of organic solvents in water varied from 0 to 10% in 2% intervals. Then, EG/water and FA/water mixtures were used as solvents in the preparation for micellar solutions.

Table 3.1. Electrical conductivities data (κ) of DTMABr/LiBr/water solutions as a function of DTMABr concentration (C) at constant LiBr concentration.

C/mmol kg ⁻¹	κ /mS cm ⁻¹	SD/ $\pm$ mS cm ⁻¹	C/mmol kg ⁻¹	κ /mS cm ⁻¹	SD/ $\pm$ mS cm ⁻¹
0.00	3.0743	0.0556	22.24	3.9656	0.0523
0.72	3.1303	0.0572	22.95	3.9798	0.0527
11.44	3.1861	0.0588	23.66	3.9941	0.0530
2.17	3.2416	0.0603	24.37	4.0084	0.0533
2.89	3.2966	0.0615	25.09	4.0226	0.0537
3.61	3.3509	0.0624	25.80	4.0369	0.0540
4.33	3.4039	0.0629	26.51	4.0511	0.0544
5.05	3.4552	0.0627	27.22	4.0653	0.0548
5.77	3.5040	0.0617	27.93	4.0796	0.0551
6.49	3.5494	0,0600	28.64	4.0938	0.0555
7.21	3.5905	0.0576	29.35	4.1080	0.0558
7.93	3.6268	0.0548	30.06	4.1222	0.0562
8.64	3.6579	0.0523	30.76	4.1364	0.0565
9.36	3.6845	0.0502	31.47	4.1506	0.0569
10.08	3.7073	0.0489	32.18	4.1648	0.0572
10.80	3.7272	0.0482	32.89	4.1790	0.0576
11.52	3.7451	0.0479	33,60	4.1931	0.0580
12.23	3.7616	0,0479	34,30	4,2073	0.0583
12.95	3.7774	0.0480	35.01	4.2215	0.0587
13.67	3.7926	0.0483	35.72	4.2356	0.0590
14.38	3.8074	0.0486	36.42	4.2498	0.0594
15.10	3.8221	0.0489	37.13	4.2639	0.0598
15.81	3.8366	0.0492	37.84	4.2780	0.0601
16.53	3.8510	0.0496	38.54	4.2922	0.0605
17.24	3.8654	0.0499	39.25	4.3063	0.0609
17.96	3.8798	0.0502	39.95	4.3204	0.0612
18.67	3.8941	0.0506	40.66	4.3345	0.0616
19.39	3.9084	0.0509	41.36	4.3486	0.0620
20.10	3.9227	0.0513	42.06	4.3627	0.0623
20.81	3.9370	0.0516	42.77	4.3768	0.0627
21.53	3.9513	0.0520			

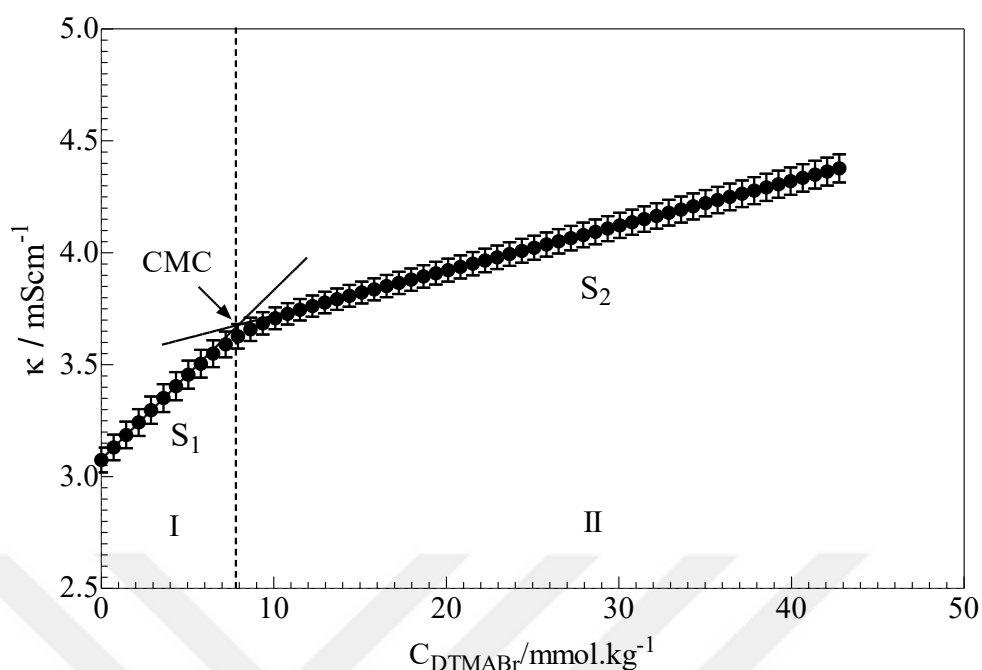


Figure 3.1. Plot of electrical conductivity of DTMABr/LiBr/water solution versus DTMABr concentration at 25.0°C. Region I and Region II correspond to the pre-micellar and post-micellar region, separately.

Table 3.2. Slopes and regressions of the linear curves for regions I and II shown in Figure 3.1. The symbol “S” in the unit of the slopes is “Siemens”. The values given with “±” correspond to the standard deviations in S_1 and S_2 values.

$S_1 / \text{S kg cm}^{-1} \text{mol}^{-1}$	R^2	$S_2 / \text{S kg cm}^{-1} \text{mol}^{-1}$	R^2
0.07566 ± 0.00041	0.9998	0.02009 ± 0.00002	1.0000

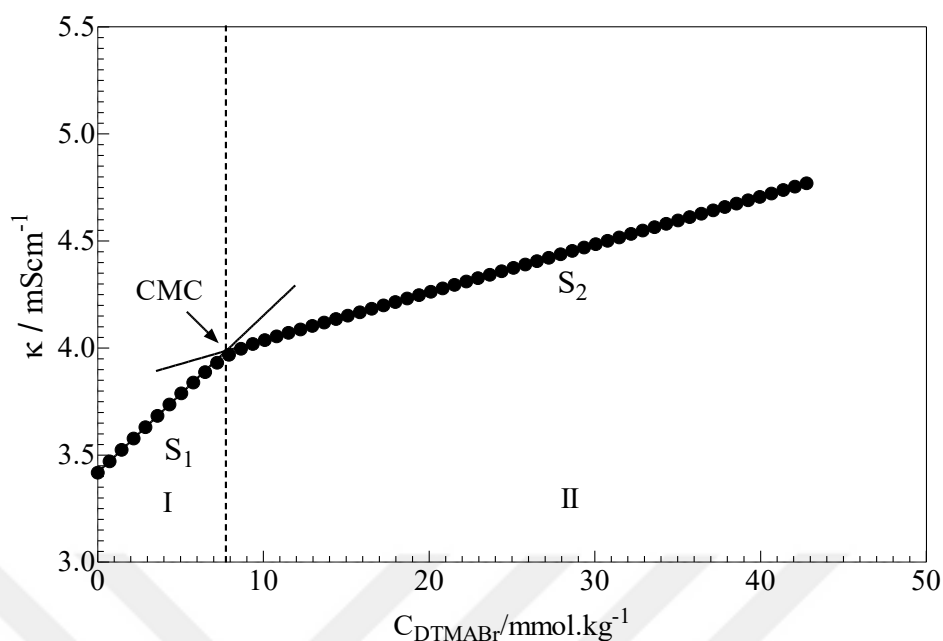


Figure 3.2. Plot of electrical conductivity of DTMABr/NaBr/water solution versus DTMABr concentration at 25.0°C.

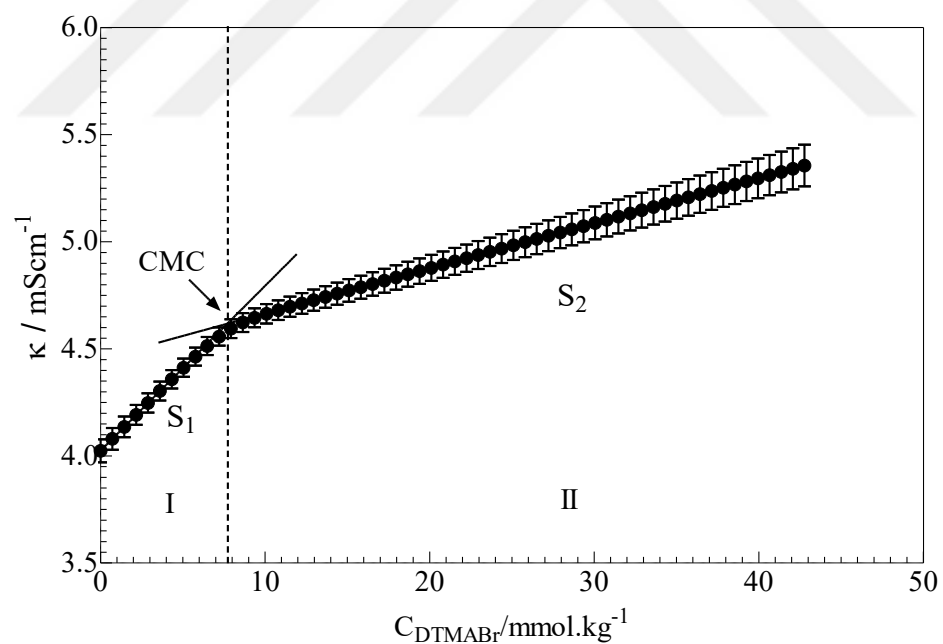


Figure 3.3. Plot of electrical conductivity of DTMABr/KBr/water solution versus DTMABr concentration at 25.0°C.

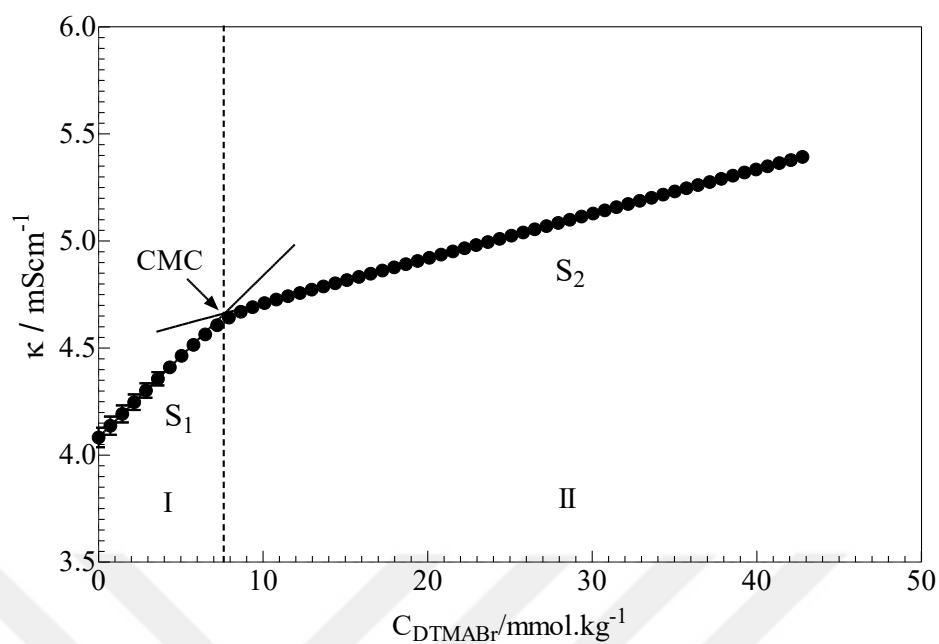


Figure 3.4. Plot of electrical conductivity of DTMABr/RbBr/water solution versus DTMABr concentration at 25.0°C.

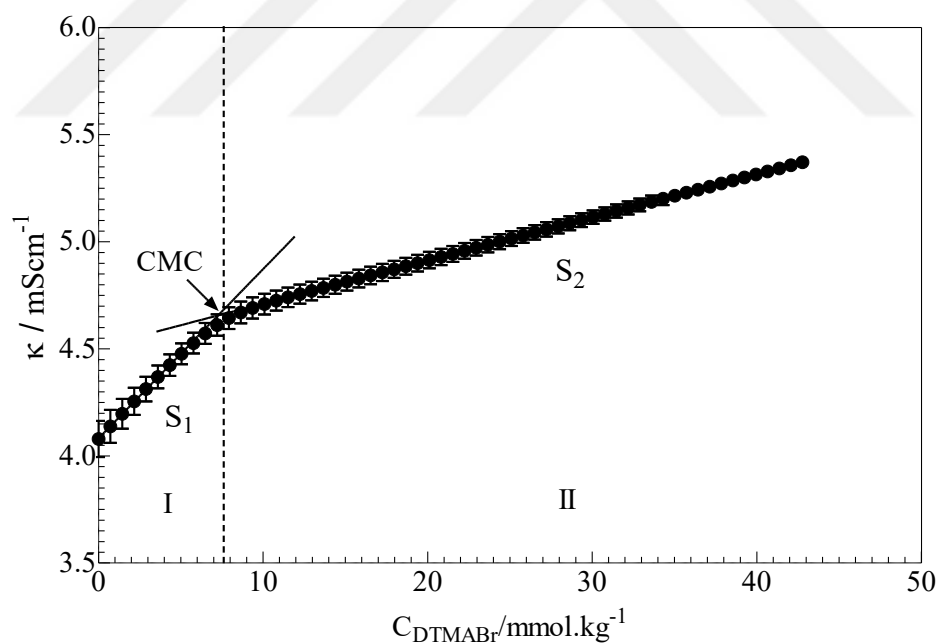


Figure 3.5. Plot of electrical conductivity of DTMABr/CsBr/water solution versus DTMABr concentration at 25.0°C.

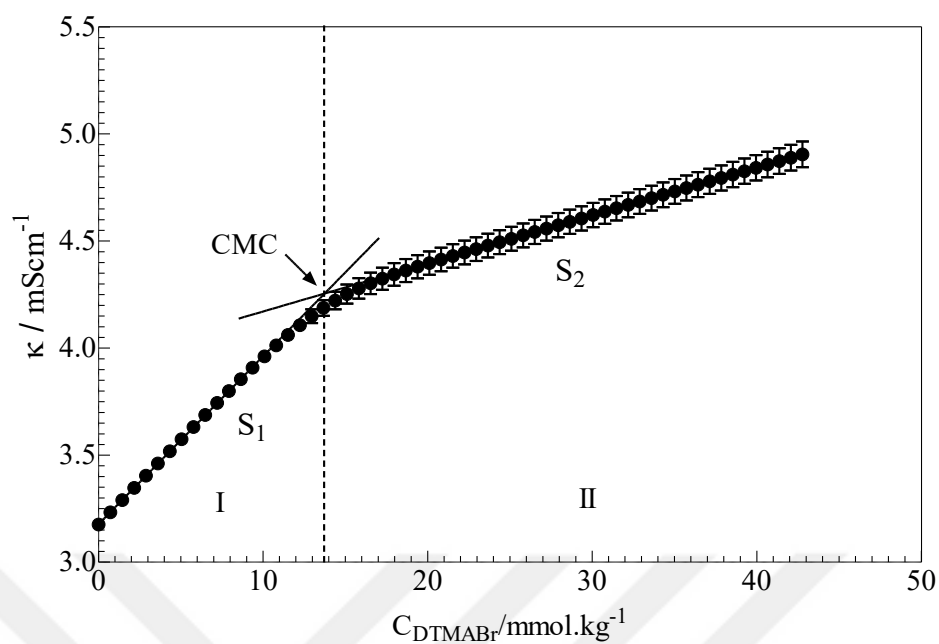


Figure 3.6. Plot of electrical conductivity of DTMABr/KF/water solution versus DTMABr concentration at 25.0°C .

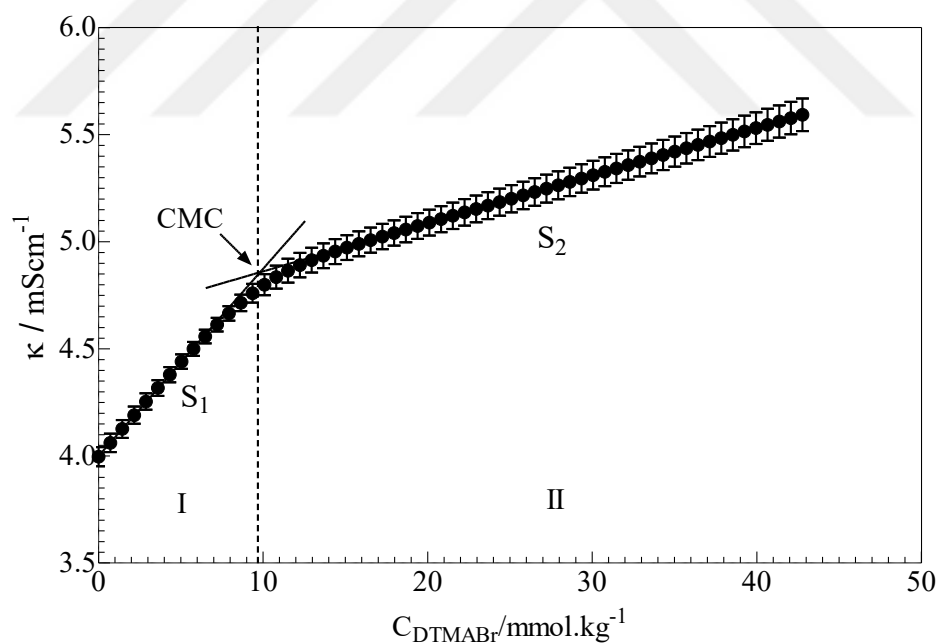


Figure 3.7. Plot of electrical conductivity of DTMABr/KCl/water solution versus DTMABr concentration at 25.0°C .

Table 3.3. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/electrolyte/ water solutions, where electrolytes are NaBr, KBr, RbBr, CsBr, KF, and KCl.

Electrolyte	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
NaBr	0.07333 ± 0.00006	1.0000	0.02234 ± 0.00000	1.0000
KBr	0.07696 ± 0.00017	1.0000	0.02118 ± 0.00000	1.0000
RbBr	0.07553 ± 0.00013	1.0000	0.02081 ± 0.00000	1.0000
CsBr	0.07906 ± 0.00051	0.9998	0.02015 ± 0.00000	1.0000
KF	0.07842 ± 0.00013	0.9998	0.02243 ± 0.00003	0.9999
KCl	0.08744 ± 0.00042	0.9998	0.02237 ± 0.00004	0.9999

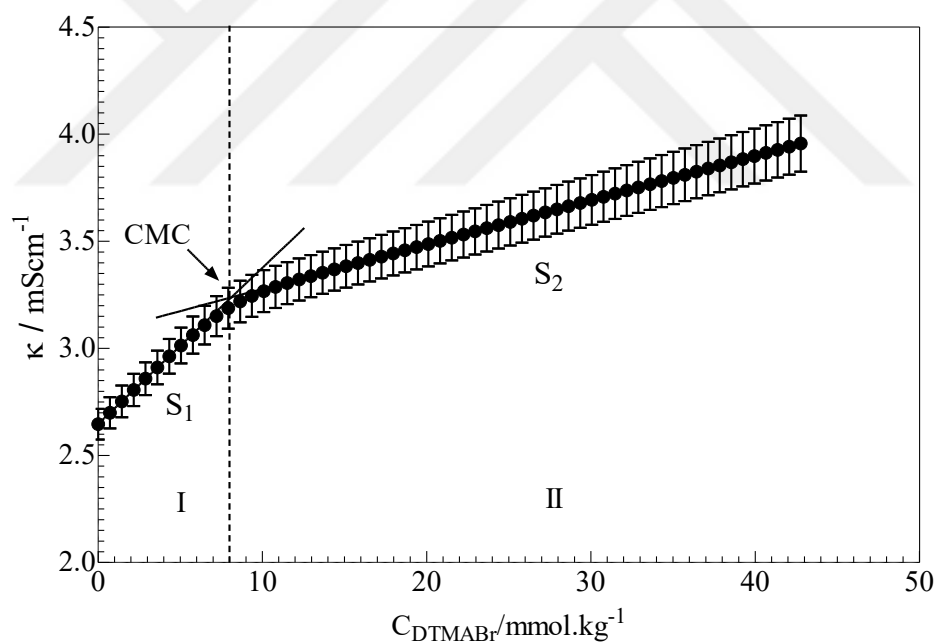


Figure 3.8. Plot of electrical conductivity of DTMABr/LiBr/2% EG-water solution versus DTMABr concentration at 25.0°C.

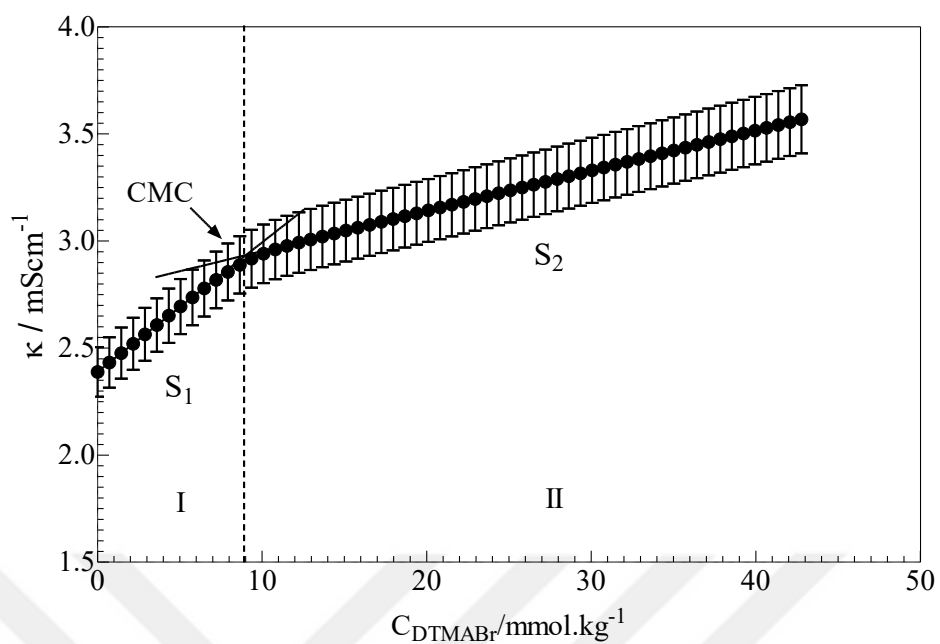


Figure 3.9. Plot of electrical conductivity of DTMABr/LiBr/4% EG-water solution versus DTMABr concentration at 25.0°C.

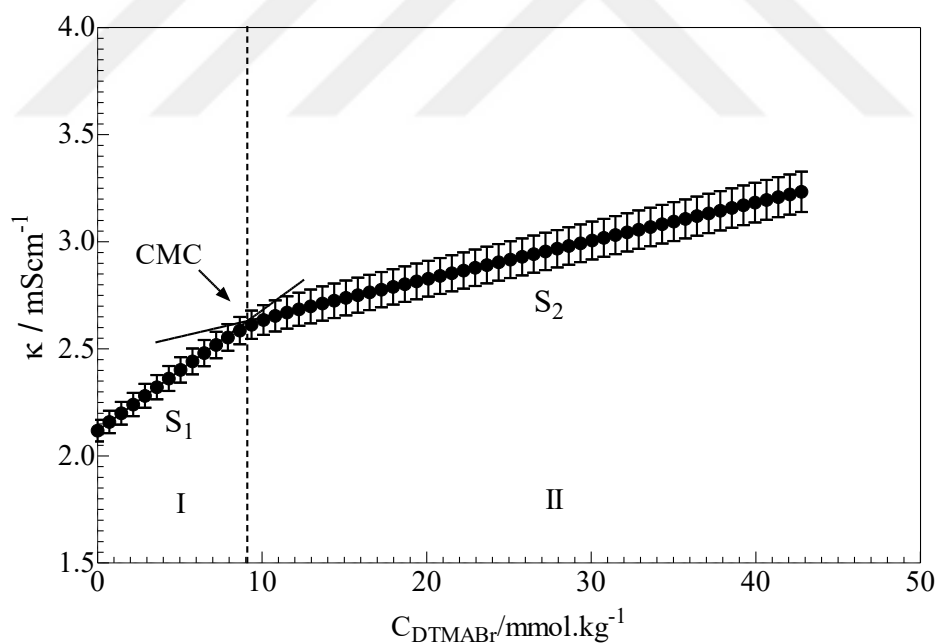


Figure 3.10. Plot of electrical conductivity of DTMABr/LiBr/6% EG-water solution versus DTMABr concentration at 25.0°C.

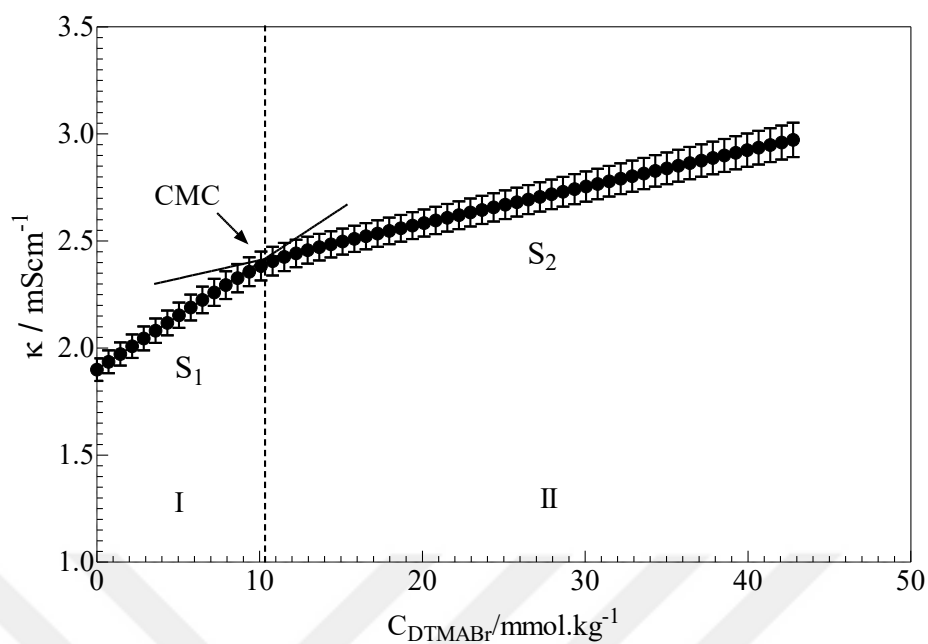


Figure 3.11. Plot of electrical conductivity of DTMABr/LiBr/8% EG-water solution versus DTMABr concentration at 25.0°C.

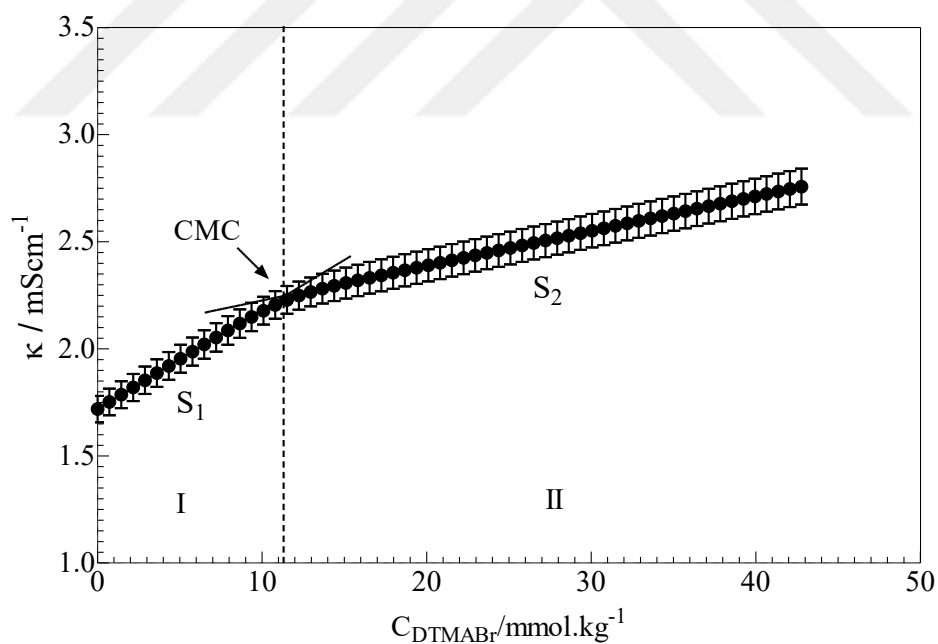


Figure 3.12. Plot of electrical conductivity of DTMABr/LiBr/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.4. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/LiBr/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07292 ± 0.00022	0.9999	0.02073 ± 0.00001	1.0000
4	0.06042 ± 0.00009	1.0000	0.01880 ± 0.00001	1.0000
6	0.05617 ± 0.00007	1.0000	0.01792 ± 0.00001	1.0000
8	0.05010 ± 0.00007	1.0000	0.01715 ± 0.00001	1.0000
10	0.04641 ± 0.00005	0.9998	0.01624 ± 0.00001	1.0000

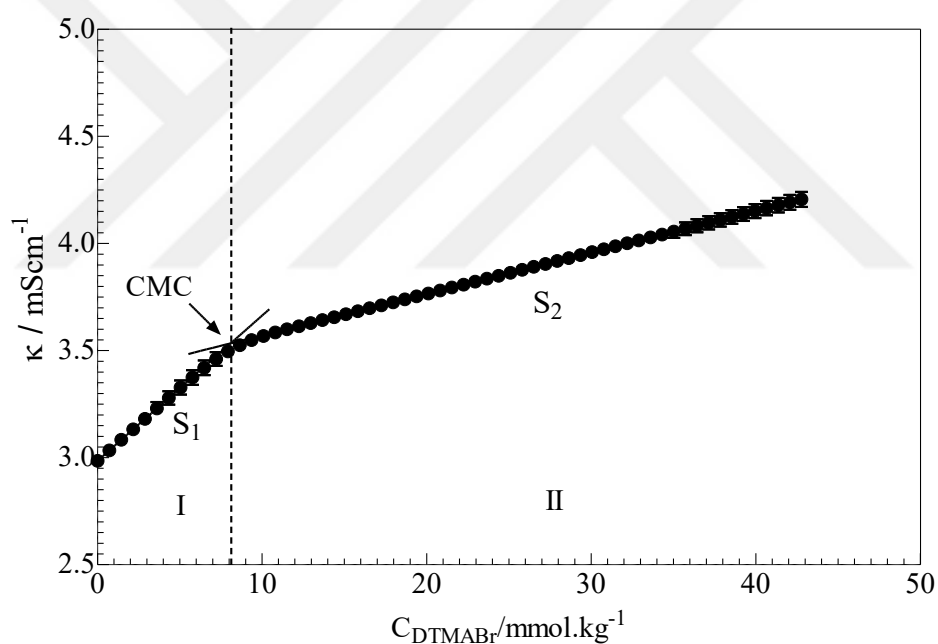


Figure 3.13. Plot of electrical conductivity of DTMABr/NaBr/2% EG-water solution versus DTMABr concentration at 25.0°C.

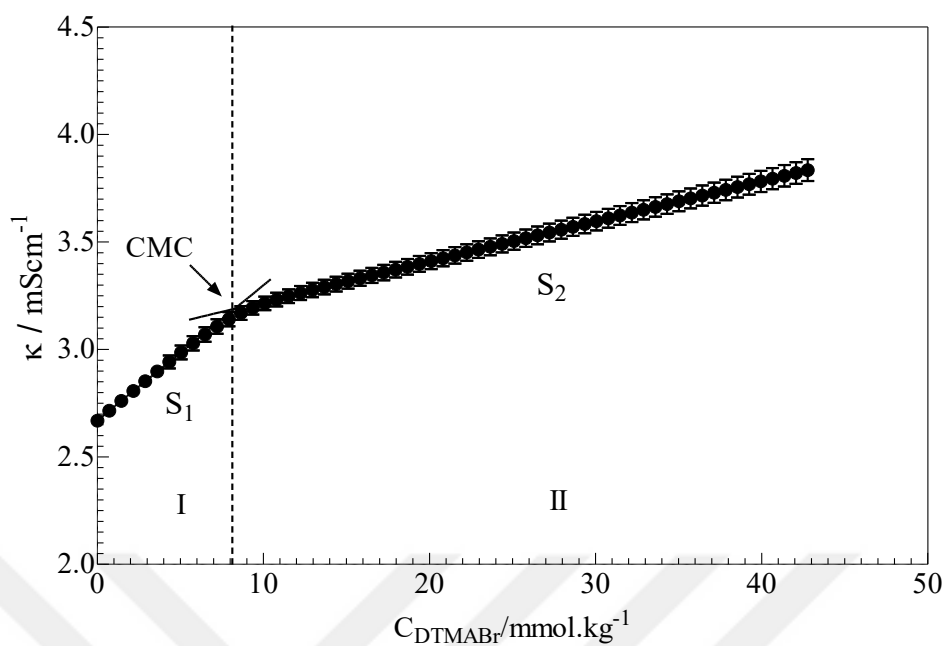


Figure 3.14. Plot of electrical conductivity of DTMABr/NaBr/4% EG-water solution versus DTMABr concentration at 25.0°C .

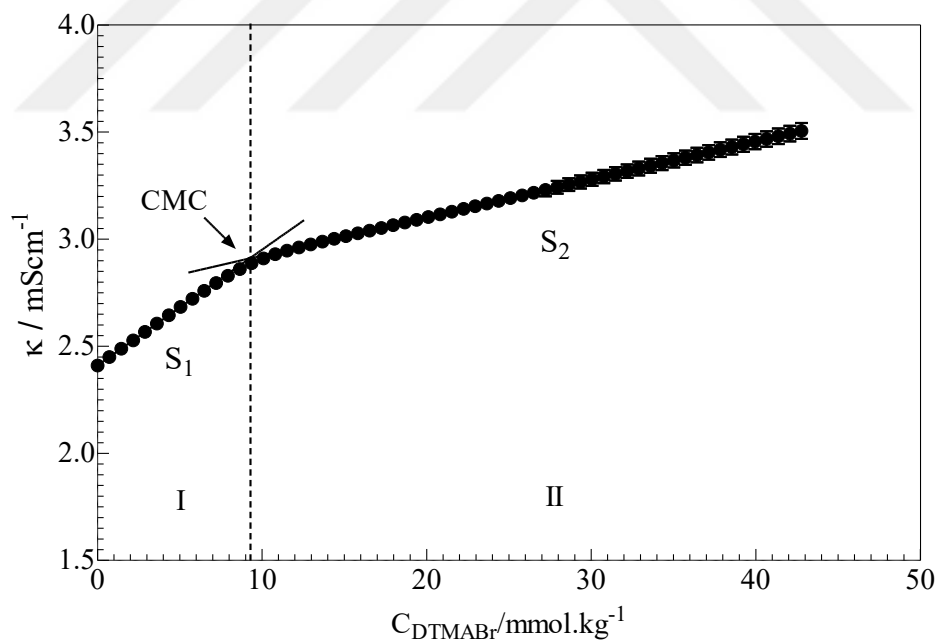


Figure 3.15. Plot of electrical conductivity of DTMABr/NaBr/6% EG-water solution versus DTMABr concentration at 25.0°C .

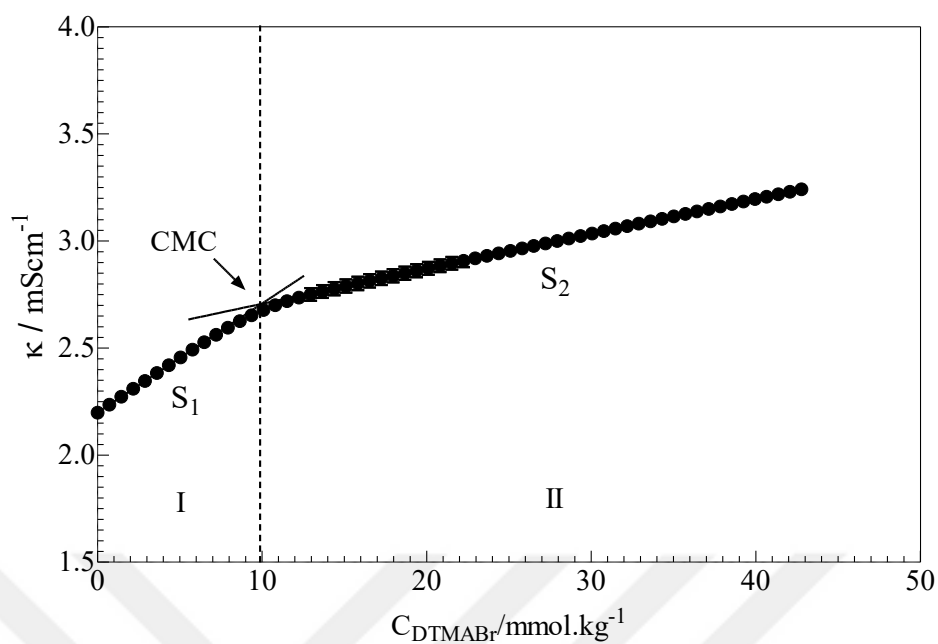


Figure 3.16. Plot of electrical conductivity of DTMABr/NaBr/8% EG-water solution versus DTMABr concentration at 25.0°C.

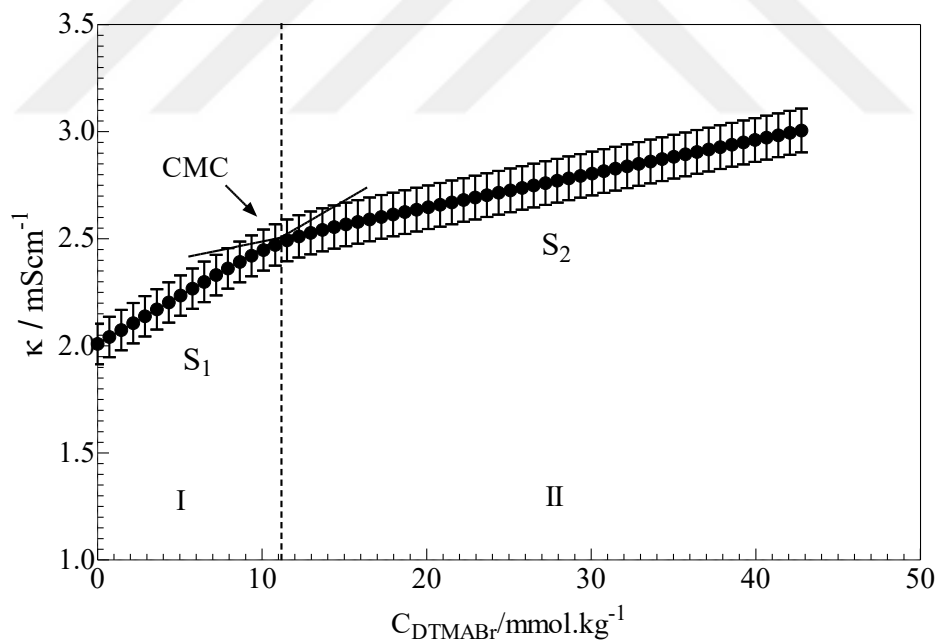


Figure 3.17. Plot of electrical conductivity of DTMABr/NaBr/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.5. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/NaBr/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.06778 ± 0.00006	1.0000	0.01938 ± 0.00000	1.0000
4	0.06288 ± 0.00015	1.0000	0.01870 ± 0.00001	1.0000
6	0.05404 ± 0.00007	1.0000	0.01776 ± 0.00001	1.0000
8	0.05090 ± 0.00012	1.0000	0.01634 ± 0.00002	1.0000
10	0.04457 ± 0.00006	1.0000	0.01583 ± 0.00001	1.0000

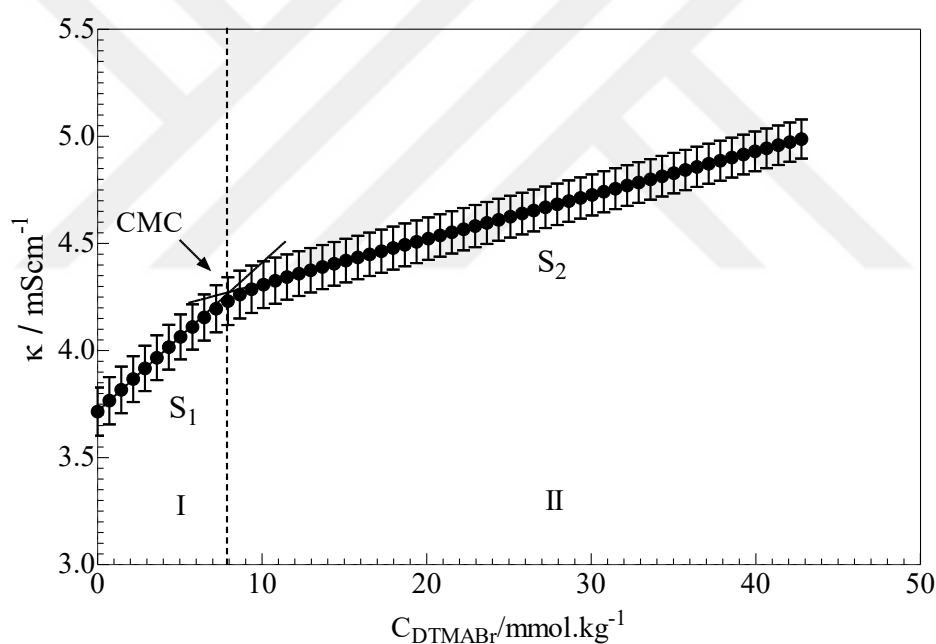


Figure 3.18. Plot of electrical conductivity of DTMABr/KBr/2% EG-water solution versus DTMABr concentration at 25.0°C.

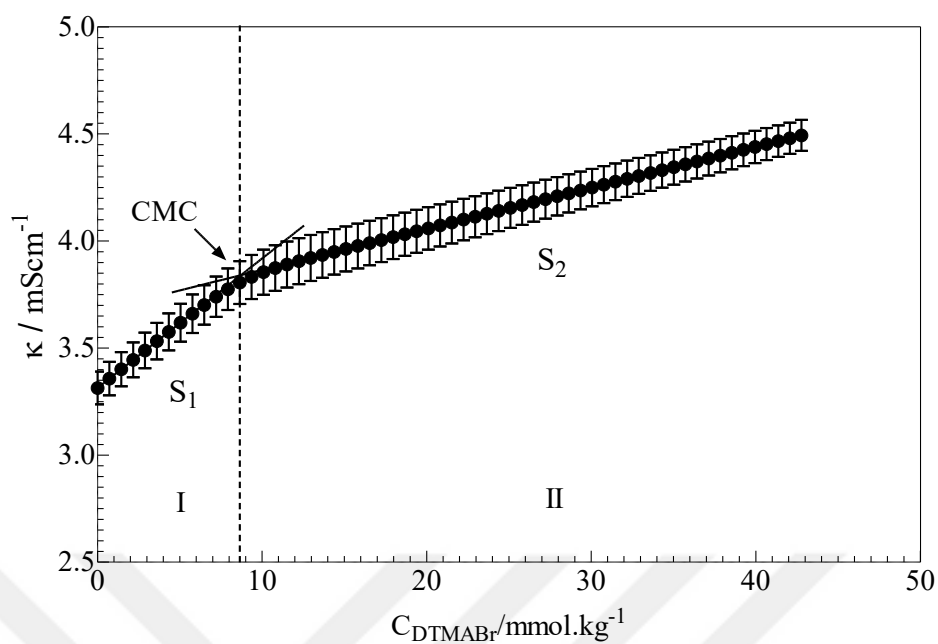


Figure 3.19. Plot of electrical conductivity of DTMABr/KBr/4% EG-water solution versus DTMABr concentration at 25.0°C.

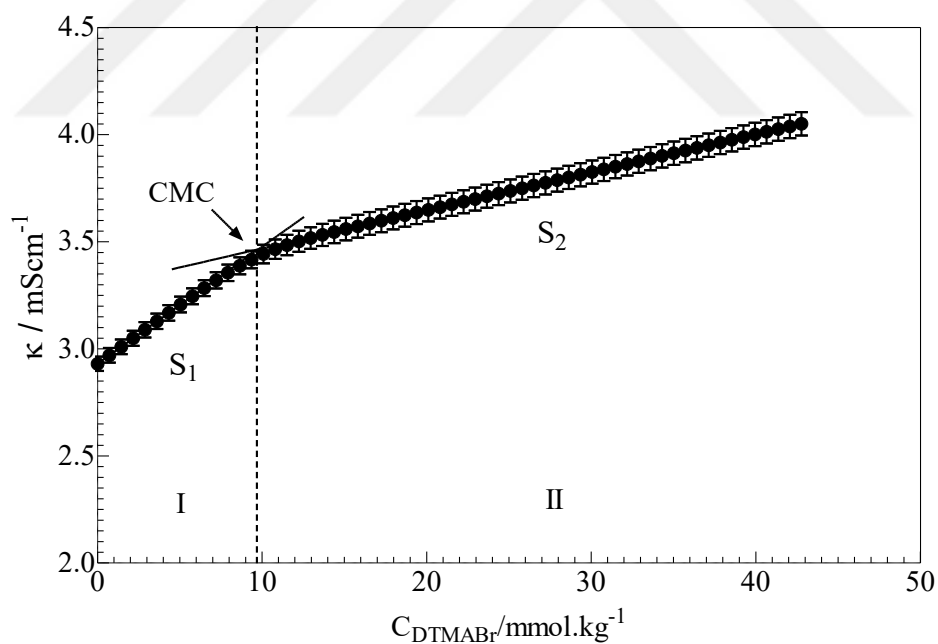


Figure 3.20. Plot of electrical conductivity of DTMABr/KBr/6% EG-water solution versus DTMABr concentration at 25.0°C.

