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Sateesh Krishna Chand Chundru

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Effect of counter ion concentration added with mixture of water and ethylene glycol on

Krafft temperature of sodium dodecyl sulfate.

by

Sateesh Krishna Chand Chundru

Thesis

Submitted to the Department of Chemistry

Eastern Michigan University

in Partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

in

Chemistry

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Ypsilanti, Michigan.

DEDICATION

To
My Family

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Finally I would like to thank the head of the chemistry department, Dr. Ross Nord, all the faculty members of chemistry department and all my friends, who helped me during my Masters at Eastern Michigan University.

ABSTRACT

Surfactants are amphiphilic organic compounds having both hydrophobic and hydrophilic groups. Surfactants in solution form aggregates known as micelles. The minimum temperature at which surfactants form micelles is known as Krafft temperature. The Krafft temperature of sodium dodecyl sulfate (SDS) was measured at various counter ion concentrations in two solvent systems, water and 10% ethylene glycol. The Krafft temperature of sodium dodecyl sulfate increased in both water and 10% ethylene glycol with increasing counter ion concentration. The Krafft temperature of sodium dodecyl sulfate in 10% ethylene glycol was higher than the Krafft temperature of sodium dodecyl sulfate in water, at the same counter ion concentration. Since the Krafft temperature of sodium dodecyl sulfate is higher in 10% ethylene glycol than in water at the same counter ion concentration, it has been concluded that the polarity of the solvent plays an important role in increasing the Krafft temperature of sodium dodecyl sulfate.

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CHAPTER 1: INTRODUCTION

1.1 Micelles

Surfactants are amphiphilic organic compounds having both hydrophobic and hydrophilic groups. Common surfactants are soaps and detergents used in daily life. These surfactant molecules form aggregates in solution known as micelles. The concentration at which a surfactant forms micelles is known as the critical micelle concentration (CMC). A micelle is an aggregate of long chained hydrocarbon surfactant molecules in aqueous solution where the hydrophilic head regions (H) are in contact with the surrounding solvent and the hydrophobic tail regions (T) are drawn towards the inside, as shown in Figure 1.1. Micelles are generally formed based on the principle of opposing forces. According to this principle, the attractive forces at the hydrophobic tail regions favor the formation of the micelles while the repulsive forces at the hydrophilic head regions prevent the aggregation.¹

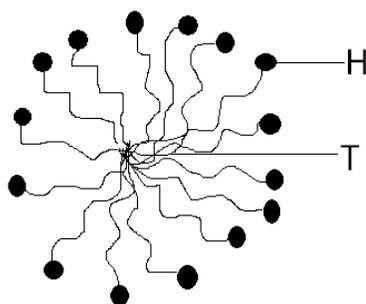


Figure 1.1. Ideal structure of surfactant micelle.

The size and shape of the micelles depends upon three main factors:

1. Surfactant concentration.
2. Temperature.
3. Ionic strength.

The size of the micelle can be increased by increasing the repulsive forces between head groups. The increase in surfactant concentration above the CMC results in the formation of larger micelles because of broad size distribution. As temperature increases, the separation of the aggregated form occurs and leads to the formation of larger micelles. An increase in hydrocarbon chain length also increases the size of the micelle, in agreement with the principle of opposing forces. In the case of ionic surfactant head groups, adding the counter ions increases the ionic strength and it leads to increases in repulsion between head groups. Micelles usually exist as spherical in shape. They may also exist in cylindrical or rod shapes. The largest micelles generally consist of many small micelles that form a continuous surface and the resulting structure looks like a rod.¹

1.2 Applications of micelles

Micelles are widely used in pharmaceutical industries, medicine, cosmetics, food, and for enhanced oil recovery.^{2,3} These micelles can also be used in solubilizing partially water soluble and water insoluble drugs. Hydrophobic drugs are solubilized in the inner core (hydrophobic region) of the micelle.⁴ Polymeric micelles can be used to transport hydrophobic drugs used in photodynamic therapy. Due to the electrostatic interaction between drug and polymer, the drug is physically entrapped in the

hydrophobic core. These micelles are helpful in preventing drug degradation and side effects.⁵

In solar energy conversion systems, binding the photo sensitizers with micelles decreases the rate of deactivation through the photoactive d-d state which leads to an increase in efficiency and lifetime of photo sensitizers.⁶ Gangotri *et al.* found an increase in electrical output of photo galvanic cells was caused by increasing the surfactant concentration.⁷ The effect of the anionic micelles in photo galvanic cells was high when compared to the cationic and neutral micelles. In most industrial applications involving surfactant micelles, the stability of micelle plays an important role.

1.3 Micellar properties

Critical micelle concentration, aggregation number and Krafft temperature are all micellar properties. Since physical properties of micelles like conductivity change suddenly with concentration and temperature,^{3, 8} critical micelle concentration and Krafft temperature can be determined using conductivity measurements at various concentrations and temperatures. The conductivity of the micelles can be increased by small pre-micelles and can be decreased by the association of ion pairs. The micellar properties are affected by changes in counter ion concentration and solvent system. It has been proven that the solubility of hydrocarbons increases in an ethylene glycol-water mixture when compared to water.⁹ Using an ethylene glycol-water mixture as solvent leads to a more negative enthalpy of micelle formation and less positive entropy, which indicates that the energetic interactions take precedence over hydrophobic effects.