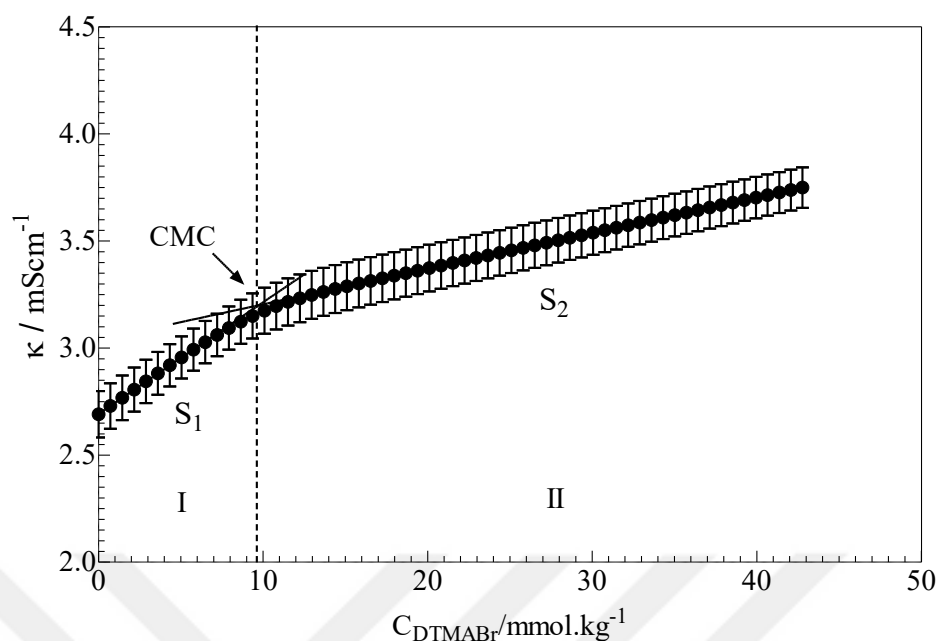


Figure 3.21. Plot of electrical conductivity of DTMABr/KBr/8% EG-water solution versus DTMABr concentration at 25.0°C.

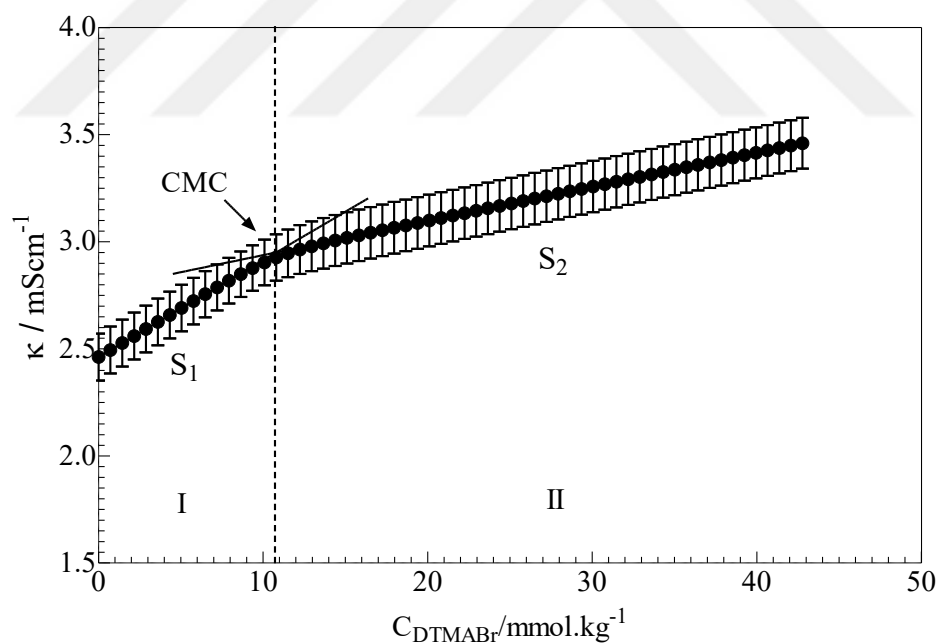


Figure 3.22. Plot of electrical conductivity of DTMABr/KBr/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.6. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KBr/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.06949 ± 0.00016	1.0000	0.02056 ± 0.00001	1.0000
4	0.06045 ± 0.00008	1.0000	0.01917 ± 0.00001	1.0000
6	0.05462 ± 0.00012	1.0000	0.01777 ± 0.00001	1.0000
8	0.05212 ± 0.00025	0.9998	0.01667 ± 0.00002	0.9999
10	0.04522 ± 0.00005	1.0000	0.01596 ± 0.00001	1.0000

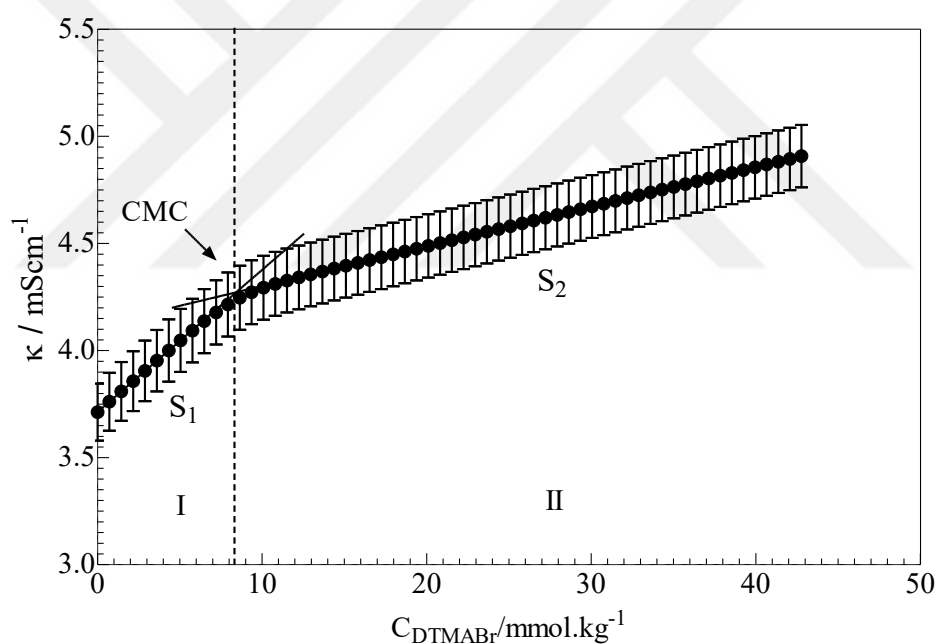


Figure 3.23. Plot of electrical conductivity of DTMABr/RbBr/2% EG-water solution versus DTMABr concentration at 25.0°C.

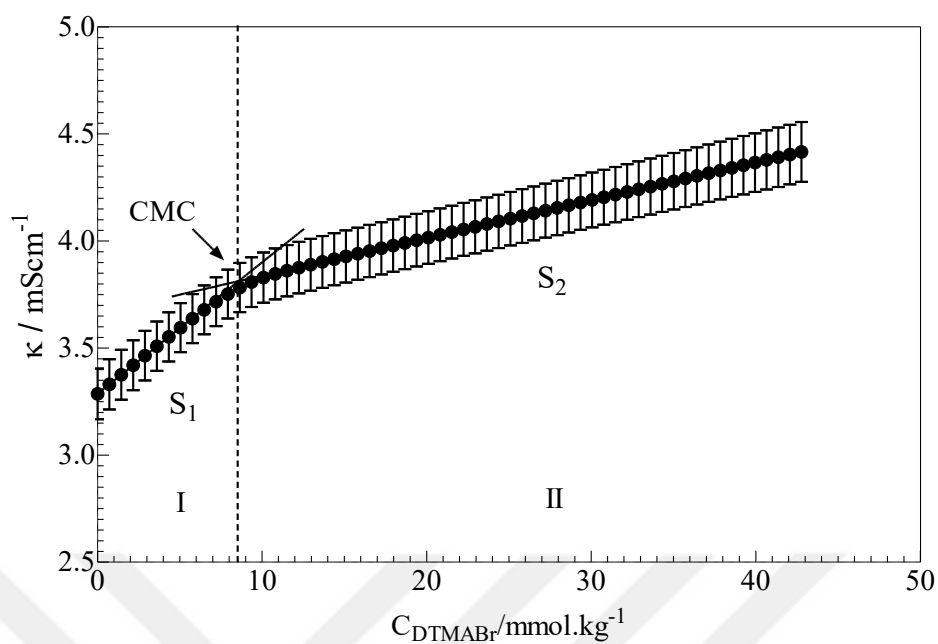


Figure 3.24. Plot of electrical conductivity of DTMABr/RbBr/4% EG-water solution versus DTMABr concentration at 25.0°C.

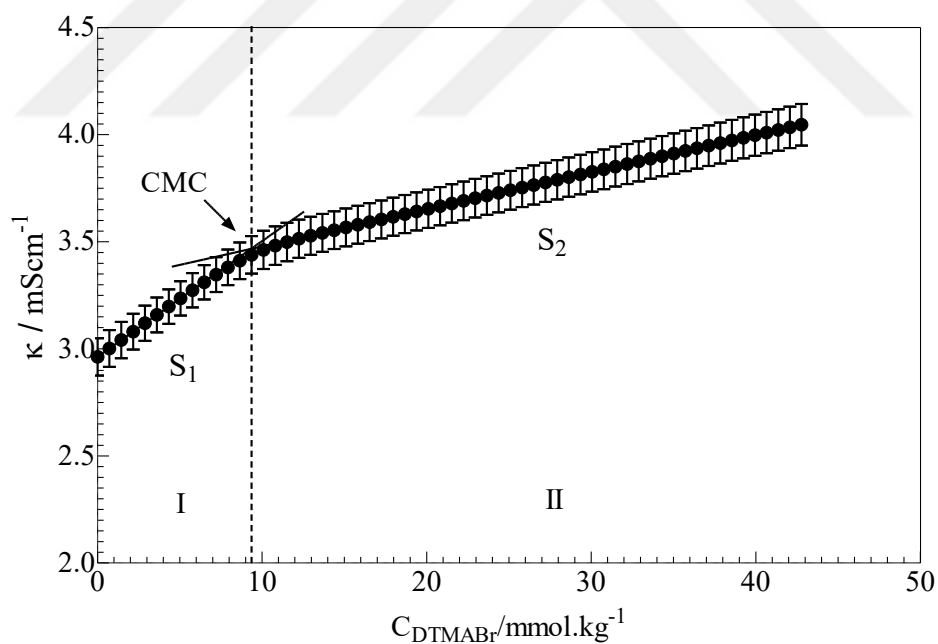


Figure 3.25. Plot of electrical conductivity of DTMABr/RbBr/6% EG-water solution versus DTMABr concentration at 25.0°C.

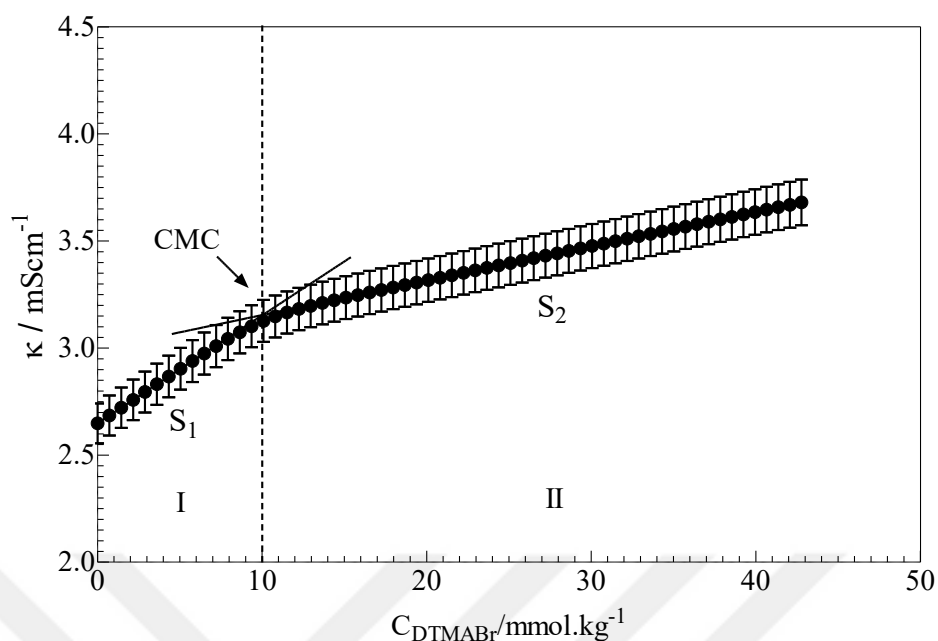


Figure 3.26. Plot of electrical conductivity of DTMABr/RbBr/8% EG-water solution versus DTMABr concentration at 25.0°C.

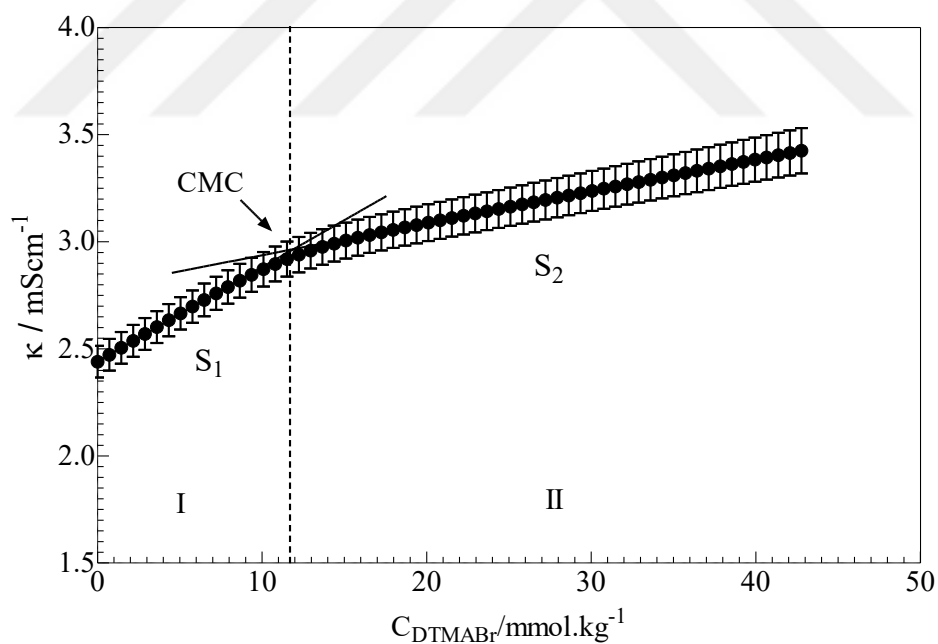


Figure 3.27. Plot of electrical conductivity of DTMABr/RbBr/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.7. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/RbBr/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.06635 ± 0.00011	1.0000	0.01852 ± 0.00001	1.0000
4	0.06138 ± 0.00012	1.0000	0.01766 ± 0.00001	1.0000
6	0.05400 ± 0.00011	1.0000	0.01734 ± 0.00001	1.0000
8	0.05037 ± 0.00008	1.0000	0.01609 ± 0.00002	1.0000
10	0.04395 ± 0.00019	0.9998	0.01494 ± 0.00003	0.9998

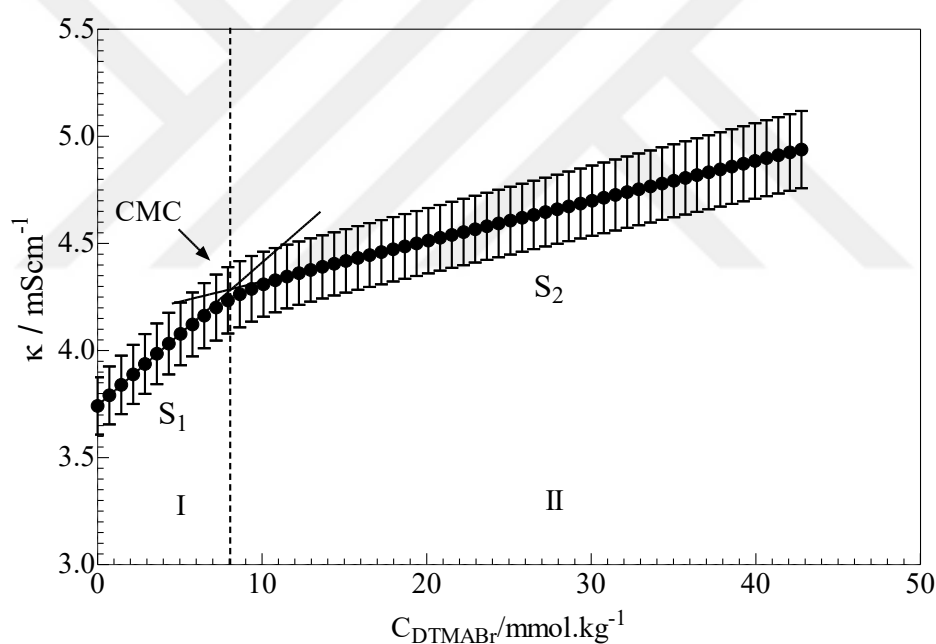


Figure 3.28. Plot of electrical conductivity of DTMABr/CsBr/2% EG-water solution versus DTMABr concentration at 25.0°C.

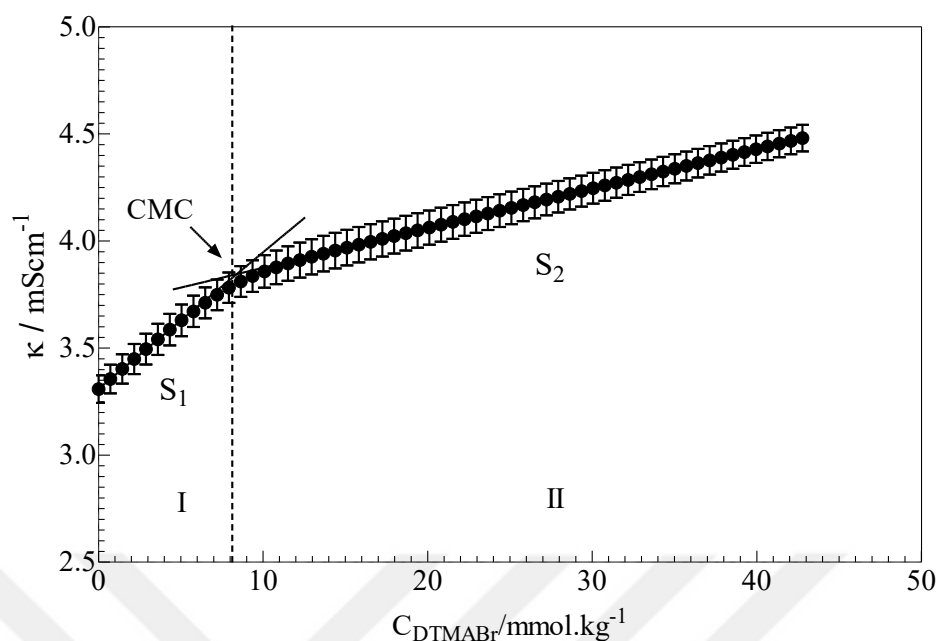


Figure 3.29. Plot of electrical conductivity of DTMABr/CsBr/4% EG-water solution versus DTMABr concentration at 25.0°C.

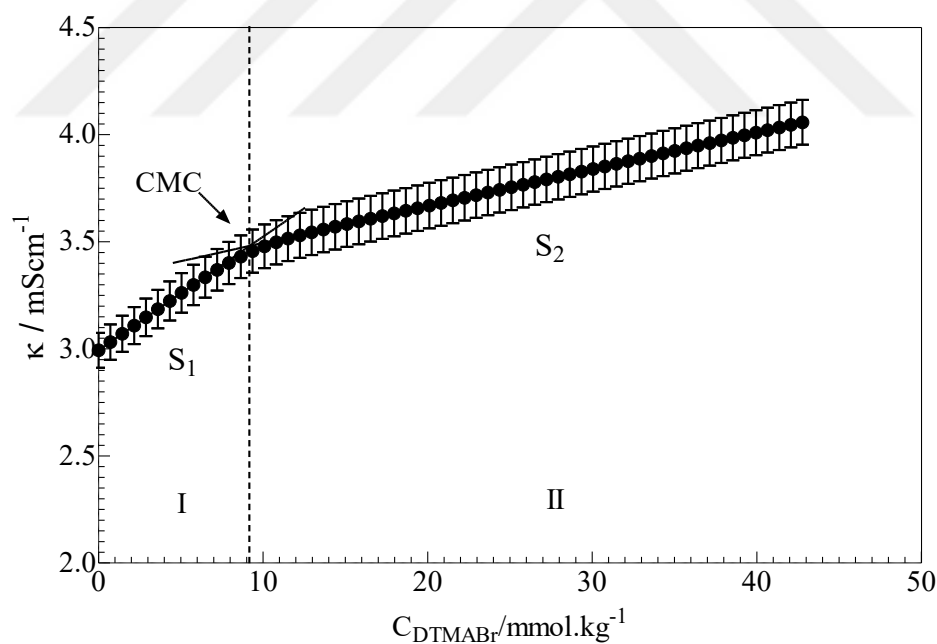


Figure 3.30. Plot of electrical conductivity of DTMABr/CsBr/6% EG-water solution versus DTMABr concentration at 25.0°C.

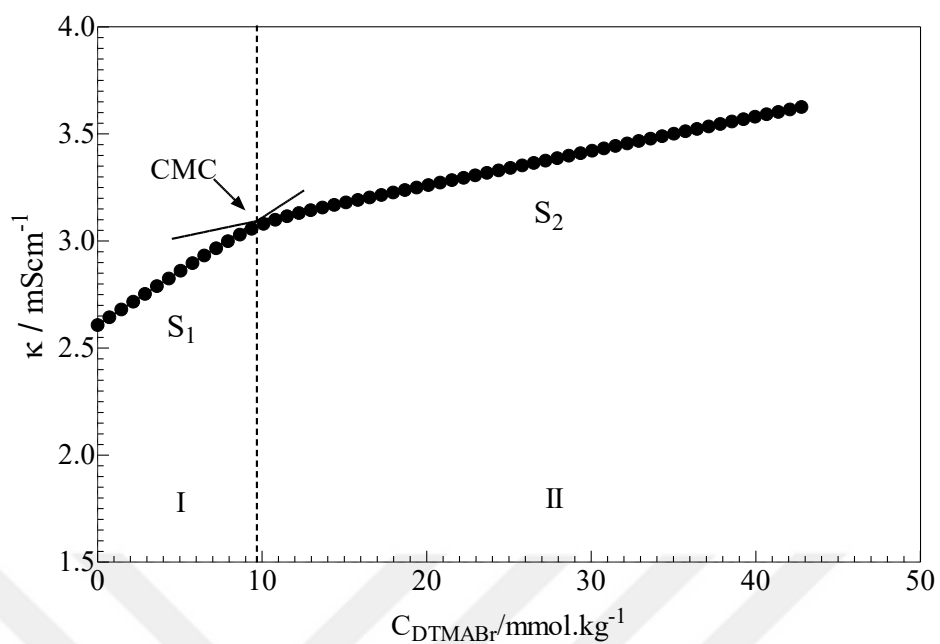


Figure 3.31. Plot of electrical conductivity of DTMABr/CsBr/8% EG-water solution versus DTMABr concentration at 25.0°C.

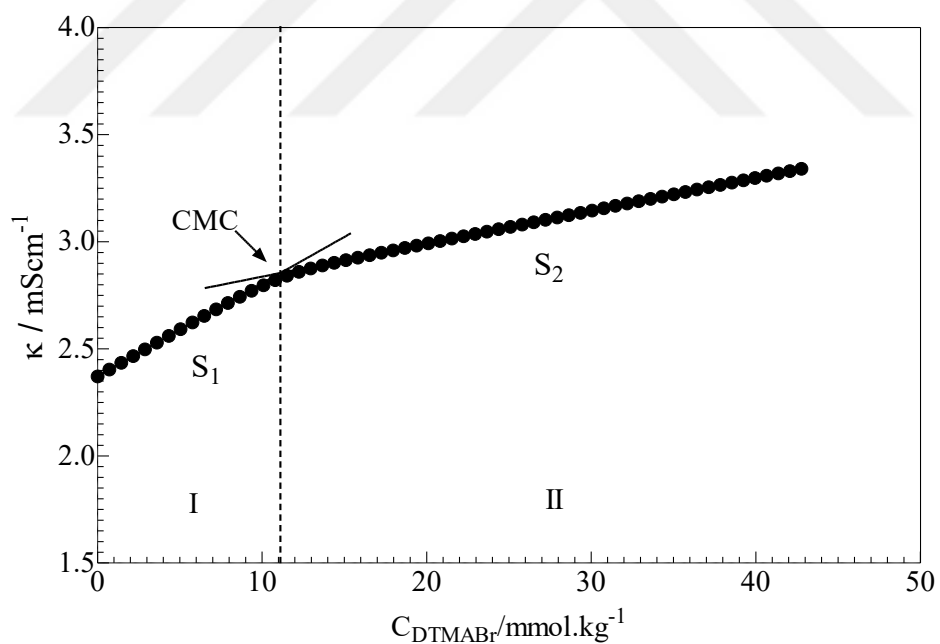


Figure 3.32. Plot of electrical conductivity of DTMABr/CsBr/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.8. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/CsBr/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.06680 ± 0.00030	0.9999	0.01882 ± 0.00002	1.0000
4	0.06377 ± 0.00031	0.9999	0.01851 ± 0.00002	1.0000
6	0.05302 ± 0.00011	1.0000	0.01718 ± 0.00001	1.0000
8	0.05007 ± 0.00007	1.0000	0.01610 ± 0.00001	1.0000
10	0.04336 ± 0.00008	1.0000	0.01540 ± 0.00001	1.0000

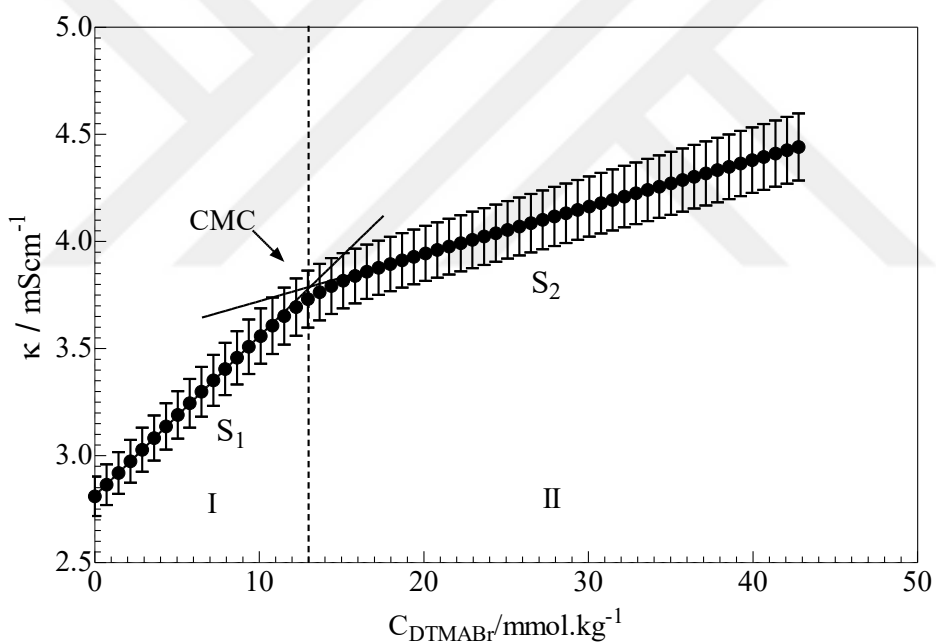


Figure 3.33. Plot of electrical conductivity of DTMABr/KF/2% EG-water solution versus DTMABr concentration at 25.0°C.

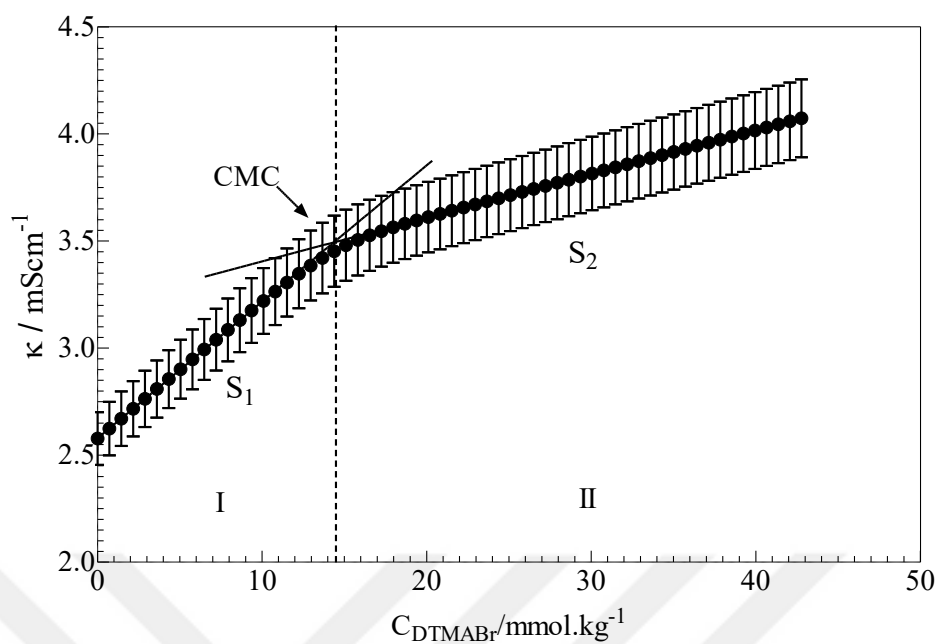


Figure 3.34. Plot of electrical conductivity of DTMABr/KF/4% EG-water solution versus DTMABr concentration at 25.0°C.

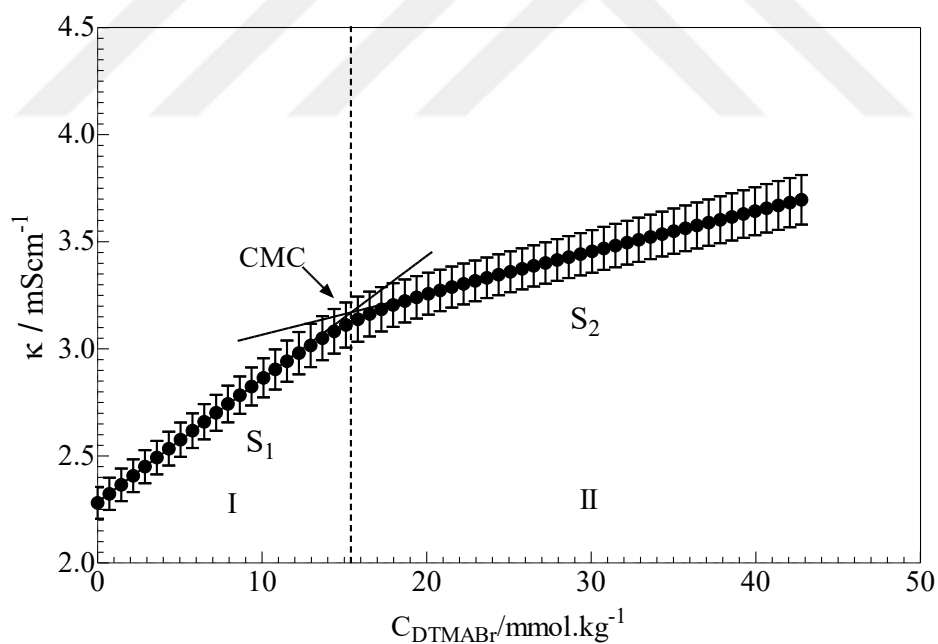


Figure 3.35. Plot of electrical conductivity of DTMABr/KF/6% EG-water solution versus DTMABr concentration at 25.0°C.

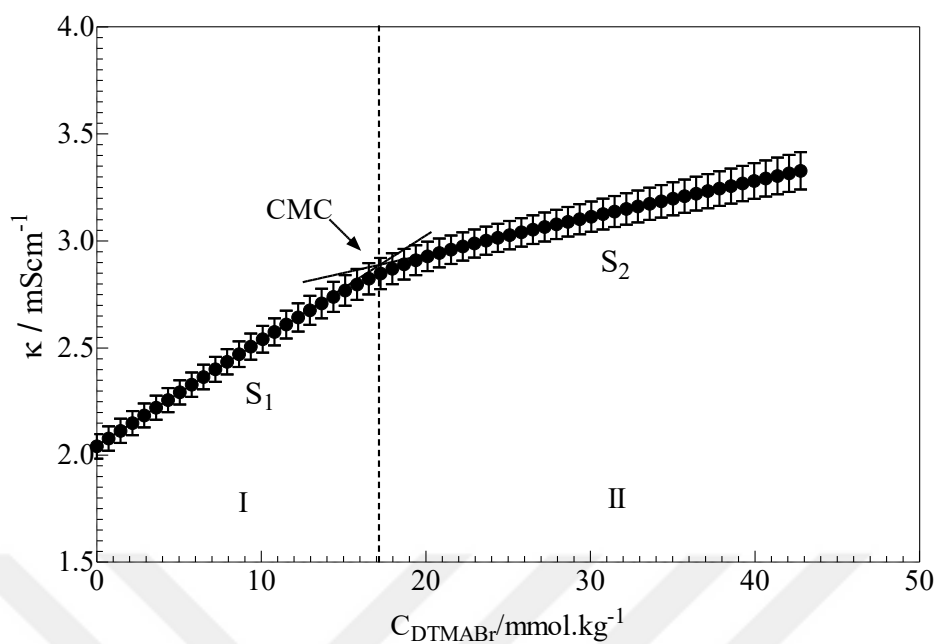


Figure 3.36. Plot of electrical conductivity of DTMABr/KF/8% EG-water solution versus DTMABr concentration at 25.0°C.

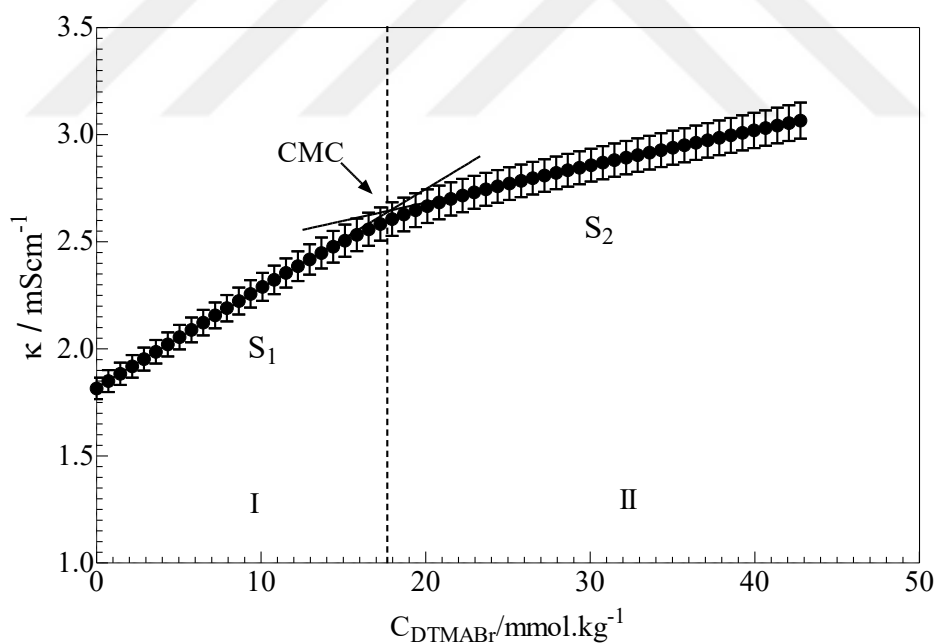


Figure 3.37. Plot of electrical conductivity of DTMABr/KF/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.9. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KF/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07455 ± 0.00018	0.9999	0.02200 ± 0.00003	0.9999
4	0.06372 ± 0.00009	1.0000	0.02044 ± 0.00003	0.9999
6	0.05748 ± 0.00019	0.9998	0.01932 ± 0.00007	0.9996
8	0.04908 ± 0.00014	0.9999	0.01729 ± 0.00008	0.9993
10	0.04634 ± 0.00017	0.9997	0.01699 ± 0.00011	0.9988

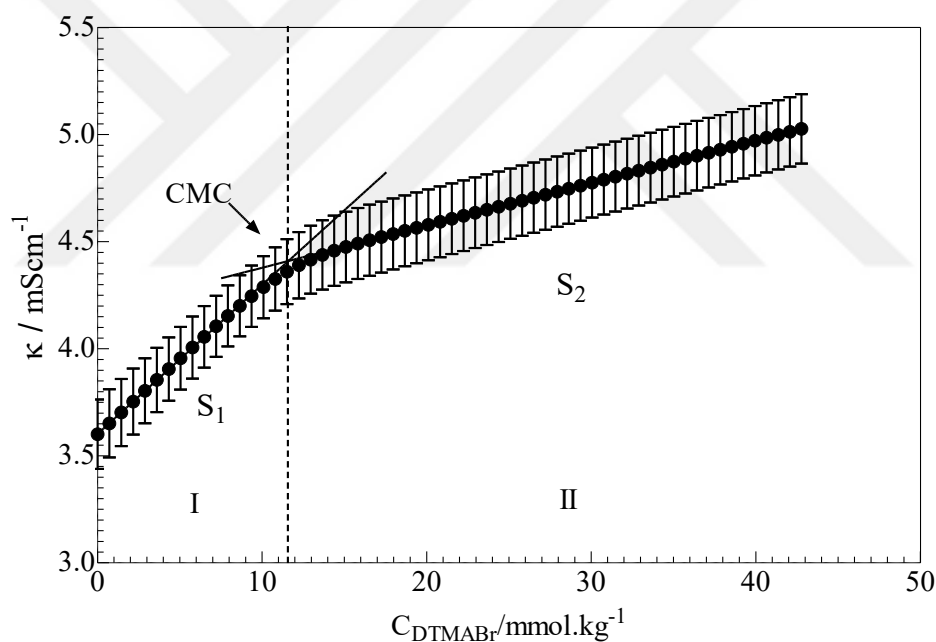


Figure 3.38. Plot of electrical conductivity of DTMABr/KCl/2% EG-water solution versus DTMABr concentration at 25.0°C.

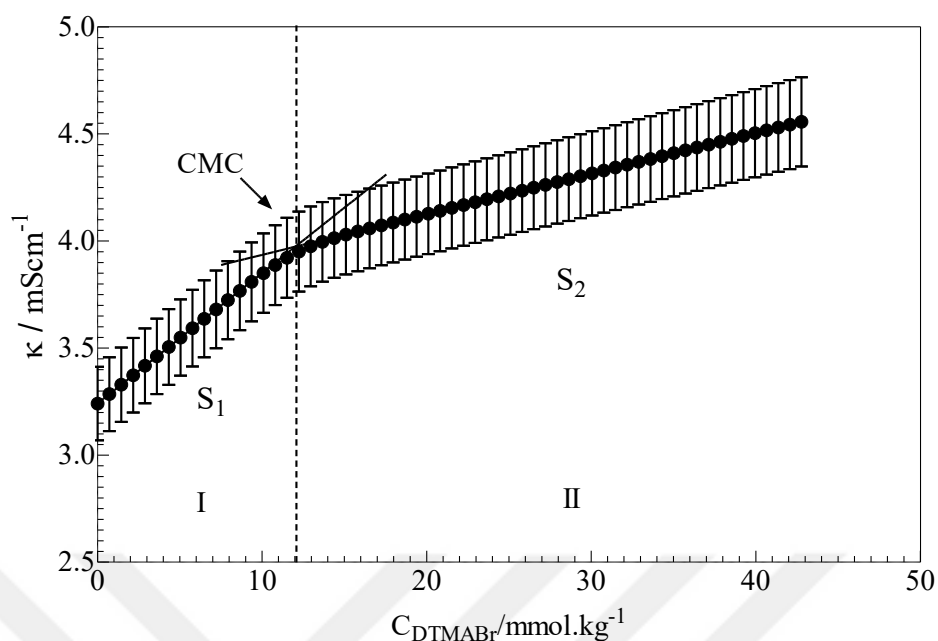


Figure 3.39. Plot of electrical conductivity of DTMABr/KCl/4% EG-water solution versus DTMABr concentration at 25.0°C.

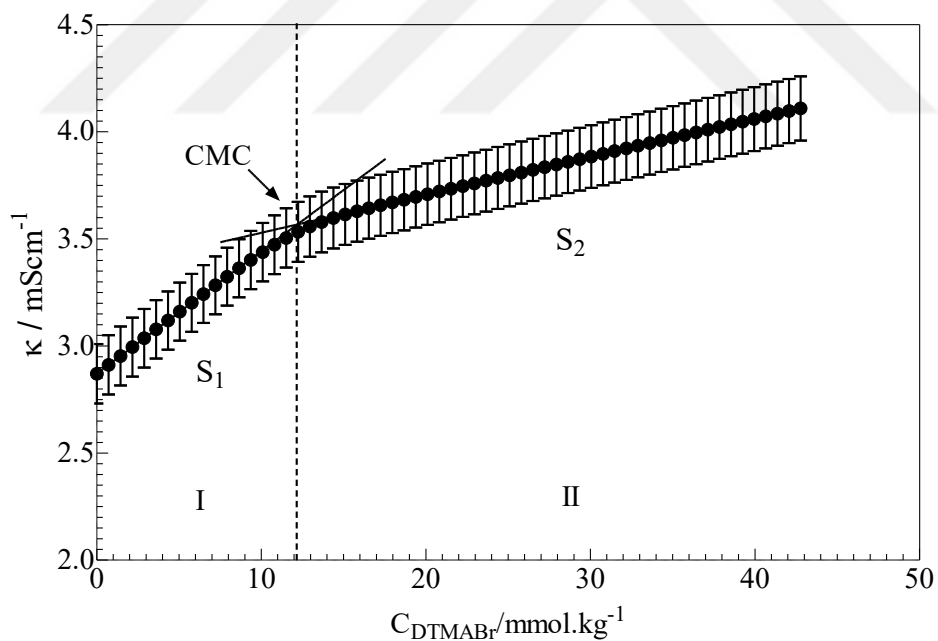


Figure 3.40. Plot of electrical conductivity of DTMABr/KCl/6% EG-water solution versus DTMABr concentration at 25.0°C.

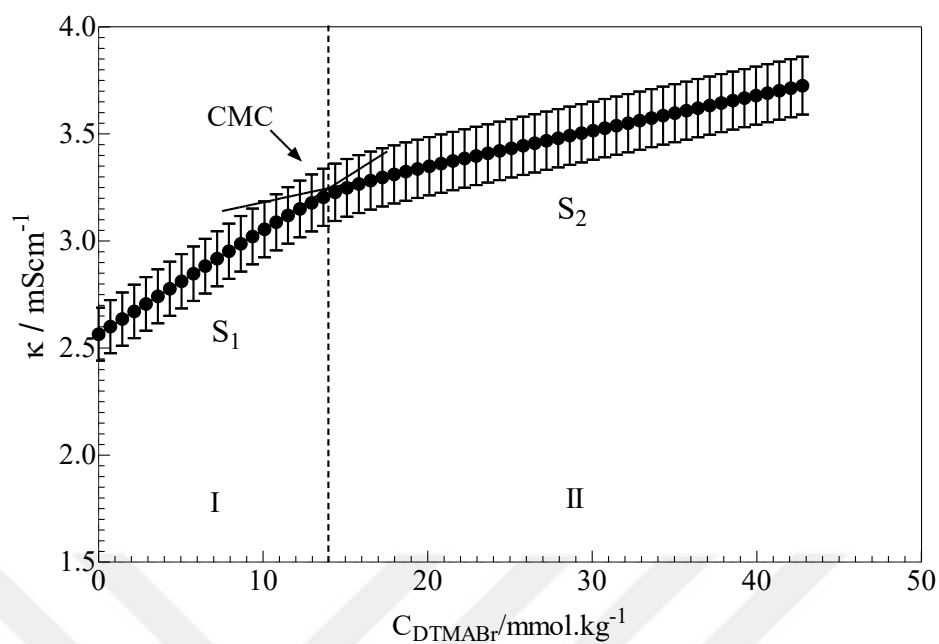


Figure 3.41. Plot of electrical conductivity of DTMABr/KCl/8% EG-water solution versus DTMABr concentration at 25.0°C.