Because of similarities between the properties of ethylene glycol and water, the hydrophobic bonds in micelles still exist in pure ethylene glycol.^{10, 11}

1.4 Krafft temperature (T_k)

Krafft temperature is also known as the critical micelle temperature. It is the minimum temperature at which surfactants form micelles. Below this temperature the surfactants do not form micelles and there is no value for the critical micelle concentration. The Krafft temperature can vary based on counter ion concentration and solvent system.

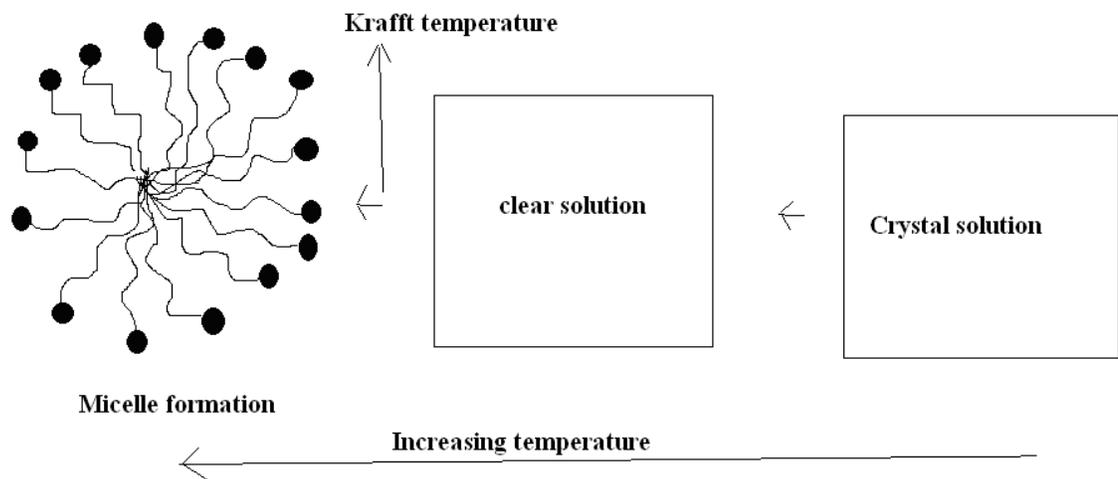


Figure 1.2. Schematic representation of micelle during Krafft temperature (T_k) determination

Bales *et al.* measured the Krafft temperature of sodium dodecyl sulfate to determine the degree of counter ion dissociation of ionic micelles.¹² Conductivity measurements were used to find the Krafft temperature of the ionic surfactants in the presence and the absence of the sodium chloride.

The concentration of counter ions (C_{aq}) provided by both the surfactant and the salt is given by

$$C_{aq} = F(C_t) \{ \alpha C_t + (1 - \alpha) C_t + C_{ad} \} \quad (1)$$

where

C_t = Concentration of total surfactant.

C_f = Concentration of surfactant in monomer form.

C_{ad} = Concentration of added salt.

α = Degree of counter ion dissociation.

and $F(C_t)$ is a volume correction factor used at higher surfactant concentrations:

$$F(C_t) = 1/1 - V C_t \quad (2)$$

In equation (2) V is the molar volume of the surfactant in L/mol which is 0.288 L/mol, taking the density of the surfactant as 1.00 g/ml.

Since different combinations of surfactant concentration (C_t) and added salt concentration (C_{ad}) will give the same value of counter ion concentration (C_{aq}), any property that is a function of C_{aq} will give same value for all these combinations. By assuming α is constant with C_{aq} , it is possible to explain a property which depends on C_{aq} by showing that it gives a common curve when plotted against $C_{aq} = F(C_t) \{ \alpha C_t + C_{ad} \}$, as follows

$$C_{aq} = F(C_t) \{ \alpha C_t + C_{ad} \} = \text{constant} \quad (3)$$

Since the concentration of surfactant in monomer form (C_f) is same for the given value of the counter ion concentration (C_{aq}), equation (3) is reasonable whether α is constant or it changes.

Figure 1.3. shows the graph plotted between the Krafft temperatures and counter ion concentrations. Salt free samples are represented by (O) while (●) represents salt added samples and (*) represents solubility data of sodium dodecyl sulfate.¹³ The Krafft temperatures increased with increasing counter ion concentration at various conditions. In figure 1.3. α was taken as 1 to calculate the counter ion concentration for all the samples.

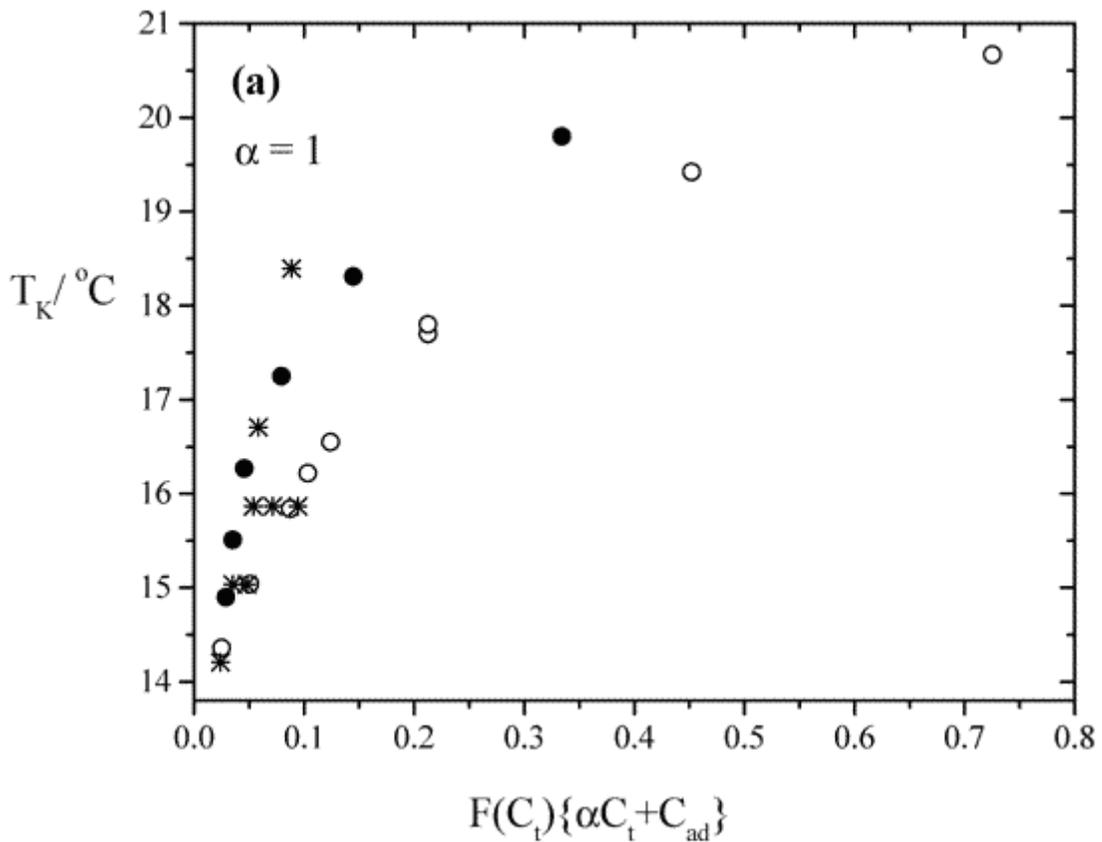


Figure 1.3. Krafft temperatures (T_k) versus $F(C_t) \{ \alpha C_t + C_{ad} \}$ for SDS ($\alpha = 1$).

Figure 1.4. shows the graph plotted between the Krafft temperatures and counter ion concentrations. Salt free samples represented by (O), (●) represents salt added samples and (*) represents solubility data of sodium dodecyl sulfate.⁷ The Krafft temperatures increased with increasing counter ion concentration at various conditions. In figure 1.4. α was taken as 0.26 to calculate the counter ion concentration for all the samples. 0.26 was taken as best fit value for α to calculate the counter ion concentration.