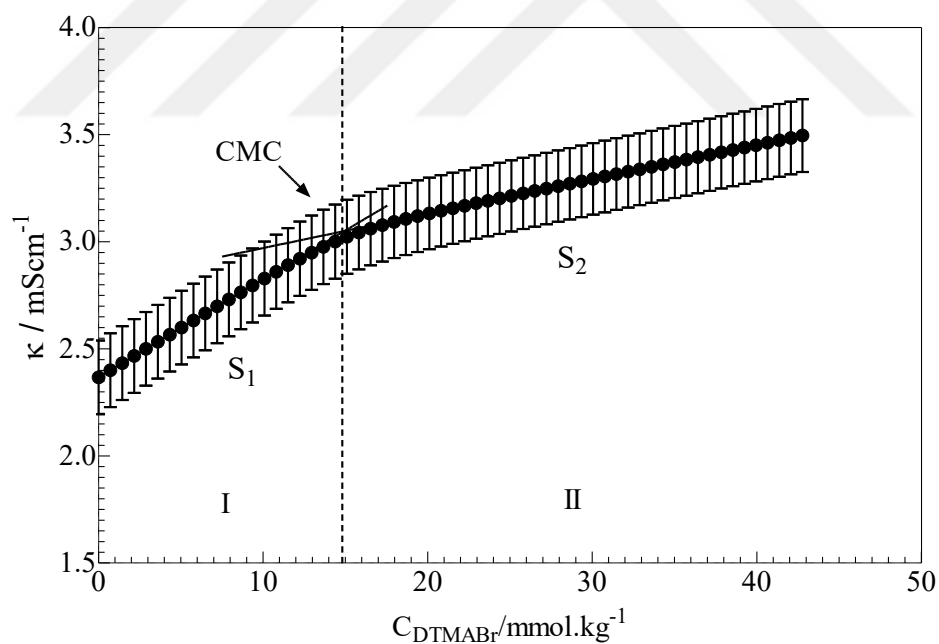


Figure 3.42. Plot of electrical conductivity of DTMABr/KCl/10% EG-water solution versus DTMABr concentration at 25.0°C.

Table 3.10. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KCl/EG-water solutions.

%EG	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.06962 ± 0.00016	0.9999	0.01981 ± 0.00002	1.0000
4	0.06097 ± 0.00004	1.0000	0.01898 ± 0.00001	1.0000
6	0.05713 ± 0.00009	1.0000	0.01775 ± 0.00002	1.0000
8	0.04860 ± 0.00009	1.0000	0.01665 ± 0.00002	0.9999
10	0.04565 ± 0.00008	1.0000	0.01606 ± 0.00003	0.9999

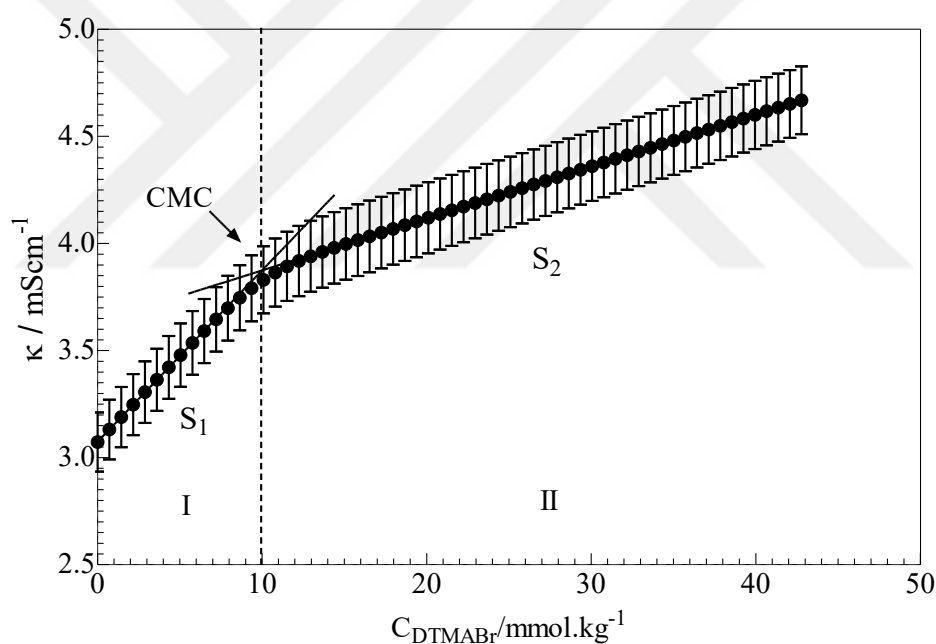


Figure 3.43. Plot of electrical conductivity of DTMABr/LiBr/2% FA-water solution versus DTMABr concentration at 25.0°C.

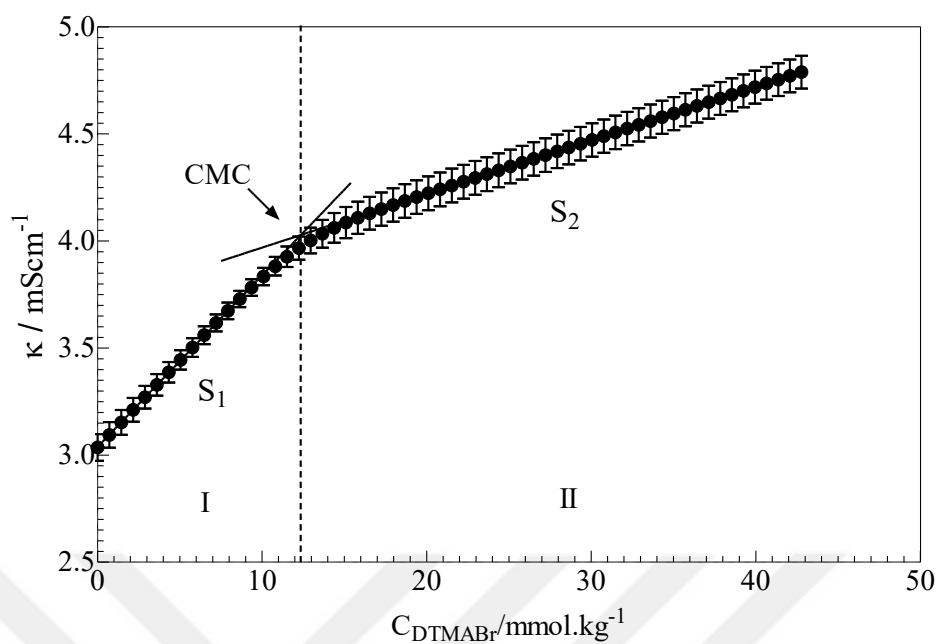


Figure 3.44. Plot of electrical conductivity of DTMABr/LiBr/4% FA-water solution versus DTMABr concentration at 25.0°C.

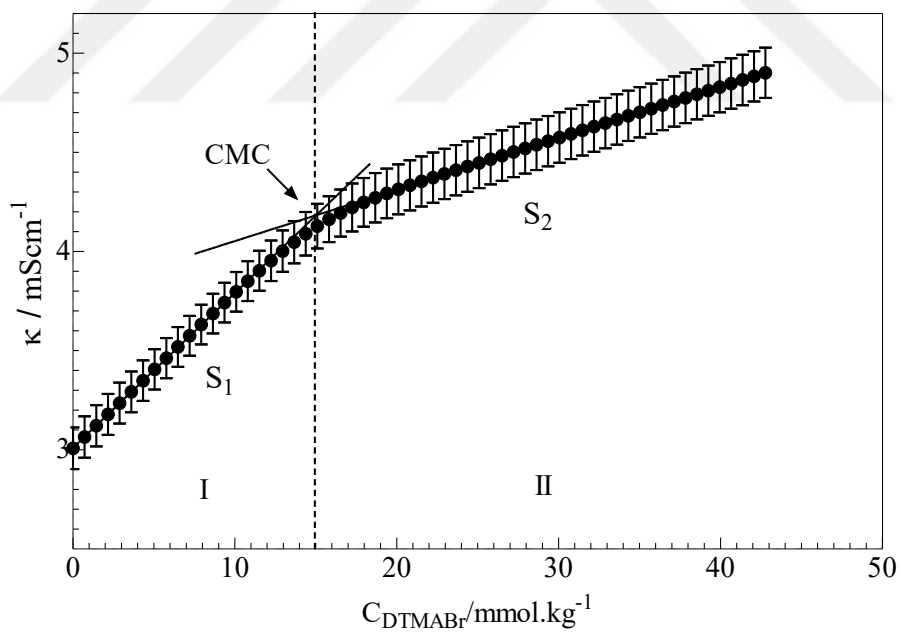


Figure 3.45. Plot of electrical conductivity of DTMABr/LiBr/6% FA-water solution versus DTMABr concentration at 25.0°C.

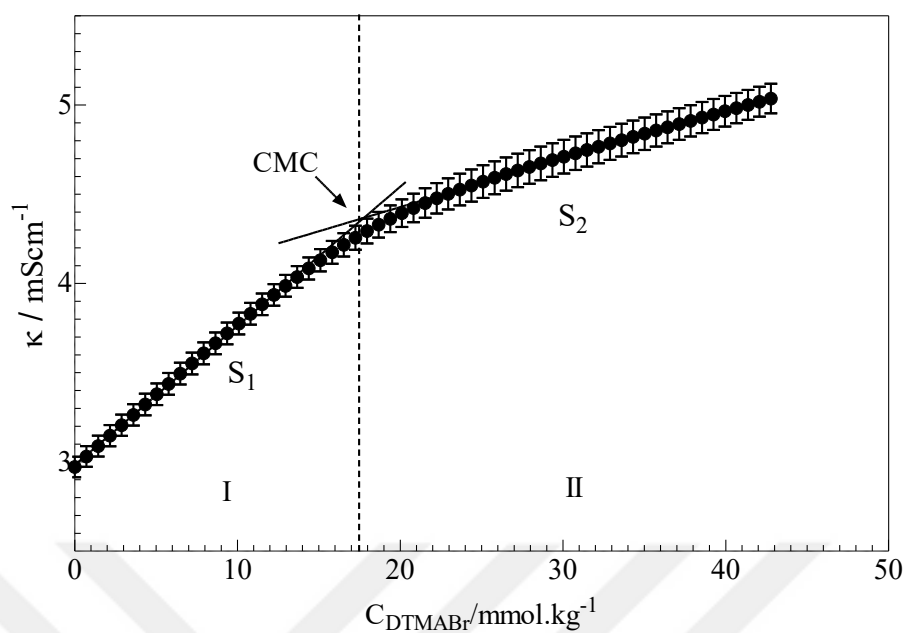


Figure 3.46. Plot of electrical conductivity of DTMABr/LiBr/8% FA-water solution versus DTMABr concentration at 25.0°C.

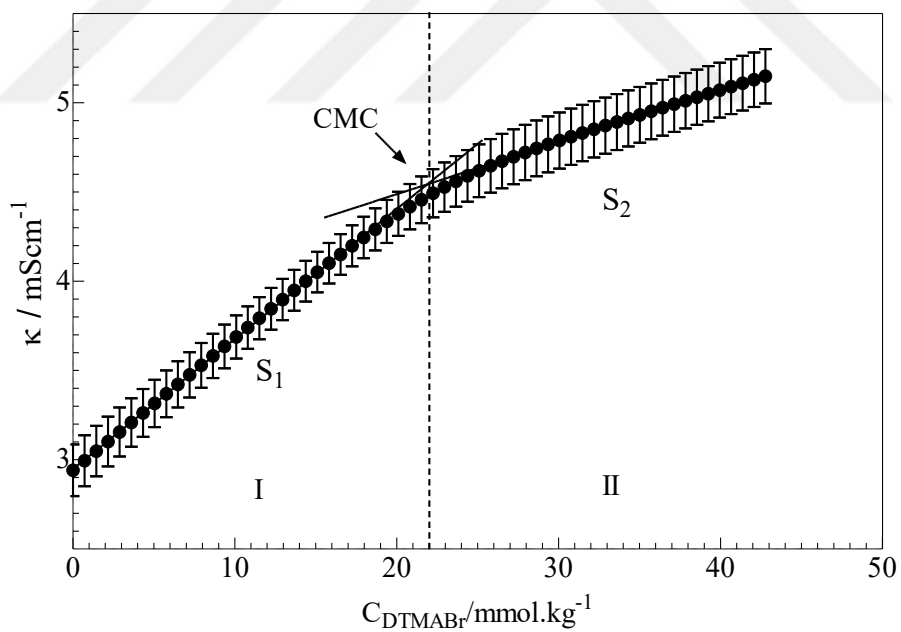


Figure 3.47. Plot of electrical conductivity of DTMABr/LiBr/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.11. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/LiBr/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.08006 ± 0.00015	1.0000	0.02426 ± 0.00002	1.0000
4	0.08011 ± 0.00021	0.9999	0.02504 ± 0.00003	1.0000
6	0.07807 ± 0.00016	0.9999	0.02597 ± 0.00006	0.9998
8	0.07801 ± 0.00040	0.9995	0.02716 ± 0.00025	0.9975
10	0.07288 ± 0.00020	0.9998	0.02934 ± 0.00023	0.9986

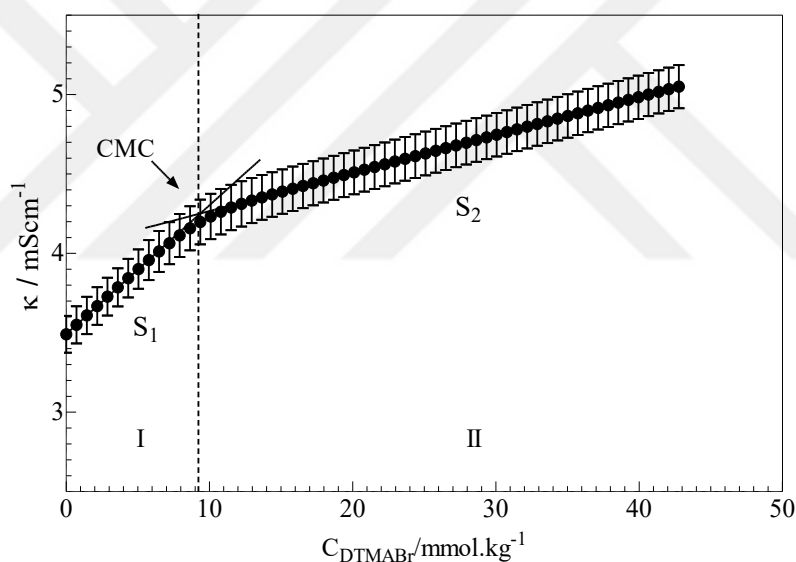


Figure3.48. Plot of electrical conductivity of DTMABr/NaBr/2% FA-water solution versus DTMABr concentration at 25.0°C.

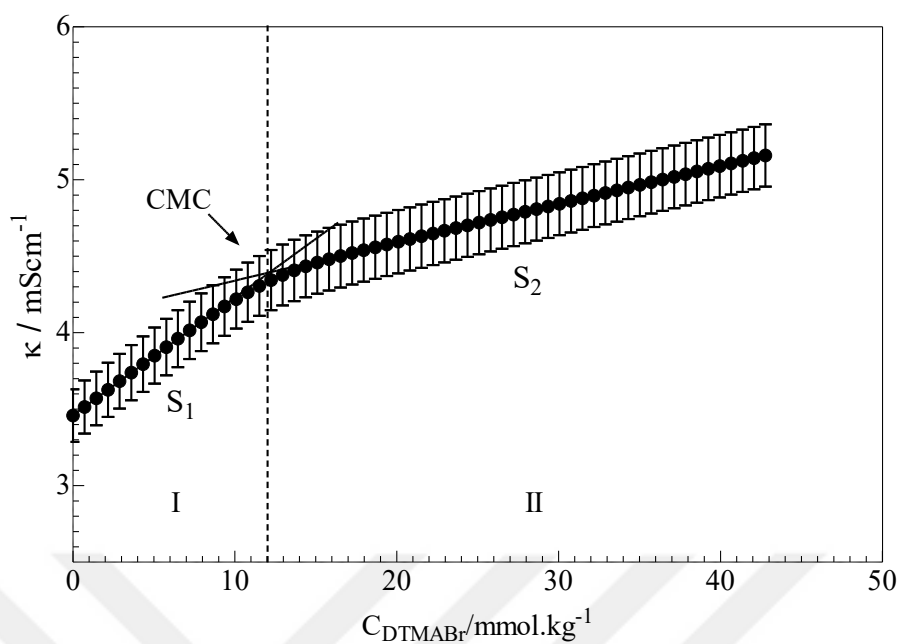


Figure 3.49. Plot of electrical conductivity of DTMABr/NaBr/4% FA-water solution versus DTMABr concentration at 25.0°C.

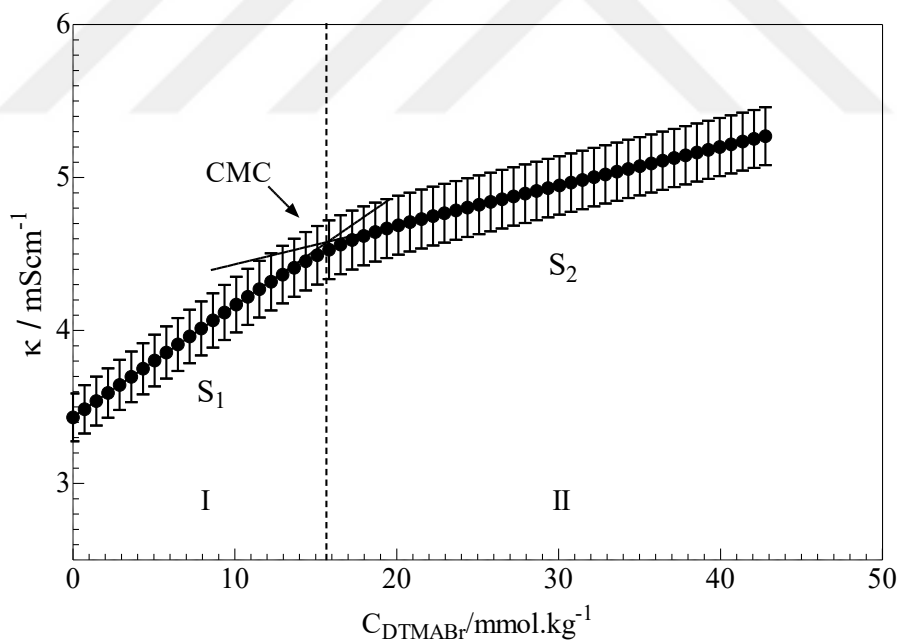


Figure 3.50. Plot of electrical conductivity of DTMABr/NaBr/6% FA-water solution versus DTMABr concentration at 25.0°C.

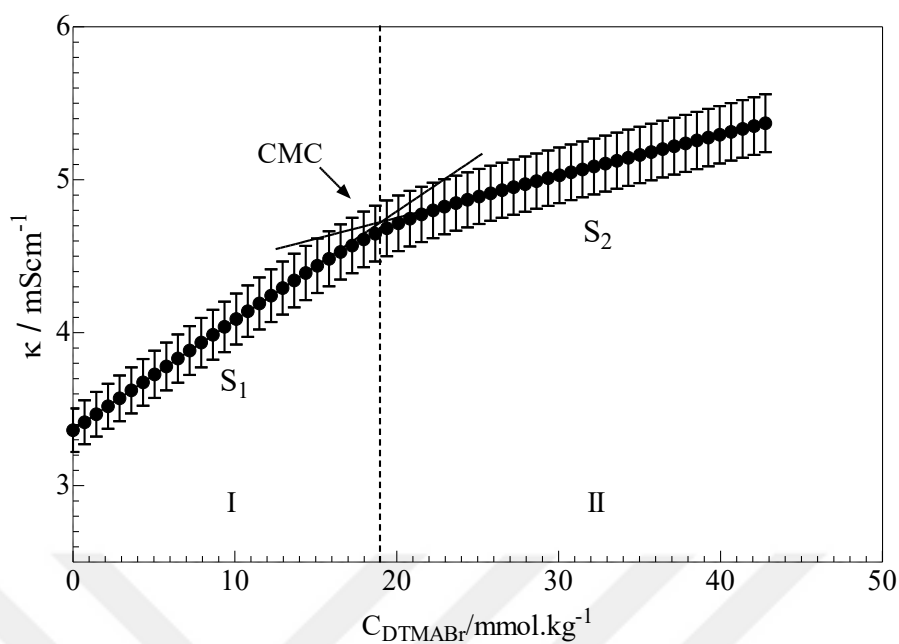


Figure 3.51. Plot of electrical conductivity of DTMABr/NaBr/8% FA-water solution versus DTMABr concentration at 25.0°C.

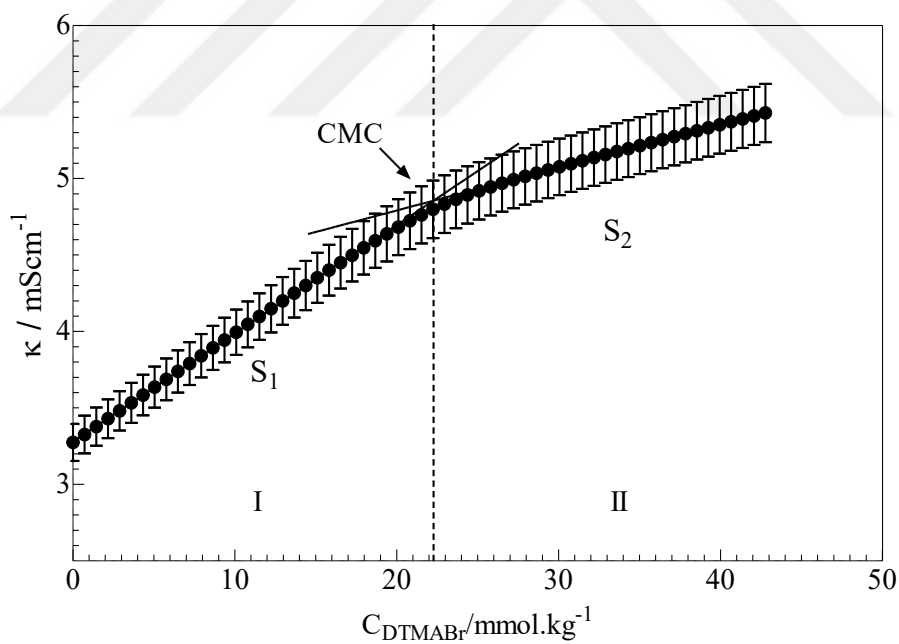


Figure 3.52. Plot of electrical conductivity of DTMABr/NaBr/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.12. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/NaBr/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.08113 ± 0.00024	0.9999	0.02394 ± 0.00003	0.9999
4	0.07691 ± 0.00020	0.9999	0.02504 ± 0.00004	0.9999
6	0.07276 ± 0.00015	0.9999	0.02564 ± 0.00007	0.9998
8	0.07134 ± 0.00017	0.9999	0.02734 ± 0.00011	0.9995
10	0.07081 ± 0.00013	0.9999	0.02812 ± 0.00012	0.9996

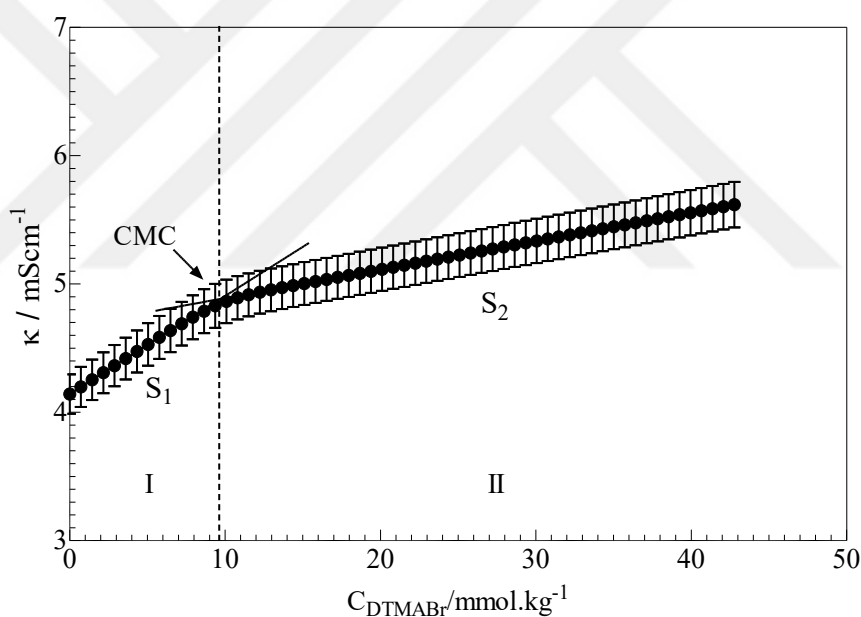


Figure 3.53. Plot of electrical conductivity of DTMABr/KBr/2% FA-water solution versus DTMABr concentration at 25.0°C.

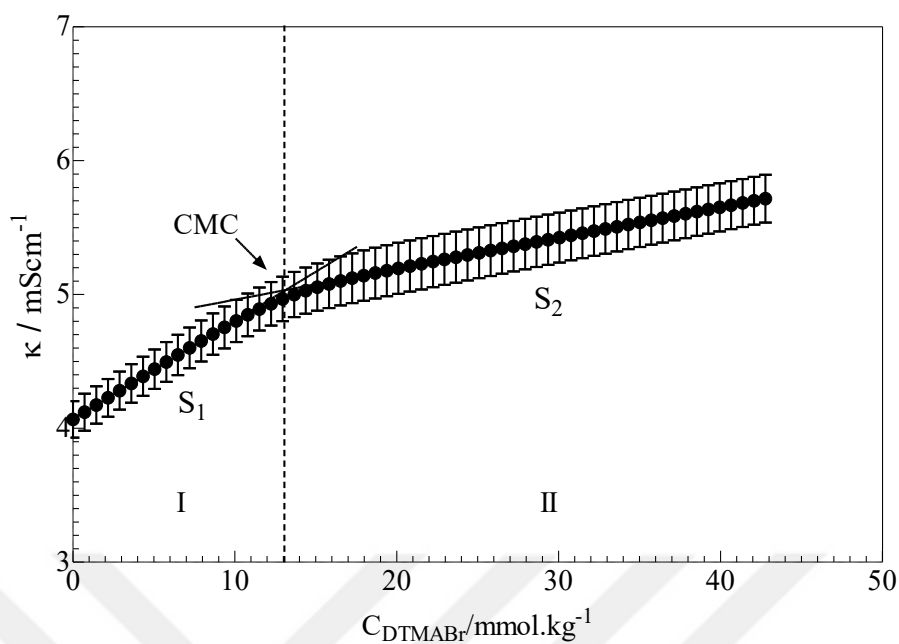


Figure 3.54. Plot of electrical conductivity of DTMABr/KBr/4% FA-water solution versus DTMABr concentration at 25.0°C.

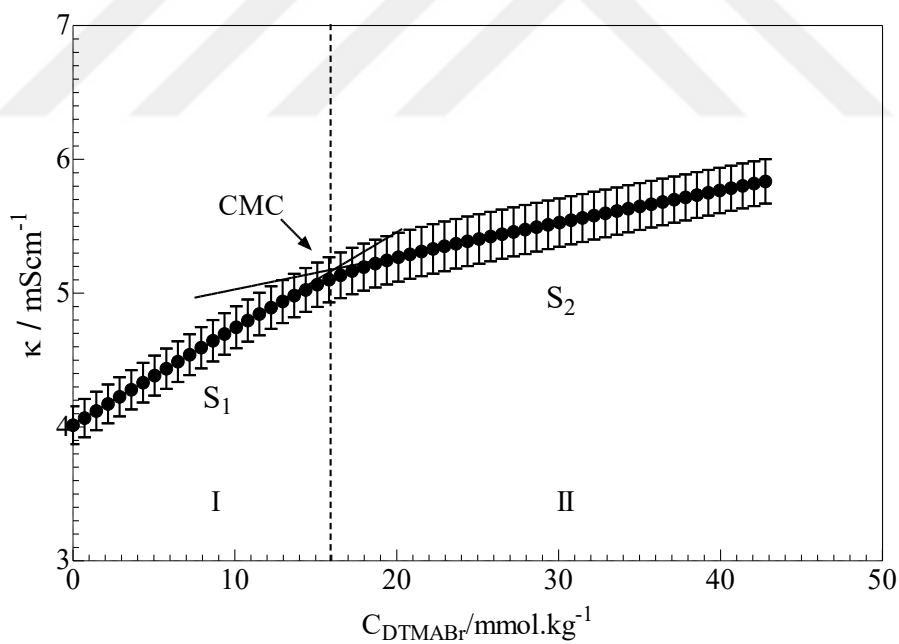


Figure 3.55. Plot of electrical conductivity of DTMABr/KBr/6% FA-water solution versus DTMABr concentration at 25.0°C.

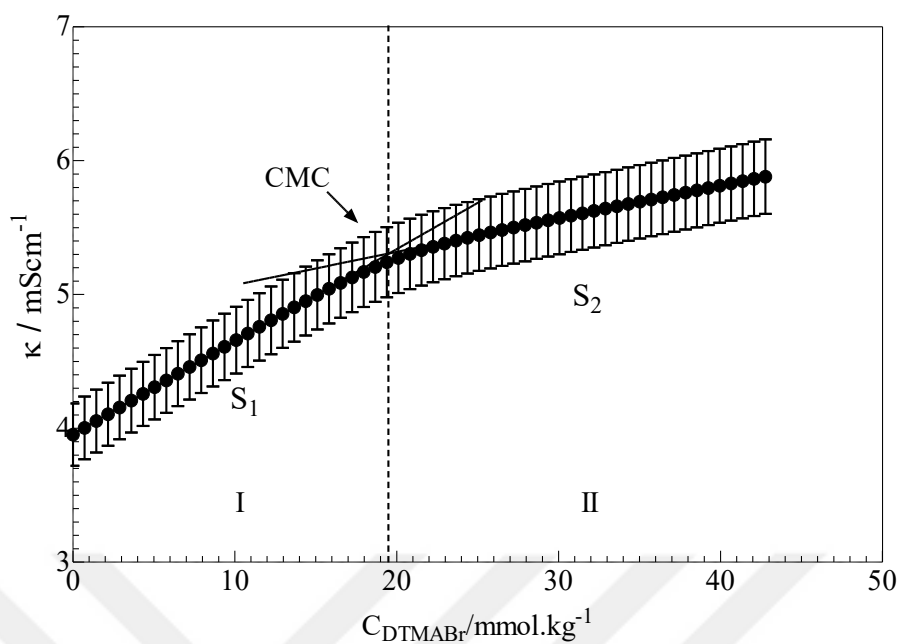


Figure 3.56. Plot of electrical conductivity of DTMABr/KBr/8% FA-water solution versus DTMABr concentration at 25.0°C.

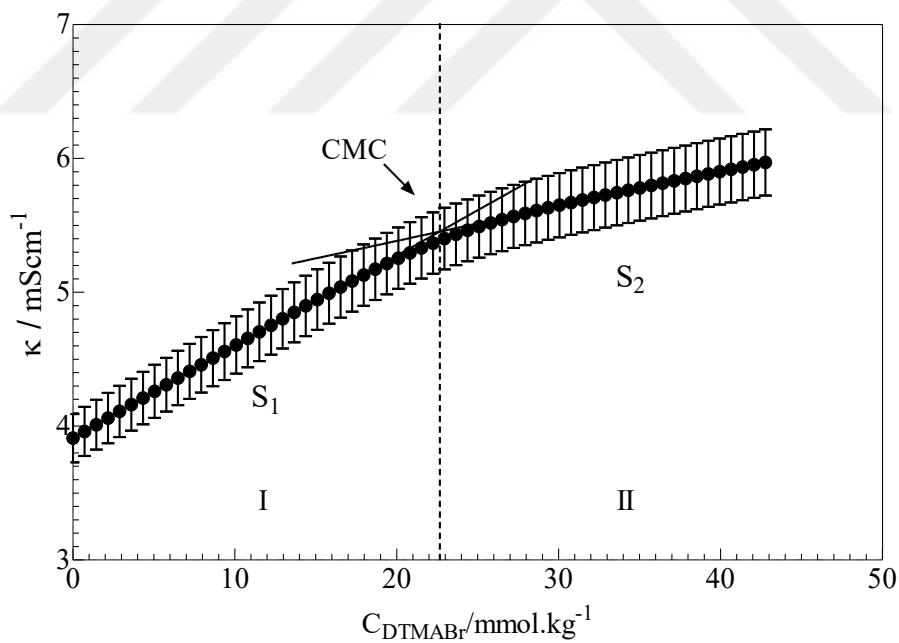


Figure 3.57. Plot of electrical conductivity of DTMABr/KBr/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.13. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KBr/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07645 ± 0.00008	1.0000	0.02221 ± 0.00001	1.0000
4	0.07336 ± 0.00023	0.9999	0.02311 ± 0.00005	0.9998
6	0.07185 ± 0.00025	0.9998	0.02476 ± 0.00010	0.9995
8	0.06905 ± 0.00019	0.9998	0.02483 ± 0.00011	0.9995
10	0.06783 ± 0.00020	0.9998	0.02609 ± 0.00025	0.9979

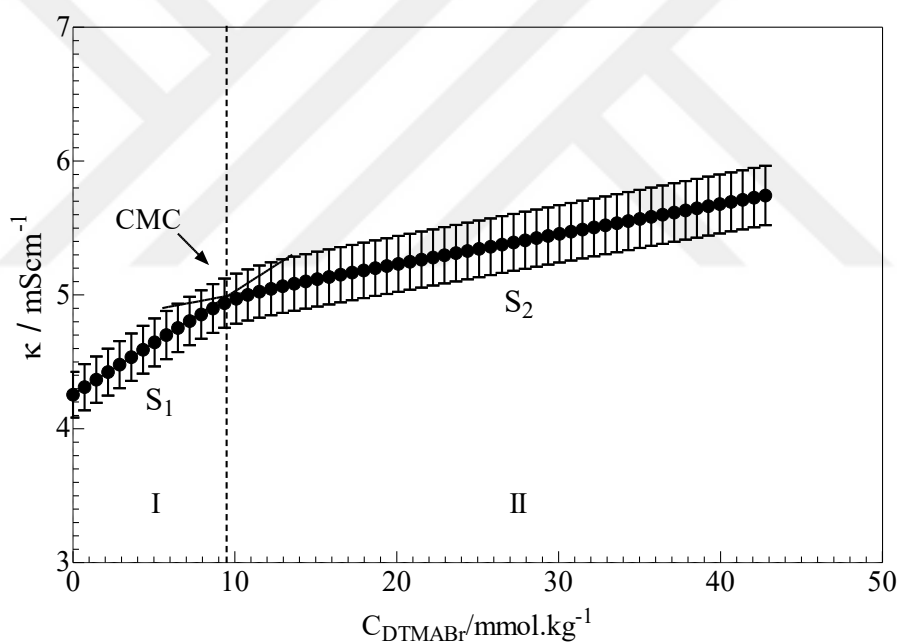


Figure 3.58. Plot of electrical conductivity of DTMABr/RbBr/2% FA-water solution versus DTMABr concentration at 25.0°C.

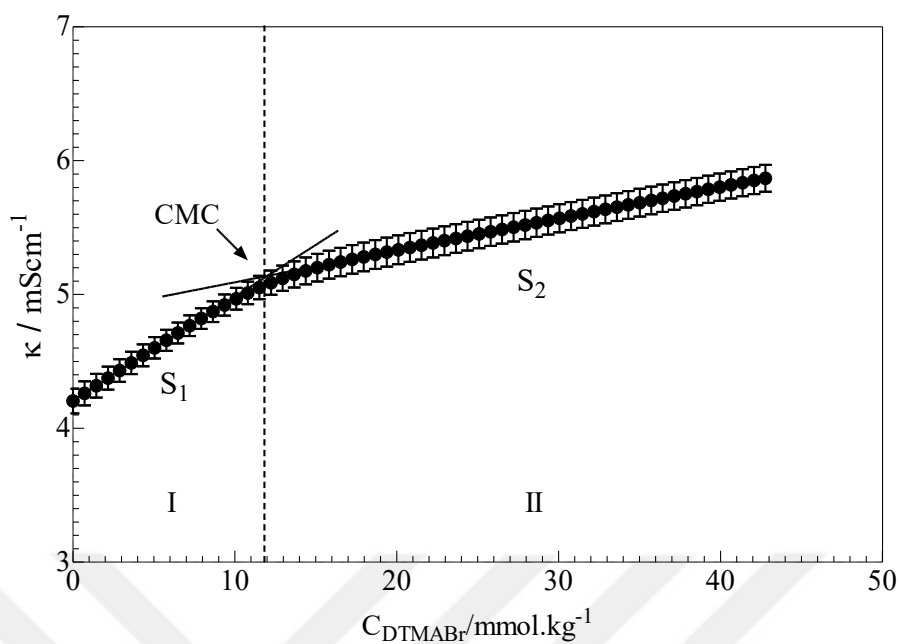


Figure 3.59. Plot of electrical conductivity of DTMABr/RbBr/4% FA-water solution versus DTMABr concentration at 25.0°C.

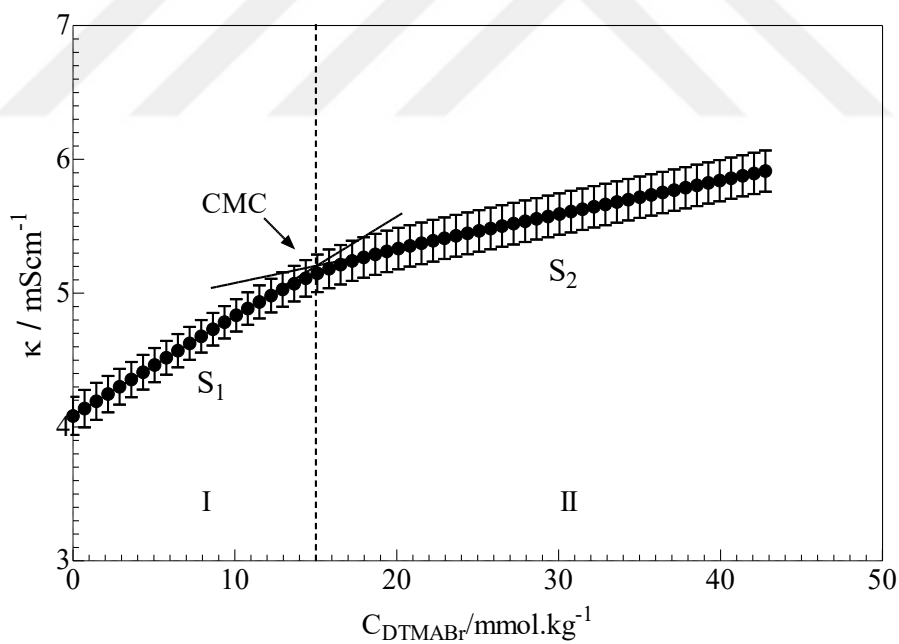


Figure 3.60. Plot of electrical conductivity of DTMABr/RbBr/6% FA-water solution versus DTMABr concentration at 25.0°C.

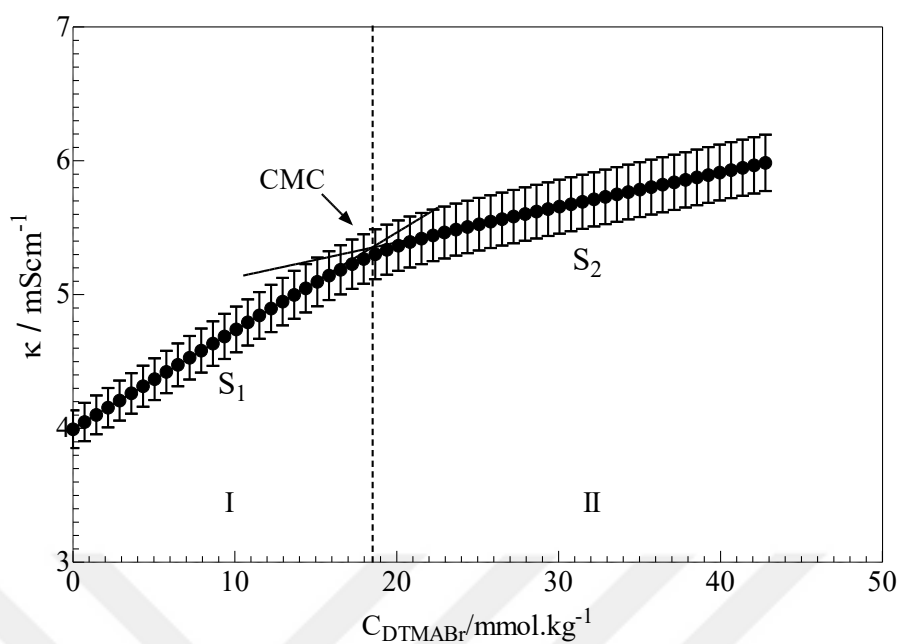


Figure 3.61. Plot of electrical conductivity of DTMABr/RbBr/8% FA-water solution versus DTMABr concentration at 25.0°C.

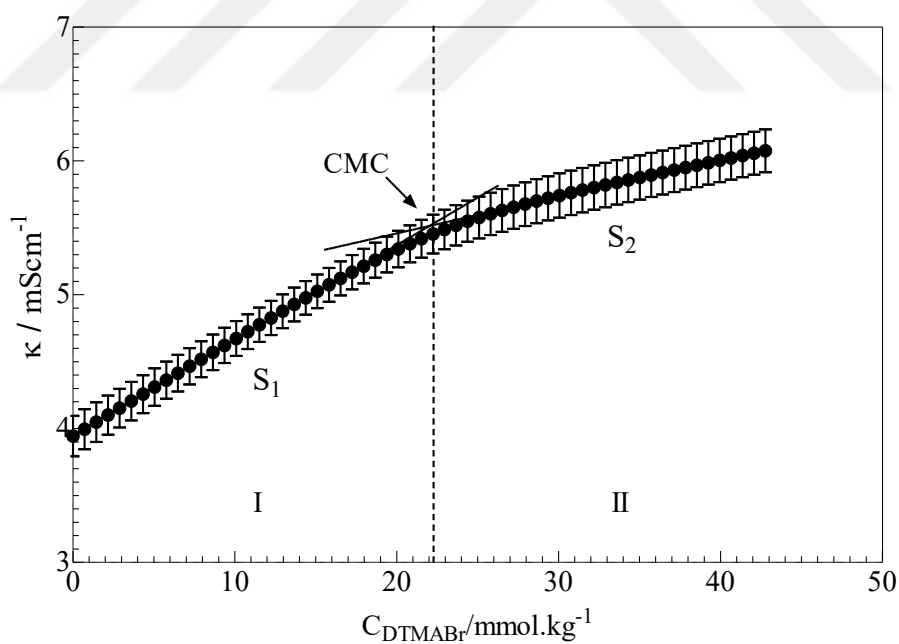


Figure 3.62. Plot of electrical conductivity of DTMABr/RbBr/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.14. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/RbBr/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07714 ± 0.00019	1.0000	0.02260 ± 0.00002	1.0000
4	0.07760 ± 0.00029	0.9998	0.02379 ± 0.00006	0.9998
6	0.07430 ± 0.00020	0.9999	0.02561 ± 0.00008	0.9997
8	0.07331 ± 0.00015	0.9999	0.02621 ± 0.00010	0.9996
10	0.07101 ± 0.00023	0.9997	0.02751 ± 0.00028	0.9976

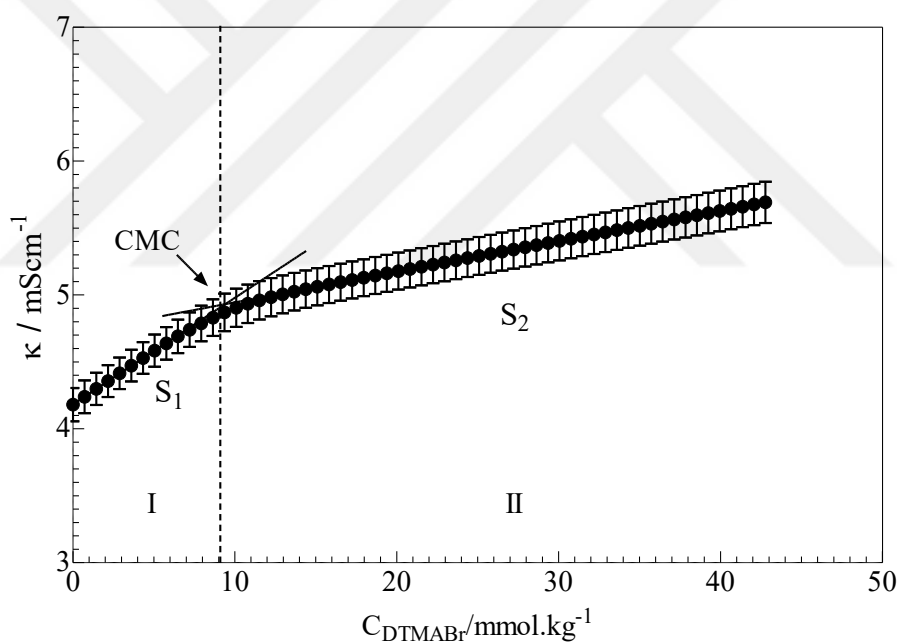


Figure 3.63. Plot of electrical conductivity of DTMABr/CsBr/2% FA-water solution versus DTMABr concentration at 25.0°C.