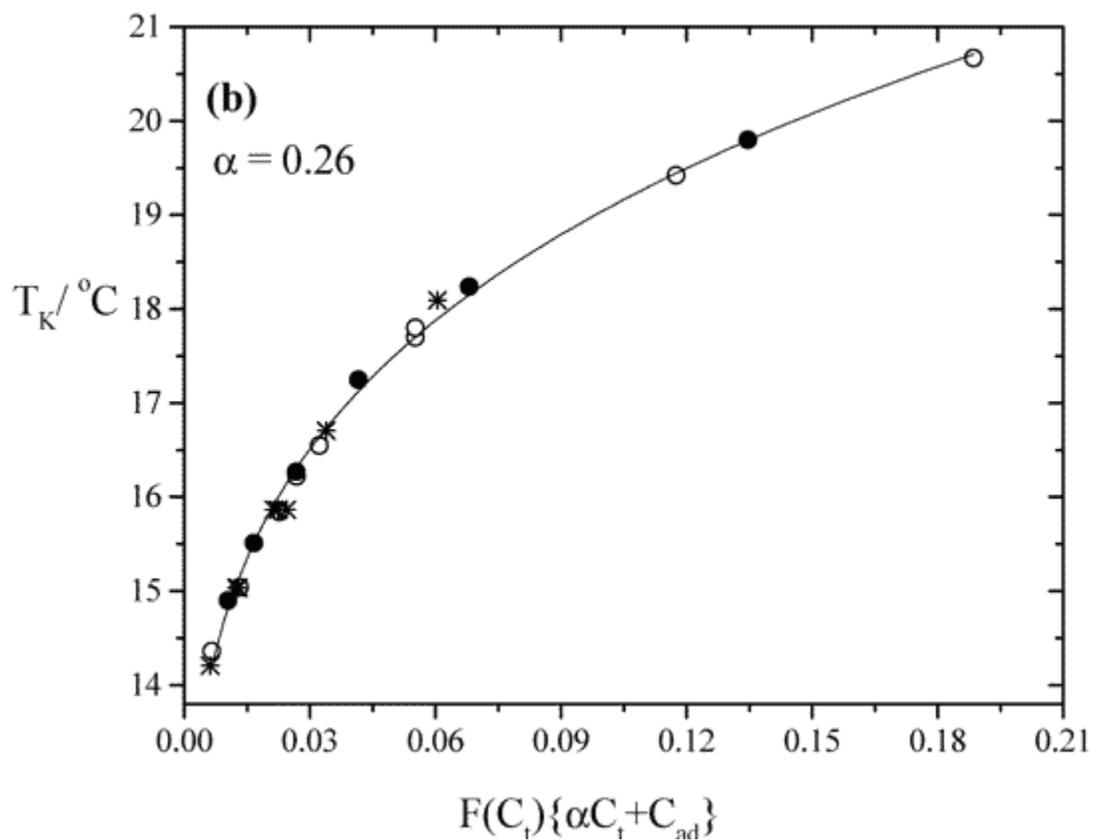


Figure 1.4. Krafft temperatures (T_K) versus $F(C_t) \{ \alpha C_t + C_{ad} \}$ for SDS ($\alpha = 0.26$).

1.5 Aggregation number (N_A)

Aggregation number is another important micellar property which can be defined as number of surfactant molecules that are associated to form a micelle. Quina *et al.* found that the aggregation number of sodium dodecyl sulfate was increased by increasing the concentration of added salt (NaCl).¹⁴

Orth *et al.* reported a method to determine the mean aggregation number of sodium dodecyl sulfate in water.¹⁵ This method was based on the quenching of a luminescent probe by a hydrophobic quencher. The ratio of luminescence intensity of a probe with quencher (I) to the luminescence intensity of a probe without quencher (I_0) is related to Q and M as shown in the equation (4).

$$\left(\frac{I}{I_0}\right) = \exp\left\{-\frac{[Q]}{[M]}\right\} \quad (4)$$

Where

[Q] = Concentration of quencher.

[M] = Micelle concentration.

Equation (5) has been derived based on the simple assumption that the surfactant molecules exist either as monomeric units or as micelles having N monomers. If the concentration of surfactant (S_0) is above the critical micelle concentration (CMC), the concentration of micelle (M) can be expressed as follows

$$[M] = [S_0]/N - \text{CMC}/N \quad (5)$$

From equations (4) and (5) the following equation (6) can be obtained.

$$\ln(I_0/I) = [Q] N / ([S_0] - CMC) \quad (6)$$

Equation (7) was obtained by rearranging equation (6) to determine the mean aggregation number (N).

$$\ln\left(\frac{I_0}{I}\right) = \frac{1}{[Q]N} [S_0] - CMC/[Q]N \quad (7)$$

1.6 Research Goals

The main focus of my research is

- To study how the Krafft temperature (T_k) of sodium dodecyl sulfate is affected by the counter ion concentration added in mixtures of water and ethylene glycol.
- To determine the Krafft temperature of sodium dodecyl sulfate at various counter ion concentrations, by increasing the sodium chloride concentration in water as solvent.
- To determine the Krafft temperature of sodium dodecyl sulfate at various counter ion concentrations, by increasing the sodium chloride concentration in 10% ethylene glycol.
- To study the mean aggregation number of the sodium dodecyl sulfate and how it is affected by the counter ion concentration in water.

CHAPTER 2:

EXPERIMENTAL

2.1 Materials

Sodium dodecyl sulfate and sodium chloride from Fisher scientific were used. Deionized water and ethylene glycol (99+% pure) from Acros Organics was used as the solvent to prepare the solutions. Tris (2, 2' - bipyridyl) dichloro - ruthenium (II) hexahydrate (Aldrich) was used as probe. 9-methylanthracene (Aldrich) was used as quencher.

2.2 Procedure

To initiate the precipitation of surfactant crystals, 100 ml of aqueous solutions of sodium dodecyl sulfate were prepared and placed in a refrigerator at 5°C for 24 hours. The precipitated micelle solution was taken in a 100 ml beaker in which both a conductivity cell (YSI 3400 SERIES conductivity cell) and a temperature probe (direct connect temperature probe) were inserted. The temperature of the micelle solution was increased gradually with constant stirring using a hot plate (Thermix stirring hot plate model 210T). The conductivity readings were taken on a YSI model 32 conductance meter. The conductivity of the solution was measured at each 0.2°C. It takes 2 – 2.5 hours to take the conductivity readings for each sample.



Figure 2.1. Picture of YSI 3400 SERIES conductivity cell

2.3 Determination of Krafft temperature

The temperature of the surfactant crystal precipitate was raised by heating on a hot plate with constant stirring. The increase in conductivity was initially slow but at one point, a sudden rise in conductivity was observed. This point is called the Krafft point (T_p , shown by arrow in Figure 2.2.), where monomer solubility is equal to the critical micelle concentration (CMC). Conductivity readings were taken until they reached a constant value. The point of abrupt change in conductivity versus temperature graph indicated by the arrow in Figure 2.2. was taken as the Krafft temperature (T_k). The slope above the Krafft temperature or critical micelle concentration occurs because of the conductivity of micelles and counter ions provided.¹⁶ When crystal solution starts to go through a transition there is a sharp increase in its conductivity. After transition, the conductivity will have a steady increase seen by a constant slope. The Krafft temperature is the last point before this constant increase in conductivity. The first derivative shows the steady increase in conductivity before and after the transition. The Krafft temperature is the last point in the first derivative plot before a constant slope value. The Krafft temperatures were reported in Table 3.1. and Table 3.2. from the 1st derivative plot. Conductivity and first derivative values for SDS (0.100 mol/L) at different temperatures are given in Table 2.1. It was observed that the micelle solution became clear when it reached the Krafft temperature. The Krafft temperatures were measured two times for each concentration and the reproducibility of the Krafft temperature measurements was reasonably good. ($\pm 0.05^\circ\text{C}$).

Table 2.1. Conductivity and first derivative values at different temperatures for SDS (0.100 mol/L) in water.

Temperature	Conductivity	First derivative
13.486	0.111	0.000983284
13.689	0.112	0.0023353
13.757	0.114	0.002089479
13.893	0.115	0.002949853
13.961	0.118	0.003441495
14.028	0.12	0.005899705
14.164	0.126	0.005776794
14.3	0.131	0.025196657
14.435	0.159	0.038225172
14.435	0.179	0.030113078
14.639	0.199	0.019665683
14.774	0.206	0.009955752
14.842	0.215	0.015117994
14.978	0.226	0.016224189
15.113	0.236	0.012045231
15.249	0.242	0.006145526
15.385	0.245	0.004178958
15.52	0.248	0.003564405
15.656	0.25	0.003687316
15.927	0.253	0.003687316
16.131	0.255	0.003933137
16.266	0.258	0.002089479
16.402	0.258	0.001106195
16.741	0.26	0.003195674
17.012	0.262	0.002949853
17.284	0.264	0.003195674
17.487	0.266	0.001106195
17.623	0.266	0.002212389
17.826	0.269	0.003318584
18.03	0.27	0.001106195
18.233	0.271	0.002089479
18.436	0.273	0.004056047
18.708	0.276	0.003072763
18.979	0.277	0.000983284
19.182	0.278	0.003195674
19.386	0.281	0.003195674
19.589	0.282	0.001229105
19.725	0.283	0.001229105
19.928	0.284	0.003195674