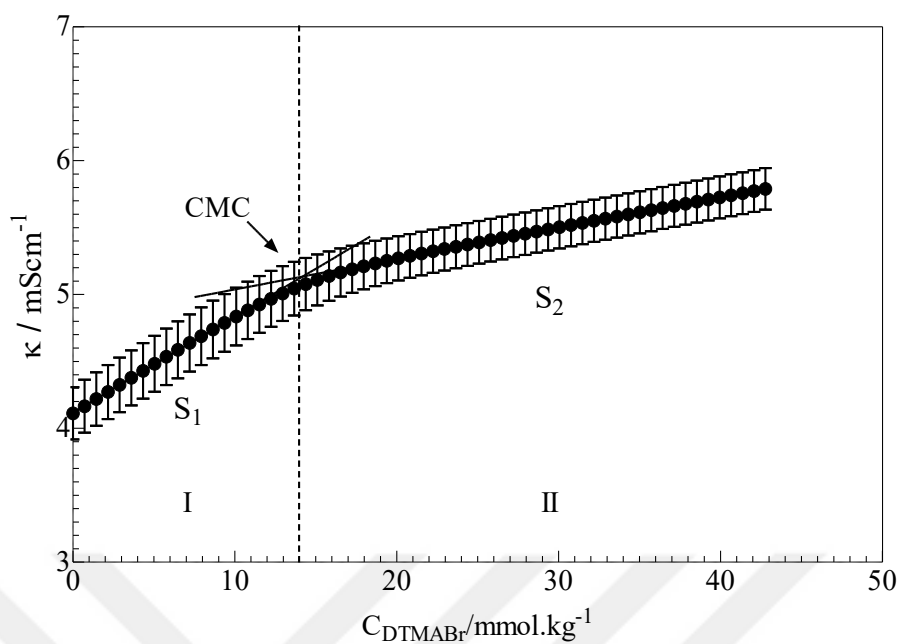


Figure 3.64. Plot of electrical conductivity of DTMABr/CsBr/4% FA-water solution versus DTMABr concentration at 25.0°C.

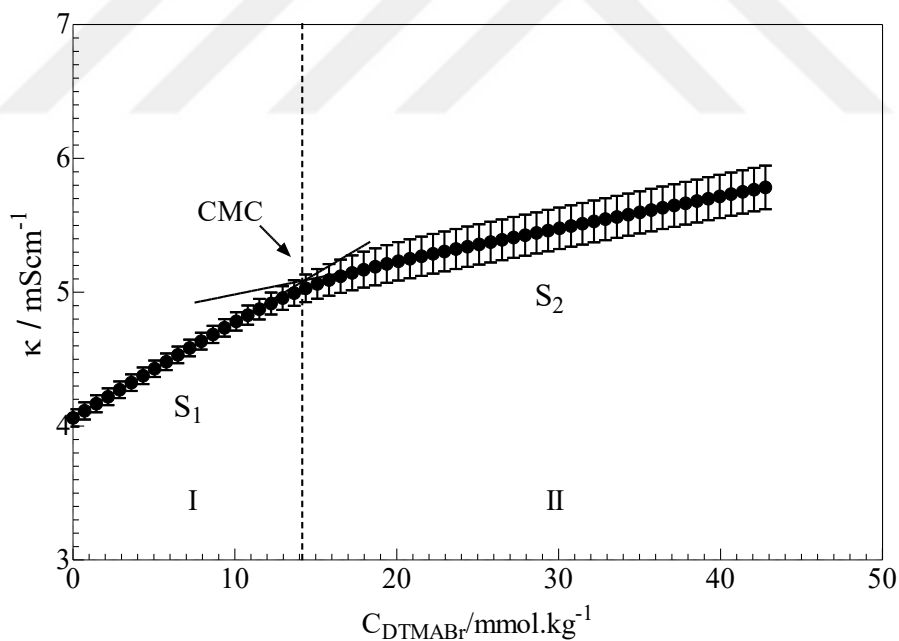


Figure 3.65. Plot of electrical conductivity of DTMABr/CsBr/6% FA-water solution versus DTMABr concentration at 25.0°C.

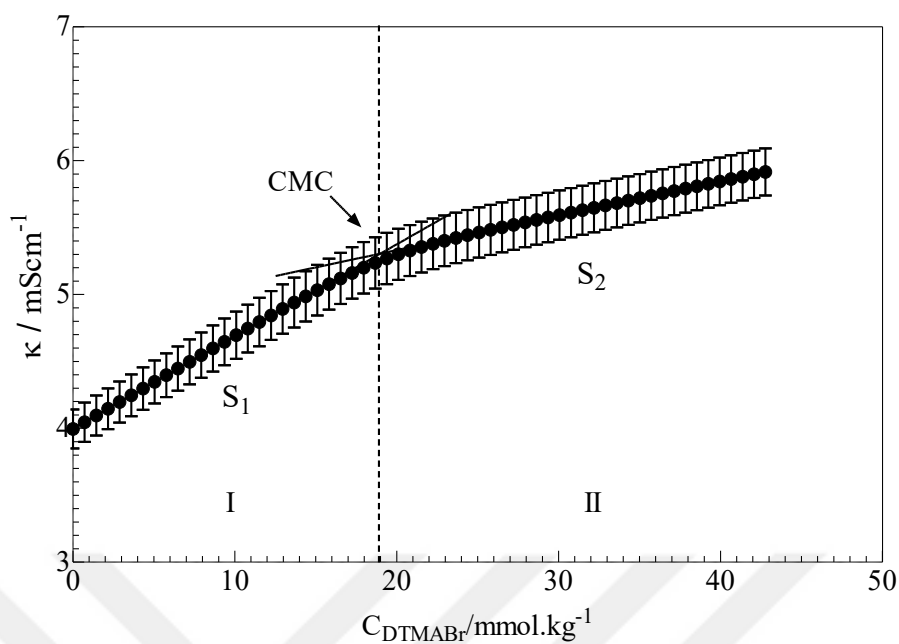


Figure 3.66. Plot of electrical conductivity of DTMABr/CsBr/8% FA-water solution versus DTMABr concentration at 25.0°C.

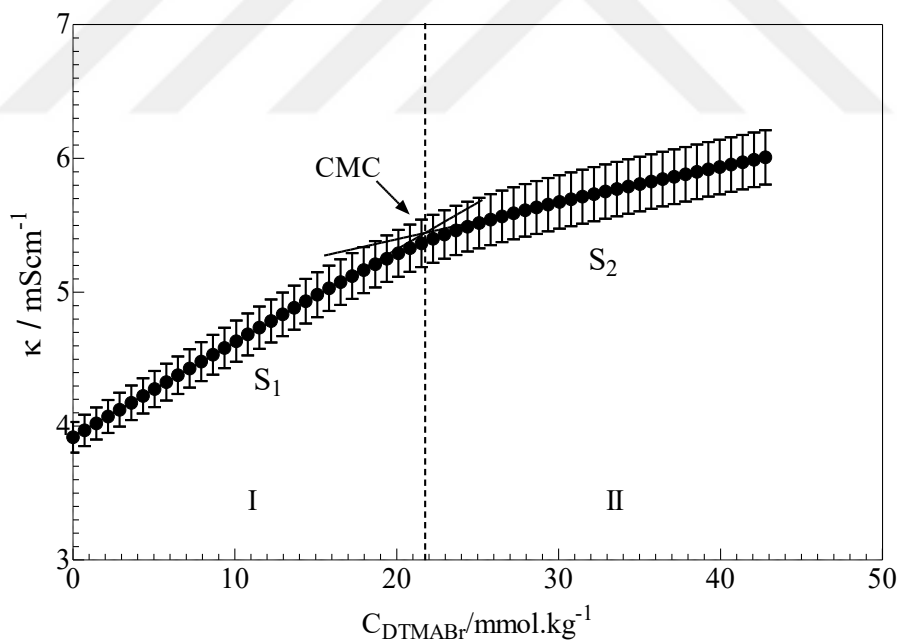


Figure 3.67. Plot of electrical conductivity of DTMABr/CsBr/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.15. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/CsBr/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07956 ± 0.00039	0.9998	0.02286 ± 0.00005	0.9998
4	0.07169 ± 0.00031	0.9997	0.02306 ± 0.00010	0.9994
6	0.07148 ± 0.00027	0.9998	0.02452 ± 0.00009	0.9995
8	0.06881 ± 0.00015	0.9999	0.02579 ± 0.00009	0.9997
10	0.06982 ± 0.00023	0.9997	0.02720 ± 0.00023	0.9983

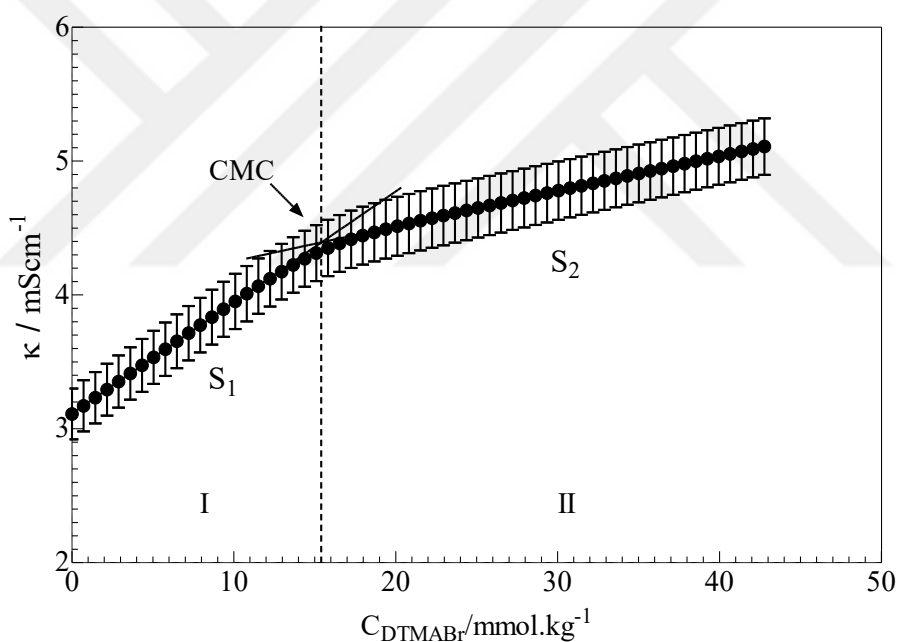


Figure 3.68. Plot of electrical conductivity of DTMABr/KF/2% FA-water solution versus DTMABr concentration at 25.0°C.

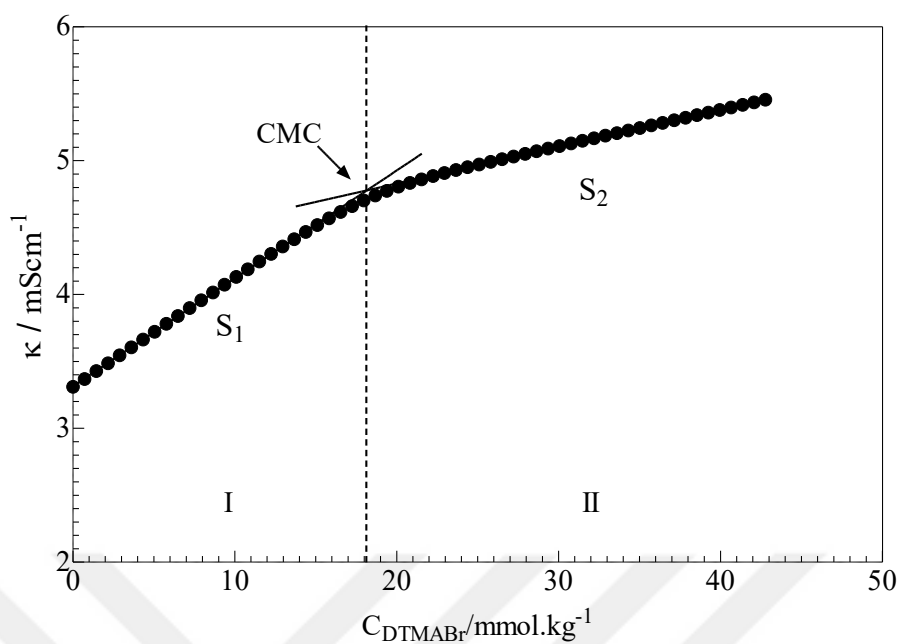


Figure 3.69. Plot of electrical conductivity of DTMABr/KF/4% FA-water solution versus DTMABr concentration at 25.0°C.

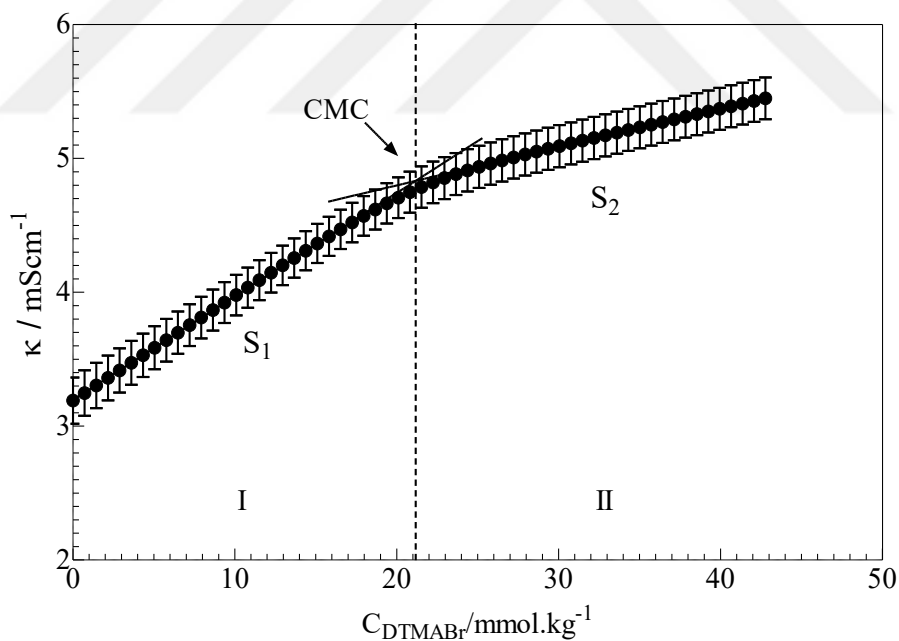


Figure 3.70. Plot of electrical conductivity of DTMABr/KF/6% FA-water solution versus DTMABr concentration at 25.0°C.

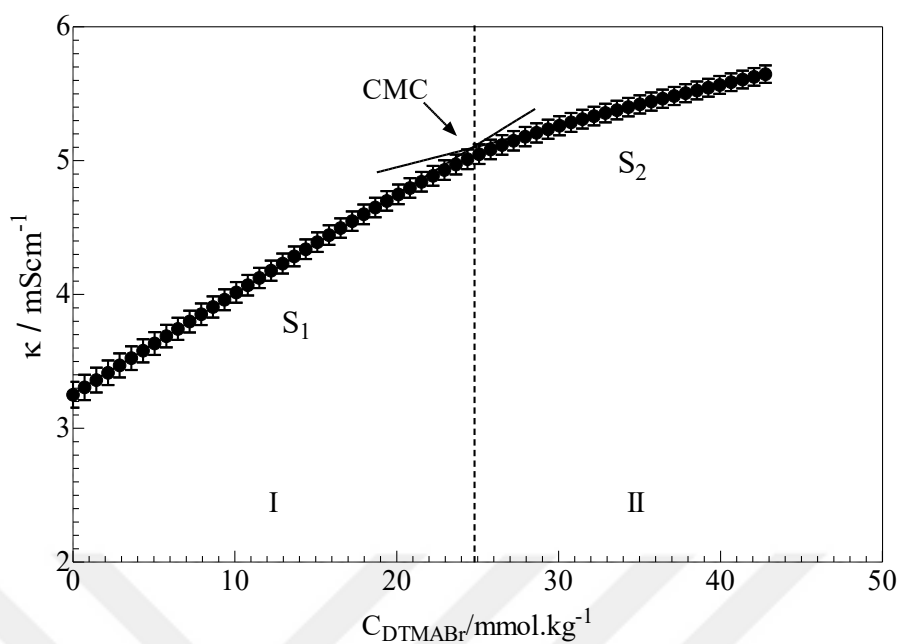


Figure 3.71. Plot of electrical conductivity of DTMABr/KF/8% FA-water solution versus DTMABr concentration at 25.0°C.

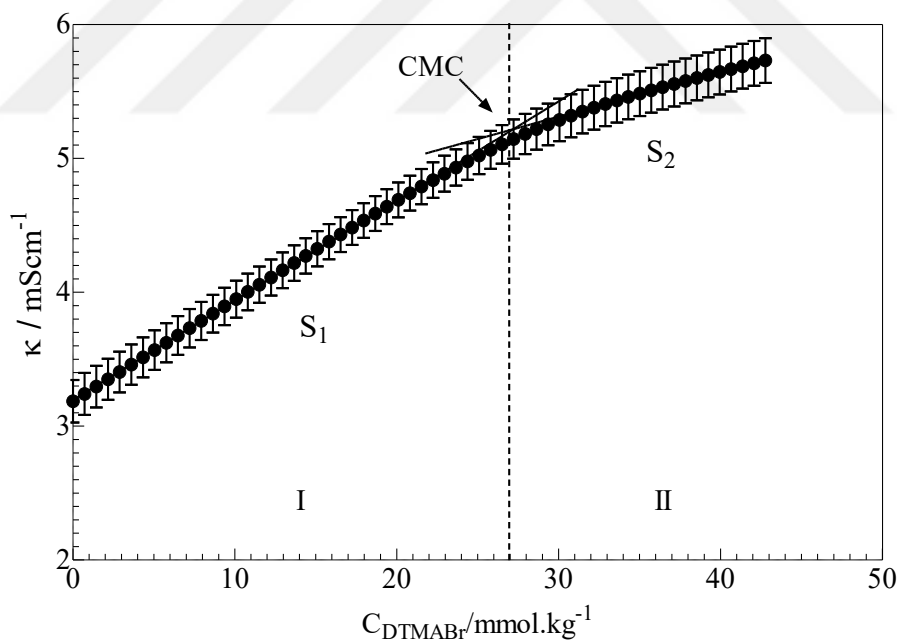


Figure 3.72. Plot of electrical conductivity of DTMABr/KF/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.16. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KF/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.08297 ± 0.00018	0.9999	0.02623 ± 0.00007	0.9998
4	0.08065 ± 0.00020	0.9999	0.02760 ± 0.00009	0.9997
6	0.07737 ± 0.00016	0.9999	0.02874 ± 0.00015	0.9994
8	0.07456 ± 0.00020	0.9998	0.03092 ± 0.00031	0.9980
10	0.07441 ± 0.00018	0.9998	0.03348 ± 0.00039	0.9980

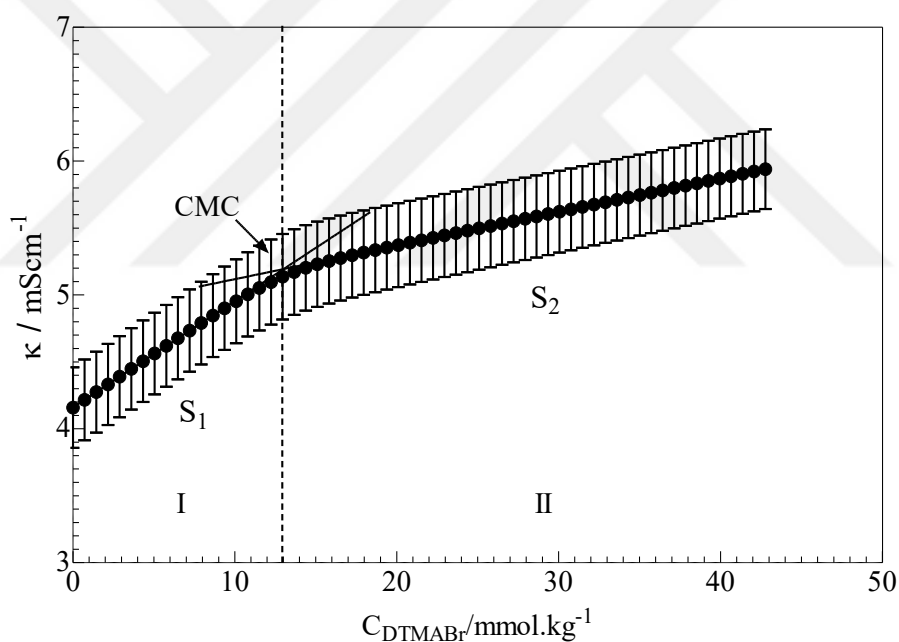


Figure 3.73. Plot of electrical conductivity of DTMABr/KCl/2% FA-water solution versus DTMABr concentration at 25.0°C.

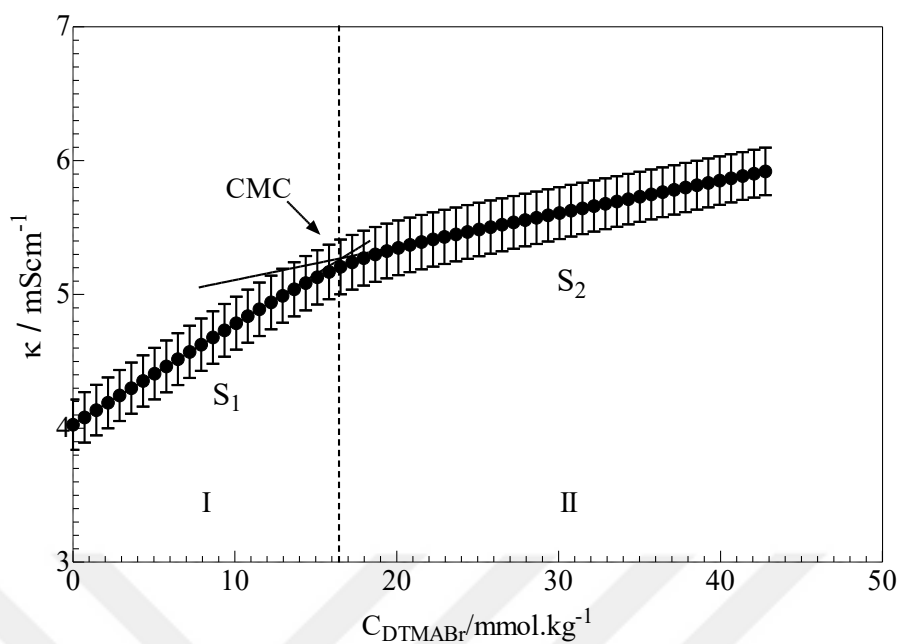


Figure 3.74. Plot of electrical conductivity of DTMABr/KCl/4% FA-water solution versus DTMABr concentration at 25.0°C.

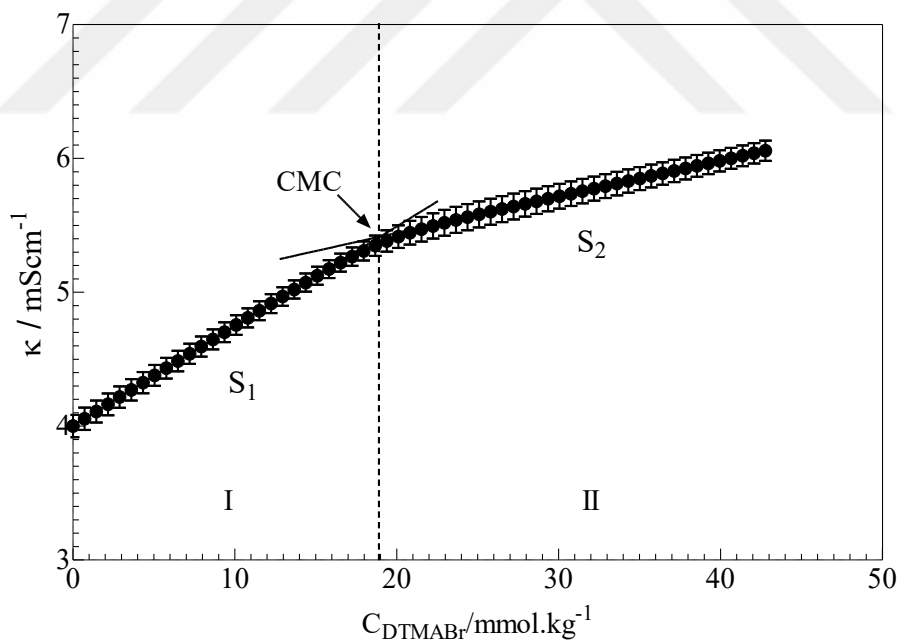


Figure 3.75. Plot of electrical conductivity of DTMABr/KCl/6% FA-water solution versus DTMABr concentration at 25.0°C.

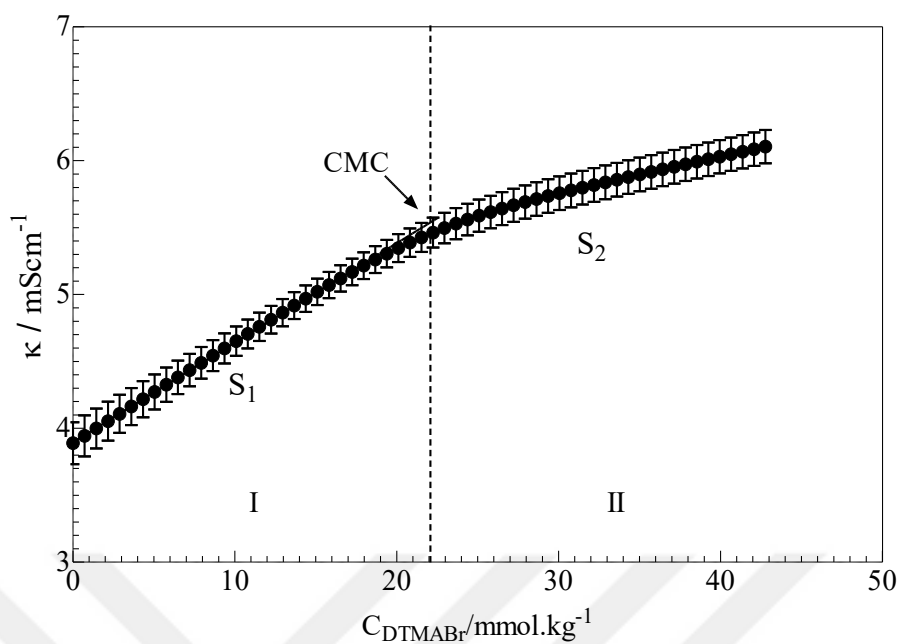


Figure 3.76. Plot of electrical conductivity of DTMABr/KCl/8% FA-water solution versus DTMABr concentration at 25.0°C.

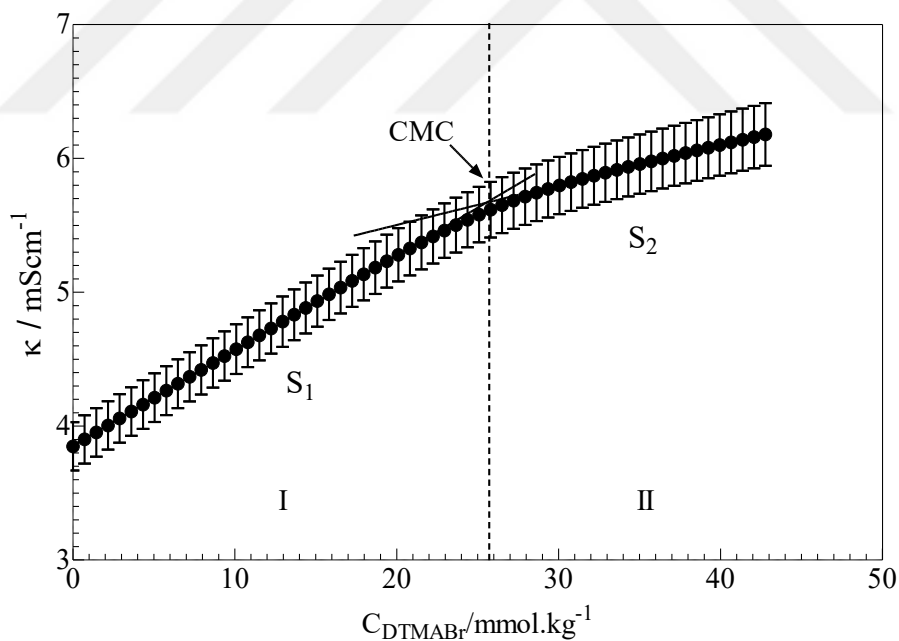


Figure 3.77. Plot of electrical conductivity of DTMABr/KCl/10% FA-water solution versus DTMABr concentration at 25.0°C.

Table 3.17. Slopes and regressions of the linear curves of regions I and II for electrical conductivity vs DTMABr concentration graphs of DTMABr/KCl/FA-water solutions.

%FA	$S_1 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2	$S_2 / S \text{ kg cm}^{-1} \text{ mol}^{-1}$	R^2
2	0.07944 ± 0.00014	1.0000	0.02511 ± 0.00003	1.0000
4	0.07475 ± 0.00016	0.9999	0.02485 ± 0.00007	0.9997
6	0.07446 ± 0.00009	1.0000	0.02705 ± 0.00007	0.9998
8	0.07441 ± 0.00021	0.9998	0.02884 ± 0.00031	0.9972
10	0.07107 ± 0.00015	0.9999	0.02997 ± 0.00026	0.9987

3.2 Results of Zeta Potential Measurements

Zeta potential measurements were performed on DTMABr/electrolyte water, DTMABr/electrolyte/10% EG-water and DTMABr/electrolyte/10% FA-water solutions at 25.0°C. The zeta potentials of the solutions were given in Table 3.18.

Table 3.18. Zeta potential values of DTMABr/electrolyte/water, DTMABr/electrolyte/10% EG-water, and DTMABr/electrolyte/10% FA-water solutions with their standard deviations.

Electrolyte	Zeta Potential / mv		
	Water	10% EG	10% FA
LiBr	46.4 ± 5.0	22.1 ± 0.4	43.3 ± 1.1
NaBr	39.9 ± 3.0	14.8 ± 0.0	40.4 ± 0.4
KBr	41.5 ± 3.3	20.5 ± 0.2	34.3 ± 2.5
RbBr	46.4 ± 1.2	26.5 ± 0.1	45.9 ± 0.8
CsBr	48.8 ± 0.3	28.1 ± 2.0	47.8 ± 1.1
KF	52.7 ± 1.3	23.7 ± 0.2	53.0 ± 0.2
KCl	45.7 ± 3.4	22.7 ± 1.9	50.0 ± 1.3

3.3 Results of SAXS Measurements

To calculate micellar average diameters, scattering vectors (q) for the solutions given in Table 2.1. were obtained from frame integrations of 2D isotropic SAXS patterns. The scattering vectors were, then, used to calculate micelle average diameters, d ($q = 2\pi/d$). The q values are given in Table 3.19.

Table 3.19. The q values of solutions s1-s12. SD: standard deviation.

Solvent	Solution	Electrolyte	$q / \text{\AA}^{-1}$	SD/ $\text{\AA}^{-1}$
Water	s1	---	0.160	7.74×10^{-4}
	s2	KBr	0.156	4.06×10^{-4}
	s3	NaBr	0.159	5.95×10^{-4}
	s4	KF	0.153	6.49×10^{-4}
10% EG	s5	---	0.132	9.57×10^{-4}
	s6	KBr	0.129	7.33×10^{-4}
	s7	NaBr	0.127	7.53×10^{-4}
	s8	KF	0.123	8.81×10^{-4}
10% FA	s9	---	0.127	8.79×10^{-4}
	s10	KBr	0.131	6.99×10^{-4}
	s11	NaBr	0.125	8.39×10^{-4}
	s12	KF	0.119	7.84×10^{-4}

4. DISCUSSION

4.1 Discussion on Conductivity Results

CMC of surfactants can be determined from some electrochemical methods (Nesměrák & Němcová, 2006). The most common methods are conductometry, fluorometry, potentiometry, calorimetry, surface tensiometry, polarography, voltammetry, electrophoresis, and isotachophoresis (Scholz et al., 2018).

Among these techniques, conductivities measurement for determining the CMC of surfactant molecules is widely preferred, as in this thesis. The conductivities (κ) of the surfactant solutions at different surfactant concentrations (C) are measured, then κ -C graph is plotted to find the break-point on the curve which corresponds to the CMC of the surfactant.

In addition to the CMC, some other micellization parameters can be also evaluated from the κ -C graphs, which consist of two different regions, below and above the CMC: the premicellar and the postmicellar region, respectively. In both regions, the κ values of the surfactant solution vary linearly with the total surfactant concentrations, i.e., linear curves are obtained with different slopes, S_1 below CMC and S_2 above CMC. The micellization parameter, so-called the degree of counterion dissociation from micelle, is calculated from the ratio of S_2 to S_1 , $\alpha = S_2/S_1$. It is related to other micellization parameter β (the degree of counterion binding to micelle) with $\beta = 1 - \alpha$.

As an acceptable approach, CMC may be assumed a transition point from surfactant monomer state to its micellar state. Thus, it is important to decide which experimental way is suitable to determine CMC with high accuracy because the transition from the premicellar region to the postmicellar region in the κ -C curve may be abrupt or gradual. In general, Williams's method (Williams et al., 1955) is used to determine CMC where the CMC can be evaluated from the intersection points of two linear curves obtained in the pre- and postmicellar regions. This method can give the CMC values with small and acceptable uncertainties in the case of abrupt transition. However, the application of the Williams's method causes high uncertainties in determining CMC values if the transition is gradual (Pérez-Rodríguez et al., 1998).

Carpena et al. proposed a very useful calculation model if the gradual transition is observed in the κ -C curve (Carpena et al., 2002), and it was successfully applied to some micellar solutions in the literature (Koya et al., 2015). Analyzing the first derivative of the κ -C curves is the starting point of their model, i.e., dependence of $d\kappa/dC$ versus surfactant concentration, C. This derivative of the κ -C curves is a sigmoidal type and can be described by the following Boltzmann type sigmoidal equation

$$\frac{d\kappa}{dC} = \frac{A_1 - A_2}{1 + e^{(C - C_0)/\Delta C}} + A_2 \quad (4.1)$$

where the parameters κ is the conductivity of the solution at each total surfactant concentration, C_0 is the center of the width of the transition (ΔC) and corresponds to CMC value, and A_1 and A_2 are the asymptotic values for small and large values of surfactant concentration (horizontal asymptote), respectively. In addition, A_1 and A_2 are the values obtained in the premicellar and postmicellar segments with $A_1 > A_2$. Carpena's method proposed that if the first derivative of the κ -C curve of the experimental raw data is fitted to Eq. 4.1 to obtain the parameters, then, because the raw data need to behave as the integral of the sigmoid (Eq. 4.2), the fitted conductivity data as a function of the surfactant concentration are determined from

$$\kappa = \kappa_0 + A_1 C + \Delta C (A_2 - A_1) \ln \left(\frac{1 + e^{(C - C_0)/\Delta C}}{1 + e^{-C_0/\Delta C}} \right) \quad (4.2)$$

The CMC value is precisely evaluated from the first derivative of the fitted data after the integration (Pérez-Rodríguez et al., 1998). Furthermore, the degree of counterion dissociation is calculated from the ratio of A_2/A_1 . For example, the experimental raw data and its non-fitted first derivative for SDS/water are given in Figure 4.1a, and their fitted curves are plotted in Figure 4.1b. considering Carpena's method (Eq. 4.2) for the comparison (Akpınar et al., 2022).

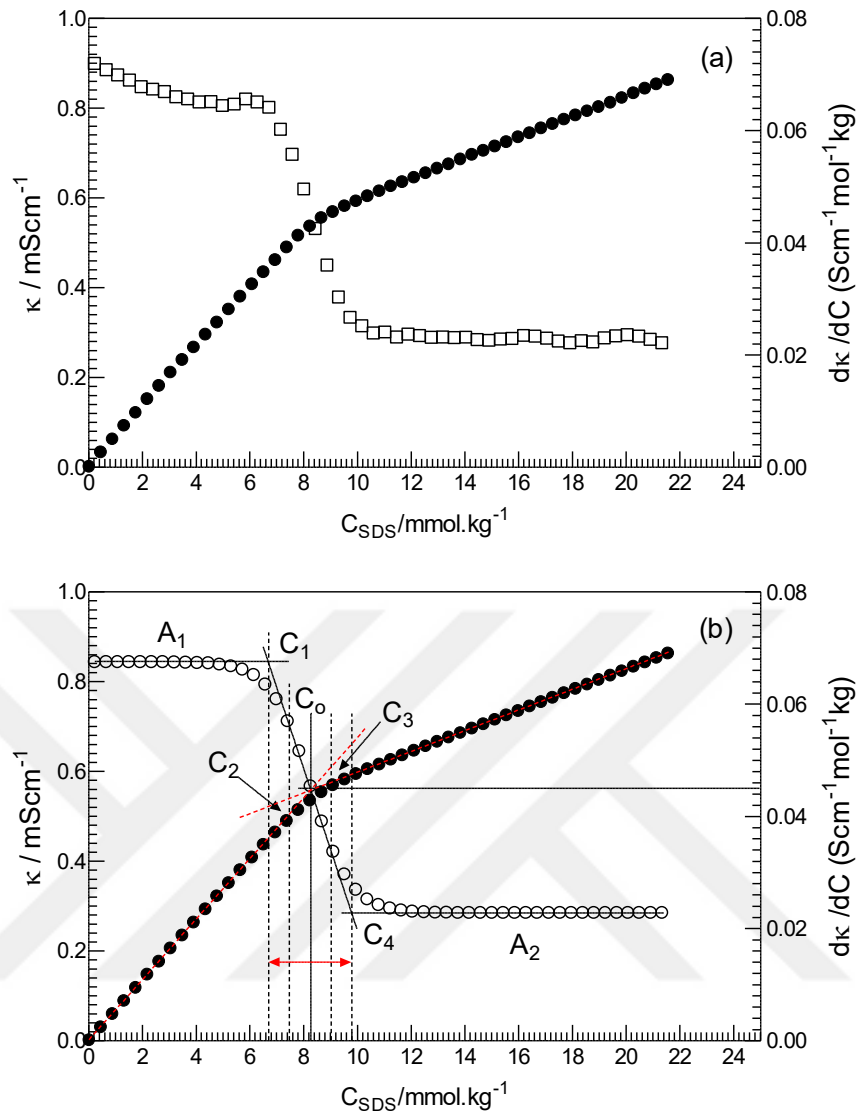


Figure 4.1. (a) Conductivity versus total surfactant concentration (κ -C) curve of experimental raw data (●) and its non-fitted first derivative, $d\kappa/dC$, (□) for SDS/water solution at 25.0°C. (b) Same curves were obtained from their fitted curves, (●) for κ -C and (○) for $d\kappa/dC$. The two-headed red arrow shows total concentration distance ($4\Delta C$) and it consists of four equal regions separated by vertical dashed lines, each of which corresponds to the concentration distance ΔC .

The micellization Gibbs energies were calculated from the following equation (Sugihara et al., 2001).

$$\Delta G_{mic} = (1 + \beta) RT \ln X_{CMC} \quad (4.3)$$

where R is ideal gas constant ($8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$), T is absolute temperature (K) and X_{cmc} is mole fraction of the surfactant at CMC. The calculated values of

CMC, α , β and ΔG_{mic} for SDS obtained from Carpena's method are 8.26 mmol/kg, 0.334, 0.666 and -36.37 kJ/mol. These values were very similar to the literature values 8.28 mmol/kg (Carpena et al., 2002), 0.369 (Chaudhary et al., 2020), 0.62 and -35.46 kJ/mol (Fenta, 2015), respectively. Thus, it can be seen that the Carpena's method can give very accurate conductivity results and it was used to evaluate the micellization parameters of DTMABr/electrolyte/water, DTMABr/electrolyte/EG-water and DTMABr/electrolyte/FA-water solutions in this thesis. The experimental results were discussed in the following parts in details.

4.1.1 Effect of the Concentration on Electrical Conductivity

4.1.1.1 DTMABr/electrolyte/EG-water Solutions

Figures 4.2-4.8 show the change in the conductivity of the surfactant solutions as a function of EG concentrations in the presence of different electrolytes. In Figures 4.2-4.6, the effect of EG concentration in the presence of electrolyte ions located in the intermicellar region, Gouy-Chapman or diffuse layer, (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) are graphically given. The effect of EG concentration in the presence of electrolyte ions F^- , Cl^- , and Br^- , which are bound to the surfactant head groups at the micelle surfaces (Stern layer), is seen in Figure 4.7, 4.8, and 4.4, respectively.

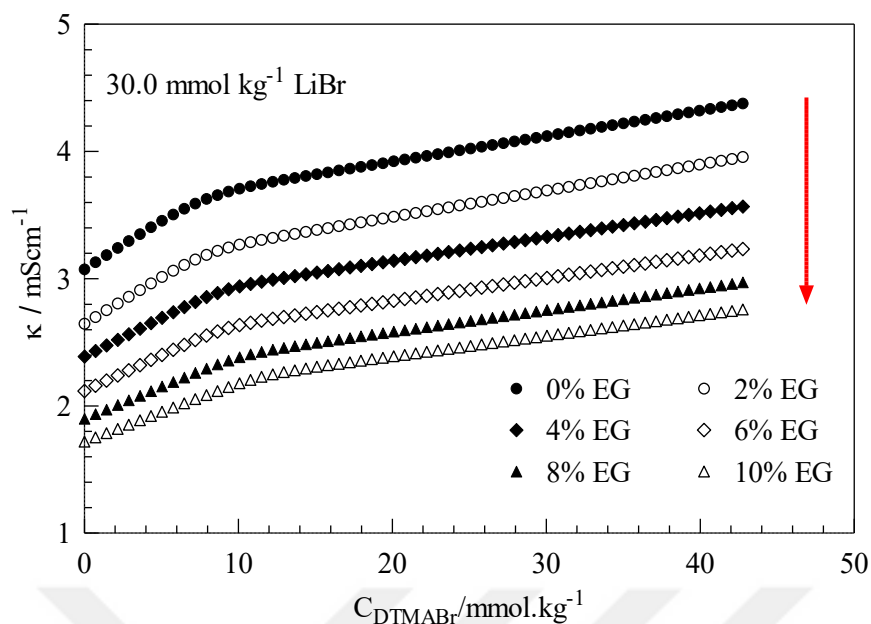


Figure 4.2. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/LiBr/EG-water solution versus DTMABr concentration at 25.0°C. Red arrow shows the direction of the change of the solution conductivity with the increase in the concentration of EG.

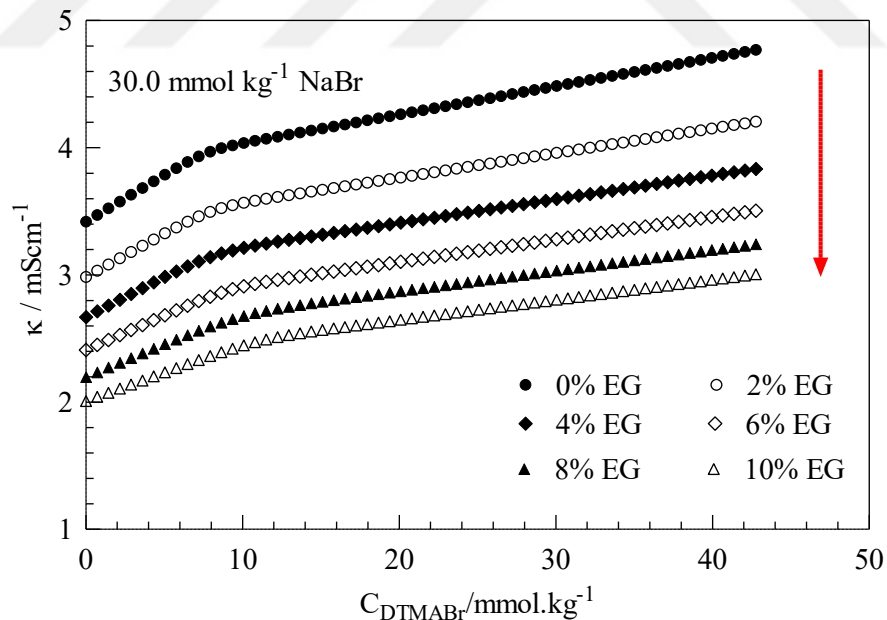


Figure 4.3. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/NaBr/EG-water solution versus DTMABr concentration at 25.0°C.