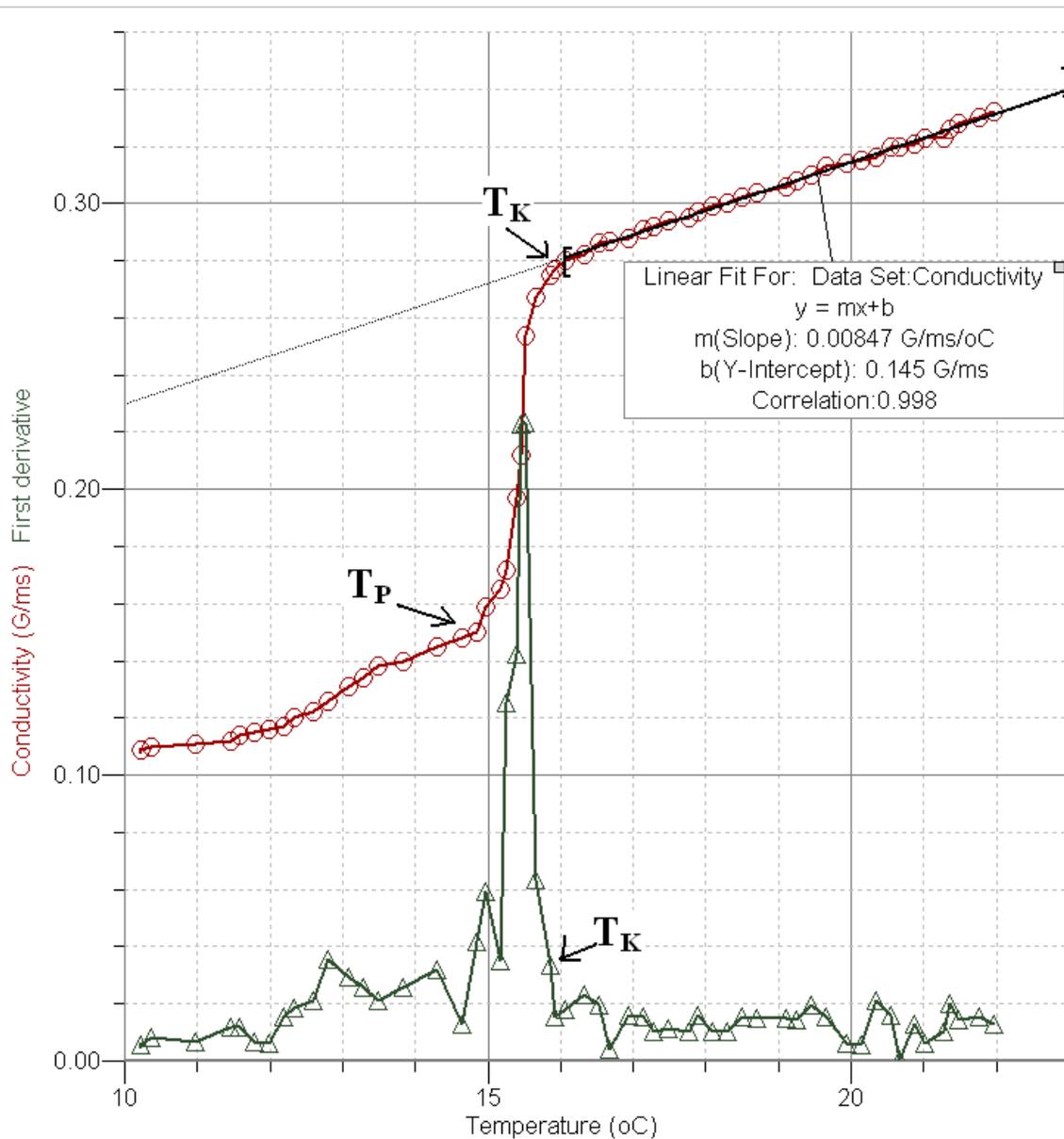


Figure 2.2. Krafft point (T_p) and Krafft temperature (T_K) indicated by arrows in temperature versus conductivity graph of SDS (0.100 mol/L) & NaCl (0.005 mol/L) in water.

2.4 Determination of mean aggregation number (N)

The concentration of Tris (2, 2'- bipyridyl) dichloro - ruthenium (II) hexahydrate was kept constant at 0.007M and 0.0005M of 9-methylanthracene was prepared using absolute ethanol. The concentration of sodium dodecyl sulfate ranged from 0.010M to 0.050M. To each surfactant solution 100 μ l of Ruthenium probe was added. The luminescence intensity of the probe in surfactant without quencher (I_0) was measured using a FP-6300 spectrofluorometer. Then 100 μ l of quencher (9-methylanthracene) was added and the luminescence intensity (I) of the surfactant system was measured. The luminescence intensities were measured at 625 nm with $\lambda_{exc} = 450$ nm. The mean aggregation number (N) of sodium dodecyl sulfate can be calculated from the regression values of slope ($1/[Q]N$) using equation (7).

$$\ln\left(\frac{I}{I_0}\right) = \frac{1}{[Q]N}[S_0] - CMC/[Q]N \quad (7)$$

CHAPTER 3:

RESULTS AND DISCUSSION

The Krafft temperature (T_k) of the sodium dodecyl sulfate (0.100 mol/L) was measured in the presence and absence of added salt (NaCl). The Krafft temperature of SDS was measured both in water and 10% ethylene glycol. The concentration of surfactant was kept constant and the concentration of the salt has been changed from 0 mol/L to 0.005, 0.010, 0.015 and 0.020 mol/L. The concentration of the counter ion was calculated from the equation (3). The conductivity versus temperature graphs of SDS at various concentrations in water and 10% ethylene glycol are shown in Figures 3.1. to 3.10. All of the data for the experimental runs is summarized in Tables 3.1. and Table 3.2.