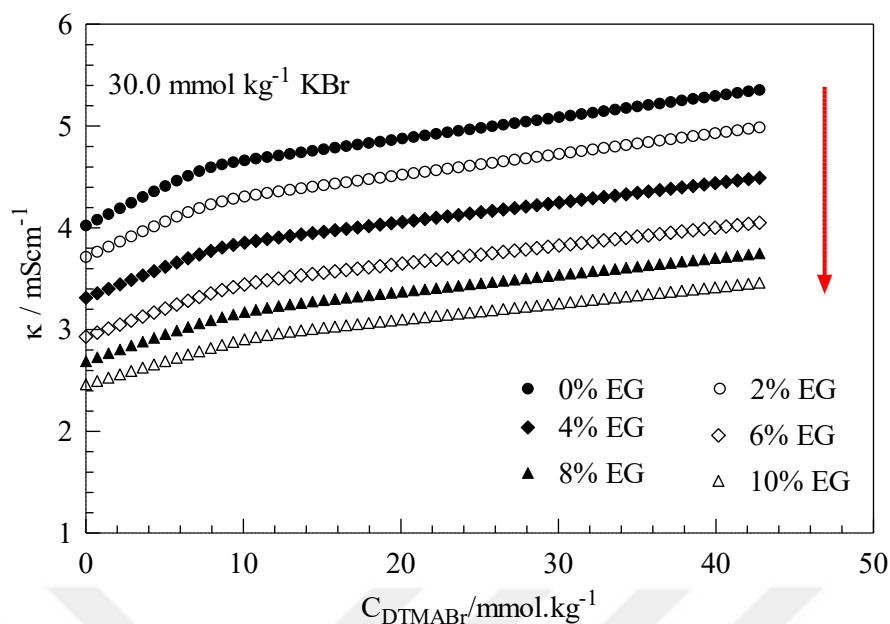


Figure 4.4. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/KBr/EG-water solution versus DTMABr concentration at 25.0°C.

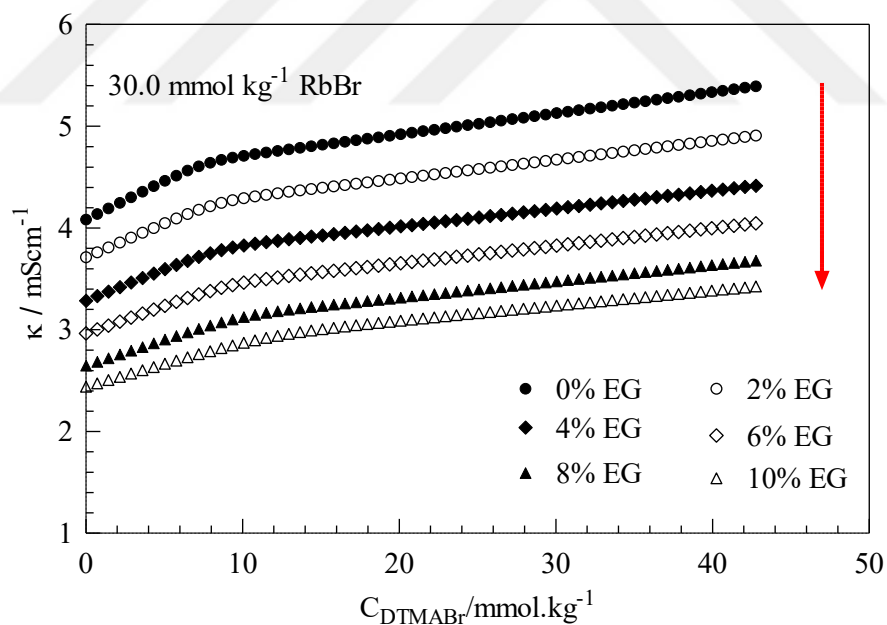


Figure 4.5. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/RbBr/EG-water solution versus DTMABr concentration at 25.0°C.

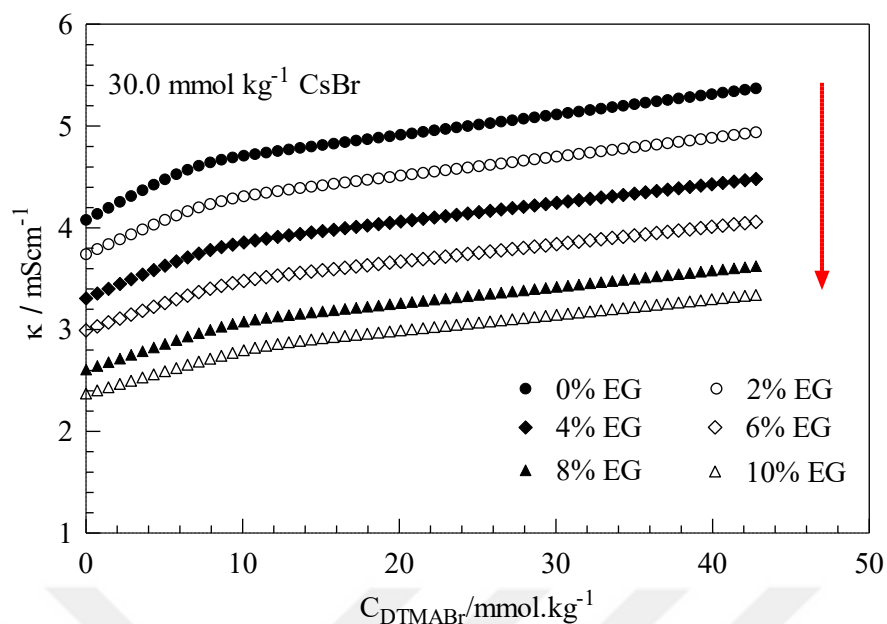


Figure 4.6. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/CsBr/EG-water solution versus DTMABr concentration at 25.0°C.

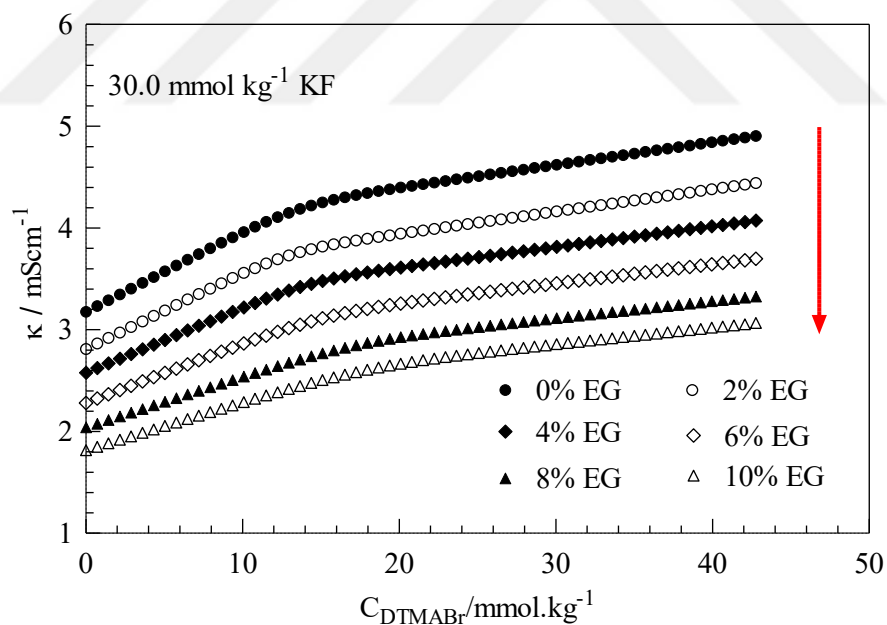


Figure 4.7. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/KF/EG-water solution versus DTMABr concentration at 25.0°C.

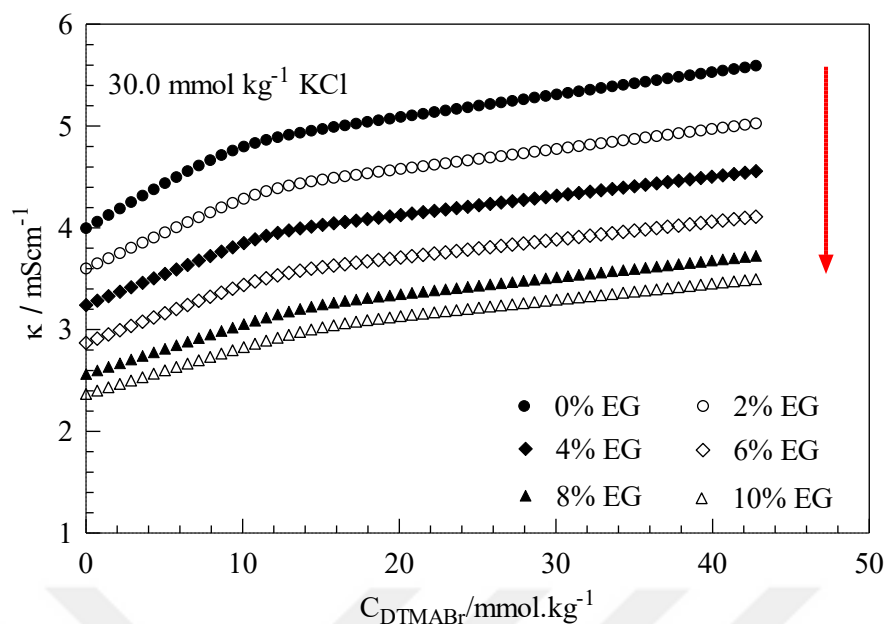


Figure 4.8. Comparison of the effect of the concentration of EG on the plot of electrical conductivity of DTMABr/KCl/EG-water solution versus DTMABr concentration at 25.0°C.

The dielectric constant of a solvent is a macroscopic parameter and a relative measure of its polarity related to the molecular interaction between the solvent and solutes, i.e., the higher the dielectric constant means the more polar solvent. The interactions between polar solvent and ionic solutes get weaker as the dielectric constant of the medium (solvent) decreases (Herrera-Pool et al., 2021). Because the dielectric constant of EG (37.7) is smaller than that of water (78.45), while the concentration of EG is increased in DTMABr/electrolyte/EG-water solutions, the dielectric constant of the medium decreases. Therefore, for all different electrolytes, the conductivities of DTMABr surfactant solutions decrease distinctly with the increase in the concentration of EG in both premicellar and postmicellar regions.

It was reported that if the hydrophilic effect is dominant in a surfactant micellar system, the conductivity or specific conductance of the bulk solution increases, however, if the hydrophobic effect is dominant, the opposite situation is observed (Al-Hatem & Ali, 2020). Thus, the conductivity results of DTMABr/electrolyte/EG-water solutions show that the decrease in the dielectric

constant of the bulk solution, arising from the increase in the concentration of EG, leads to increase in the hydrophobic effect.

4.1.1.2 DTMABr/electrolyte/FA-water Solutions

Figures 4.9-4.15 give the relation between the conductivity of the surfactant solutions and FA concentrations in the presence of different electrolytes. While the effect of FA concentration in the presence of electrolyte ions located in the intermicellar region (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) are graphically shown in Figure 4.9-4.13, that of electrolyte ions bound to the surfactant head groups at the micelle surfaces (F^- , Cl^- , and Br^-) are given in Figure 4.14., 4.15, and 4.11, respectively.

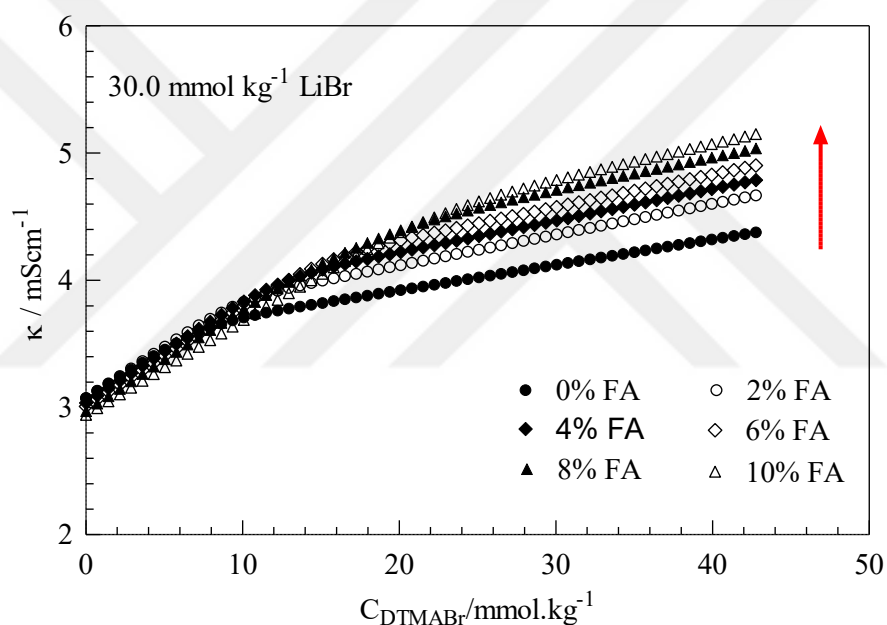


Figure 4.9. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/LiBr/FA-water solution versus DTMABr concentration at 25.0°C. Red arrow shows the direction of the change of the solution conductivity with the increase in the concentration of FA.

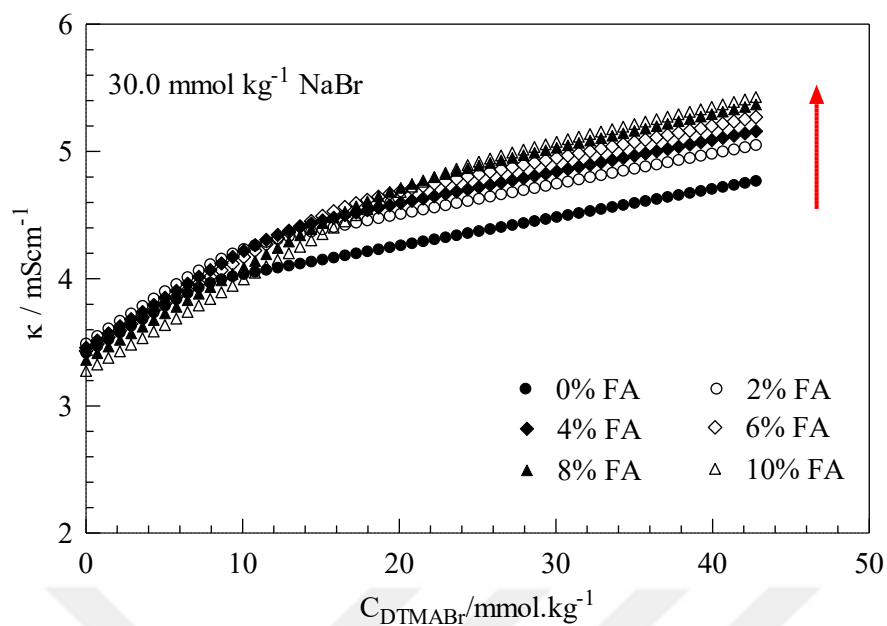


Figure 4.10. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/NaBr/FA-water solution versus DTMABr concentration at 25.0°C.

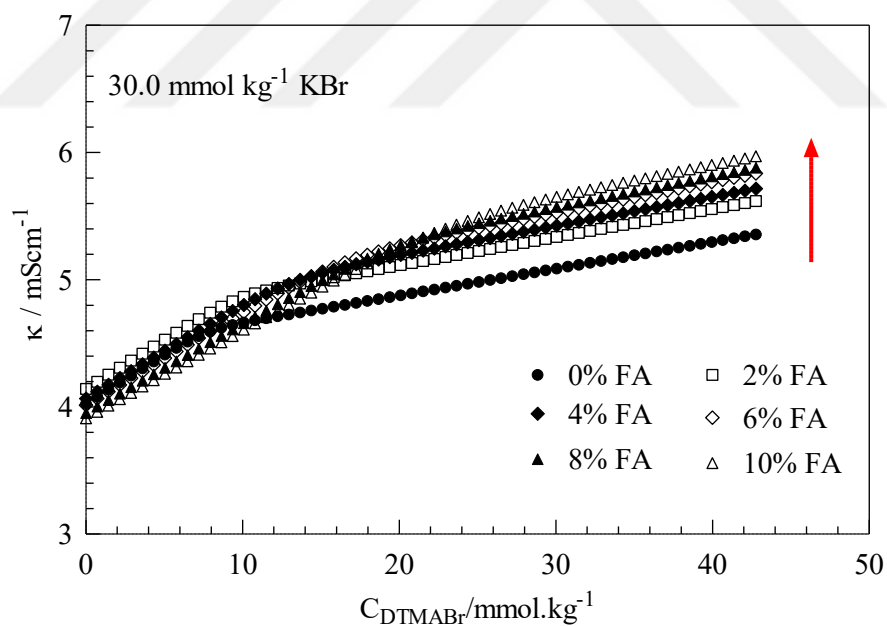


Figure 4.11. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/KBr/FA-water solution versus DTMABr concentration at 25.0°C.

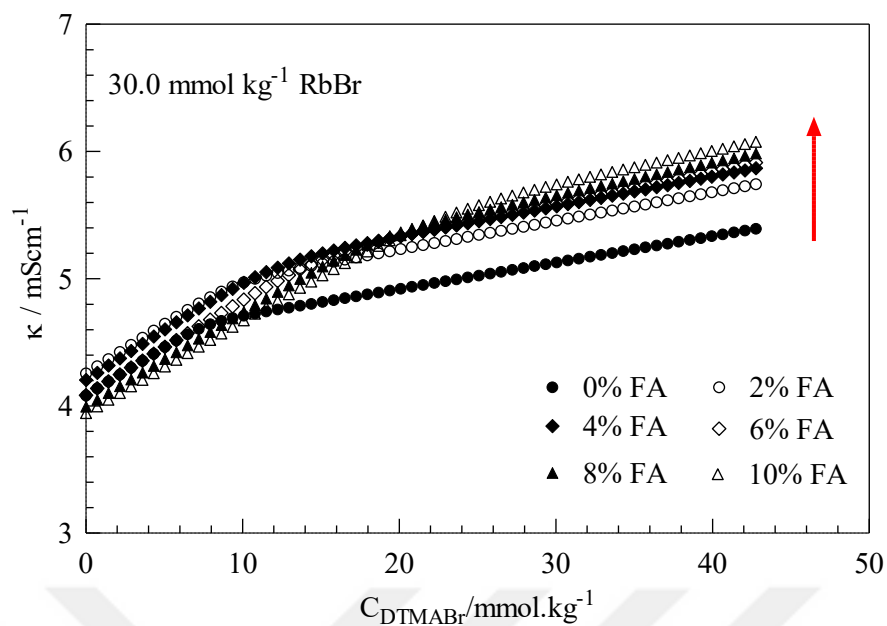


Figure 4.12. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/RbBr/FA-water solution versus DTMABr concentration at 25.0°C.

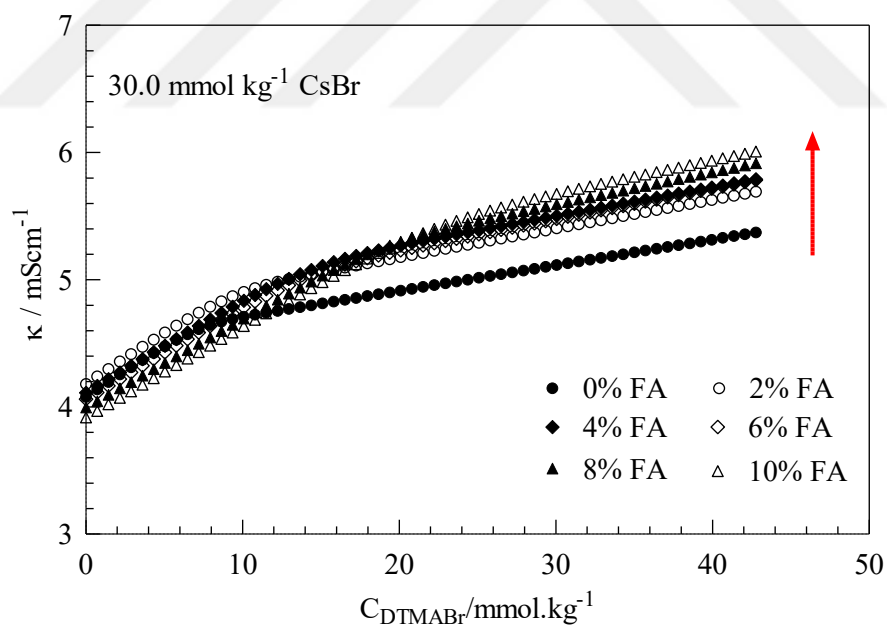


Figure 4.13. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/CsBr/FA-water solution versus DTMABr concentration at 25.0°C.

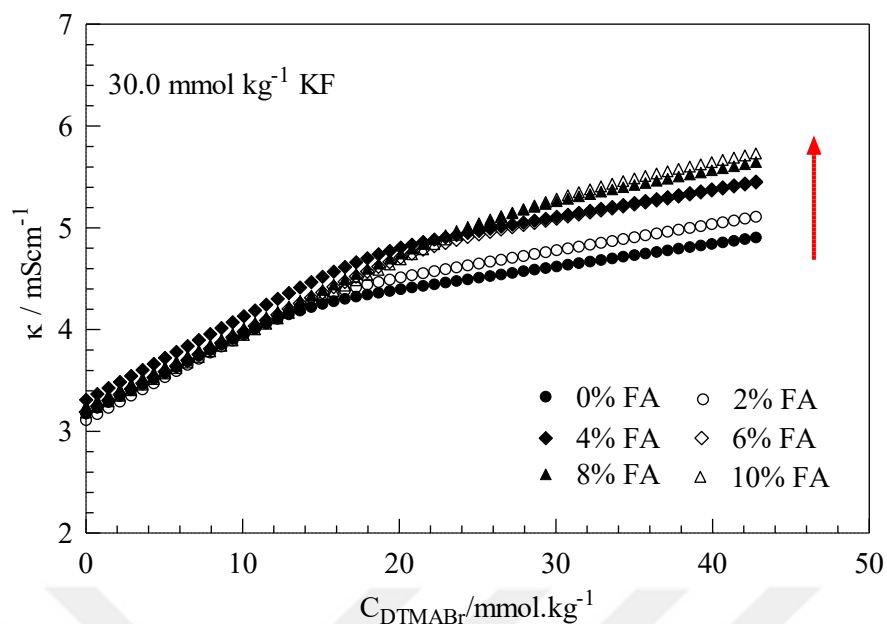


Figure 4.14. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/KF/FA-water solution versus DTMABr concentration at 25.0°C.

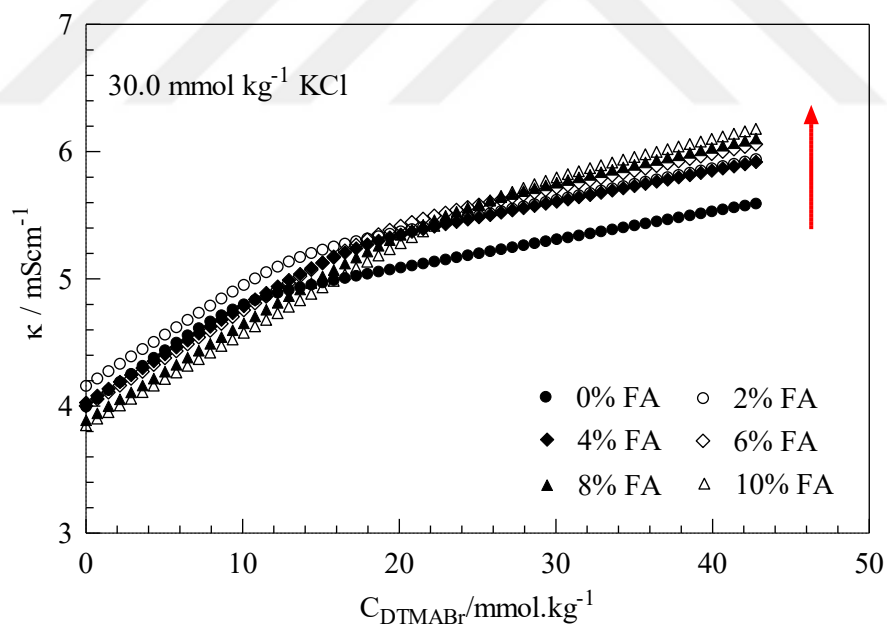


Figure 4.15. Comparison of the effect of the concentration of FA on the plot of electrical conductivity of DTMABr/KCl/FA-water solution versus DTMABr concentration at 25.0°C.

If the change in the conductivity of DTMABr/electrolyte/FA-water solutions as a function of FA concentration is compared with that of DTMABr/electrolyte/EG-water solutions, completely opposite behavior is observed. It means that when the concentration of FA is increased in the solution, the solution conductivity increases, too. This result indicates that the increase in the dielectric constant of the bulk solution by the addition of FA leads to increase in the hydrophilic effect.

In the case of EG, its effect on the conductivity of the bulk solution is so clear in both the premicellar and postmicellar regions. However, in the case of FA, while its effect is regular and clear in the postmicellar region, there is no regular effect on the solution conductivity in the premicellar region. In addition, the effect of EG on the solution properties is more dominant than that of FA, within the same concentration range. This may be attributed to the greater effect of hydrophobic effect (the case, EG) rather than the hydrophilic effect (the case, FA) on the solution conductivity.

4.1.2 Effect of the Concentration on CMC

4.1.2.1 DTMABr/electrolyte/EG-water Solutions

The effect of EG on CMC of DTMABr in mixture of electrolyte/EG-water in the presence of different electrolytes is graphically shown in Figures 4.16-4.22. For each EG concentration, the measurements were repeated at least three times and the CMC values in the figures were averaged of these three measurements with their standard deviations.

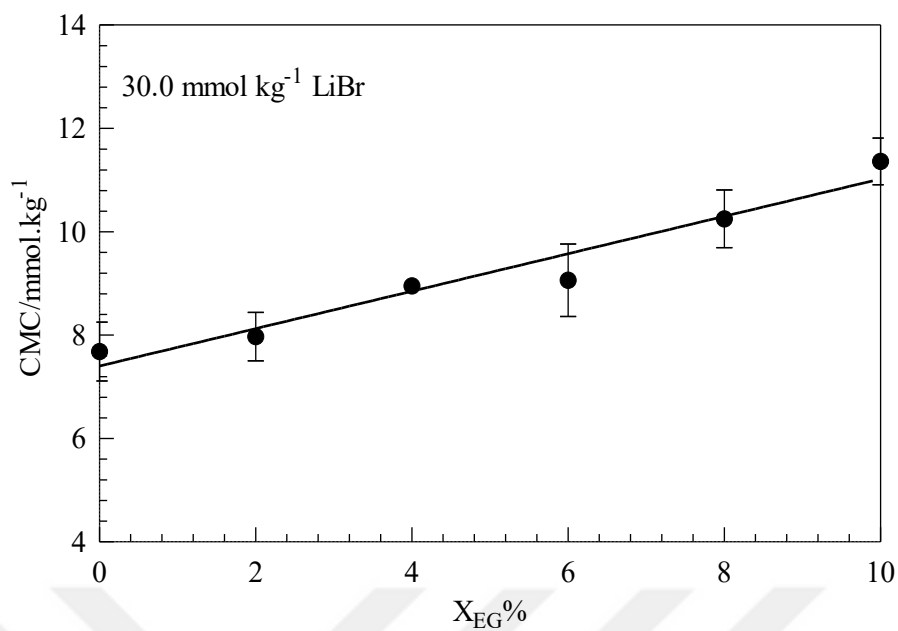


Figure 4.16. Comparison of the effect of the concentration of EG on the CMC of DTMABr/LiBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

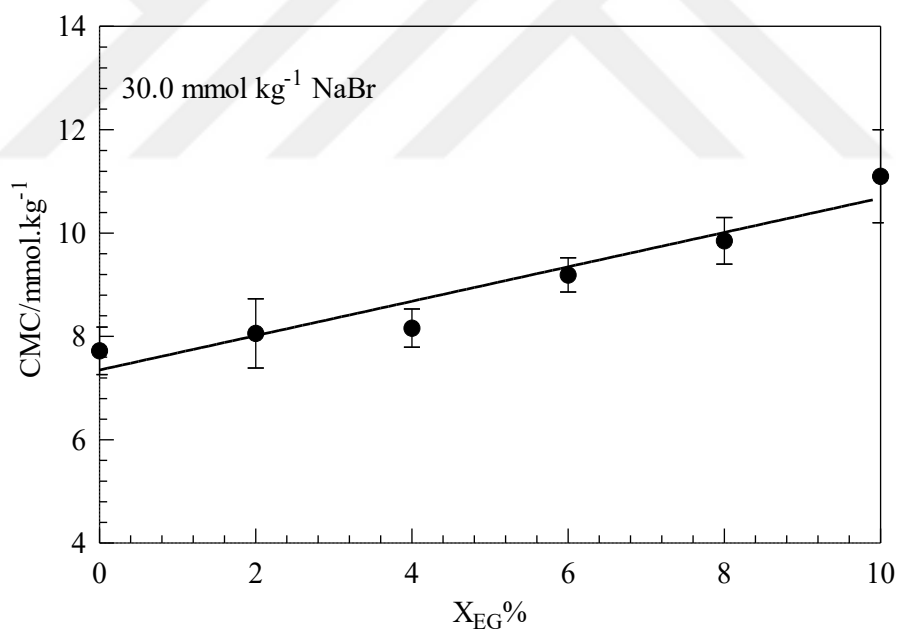


Figure 4.17. Comparison of the effect of the concentration of EG on the CMC of DTMABr/NaBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

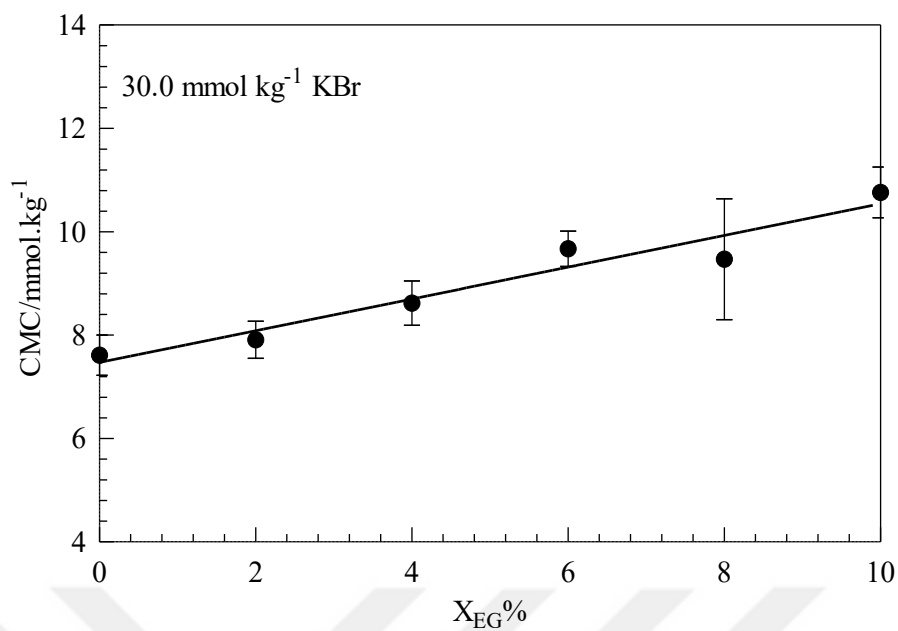


Figure 4.18. Comparison of the effect of the concentration of EG on the CMC of DTMABr/KBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

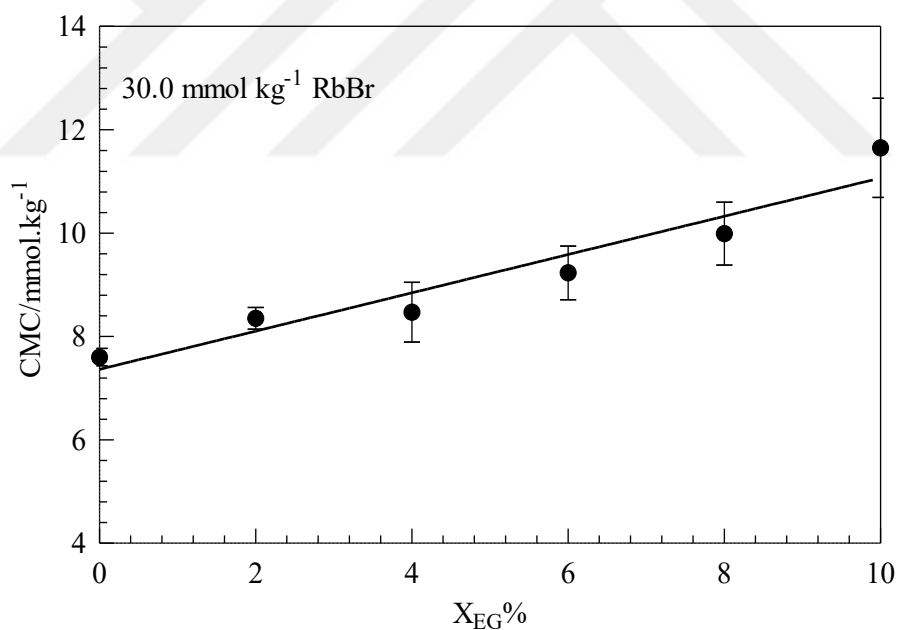


Figure 4.19. Comparison of the effect of the concentration of EG on the CMC of DTMABr/RbBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

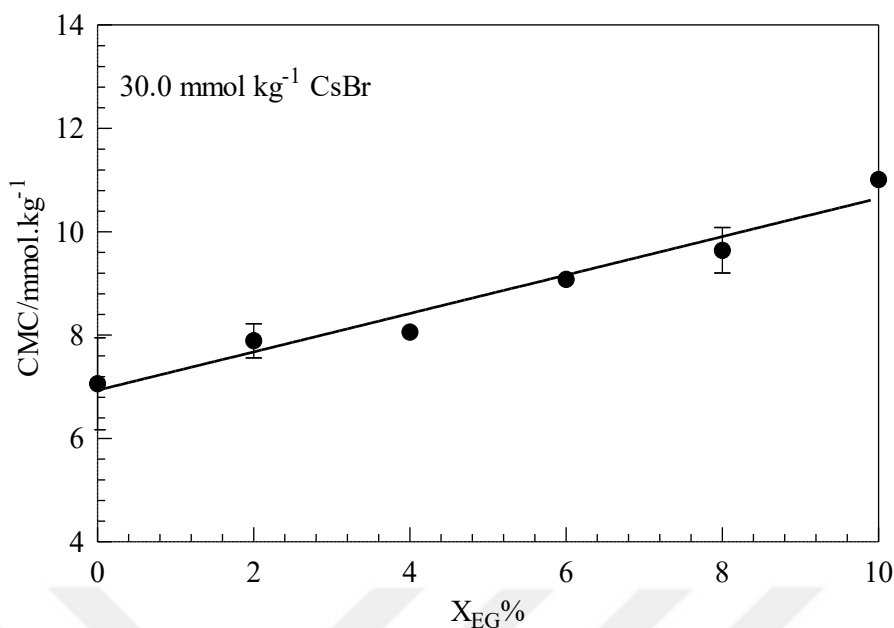


Figure 4.20. Comparison of the effect of the concentration of EG on the CMC of DTMABr/CsBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

Table 4.1. CMC values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	CMC/mmol kg ⁻¹				
	LiBr	NaBr	KBr	RbBr	CsBr
0	7.68 ± 0.57	7.72 ± 0.46	7.61 ± 0.39	7.60 ± 0.17	7.06 ± 0.89
2	7.97 ± 0.47	8.06 ± 0.67	7.91 ± 0.36	8.35 ± 0.21	7.89 ± 0.33
4	8.95 ± 0.04	8.16 ± 0.37	8.62 ± 0.43	8.47 ± 0.58	8.06 ± 0.06
6	9.06 ± 0.70	9.19 ± 0.33	9.67 ± 0.34	9.23 ± 0.52	9.08 ± 0.07
8	10.25 ± 0.56	9.85 ± 0.45	9.47 ± 1.17	9.99 ± 0.61	9.64 ± 0.44
10	11.36 ± 0.45	11.10 ± 0.90	10.76 ± 0.49	11.65 ± 0.96	11.01 ± 0.12

CMC values of DTMABr in the presence of the electrolyte ions Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺, obtained from the Figures 4.16-4.20 by applying Carpena's method, are summarized in Table 4.1. Remember that these ions cannot be located at the micelle surfaces (in Stern layer), but in the intermicellar region (Gouy-Chapman or diffuse layer). In the cases of the absence and presence of EG in the solutions, there is no significant difference in the CMC values of DTMABr for all

alkali metal ions. However, the concentration of EG affects the CMC of DTMABr, the increase in the EG concentration increases the CMC (Ghosh & Quagliotto, 2009). It means that the presence of EG unfavors the micellization of DTMABr surfactant monomers. This is due to the replacement of some water molecules with EG at the micelle surfaces, where EG molecules may penetrate between the surfactant head groups, resulting in a decrease in the dielectric constant at the micelle surfaces (Al-Hatem & Ali, 2020), which leads to a greater repulsion between the ionic head groups of the surfactant molecules and the CMC values increase (Tikariha, Ghosh & Quagliotto, 2011).

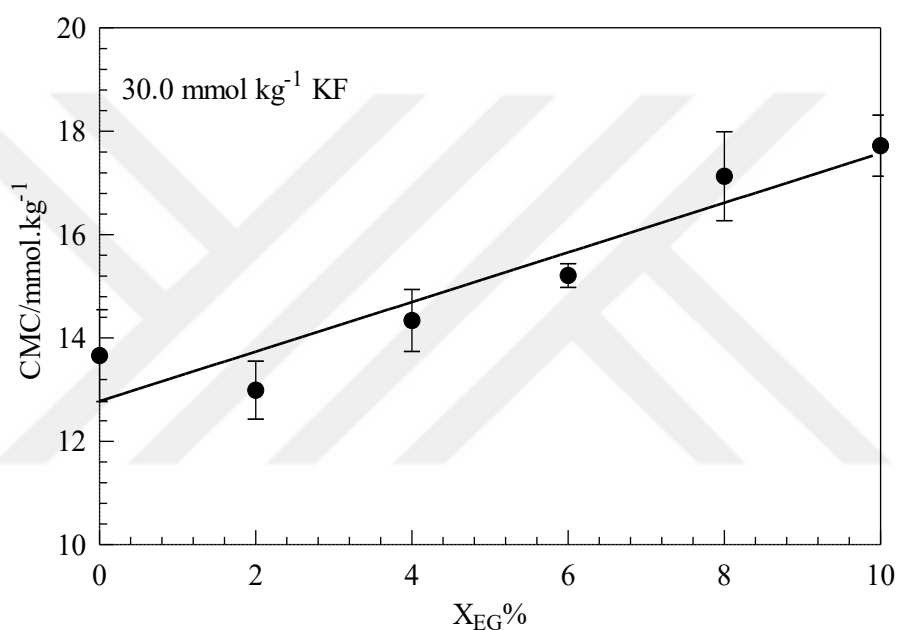


Figure 4.21. Comparison of the effect of the concentration of EG on the CMC of DTMABr/KF/EG-water solution versus percent mole fraction of EG at 25.0°C.

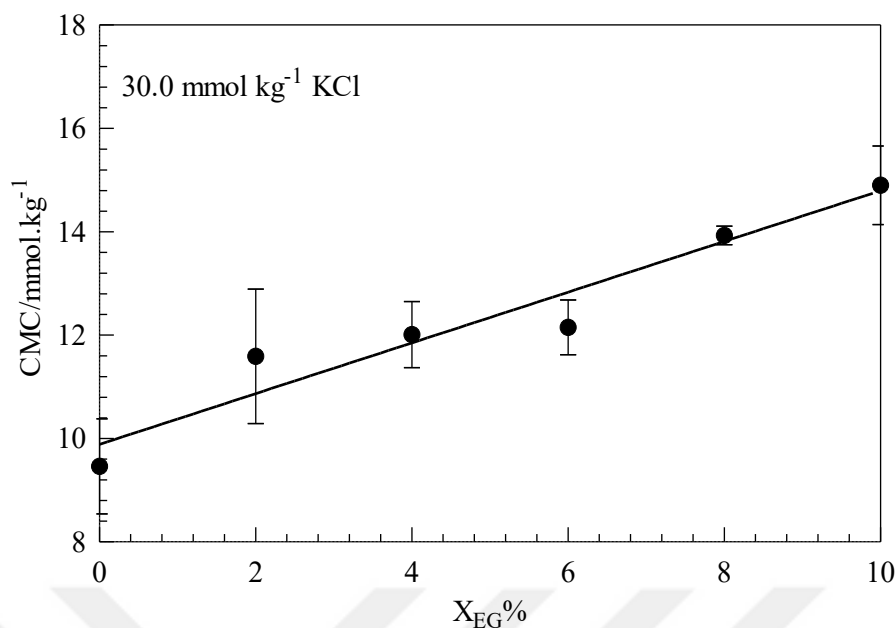


Figure 4.22. Comparison of the effect of the concentration of EG on the CMC of DTMABr/KCl/EG-water solution versus percent mole fraction of EG at 25.0°C.

Table 4.2. CMC values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	CMC/mm mol kg^{-1}		
	KF	KCl	KBr
0	13.66 ± 0.89	9.46 ± 0.92	7.61 ± 0.39
2	12.99 ± 0.56	11.59 ± 1.30	7.91 ± 0.36
4	14.34 ± 0.60	12.01 ± 0.64	8.62 ± 0.43
6	15.21 ± 0.23	12.15 ± 0.53	9.67 ± 0.34
8	17.13 ± 0.86	13.93 ± 0.18	9.47 ± 1.17
10	17.72 ± 0.59	14.90 ± 0.76	10.76 ± 0.49

If the results given in Figures 4.21 and 4.22 are compared with those in Figure 4.18, going from F⁻ to Br⁻, CMC of DTMABr significantly decreases in water and in EG-water. Furthermore, as the concentration of EG is increased for three electrolytes, CMC increases, too. This result may be explained by the following way: The dispersed electrolyte ions in solutions disturb the extent of hydrogen bonding of water molecules with these ions, which lead to a dramatic

effect on the structure of water (Rafiee & Frouzesh, 2016). In other words, ions can change the local structure of the hydrogen-bond network of water (Bakker & Skinner, 2010). From this respect, the ions may either enhance or diminish the degree of hydrogen bonding in water molecules (Naseem et al., 2021). Ions for the former and latter cases are called “kosmotropic” and “chaotropic” ions, respectively. Kosmotropic and chaotropic ions are also known as “structure maker” and “structure breaker”, respectively (Marcus, 2009). How those ions affect the water structure can be explained by Collins’s approach, although it was proposed for the interactions in the macromolecular solutes-electrolyte ions systems. In the Collins’s approach (Collins, 2004), the interface of the macromolecular solutes in the aqueous solution into three layers (Figure 4.23): **hydration layer** includes water molecules next to the surface of the solute; **transition layer** is the second water molecule layer next to the hydration layer; the **third layer** consists of water molecules next to the bulk solution. Note that the third layer of water molecules can act on the hydration layer through the transition layer and thus indirectly changes the solvation behavior of the solute molecules (Figure 4.23b) (Wei et al., 2022).

The effect of the presence of kosmotropic or chaotropic ions in the solution can be explained as follows: kosmotropic ions diffuse to the third layer of water molecules, and the water molecules in the transition layer mainly participate in the hydration of kosmotropes, which leads to weakening the interaction with the solute in the hydration layer, (Figure 4.23a). In the case of the presence of chaotropic ions, they are in the third molecular layer, and their binding to water molecules is difficult, which leads to facilitating the interaction between water molecules in the transition layer and the solutes in the hydration layer, thus promoting dissolution of solutes (Figure 4.23c).

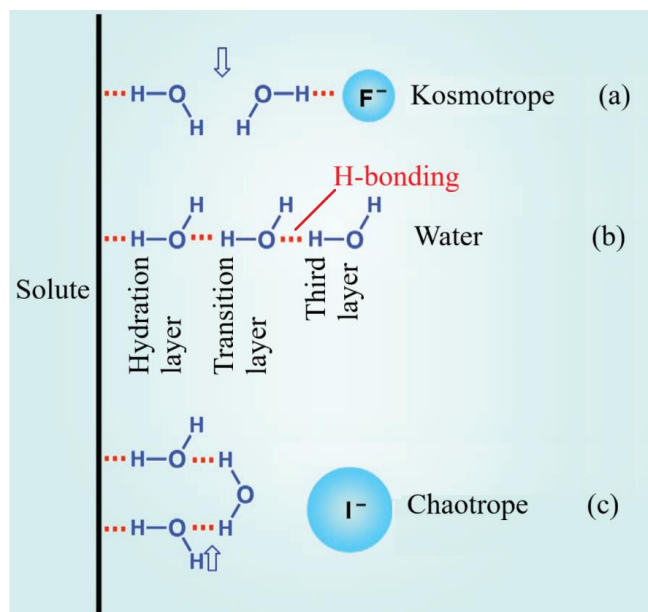


Figure 4.23. The interaction between kosmotropic or chaotropic ions and interfacial water molecules near the surface of solutes (This figure is adapted from one given in (Wei et al., 2022)).

The ionic surfactants are also classified as kosmotrope and chaotrope, similar to the electrolyte ions, because they have ionic head groups. For instance, the head group of DTMABr surfactant (TMA^+) exhibits a chaotropic character. It is well-known that the ionic species with similar (different) extent of the kosmotropic/chaotropic characters results in the formation of close contact (loosely bound) ion pairs (Conway, 1981), Figure 4.24.

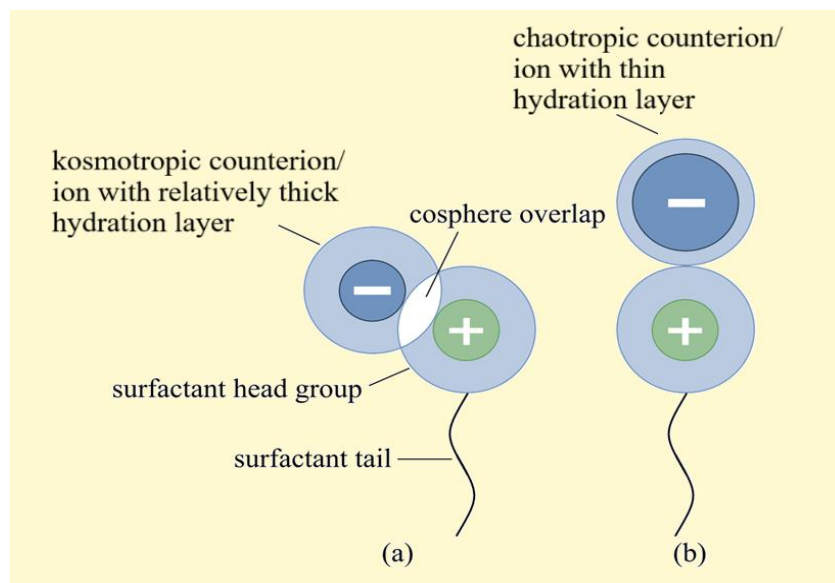


Figure 4.24. Schematic representation of formation of the different ion pairs, considering the interactions between, for example, the positively charged kosmotropic surfactant head group and (a) strongly kosmotropic, and (b) strongly chaotropic, counterion/ion, separately (Moreira & Firoozabadi, 2010). In (a) and (b), a tightly and a loosely bound ion pairs are produced, respectively (Adapted from (Akpınar & Figueiredo Neto, 2019)).

Now, we can comprehensively discuss the effects of electrolyte ions on the CMC of DTMABr by combining Collins's approach (Figure 4.23) with the formation of contact ions pairs (Figure 4.24), except that the term charged "micelle" surface should be considered instead of "solute" surface in Figure 4.23. When the electrolyte ions are added to the solutions, their oppositely charged ions with respect to the surfactant head groups may penetrate the first hydration layer (Stern layer of micellar systems) by reducing the repulsions between surfactant head groups, which favors the micellization, i.e., CMC decreases. In the case of alkali metal bromides (Table 4.1), CMC of DTMABr in the absence of EG and in the presence of constant EG concentration does not change significantly from LiBr to CsBr. This states that the cations of those electrolytes cannot modify the interactions in the Stern layer because they mainly prefer to be in the third hydration layer (electric double layer, diffuse layer or Gouy-Chapman layer of micellar systems). However, the anions of potassium halides (KF, KCl and KBr) have a significant effect on CMC of DTMABr. Considering kosmotropic character of F^- and chaotropic characters of both Cl^- and Br^- (the latter is more

chaotropic than the former one), Table 4.2, the degree of strong (weak) interaction between TMA^+ and Br^- (F^-) ions, coming from KBr (KF), in the first hydration layer favors (unfavors) micellization. The favoring the micellization of DTMABr follows the order $\text{KBr} > \text{KCl} > \text{KF}$.

The increase in CMC of the surfactant DTMABr with the increase in EG concentration can only be explained by removing some part of oppositely charged ions (surfactant counterions or electrolyte ions) in the first hydration layer next to the micelle surfaces, which increases the repulsions between the surfactant head groups and unfavour the micellization.

4.1.2.2 DTMABr/electrolyte/FA-water Solutions

The effect of FA on CMC of DTMABr in mixture of electrolyte/FA-water in the presence of different electrolytes are graphically shown in Figures 4.25-4.31. The measurements were repeated at least three times and the CMC values in the figures were averaged of these three measurements with their standard deviations.

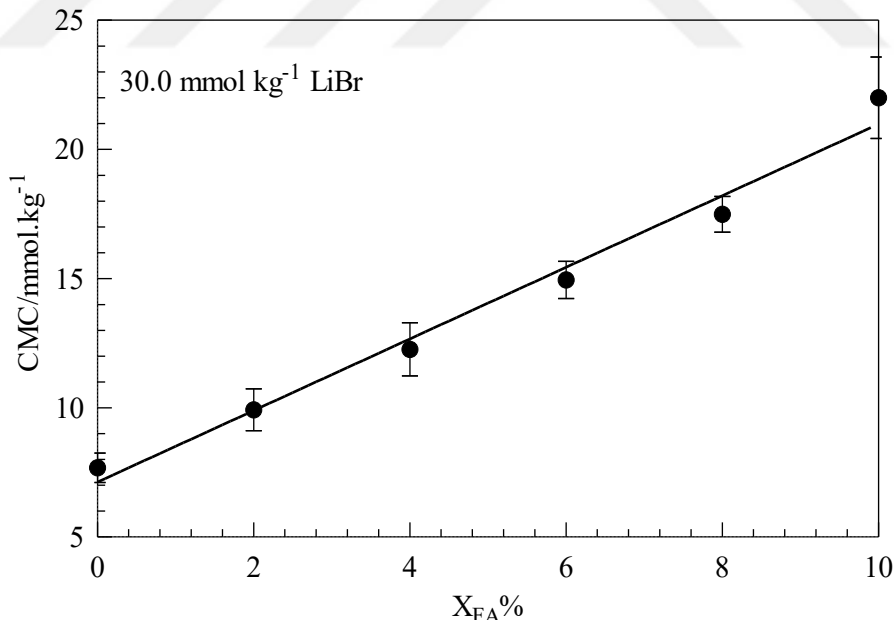


Figure 4.25. Comparison of the effect of the concentration of FA on the CMC of DTMABr/LiBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

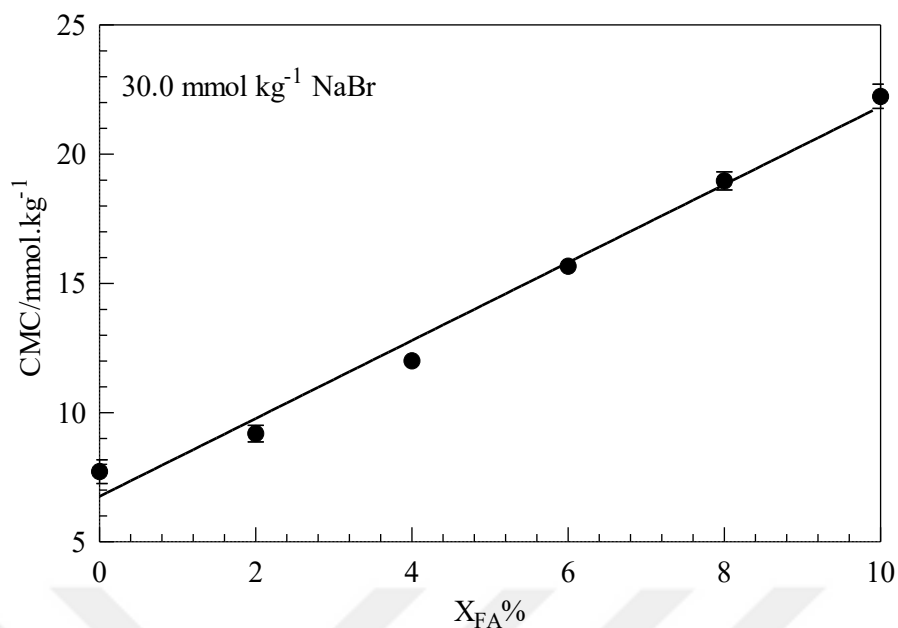


Figure 4.26. Comparison of the effect of the concentration of FA on the CMC of DTMABr/NaBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

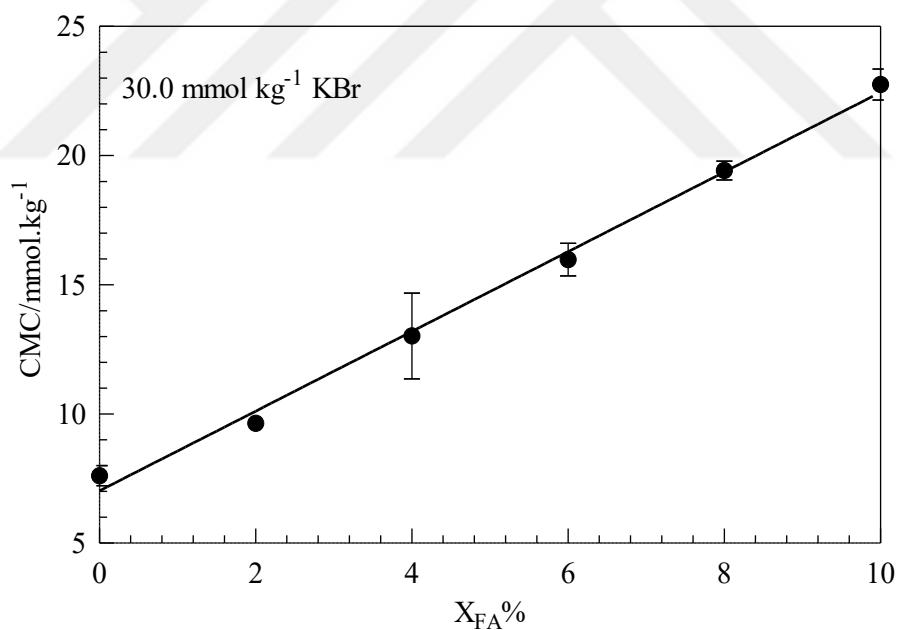


Figure 4.27. Comparison of the effect of the concentration of FA on the CMC of DTMABr/KBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

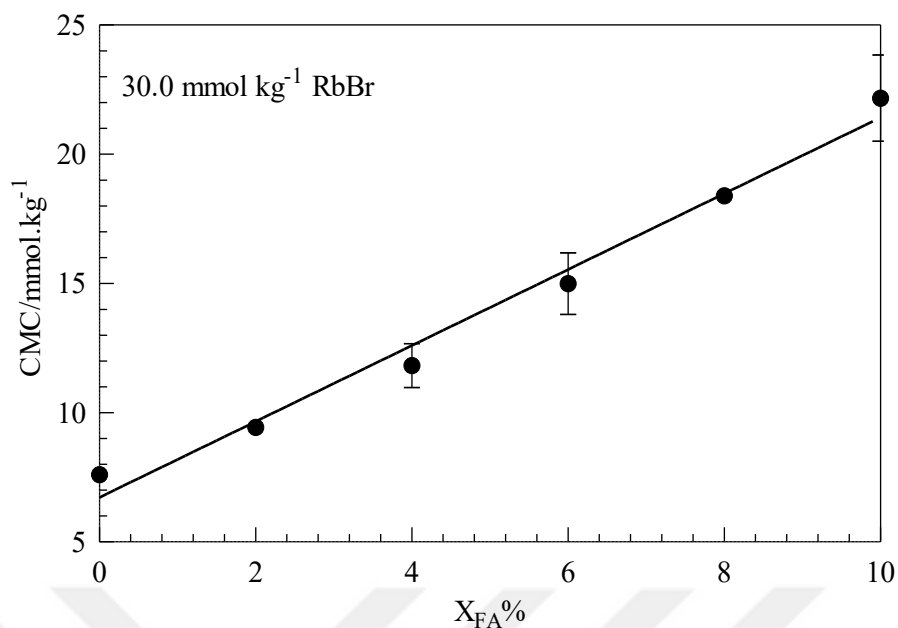


Figure 4.28. Comparison of the effect of the concentration of FA on the CMC of DTMABr/RbBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

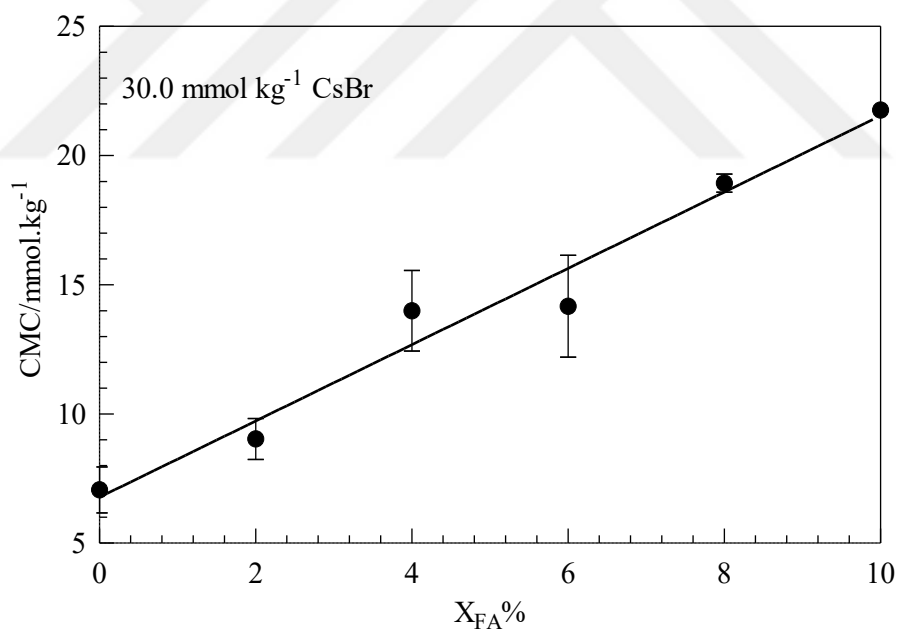


Figure 4.29. Comparison of the effect of the concentration of FA on the CMC of DTMABr/CsBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

Table 4.3. CMC values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations ($30.0 \text{ mmol kg}^{-1}$) and FA at different percent mole fractions at 25.0°C .

FA%	CMC/ mmol kg^{-1}				
	LiBr	NaBr	KBr	RbBr	CsBr
0	7.68 ± 0.57	7.72 ± 0.46	7.61 ± 0.39	7.60 ± 0.17	7.06 ± 0.89
2	9.92 ± 0.81	9.19 ± 0.32	9.64 ± 0.36	9.43 ± 0.23	9.03 ± 0.79
4	12.26 ± 1.03	12.00 ± 0.17	13.20 ± 1.66	11.82 ± 0.85	13.99 ± 1.56
6	14.95 ± 0.72	15.67 ± 0.08	15.97 ± 0.63	14.99 ± 1.19	14.17 ± 1.97
8	17.49 ± 0.69	18.97 ± 0.35	19.42 ± 0.36	18.39 ± 0.08	18.93 ± 0.35
10	22.00 ± 1.58	22.24 ± 0.47	22.75 ± 0.60	22.17 ± 1.67	21.76 ± 0.02

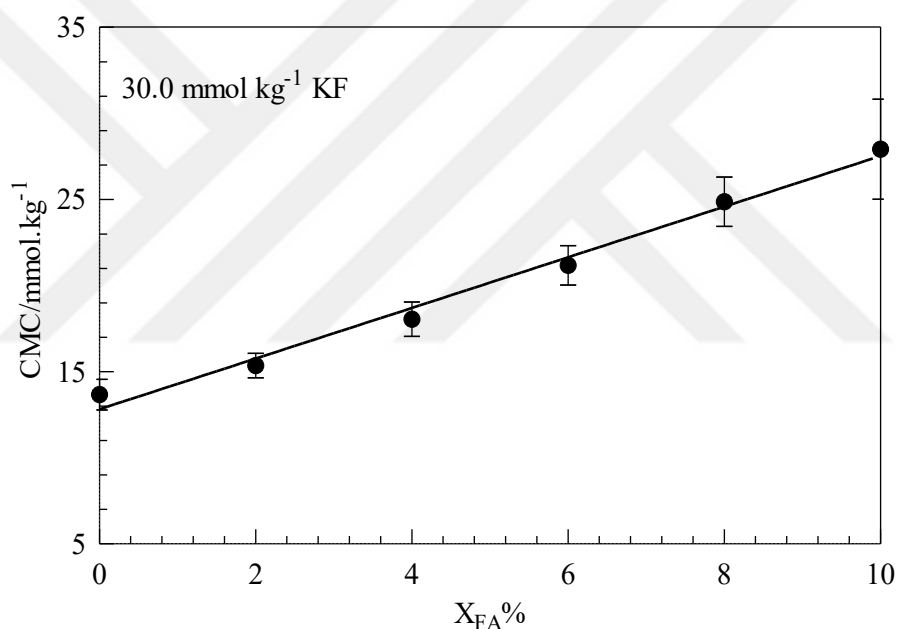


Figure 4.30. Comparison of the effect of the concentration of FA on the CMC of DTMABr/KF/FA-water solution versus percent mole fraction of FA at 25.0°C .

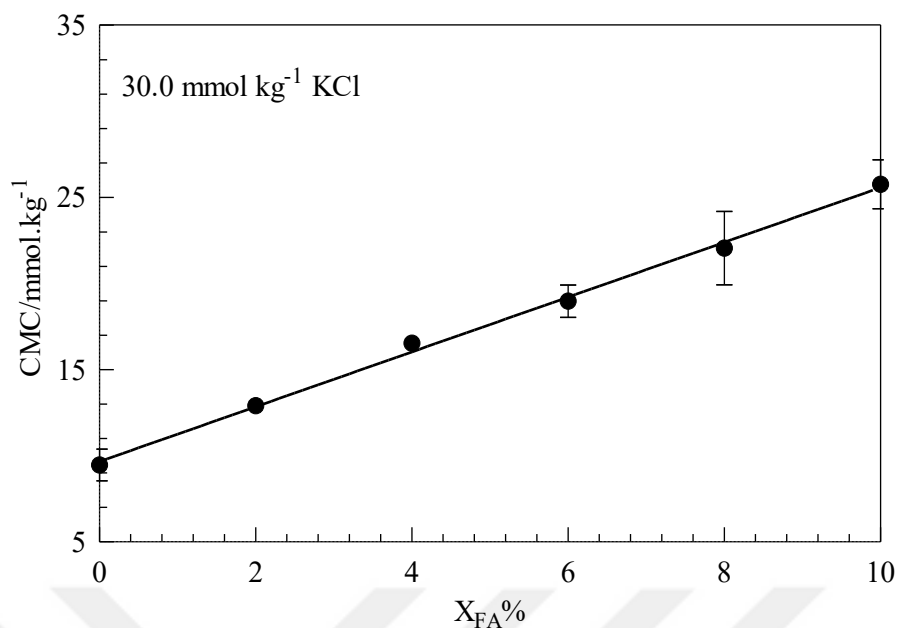


Figure 4.31. Comparison of the effect of the concentration of FA on the CMC of DTMABr/KCl/FA-water solution versus percent mole fraction of FA at 25.0°C.

Table 4.4. CMC values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	CMC/mmole kg ⁻¹		
	KF	KCl	KBr
0	13.66 ± 0.89	9.46 ± 0.92	7.61 ± 0.39
2	15.35 ± 0.71	12.91 ± 0.15	9.64 ± 0.36
4	18.04 ± 1.00	16.63 ± 0.12	13.20 ± 1.66
6	21.17 ± 1.14	18.97 ± 0.94	15.97 ± 0.63
8	24.86 ± 1.43	22.05 ± 2.13	19.42 ± 0.36
10	27.91 ± 2.90	25.76 ± 1.42	22.75 ± 0.60

If the effects of EG and FA on the critical micelle concentration of DTMABr are compared, similar results were obtained within the experimental error limits for the constant FA concentration. However, while CMC of DTMABr increases by ~4 mmol/kg as the concentration of EG was changed from 0% to 10%, it increases by ~14-15 mmol/kg in the case of FA. This result indicates that FA causes the removal of the counterions/oppositely charged electrolyte ions from

the micelle surfaces (first hydration layer) or the weakening the interactions between surfactant head groups and counterions/oppositely charged electrolyte ions at the micelle surfaces more efficiently than EG. The ionization degree of counterions from the micelles (α) values may help which factor is dominant in the presence of EG or FA (see the next part).

4.1.3 Effect of the Concentration on α and β Values

4.1.3.1 DTMABr/electrolyte/EG-water Solutions

The degrees of counterion ionization from micelle, α , for DTMABr/electrolyte/water and DTMABr/electrolyte/EG-water solutions were evaluated from the conductivity measurements at different EG concentrations. From this parameter, the degrees of counterion binding to the micelle, β , were also determined. The changes in both parameters were plotted against the change in the concentration of EG at constant alkali bromides concentrations and potassium halides concentrations, separately. The results are given in Figures 4.32-4.38 and summarized in Tables 4.5-4.8.

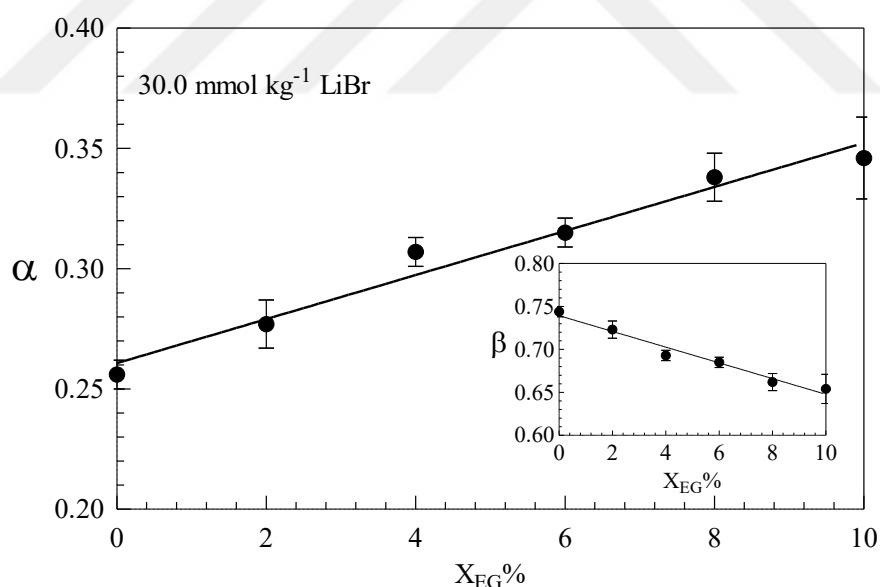


Figure 4.32. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/LiBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

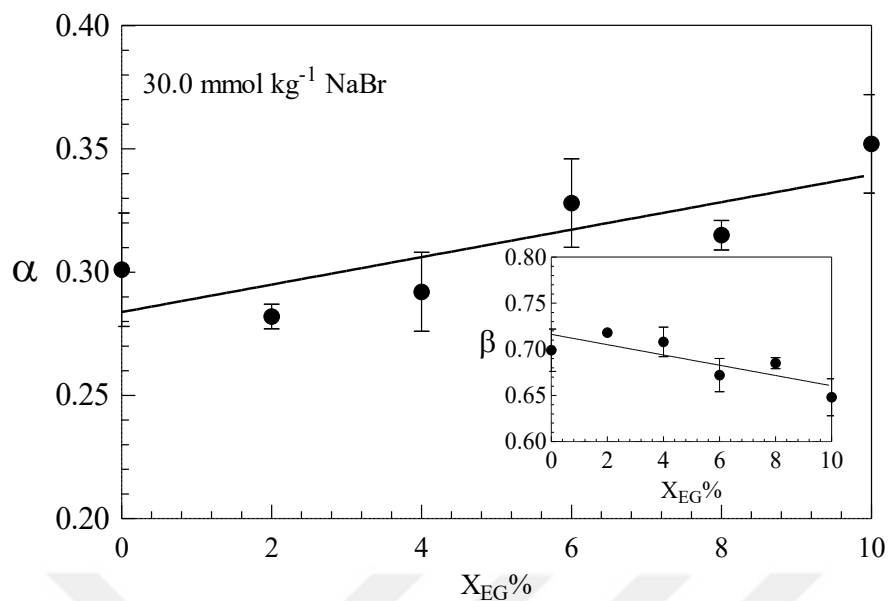


Figure 4.33. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/NaBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

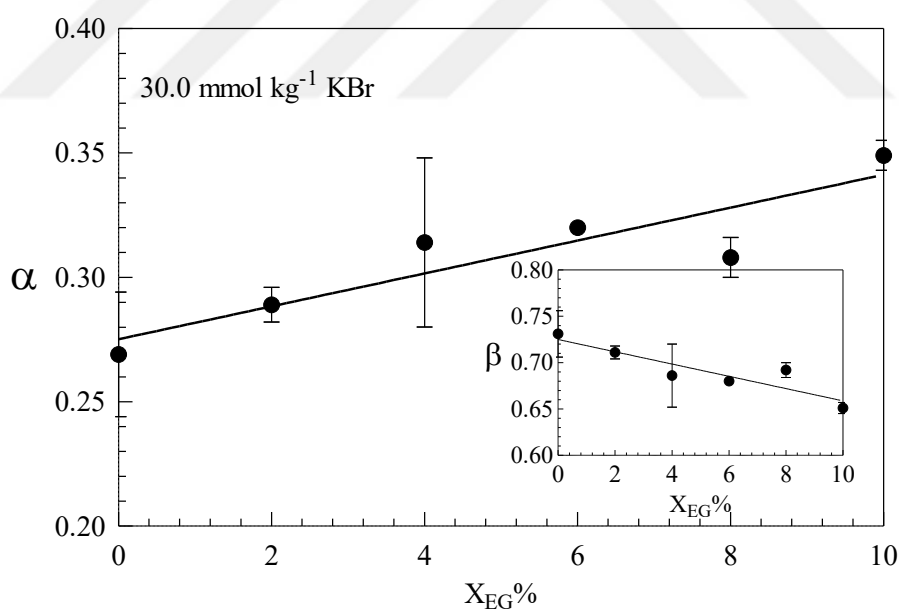


Figure 4.34. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/KBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

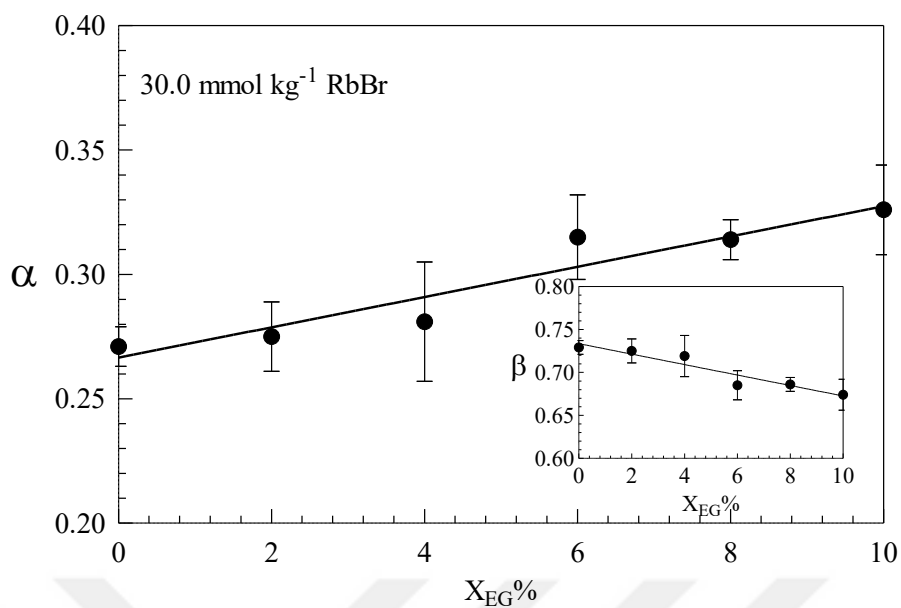


Figure 4.35. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/RbBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

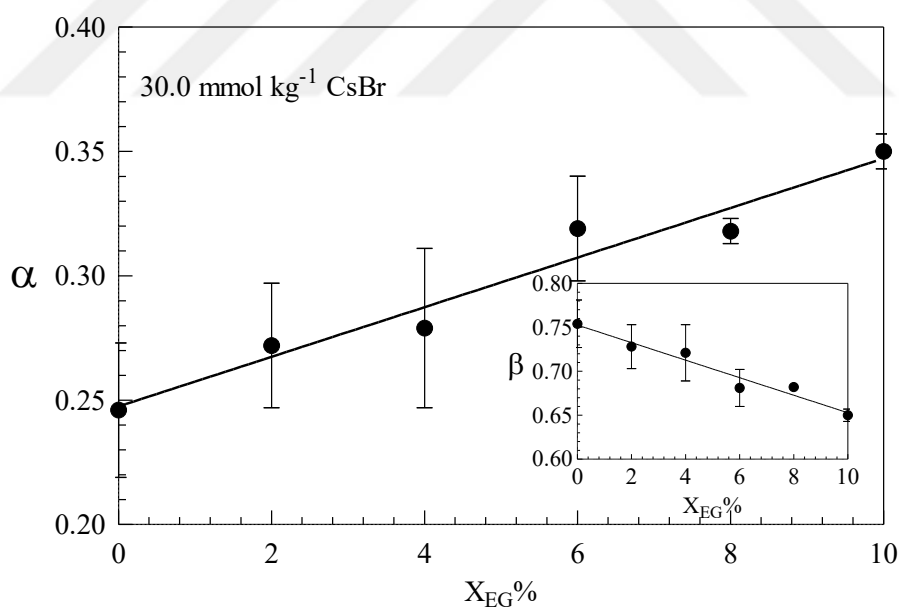


Figure 4.36. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/CsBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

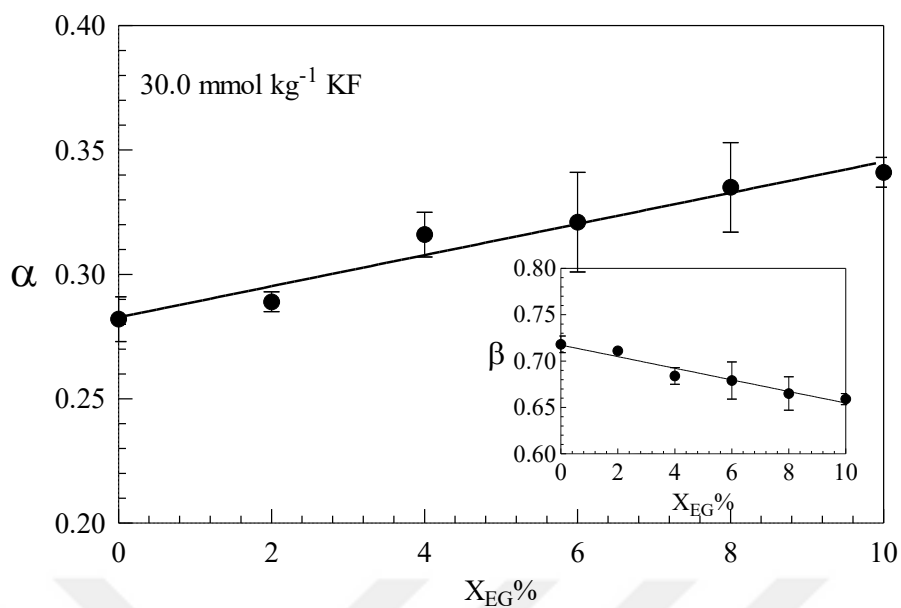


Figure 4.37. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/KF/EG-water solution versus percent mole fraction of EG at 25.0°C.

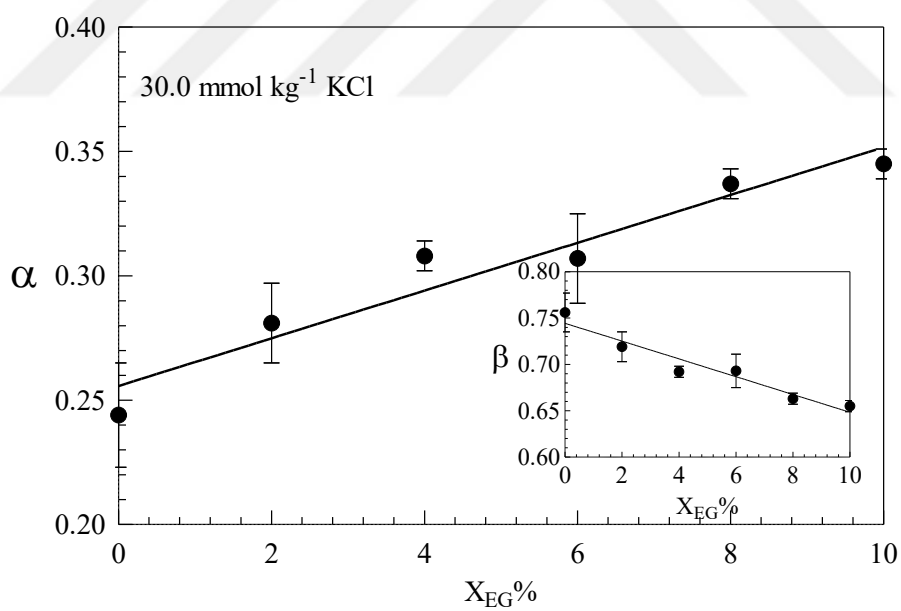


Figure 4.38. Comparison of the effect of the concentration of EG on α and β (inset) values of DTMABr/KCl/EG-water solution versus percent mole fraction of EG at 25.0°C.

Table 4.5. α values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	α				
	LiBr	NaBr	KBr	RbBr	CsBr
0	0.256±0.006	0.301±0.023	0.269±0.025	0.271±0.008	0.246±0.027
2	0.277±0.010	0.282±0.005	0.289±0.007	0.275±0.014	0.272±0.025
4	0.307±0.006	0.292±0.016	0.314±0.034	0.281±0.024	0.279±0.032
6	0.315±0.006	0.328±0.018	0.320±0.003	0.315±0.017	0.319±0.021
8	0.338±0.010	0.315±0.006	0.308±0.008	0.314±0.008	0.318±0.005
10	0.346±0.017	0.352±0.020	0.349±0.006	0.326±0.018	0.350±0.007

Table 4.6. β values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	β				
	LiBr	NaBr	KBr	RbBr	CsBr
0	0.744±0.006	0.699±0.023	0.731±0.025	0.729±0.008	0.754±0.027
2	0.723±0.010	0.718±0.005	0.711±0.007	0.725±0.014	0.728±0.025
4	0.693±0.006	0.708±0.016	0.686±0.034	0.719±0.024	0.721±0.032
6	0.685±0.006	0.672±0.018	0.680±0.003	0.685±0.017	0.681±0.021
8	0.662±0.010	0.685±0.006	0.692±0.008	0.686±0.008	0.682±0.005
10	0.654±0.017	0.648±0.020	0.651±0.006	0.674±0.018	0.650±0.007

According to the α (β) values given in Table 4.5 (Table 4.6), for all alkali metal bromides, the increase in the concentration of EG in the solutions results in an increase (decrease) in the α (β) values. This is due to the ionization of counterions from the micelle surfaces because of the decrease in the dielectric constant at micelle surfaces, arising from replacement of some water molecules by EG in the first hydration layer (Stern layer). This explanation is in good agreement with the discussion of the effect of EG concentration on CMC of DTMABr. Within the experimental error limits (standard deviations), at constant

EG concentrations and for EG-free solutions, there are no significance difference between the α (β) values.

Table 4.7. α values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	α		
	KF	KCl	KBr
0	0.281 ± 0.009	0.244 ± 0.021	0.269 ± 0.025
2	0.289 ± 0.004	0.281 ± 0.016	0.289 ± 0.007
4	0.316 ± 0.009	0.308 ± 0.006	0.314 ± 0.034
6	0.321 ± 0.020	0.307 ± 0.018	0.320 ± 0.003
8	0.335 ± 0.018	0.337 ± 0.006	0.308 ± 0.008
10	0.341 ± 0.006	0.345 ± 0.006	0.349 ± 0.006

Table 4.8. β values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	β		
	KF	KCl	KBr
0	0.719 ± 0.009	0.756 ± 0.021	0.731 ± 0.025
2	0.711 ± 0.004	0.719 ± 0.016	0.711 ± 0.007
4	0.684 ± 0.009	0.692 ± 0.006	0.686 ± 0.034
6	0.679 ± 0.020	0.693 ± 0.018	0.680 ± 0.003
8	0.665 ± 0.018	0.663 ± 0.006	0.692 ± 0.008
10	0.651 ± 0.006	0.655 ± 0.006	0.651 ± 0.006

For the potassium halides (Tables 4.7 and 4.8), it was surprisingly observed similar trends in the α and β values as we observed for alkali metal bromides at constant EG-concentration. We expected that some parts of anions coming from the electrolytes (F⁻, Cl⁻ and Br⁻) would bind to the micelle surfaces because CMC of DTMABr in the presence of these anions decreases following

the order $\text{Br}^- > \text{Cl}^- > \text{F}^-$ following the chaotropic order of these anions. Thus, while the α and β values are almost same values, within the experimental error limits, at constant EG-concentration in DTMABr/electrolyte/EG/water and for EG-free solutions, this result may be attributed to increase in the surfactant head group-counterions/electrolyte ions interactions, going from F^- to Br^- . If we compare the results of cations located in the intermicellar region with the results of anions, which prefer to bind to the micelle surfaces, both types of ions exhibit almost same effects on the ionization or binding of ions.

4.1.3.2 DTMABr/electrolyte/FA-water Solutions

Figures 4.39-4.45 show FA concentration dependences of the degrees of counterion ionization from micelle, α , and of counterion binding to the micelle, β , for DTMABr/electrolyte/water and DTMABr/electrolyte/FA-water solutions. The results are summarized in Tables 4.9-4.12.

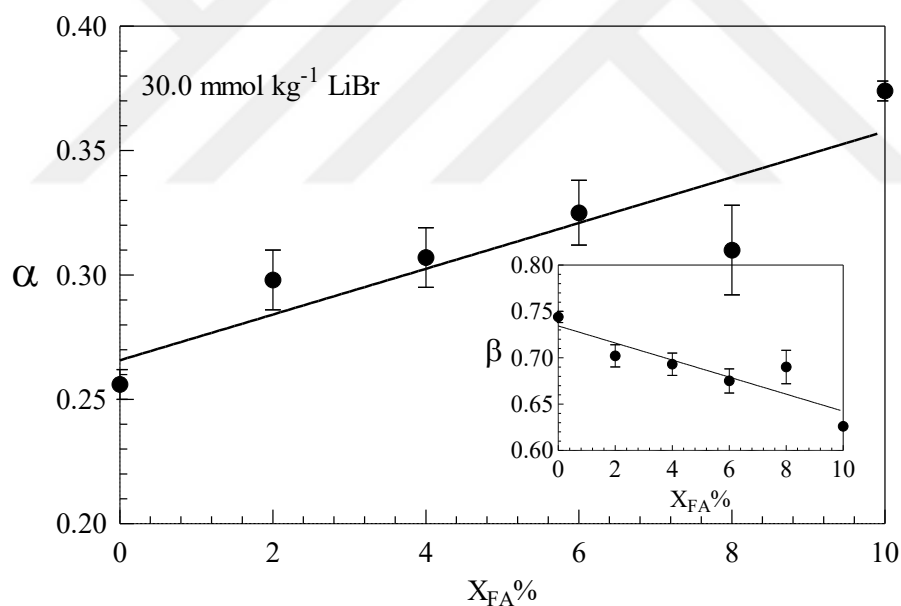


Figure 4.39. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/LiBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

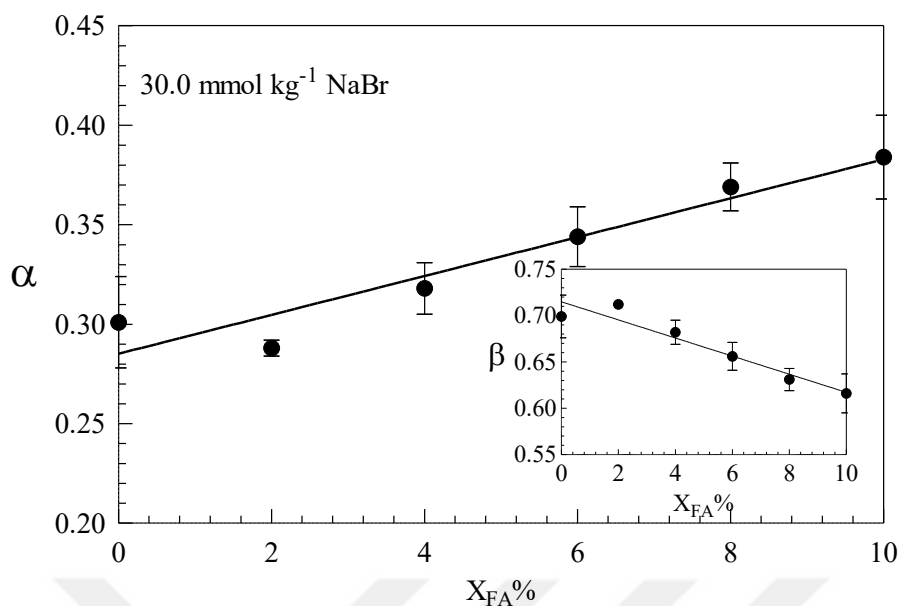


Figure 4.40. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/NaBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

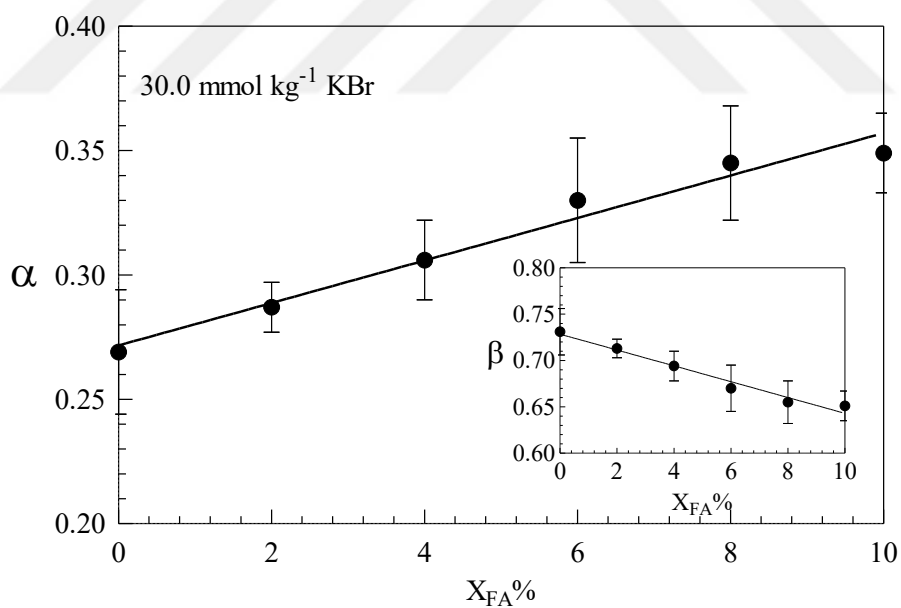


Figure 4.41. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/KBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

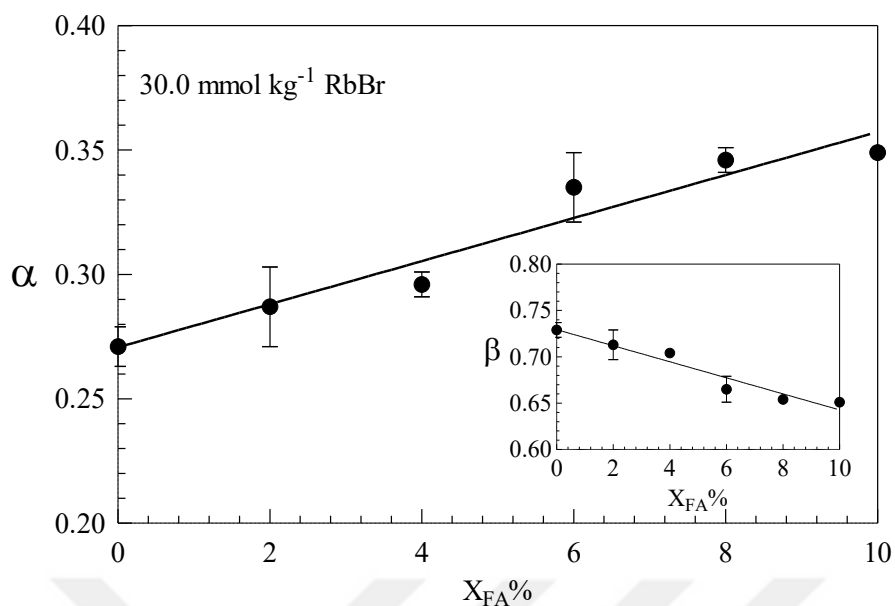


Figure 4.42. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/RbBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

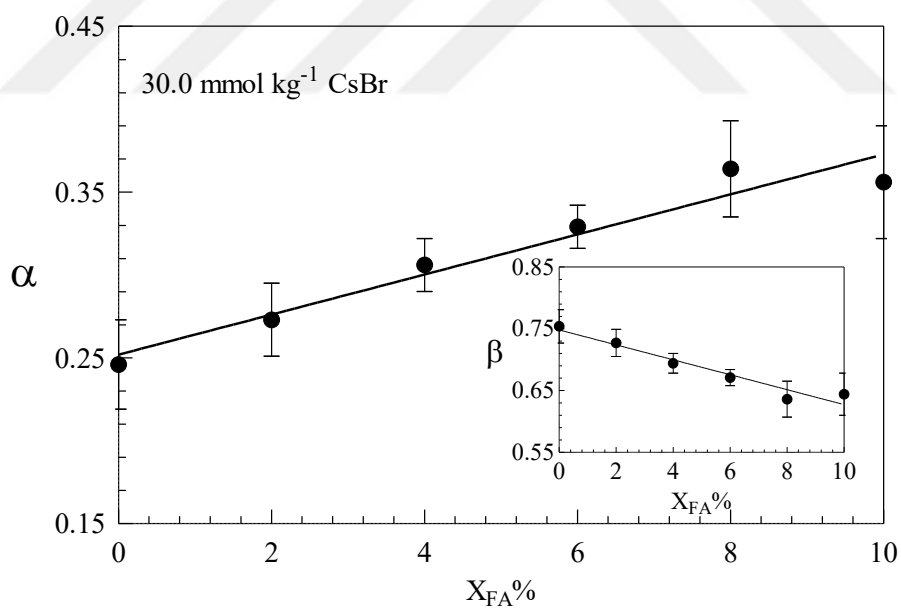


Figure 4.43. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/CsBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

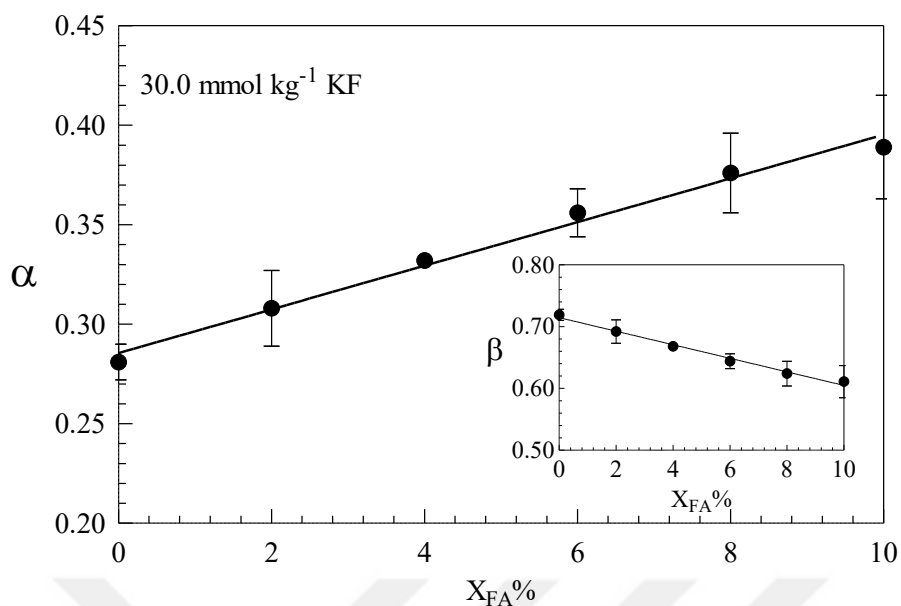


Figure 4.44. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/KF/FA-water solution versus percent mole fraction of FA at 25.0°C.