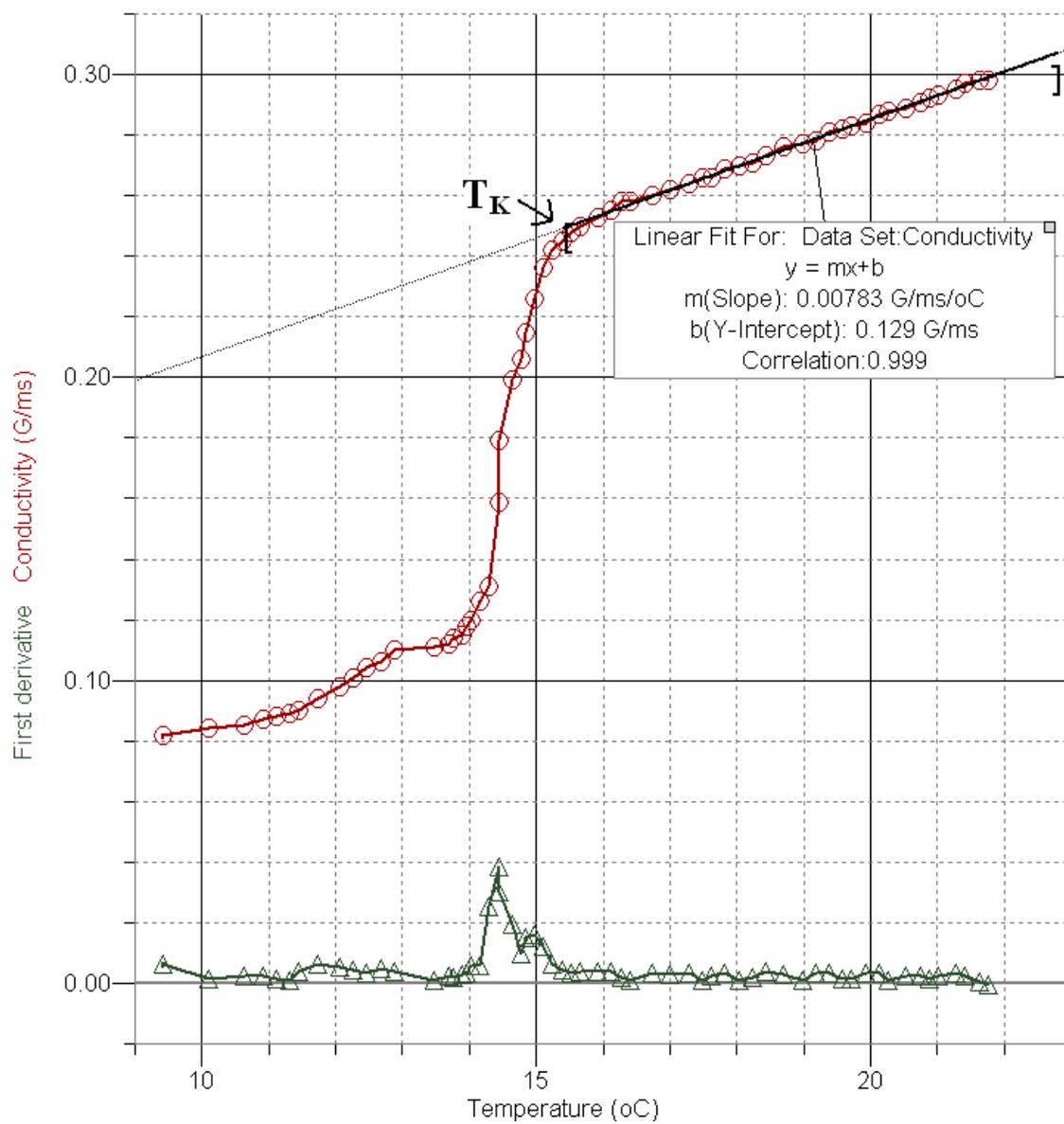


Figure 3.1. Temperature versus conductivity graph for SDS (0.100 mol/L) in water.