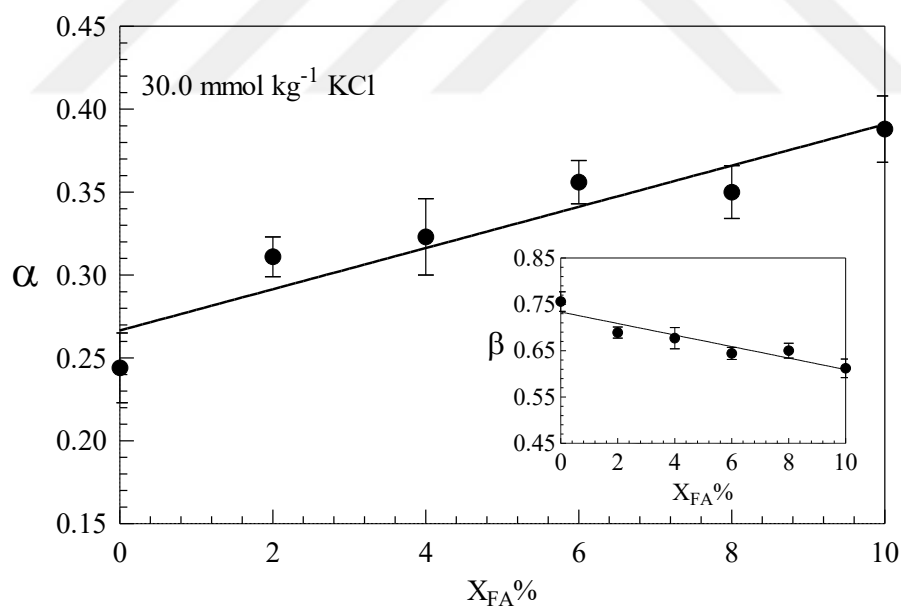


Figure 4.45. Comparison of the effect of the concentration of FA on α and β (inset) values of DTMABr/KCl/FA-water solution versus percent mole fraction of FA at 25.0°C.

Table 4.9. α values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	α				
	LiBr	NaBr	KBr	RbBr	CsBr
0	0.256±0.006	0.301±0.023	0.269±0.025	0.271±0.008	0.246±0.027
2	0.298±0.012	0.288±0.004	0.287±0.010	0.287±0.016	0.273±0.022
4	0.307±0.012	0.318±0.013	0.306±0.016	0.296±0.005	0.306±0.016
6	0.325±0.013	0.344±0.015	0.330±0.025	0.335±0.014	0.329±0.013
8	0.310±0.018	0.369±0.012	0.345±0.023	0.346±0.005	0.364±0.026
10	0.374±0.004	0.384±0.021	0.349±0.016	0.349±0.003	0.356±0.034

Table 4.10. β values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	β				
	LiBr	NaBr	KBr	RbBr	CsBr
0	0.744±0.006	0.699±0.023	0.731±0.025	0.729±0.008	0.754±0.027
2	0.702±0.012	0.712±0.004	0.713±0.010	0.713±0.016	0.727±0.022
4	0.693±0.012	0.682±0.013	0.694±0.016	0.704±0.005	0.694±0.016
6	0.675±0.013	0.656±0.015	0.670±0.025	0.665±0.014	0.671±0.013
8	0.690±0.018	0.631±0.012	0.655±0.023	0.654±0.005	0.636±0.029
10	0.626±0.004	0.616±0.021	0.651±0.016	0.651±0.003	0.644±0.034

Table 4.11. α values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	α		
	KF	KCl	KBr
0	0.281 ± 0.009	0.244 ± 0.021	0.269 ± 0.025
2	0.308 ± 0.019	0.311 ± 0.012	0.287 ± 0.010
4	0.332 ± 0.003	0.323 ± 0.023	0.306 ± 0.016
6	0.356 ± 0.012	0.356 ± 0.013	0.330 ± 0.025
8	0.376 ± 0.020	0.350 ± 0.016	0.345 ± 0.023
10	0.389 ± 0.026	0.388 ± 0.020	0.349 ± 0.016

Table 4.12. β values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	β		
	KF	KCl	KBr
0	0.719 ± 0.009	0.756 ± 0.021	0.731 ± 0.025
2	0.692 ± 0.019	0.689 ± 0.012	0.713 ± 0.010
4	0.668 ± 0.003	0.677 ± 0.023	0.694 ± 0.016
6	0.644 ± 0.012	0.644 ± 0.013	0.670 ± 0.025
8	0.624 ± 0.020	0.650 ± 0.016	0.655 ± 0.023
10	0.611 ± 0.026	0.612 ± 0.020	0.651 ± 0.016

From the data given in Tables 4.9-4.12, FA affect the α and β values of DTMABr with similar ways as EG. This shows that the cations in the intermicellar region have the same effect as the anions on the micelle surfaces, even if the dielectric constant of the medium increases compared to water.

4.1.4 Effect of the Concentration on ΔG_{mic}

4.1.4.1 DTMABr/electrolyte/EG-water Solutions

ΔG_{mic} , the Gibbs energy change for micellization, gives valuable information on spontaneous micellization of surfactant molecules (Pires et al., 2012), arising from the transfer of hydrophobic surfactant tails from the bulk solution to the micellar region (Fenta, 2015). The more negative value of ΔG_{mic} indicates the favorable micellization (El-Dossoki et al., 2024).

The calculated ΔG_{mic} values can be seen in Figures 4.46-4.52 for DTMABr/electrolyte/EG-water solutions as a function of EG concentrations.

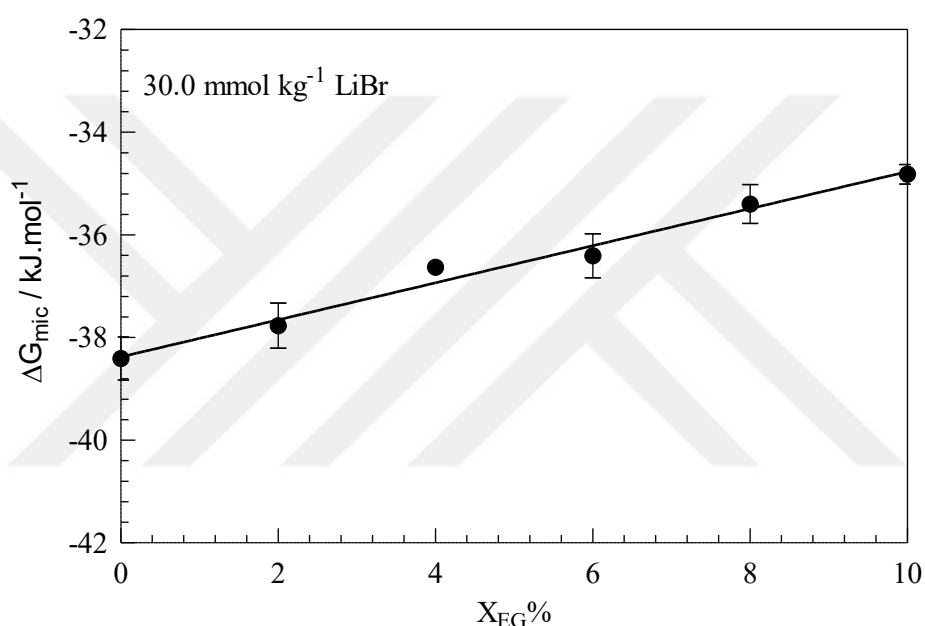


Figure 4.46. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/LiBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

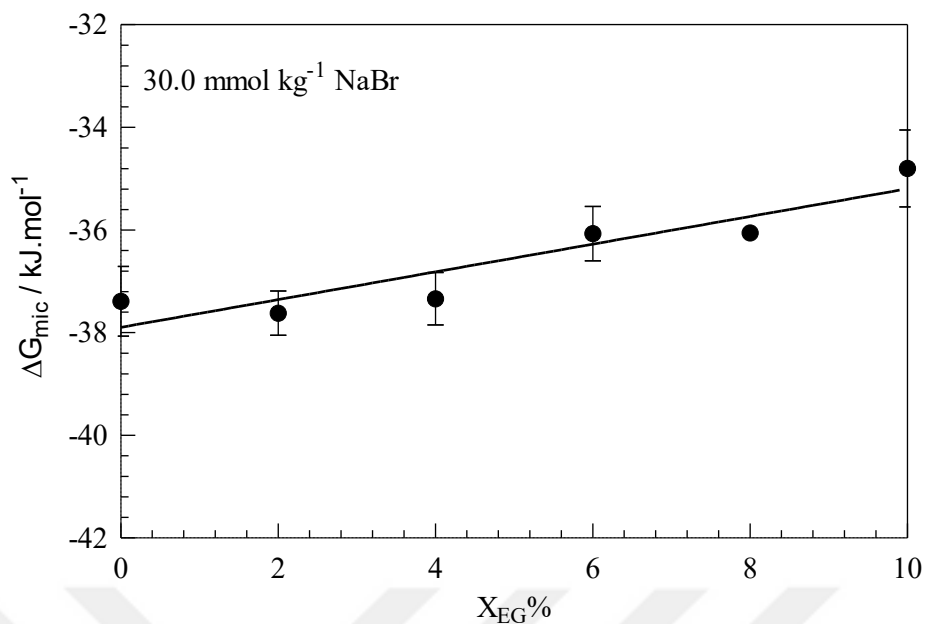


Figure 4.47. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/NaBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

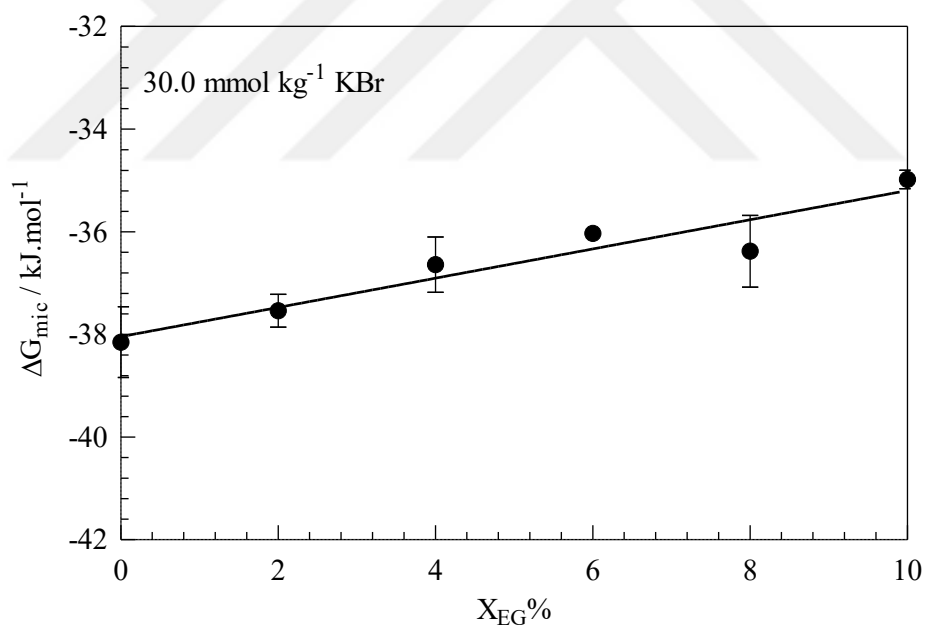


Figure 4.48. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/KBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

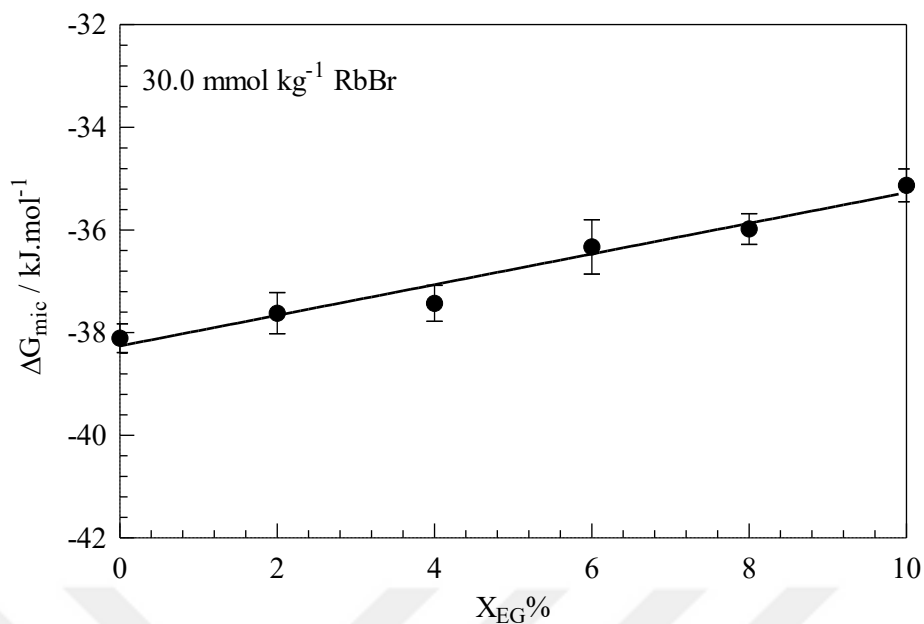


Figure 4.49. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/RbBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

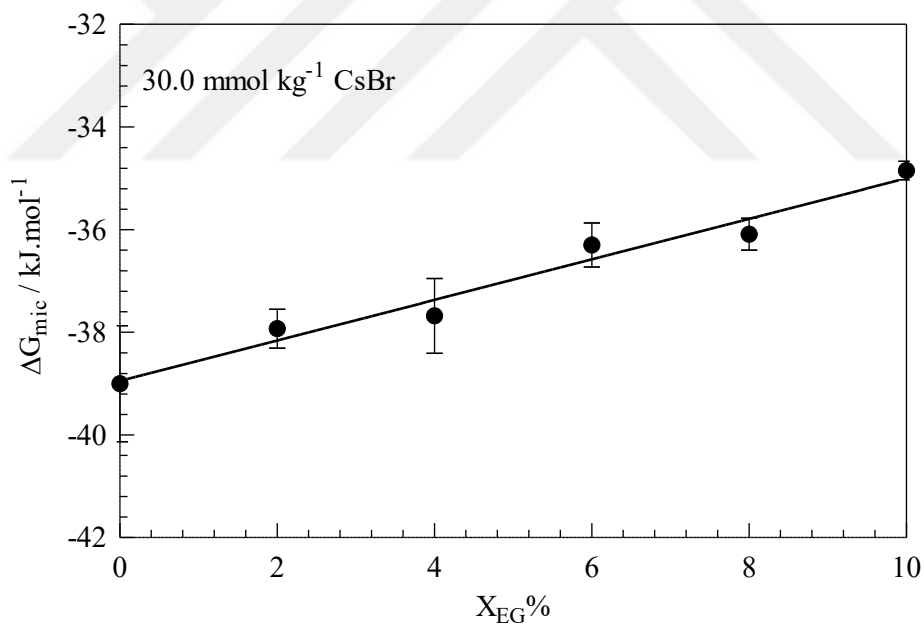


Figure 4.50. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/CsBr/EG-water solution versus percent mole fraction of EG at 25.0°C.

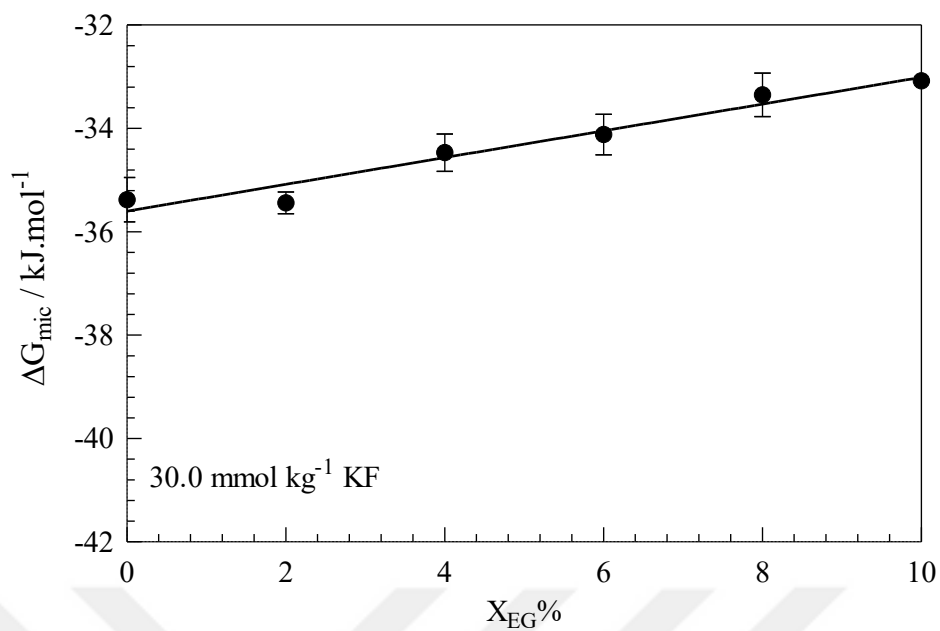


Figure 4.51. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/KF/EG-water solution versus percent mole fraction of EG at 25.0°C.

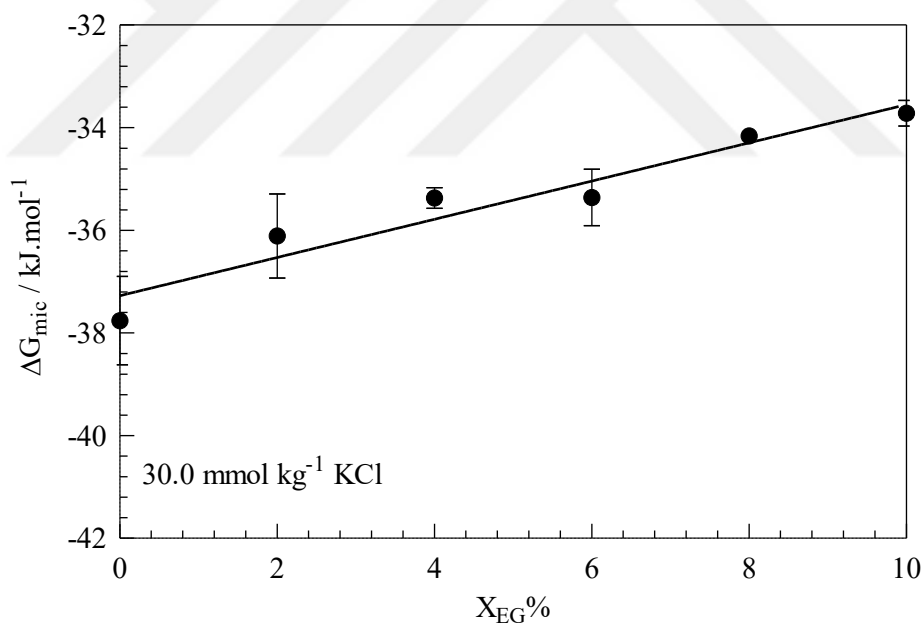


Figure 4.52. Effect of the concentration of EG on ΔG_{mic} values of DTMABr/KCl/EG-water solution versus percent mole fraction of EG at 25.0°C.

Table 4.13. ΔG_{mic} values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	$\Delta G_{mic}/\text{kJ mol}^{-1}$				
	LiBr	NaBr	KBr	RbBr	CsBr
0	-38.41±0.42	-37.39±0.68	-38.15±0.69	-38.11±0.28	-39.00±1.13
2	-37.77±0.44	-37.62±0.43	-37.54±0.32	-37.62±0.40	-37.93±0.38
4	-36.63±0.12	-37.34±0.51	-36.64±0.54	-37.43±0.35	-37.68±0.73
6	-36.41±0.43	-36.07±0.53	-36.30±0.08	-36.63±0.53	-36.30±0.43
8	-35.40±0.38	-36.06±0.10	-36.38±0.70	-35.98±0.30	-36.09±0.31
10	-34.82±0.19	-34.80±0.75	-34.98±0.18	-35.13±0.32	-34.85±0.18

Table 4.14. ΔG_{mic} values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and EG at different percent mole fractions at 25.0°C.

EG%	$\Delta G_{mic}/\text{kJ mol}^{-1}$		
	KF	KCl	KBr
0	-35.39 ± 0.42	-37.76 ± 0.86	-38.15 ± 0.69
2	-35.44 ± 0.21	-36.11 ± 0.82	-37.54 ± 0.32
4	-34.47 ± 0.36	-35.37 ± 0.20	-36.64 ± 0.54
6	-34.12 ± 0.39	-35.36 ± 0.55	-36.30 ± 0.08
8	-33.35 ± 0.42	-34.16 ± 0.10	-36.38 ± 0.70
10	-33.08 ± 0.02	-33.72 ± 0.25	-34.98 ± 0.18

ΔG_{mic} values of DTMABr in the presence of electrolytes are given in Tables 4.13. and 4.14. For LiBr, NaBr, KBr, RbBr, and CsBr electrolytes, ΔG_{mic} values are almost same at constant EG concentration. However, on increasing EG concentration, ΔG_{mic} values increase, i.e., become less negative. This may be ascribed to the unfavorable tendency of the transfer of DTMABr alkyl tails from the bulk solution to the interior of the micelles, which unfavors the micellization. This is supported by the results of EG-concentration dependence of CMC of DTMABr (Table 4.1).

Table 4.14 shows the ΔG_{mic} values of DTMABr in the presence of electrolytes KF, KCl and KBr, whose anions may penetrate the first hydration layer (Stern layer) around the micelle surfaces. The effect of those anions follows their kosmotropic/chaotropic characters, the higher the chaotropic character the negatively higher ΔG_{mic} . The effect of the increase in EG concentration exhibits similar trends as the alkali metal bromides, i.e., the increase in the concentration of EG turns the micellization into less favorable and ΔG_{mic} increases or becomes less negative.

4.1.4.2 DTMABr/electrolyte/FA-water Solutions

The effect of FA on the ΔG_{mic} of DTMABr was also studied in the frame of this thesis. Figure 4.53-4.59 show the FA concentration dependence of the ΔG_{mic} of DTMABr at different FA-concentration and at constant electrolyte concentrations.

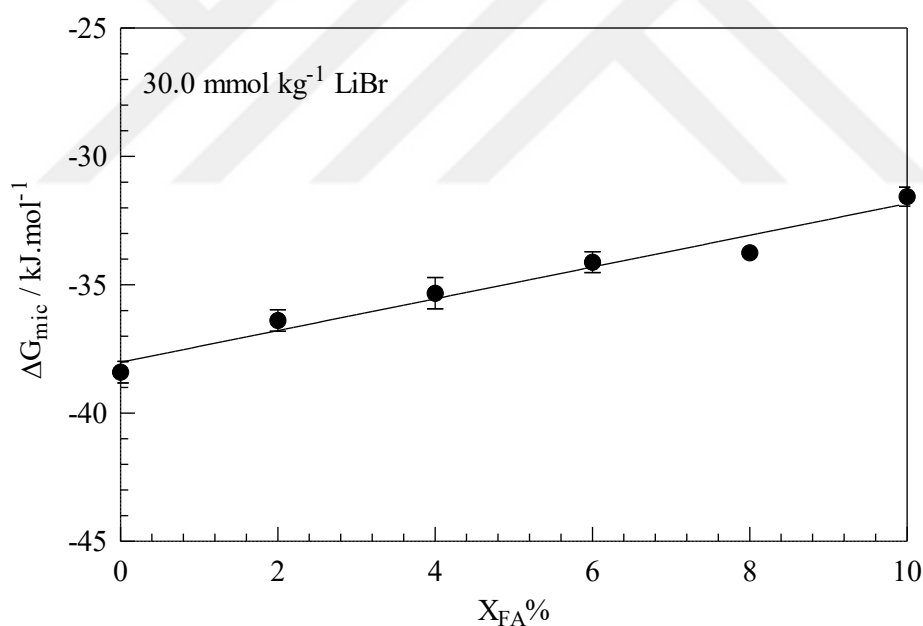


Figure 4.53. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/LiBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

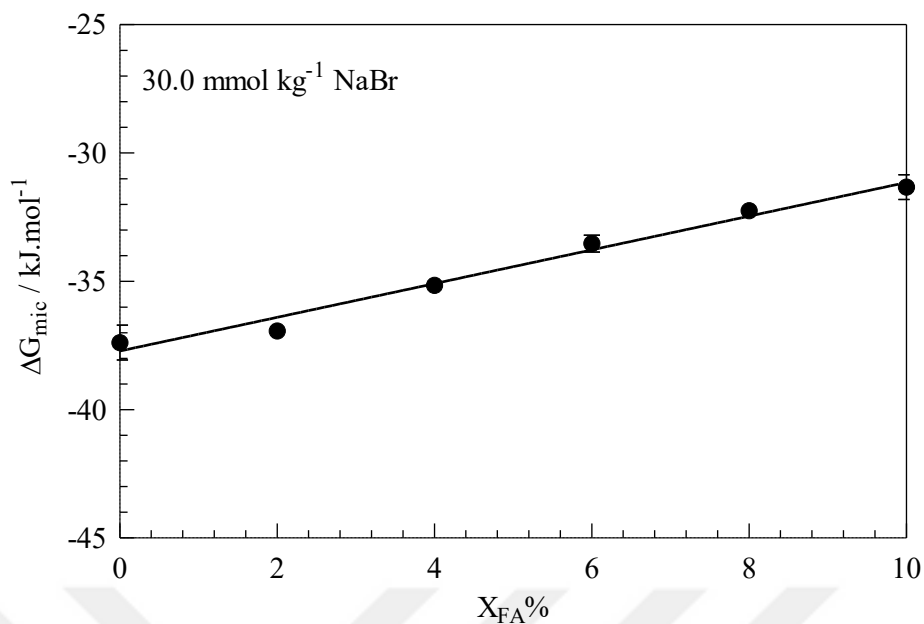


Figure 4.54. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/NaBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

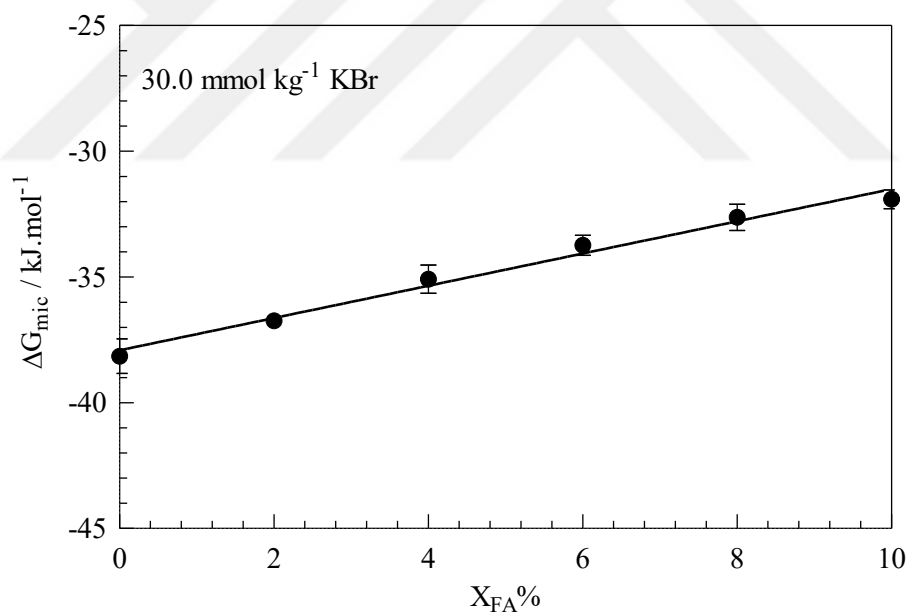


Figure 4.55. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/KBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

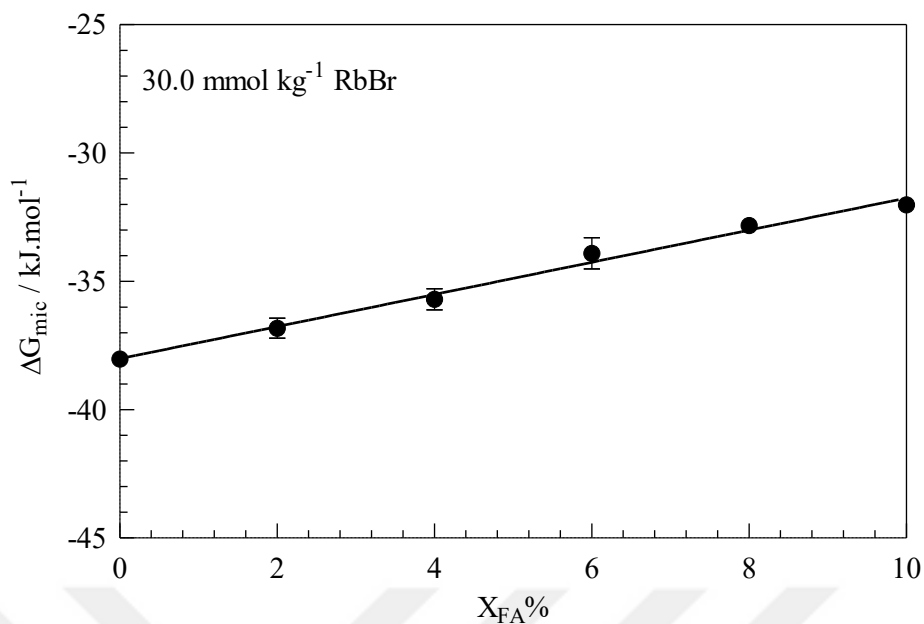


Figure 4.56. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/RbBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

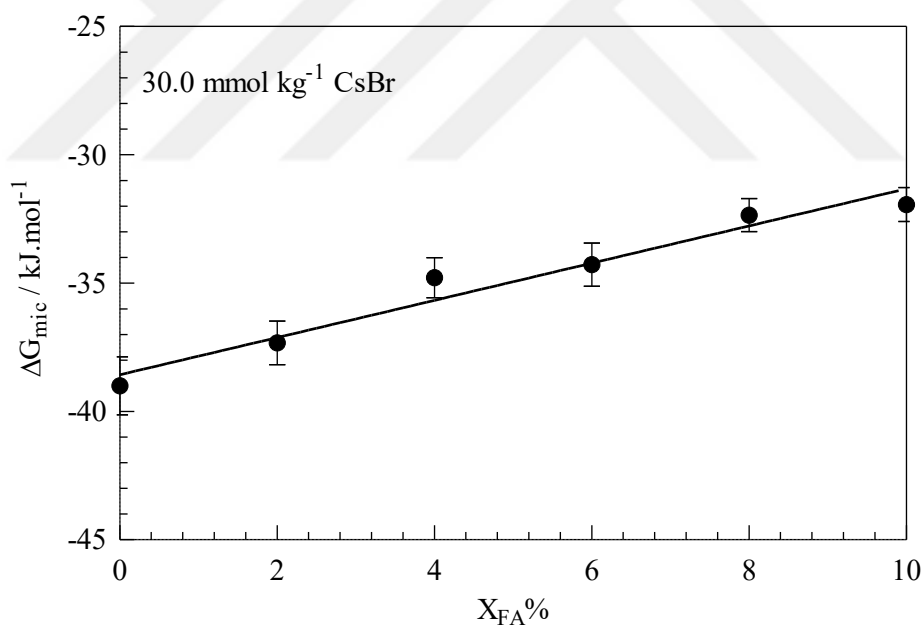


Figure 4.57. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/CsBr/FA-water solution versus percent mole fraction of FA at 25.0°C.

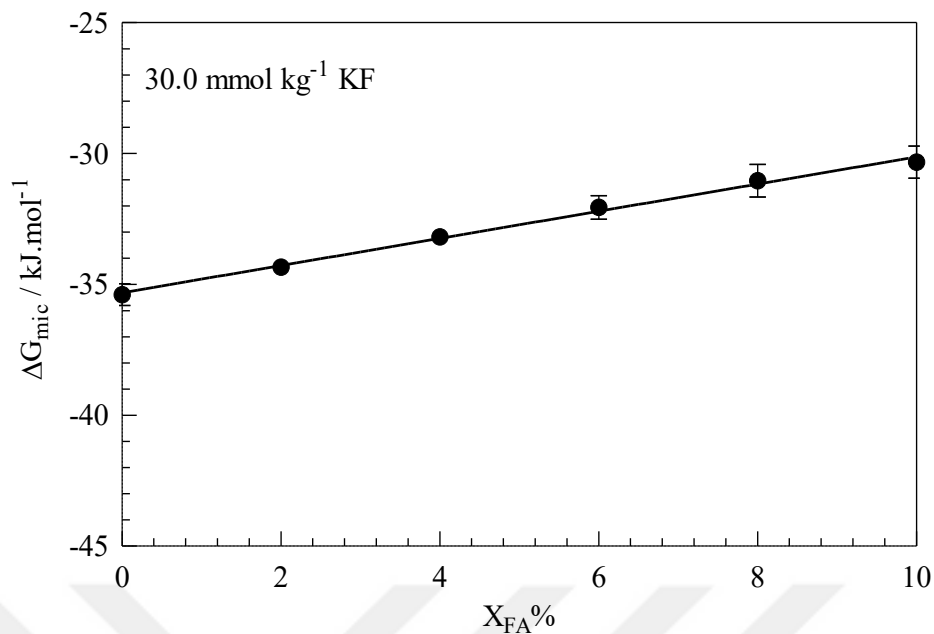


Figure 4.58. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/KF/FA-water solution versus percent mole fraction of FA at 25.0°C.

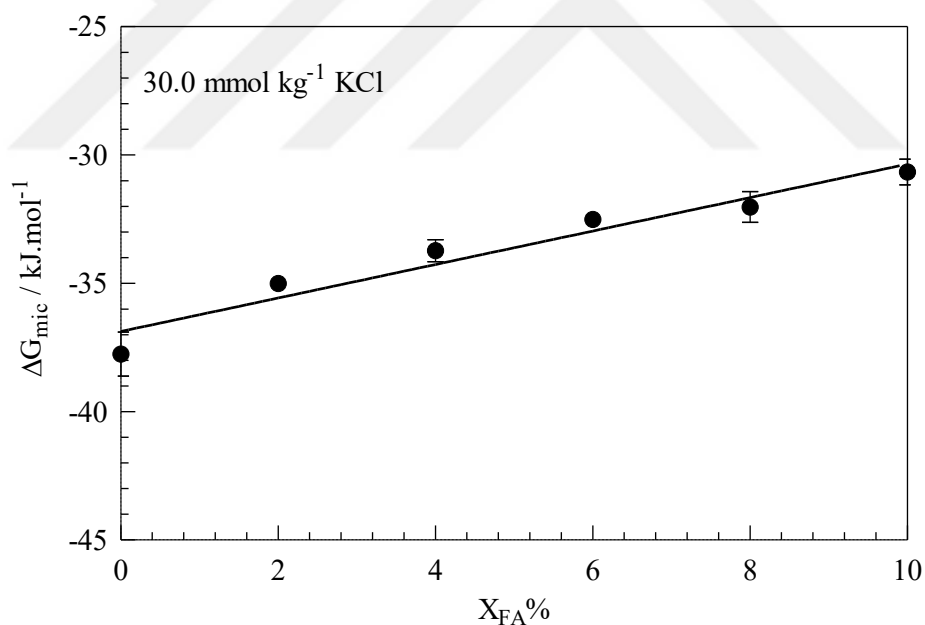


Figure 4.59. Effect of the concentration of FA on ΔG_{mic} values of DTMABr/KCl/FA-water solution versus percent mole fraction of FA at 25.0°C.

Table 4.15. ΔG_{mic} values of DTMABr in the presence of electrolytes (LiBr, NaBr, KBr, RbBr, CsBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	$\Delta G_{mic}/\text{kJ mol}^{-1}$				
	LiBr	NaBr	KBr	RbBr	CsBr
0	-38.41±0.42	-37.39±0.68	-38.15±0.69	-38.03±0.24	-39.00±1.13
2	-36.39±0.42	-36.94±0.06	-36.74±0.27	-36.83±0.39	-37.33±0.85
4	-35.33±0.61	-35.16±0.22	-35.09±0.56	-35.70±0.41	-34.79±0.78
6	-34.12±0.41	-33.53±0.33	-33.74±0.40	-33.91±0.61	-34.28±0.84
8	-33.76±0.19	-32.25±0.29	-32.63±0.52	-32.83±0.12	-32.35±0.64
10	-31.57±0.37	-31.33±0.48	-31.91±0.37	-32.02±0.27	-31.94±0.66

Table 4.16. ΔG_{mic} Values of DTMABr in the presence of electrolytes (KF, KCl, KBr) at constant concentrations (30.0 mmol kg⁻¹) and FA at different percent mole fractions at 25.0°C.

FA%	$\Delta G_{mic}/\text{kJ mol}^{-1}$		
	KF	KCl	KBr
0	-35.39 ± 0.42	-37.76 ± 0.86	-38.15 ± 0.69
2	-34.34 ± 0.25	-35.01 ± 0.19	-36.74 ± 0.27
4	-33.19 ± 0.28	-33.73 ± 0.43	-35.09 ± 0.56
6	-32.06 ± 0.45	-32.51 ± 0.07	-33.74 ± 0.40
8	-31.04 ± 0.62	-32.03 ± 0.60	-32.63 ± 0.52
10	-30.33 ± 0.61	-30.66 ± 0.50	-31.91 ± 0.37

The effect of FA on the ΔG_{mic} values of DTMABr in the presence of all electrolytes at constant concentrations is very similar to that of EG. But, if the effect of an increase in the concentration FA on ΔG_{mic} values of DTMABr is compared with EG, FA causes the micellization unfavorable than EG (its effect is about two times greater than EG). Furthermore, the ΔG_{mic} results of FA, like EG, are in good agreement with the results of CMC, i.e., they are supported by each other.

If the effect of the concentration of EG and FA on the ΔG_{mic} values are considered together, the effect of the electrolyte ions located in the intermicellar region and those at the micelle surfaces are, in general, similar.

4.2 Discussion of Zeta Potential Results

Modifications in the intermicellar region (such as the addition of a strong electrolyte, interactions of electrolyte ions with water and oppositely charged ions on micelle surfaces, changes in the dielectric constant of the medium, etc.) affect the repulsive and/or attractive forces between micelles with charged surfaces, enabling them to remain stable at a distance in solution. The question here is, which parameters can be used to evaluate these repulsive/attractive forces? Information about the stability of an electrically charged particle (like micelles) can be determined by the magnitude of the "zeta potential" values of the surface charged particle (Buckton, 2000). From this respect, zeta potential can be assumed as a parameter that gives the degree of repulsion between charged particles dispersed in the medium (Samimi et al., 2019).

A high zeta potential value indicates the presence of highly charged particles, and in this case, repulsive forces prevent these particles from coming together and clustering (Gumustas et al., 2017). If the zeta potential of the system is low, the attractive forces between charged particles suppress the repulsive forces, and coagulation occurs in solution (Das & Chaudhury, 2011). It is stated in literature that there should be an optimum zeta potential value for good stabilization of nanodispersions, i.e. structures such as micelles, in the medium (Freitas & Müller, 1998).

Zeta potential depends on the pH value of the medium, temperature, the nature of the medium (solution), the concentration of the components added to the medium (such as electrolyte) and the ionic strength of the medium (Dunstan & White, 1990). Zeta potential decreases with the addition of electrolyte, electrolyte concentration, and surface charge density of an ion (Chiu et al., 2000). In addition, zeta potential is used to study the interactions between colloidal particles and electrolytes (Rajpoot & Tekade, 2019). It is also known that the type and size of electrolyte ions or surfactant counterions bound to micelle surfaces (F, Cl, Br, etc.) have a significant effect on the zeta potential (Tokiwa & Ohki, 1969).

Although zeta potential is not the surface potential in the general sense, it provides useful information about the electrical repulsion between charged particles on the shear surface (slipping plane) (Tokiwa, 1968), Figure 4.60. It is also known from the literature that zeta potential provides important information about the binding of Hofmeister series ions, added into the medium, to the micelle surfaces (Iso & Okada, 2000). For example, ClO_4^- ion, which binds to trimethylammonium groups on the surfaces of zwitterionic hexadecyl phosphorylcholine-HPC micelles (like DTMA^+ in the DTMABr), affects the zeta potential more than Cl^- ion (Priebe et al., 2010). Therefore, it should be expected that zeta potential measurements will be useful in determining the change in micelle surface charge density due to the presence of counter ions/electrolyte ions on micelle surfaces or in the intermicellar region.

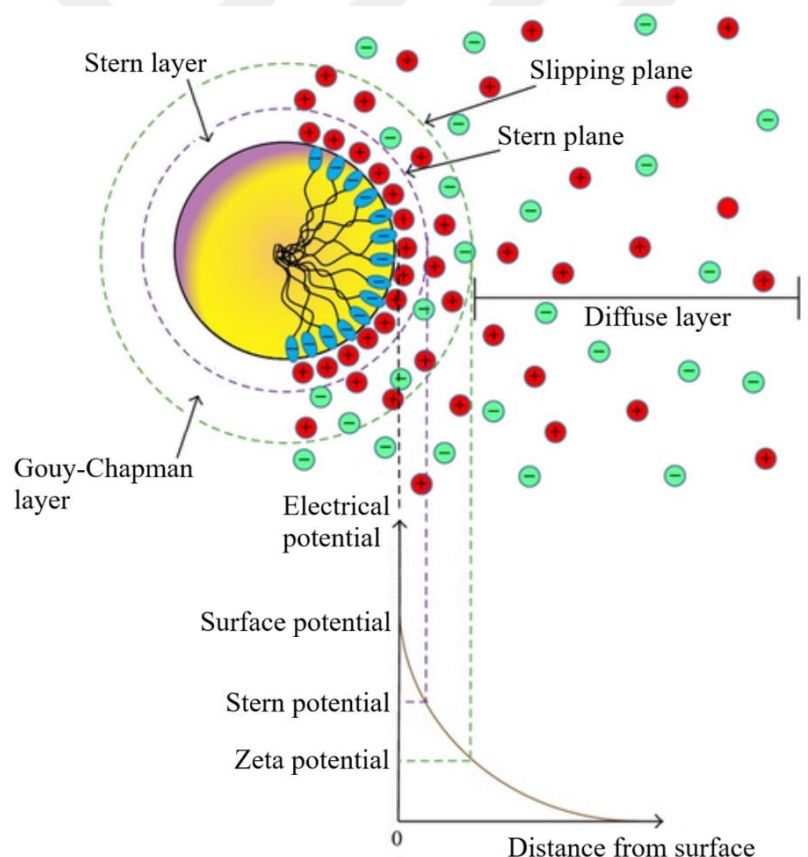


Figure 4.60. Schematic representation of the electrical potentials at micelle surface (surface potential), Stern plane (Stern potential) and slipping or shear plane (zeta potential) for self-assembled surfactant molecules with, for example, negatively charged head groups (Adopted from Lombardo et al., 2015).

Zeta potential results of DTMABr/electrolyte/water, DTMABr/electrolyte/EG-water and DTMABr/electrolyte/FA-water solutions are compared at constant EG and FA concentration, and at constant electrolyte concentrations. By this way, we could determine the effects of both dielectric constant of the solution and the kosmotropic-chaotropic characters of the electrolyte ions.

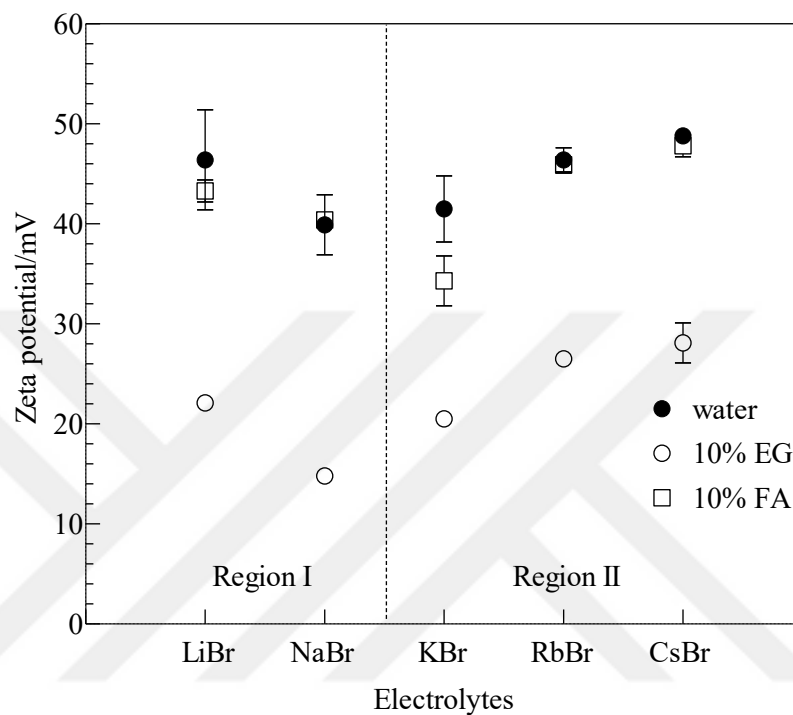


Figure 4.61. Comparison of the change in zeta potentials (with standard deviations) of DTMABr/electrolyte/solvent solutions for alkali metal bromides, where solvent is water, 10% aqueous EG and 10% aqueous FA, separately.

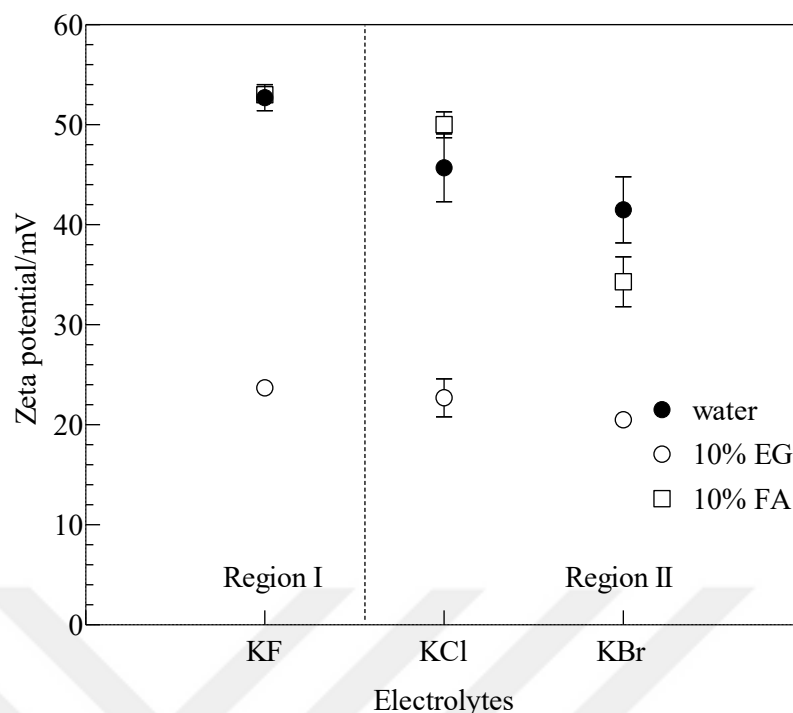


Figure 4.62. Comparison of the change in zeta potentials (with standard deviations) of DTMABr/electrolyte/solvent solutions for potassium halides, where solvent is water, 10% aqueous EG and 10% aqueous FA, separately.

Naskar et. al. stated that addition of an electrolyte such as NaCl or NaBr into ionic surfactant solutions causes the decrease in the zeta potential and also the decrease in the thickness of Gouy-Chapman layer (Naskar et al., 2013), arising from the binding of counterions to micelles, i.e., an increase in the number of the counterions adsorbed on the micelle (Sabaté et al., 2000). Furthermore, the magnitude of the zeta potential may give information about dispersion stability (Riddick, 1968; Hunter, 2013). It is reported that if the solution has zeta potential $> \pm 30$ mV, the dispersion of charged particles (or micelles) can, in general, be considered moderately stable against aggregation due to charge stabilization, i.e. the electrostatic repulsive forces are high enough to prevent aggregation (Lowry et al., 2016).

The regions labelled as I and II in Figures 4.61 and 4.62 correspond to the zeta potentials of the solutions including kosmotropic cations/anions (Li^+ , Na^+/F^-) and chaotropic cations/anions (K^+ , Rb^+ , Cs^+/Cl^- , Br^-). In the case of the electrolyte cations of alkali metal bromides, which prefer to be in Gouy-Chapman

and/or diffuse layers, while the zeta potential of the solution decreases in Region I, it increases in Region II. It means that Gouy-Chapman layer gets thinner (thicker) in Region I (Region II). However, in the case of F^- , Cl^- and Br^- (Figure 4.62), the zeta potential of the solution continuously decreases going from Region I to Region II, i.e., while the kosmotropic ion F^- causes the formation of relatively thicker Gouy-Chapman layer, the chaotropic Cl^- and Br^- ions favor thinner Gouy-Chapman layer.

In terms of dispersion stabilities of micelles against their aggregations, DTMABr/electrolyte/water and DTMABr/electrolyte/FA-water (DTMABr/electrolyte/EG-water) solutions have zeta potential values greater (smaller) than 30 mV. This states that dielectric constant of the medium affects the stability of micellar dispersions, i.e., the lower the dielectric constant the lower the stability of micellar dispersion because the order of dielectric constants of the selected solvents is $EG < \text{water} < FA$ or $10\% \text{ aqueous } EG < \text{pure water} < 10\% \text{ aqueous } FA$.

4.3 Discussion of SAXS Results

Small-angle X-ray scattering is available to evaluate some micellar structural parameters. In the frame of this thesis, we evaluated micelle average diameters for micellar solutions (from scattering vector), assuming that micelles are spherical in these solutions due to relatively low DTMABr surfactant concentration (around its CMC). The last situation was also confirmed by 2D isotropic SAXS patterns (Photo 2.4).

Experimental raw data of SAXS measurements of solutions s1-s12 (Table 2.1) were fitted to “best fit” curves as shown in Figure 4.63-4.74. The evaluated micelle average diameters with the standard deviations are given in Table 4.17.

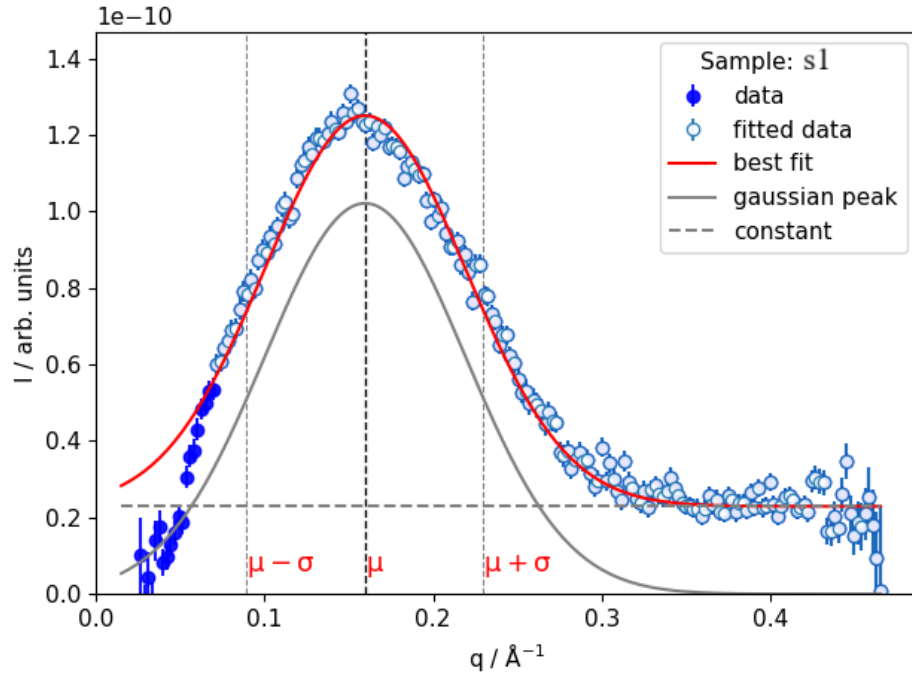


Figure 4.63. Frame integration of the 2D isotropic SAXS patterns of sample s1: scattering intensity (I) versus scattering vector (q). μ and σ are the fitting parameters.

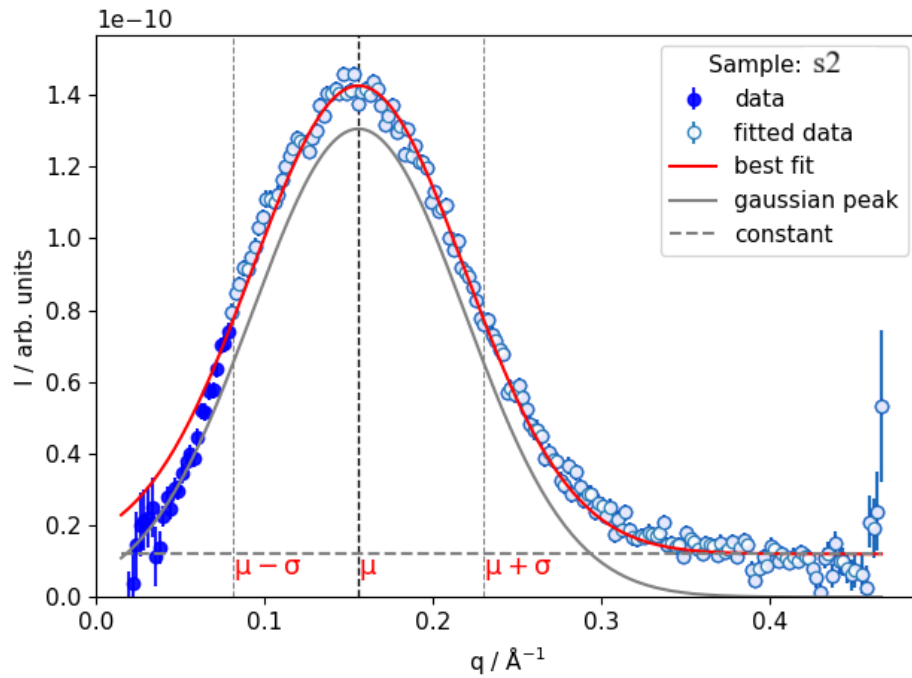


Figure 4.64. Frame integration of the 2D isotropic SAXS patterns of sample s2.

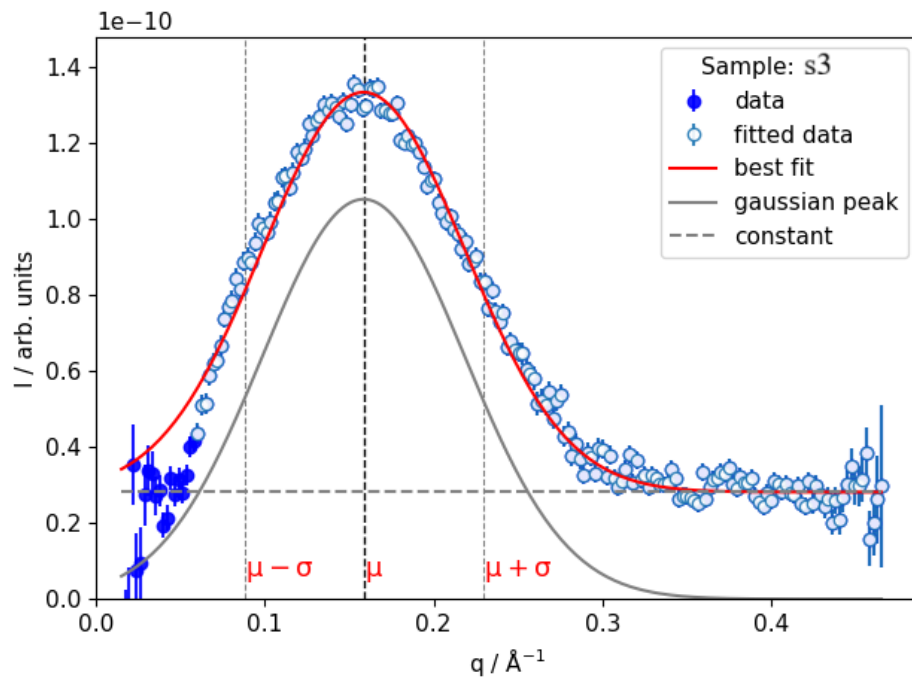


Figure 4.65. Frame integration of the 2D isotropic SAXS patterns of sample s3.

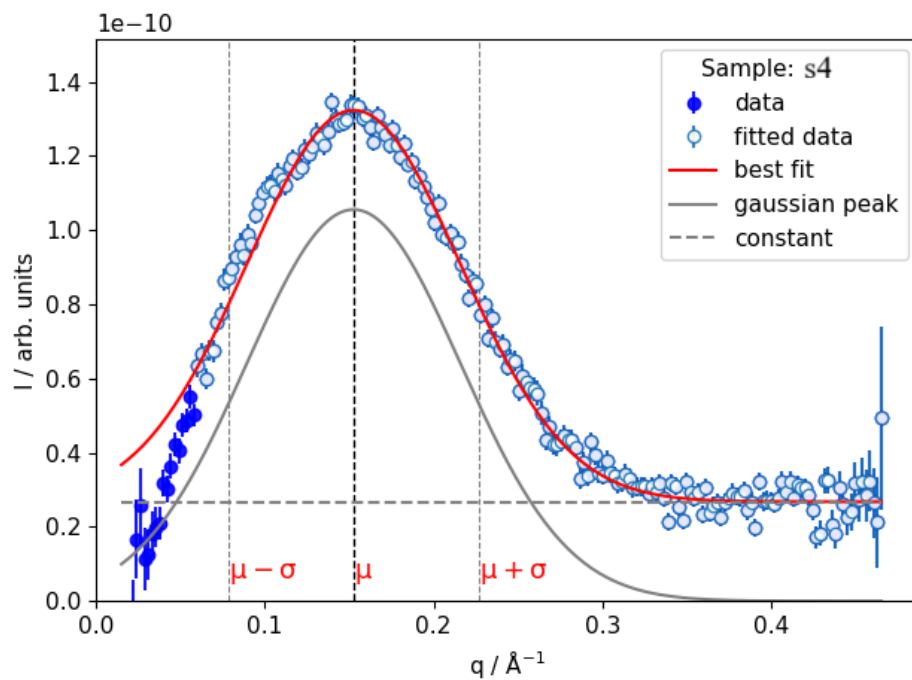


Figure 4.66. Frame integration of the 2D isotropic SAXS patterns of sample s4.

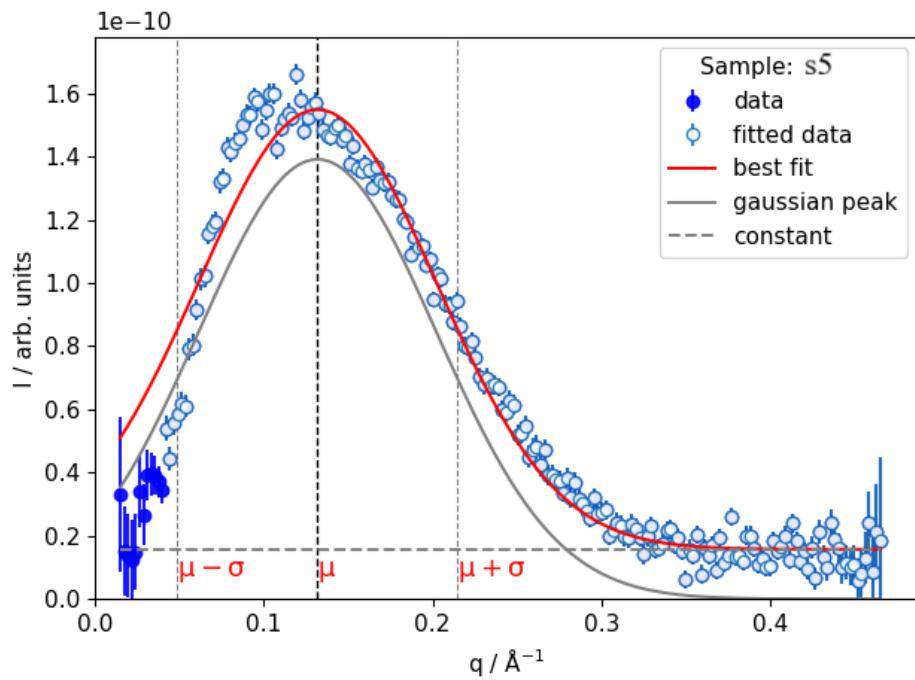


Figure 4.67. Frame integration of the 2D isotropic SAXS patterns of sample s5.

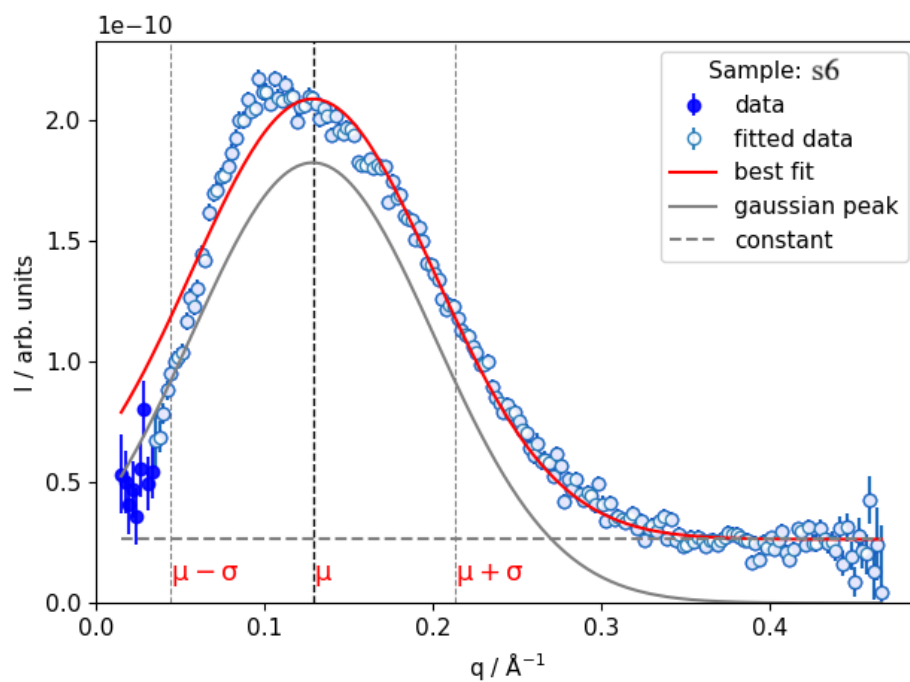


Figure 4.68. Frame integration of the 2D isotropic SAXS patterns of sample s6.

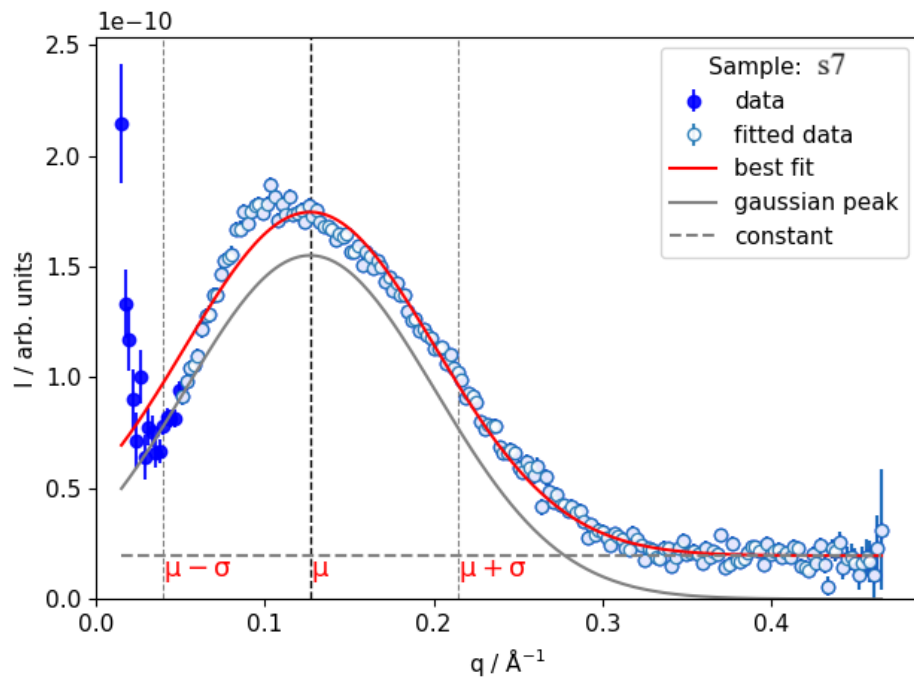


Figure 4.69. Frame integration of the 2D isotropic SAXS patterns of sample s7.

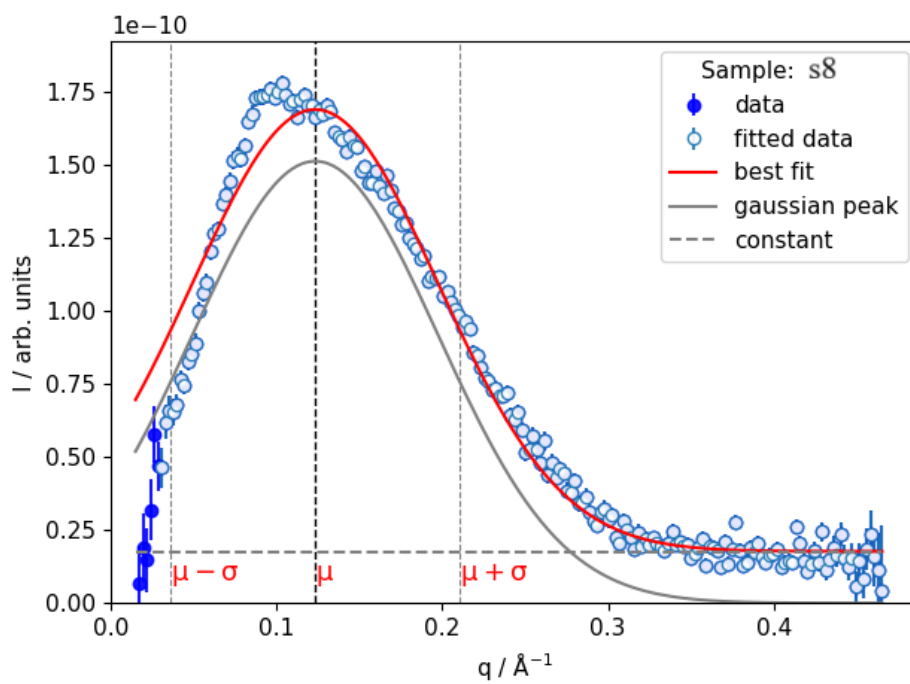


Figure 4.70. Frame integration of the 2D isotropic SAXS patterns of sample s8.

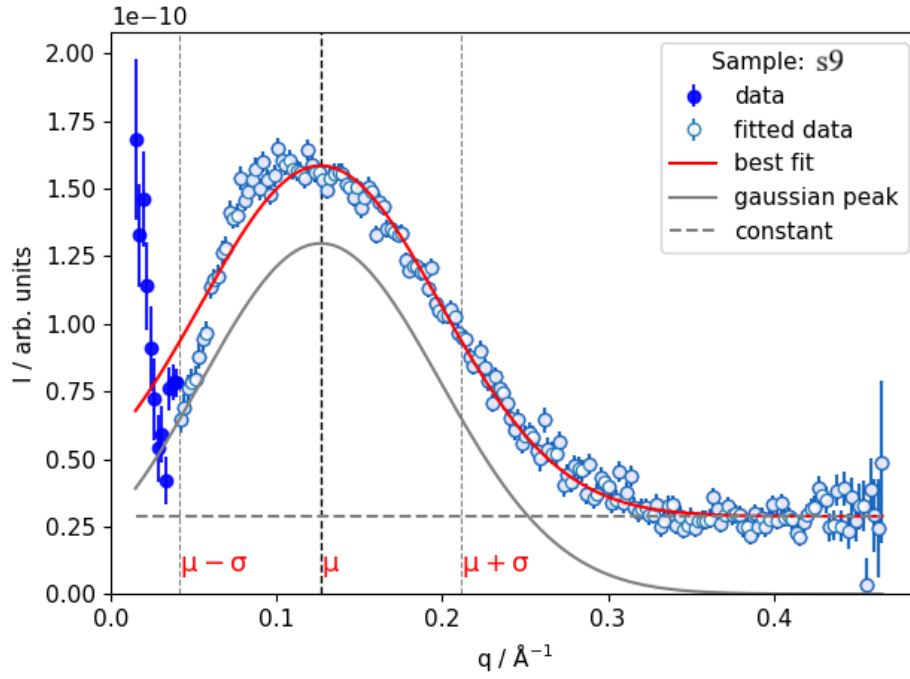


Figure 4.71. Frame integration of the 2D isotropic SAXS patterns of sample s9.

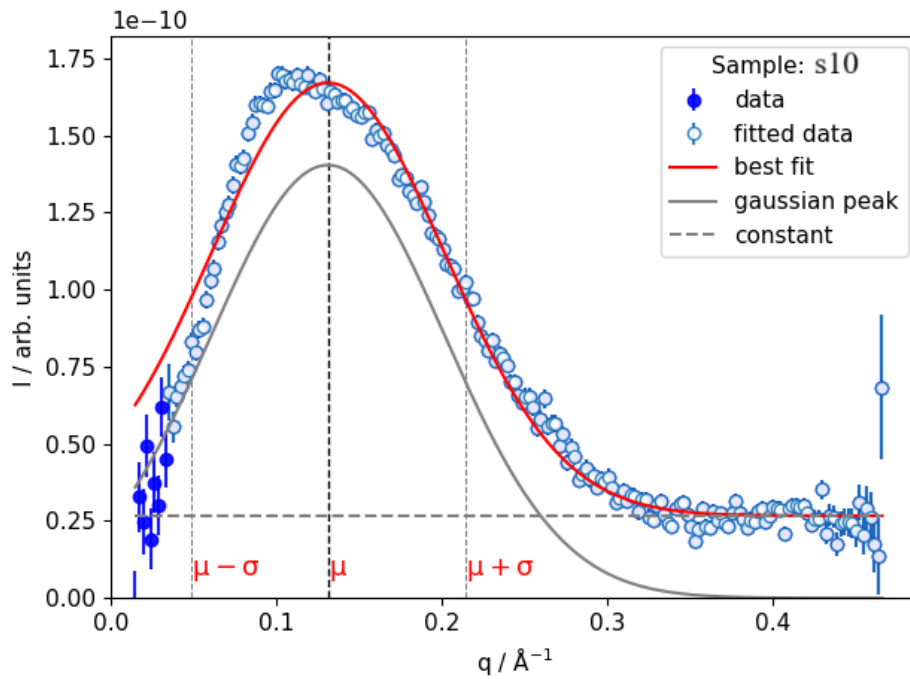


Figure 4.72. Frame integration of the 2D isotropic SAXS patterns of sample s10.

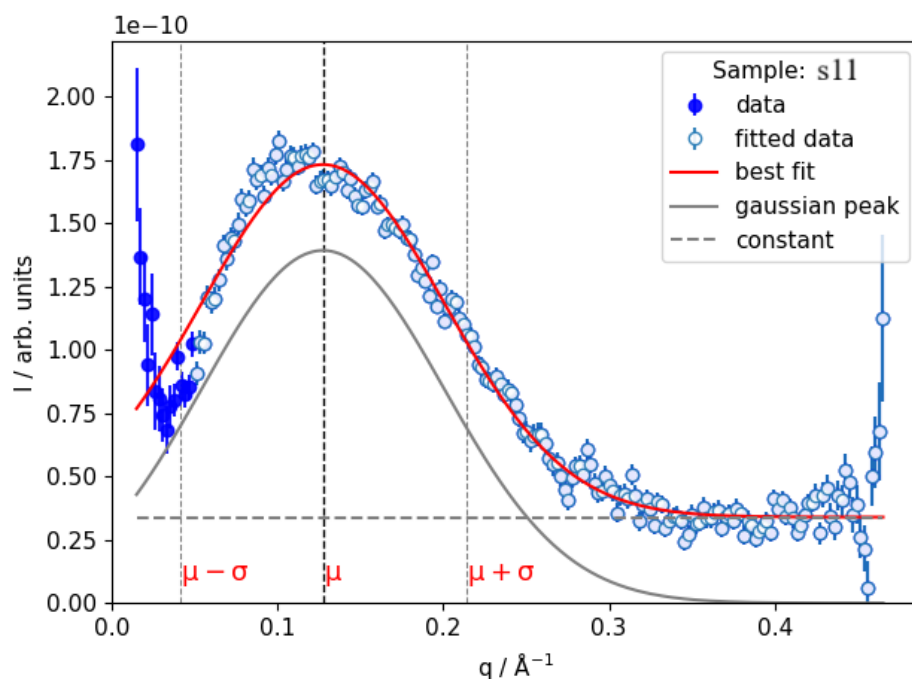


Figure 4.73. Frame integration of the 2D isotropic SAXS patterns of sample s11.

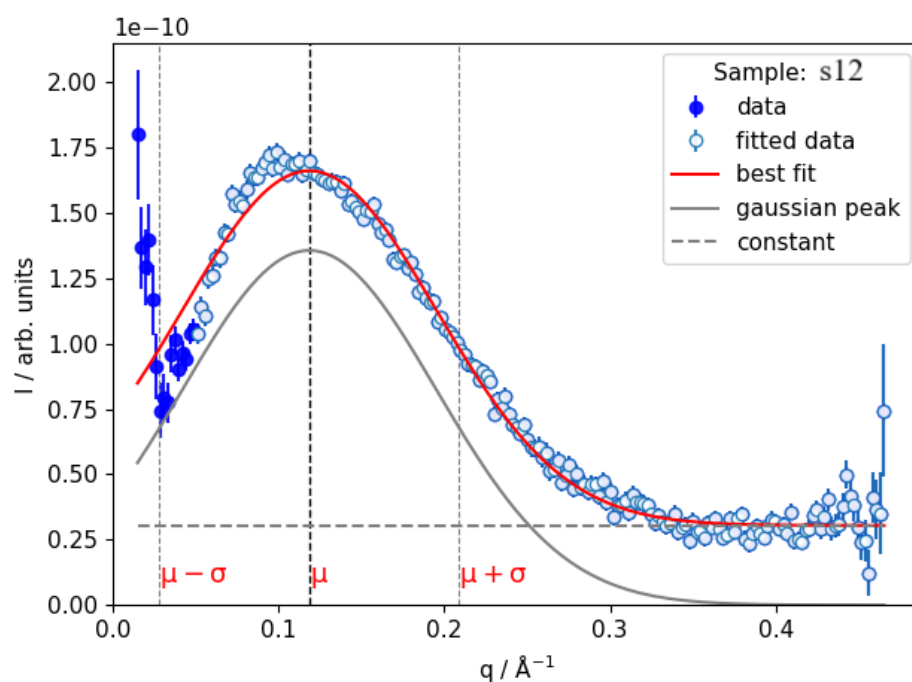


Figure 4.74. Frame integration of the 2D isotropic SAXS patterns of sample s12.

For SAXS measurements, some specific electrolytes were chosen: KF, KBr and NaBr. Remember that Na^+ (F^-) and K^+ (Br^-) are kosmotropic cation (anion) and chaotropic cation (anion), respectively. First, we will discuss the

results obtained from the surfactant solutions of KF and KBr, and then of KBr and NaBr. By this way, we may make a comprehensive interpretation on the location of electrolytes in different regions of micellar solutions.

Table 4.17. Micelle average diameters obtained from the evaluation of SAXS data for the solutions s1-s12 at constant solution compositions.

Solvent	Micelle average diameter, $d / \text{\AA}$			
	No electrolyte	KBr	NaBr	KF
Water	39.35 ± 0.18 (s1)	40.36 ± 0.11 (s2)	39.64 ± 0.15 (s3)	41.17 ± 0.17 (s4)
10% EG	47.66 ± 0.35 (s5)	48.87 ± 0.28 (s6)	49.54 ± 0.29 (s7)	50.90 ± 0.36 (s8)
10% FA	49.57 ± 0.34 (s9)	47.86 ± 0.25 (s10)	49.27 ± 0.32 (s11)	52.93 ± 0.35 (s12)

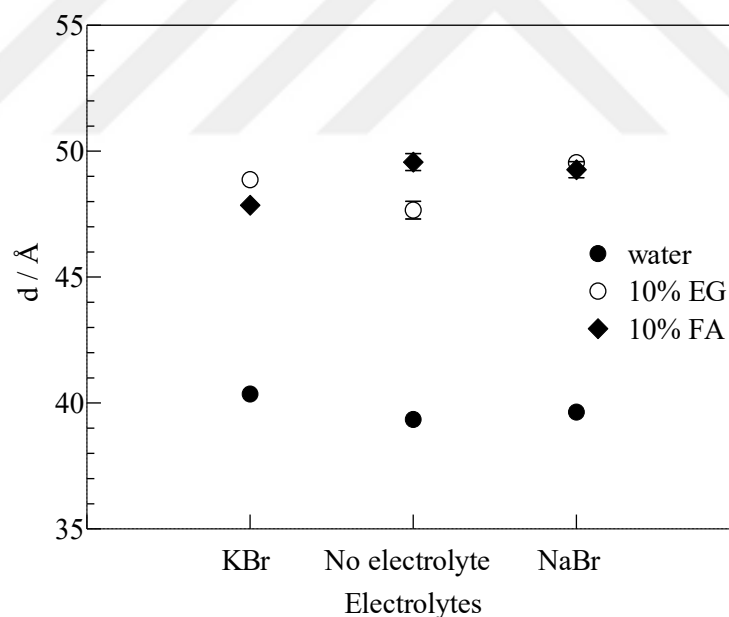


Figure 4.75. Relative effect of kosmotropic Na^+ and chaotropic K^+ ions, which prefer to be located in the intermicellar region (Gouy-Chapman layer).

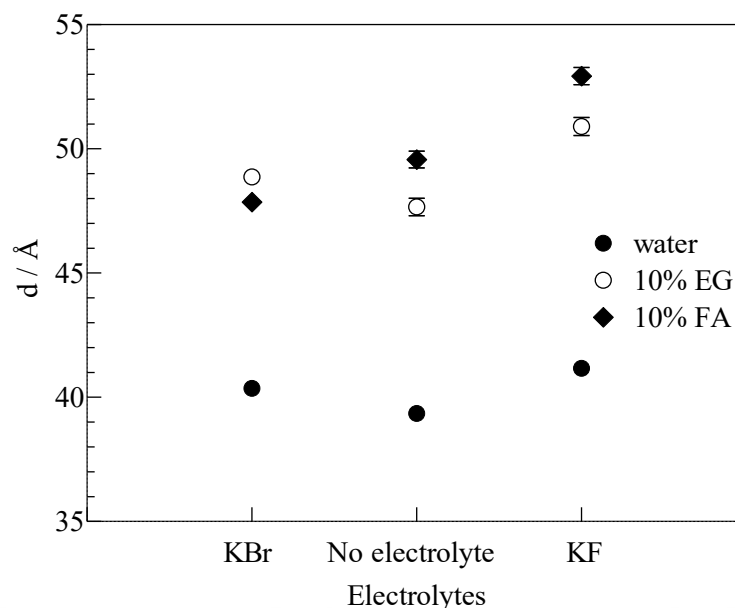


Figure 4.76. Relative effect of kosmotropic F^- and chaotropic Br^- ions, which prefer to be located at the micelle surfaces (Stern layer).

Table 4.17 and Figures 4.75-4.76 show the relative micelle average diameters for the solutions DTMABr/electrolyte/water, DTMABr/electrolyte/10% EG-water, and DTMABr/electrolyte/10% FA-water, along with their standard deviations. In general, electrolyte-included solutions consist of micelles with relatively higher micelle diameters than electrolyte-free solutions. This is an expected result because it is well-known that the addition of electrolytes in micellar solutions leads to micellar growth. If we compare NaBr with KBr, their cations cannot penetrate the first hydration layer (Stern layer) next to the micelle surface. They prefer to be in the Gouy-Chapman layer or diffuse layer. The relative effect of those cations is $Na^+ < K^+$ ($Na^+ < K^+$) in water, $Na^+ > K^+$ ($Na^+ < K^+$) in EG, and $Na^+ > K^+$ ($Na^+ > K^+$) in FA, where the relation in the parentheses represents the relative effect of those cations on the zeta potentials of solutions. If KF is compared with KBr, now the relative effect of F^- and Br^- , which penetrate the Stern layer (micelle surface), on the change in micelle diameter can be understood: $F^- > Br^-$ ($F^- > Br^-$) in water, $F^- > Br^-$ ($F^- > Br^-$) in EG, and $F^- > Br^-$ ($F^- > Br^-$). Except for the relation between Na^+ and K^+ , the change in the micelle diameter by the addition of kosmotropic/chaotropic ions follows the change in the zeta potentials of solutions. In other words, the results of SAXS and zeta potential

measurements can be assumed in good agreement with each other, i.e., the kosmotropic/chaotropic character of ions may change the thickness of the layer around the dry micelles, depending on which ions prefer to be located in which layer.



5. CONCLUSION

The effects of (a) dielectric constant of the bulk solution, and (b) location of electrolyte ions at the micelle surfaces (the Stern layer) and in the intermicellar region (the Gouy-Chapman or diffuse layer), from the specific interactions between surfactant head groups and ions in those region point of view, on the micellization properties of DTMABr were investigated by electrical conductivity, zeta potential, and Small-angle X-ray scattering measurements in this thesis. The following conclusions can be drawn from the experimental results of this thesis.

(1) While the increase in the concentration of EG in DTMABr/electrolyte/polar solvent-water solutions decreased the conductivity of surfactant solutions, the increase in the concentration of FA caused an increase in the solution's conductivity due to the change in the dielectric constant of the solution: the lower (higher) the dielectric constant of the bulk solution, the lower (higher) the solution conductivity as a result of the higher the hydrophobic (hydrophilic) effect. Furthermore, the effect of EG on the solution properties was more dominant than that of FA. This may be attributed to the greater effect of the "hydrophobic effect" (the case EG) than the "hydrophilic effect" (the case FA) on the solution conductivity.

(2) CMC of DTMABr increased by increasing EG and FA concentration in the solutions. This showed that polar organic solvents may remove some parts of oppositely charged ions (surfactant counterions or electrolyte ions) in the first hydration layer next to the micelle surfaces (the Stern layer) and the repulsions between the surfactant head groups increase which unfavor the micellization. If the effects of EG and FA on the critical micelle concentration of DTMABr are relatively compared in their same concentration range, CMC of DTMABr increased by ~4 mmol/kg as the concentration of EG was changed it increased by ~14-15 mmol/kg. in the case of FA. This result indicated that FA caused (a) the removal of the counterions/oppositely charged electrolyte ions from the micelle surfaces or (b) the weakening the interactions between surfactant head groups and counterions/oppositely charged electrolyte ions at the micelle surfaces more efficiently than EG. The similar ionization degree of counterions from the micelles (α) values for EG and FA showed that the case (b) is more dominant in the presence organic solvent FA.

(3) The α (β) values for all alkali metal bromides in the presence of EG or FA in the solutions, the increase in the concentration of EG/FA lead to an increase (decrease) in the α (β) values due to the ionization of counterions from the micelle surfaces because of the decrease in the dielectric constant at micelle surfaces, arising from replacement of some water molecules by EG/FA in the first hydration layer (Stern layer). This explanation was in good agreement with the discussion of the effect of polar solvent concentration on CMC of DTMABr. Within the experimental error limits (standard deviations), at constant polar organic solvents and for polar organic solvent-free solutions, no significant difference was observed between the α (β) values.

For the potassium halides, similar trends in the α and β values were observed as for alkali metal bromides at constant polar organic solvent concentration, i.e., the α and β values were almost the same, within the experimental error limits, at constant polar organic solvent concentration in DTMABr/electrolyte/polar organic solvent-water and for polar organic solvent-free solutions. This indicated that there should be an increase in the surfactant head group-counterions/electrolyte ions interactions, going from F^- to Br^- .

Consequently, if the results of cations located in the intermicellar region were compared with the results of anions, which prefer to bind to the micelle surfaces, both types of ions exhibited almost the same effects from the ionization or binding of ions point of view. In other words, the cations in the intermicellar region had the same effect as the anions on the micelle surfaces, even if the dielectric constant of the medium decreased or increased compared to water.

(4) ΔG_{mic} values of DTMABr in the presence of electrolytes LiBr, NaBr, KBr, RbBr, and CsBr were almost the same at constant EG/FA concentration. However, on increasing EG/FA concentration, ΔG_{mic} values increase, i.e., becoming less negative. This was ascribed to the unfavorable tendency of the transfer of DTMABr alkyl tails from the bulk solution to the interior of the micelles, which unfavours the micellization.

The change in the ΔG_{mic} values of DTMABr in the presence of electrolytes KF, KCl, and KBr, whose anions may penetrate the first hydration layer (Stern layer) around the micelle surfaces, follows the kosmotropic/chaotropic characters of the anions: the higher the chaotropic character the negatively high ΔG_{mic} .

The increase in polar organic solvent concentration for the alkali metal bromides and for the potassium halides was similar, i.e., the increase in the concentration of polar organic solvents turned the micellization less favorable.

Although the effect of FA on the ΔG_{mic} values of DTMABr in the presence of all electrolytes at constant concentrations was very similar to that of EG, the effect of an increase in the concentration of FA on ΔG_{mic} values of DTMABr was more dominant than that of EG, i.e., FA caused the micellization to be more unfavorable than EG.

If the effect of the concentration of EG and FA on the ΔG_{mic} values were considered together, the effect of the electrolyte ions located in the intermicellar region and those at the micelle surfaces were, in general, similar.

(5) In the case of alkali metal bromides, whose cations prefer to be in Gouy-Chapman and/or diffuse layers, while the zeta potential of the solution decreased for kosmotropic cations, it increased for chaotropic cations. These results were attributed to getting Gouy-Chapman layer thinner and thicker for those cations, respectively. However, in the case of F^- , Cl^- and Br^- , the zeta potential of the solution continuously decreased going from kosmotropic to chaotropic anions, i.e., while the kosmotropic ion F^- caused the formation of relatively thicker Gouy-Chapman layer, the chaotropic Cl^- and Br^- ions favored thinner Gouy-Chapman layer.

It was also observed that dielectric constant of the medium affected the stability of micellar dispersions. Because the zeta potential is related to the dispersion stability (the higher zeta potential than 30 mV, the higher the micellar stability), the stability of micellar solutions followed the order of dielectric constants of the selected solvents: EG < water < FA.

(6) Electrolyte-included solutions consisted of micelles with relatively higher micelle diameters due to the micellar growth. The relative effect of the cations, which tend to locate in the Gouy-Chapman layer, was $Na^+ < K^+$ in water, $Na^+ > K^+$ in EG, and $Na^+ > K^+$ in FA. The relative effect of F^- and Br^- , which penetrate the Stern layer (micelle surface), on the change in micelle diameter followed the order $F^- > Br^-$ in water, $F^- > Br^-$ in EG, and $F^- > Br^-$. The results showed that the change in the micelle diameter by the addition of kosmotropic/chaotropic ions follows the change in the zeta potentials of solutions. In other words, the results of SAXS and zeta potential measurements were

accepted as in good agreement with each other, i.e., the kosmotropic/chaotropic character of ions could change the thickness of the layer around the dry micelles, depending on which ions prefer to be located in which layer.



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