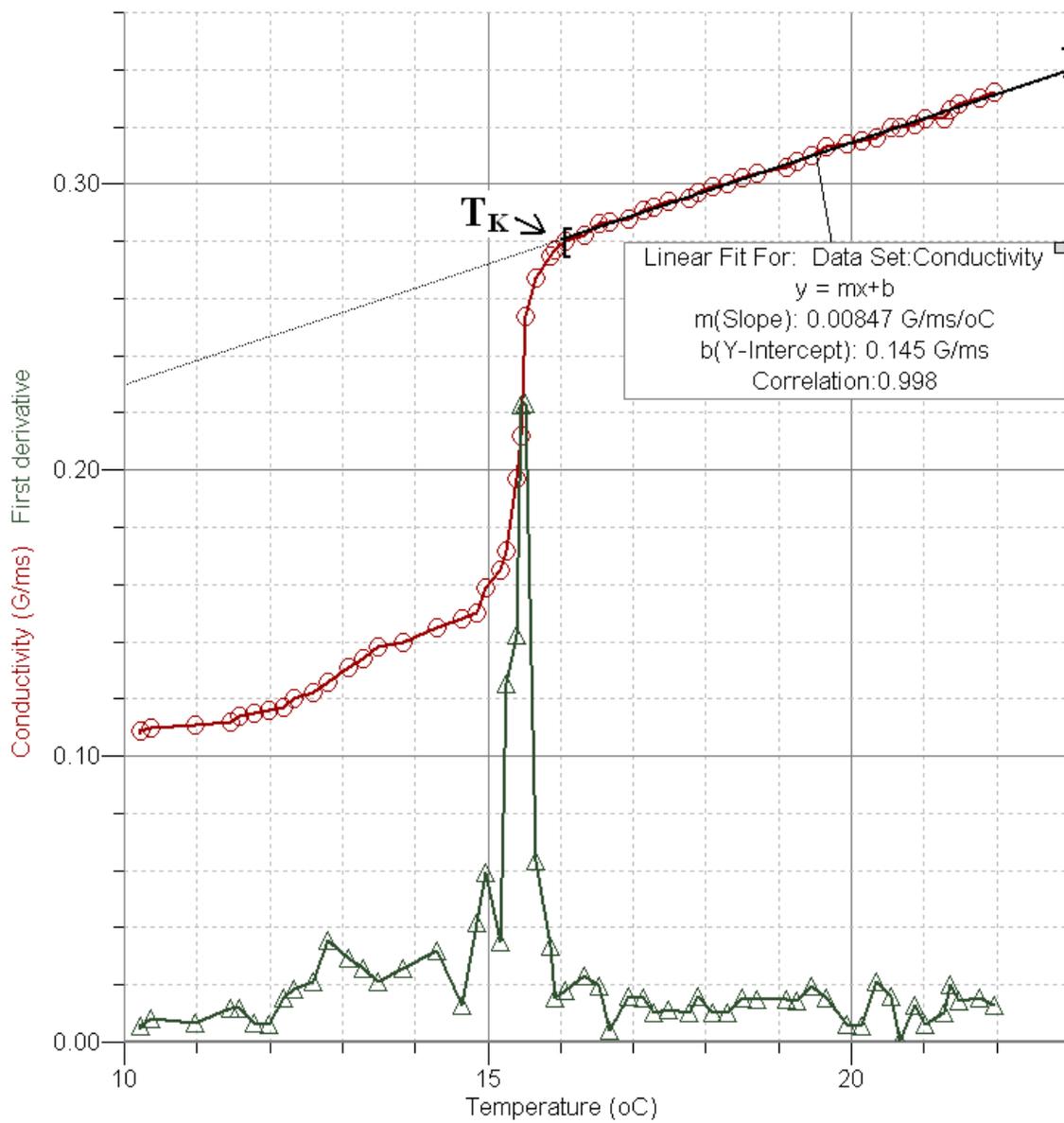


Figure 3.2. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.005 mol/L) in water.

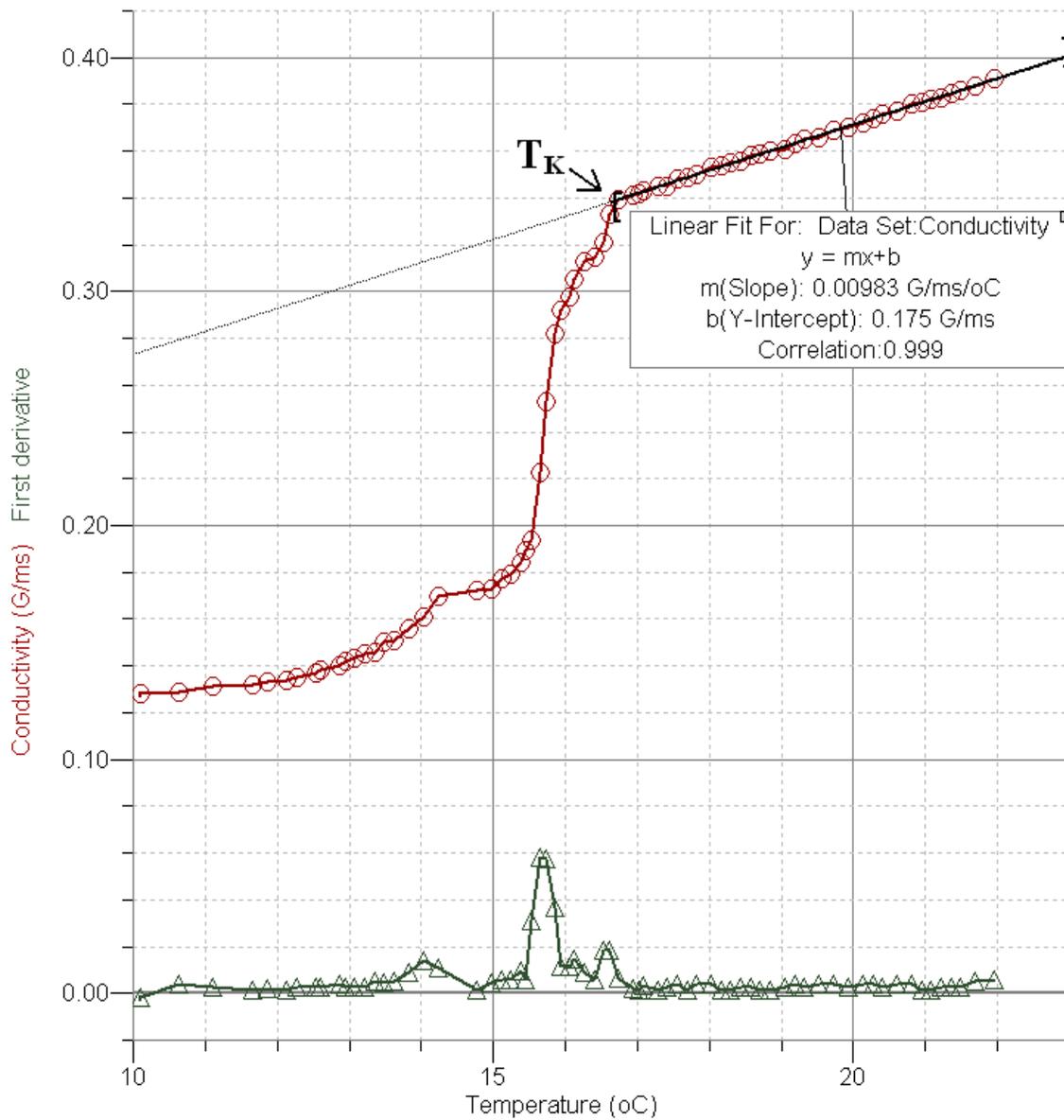


Figure 3.3. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.010 mol/L) in water.

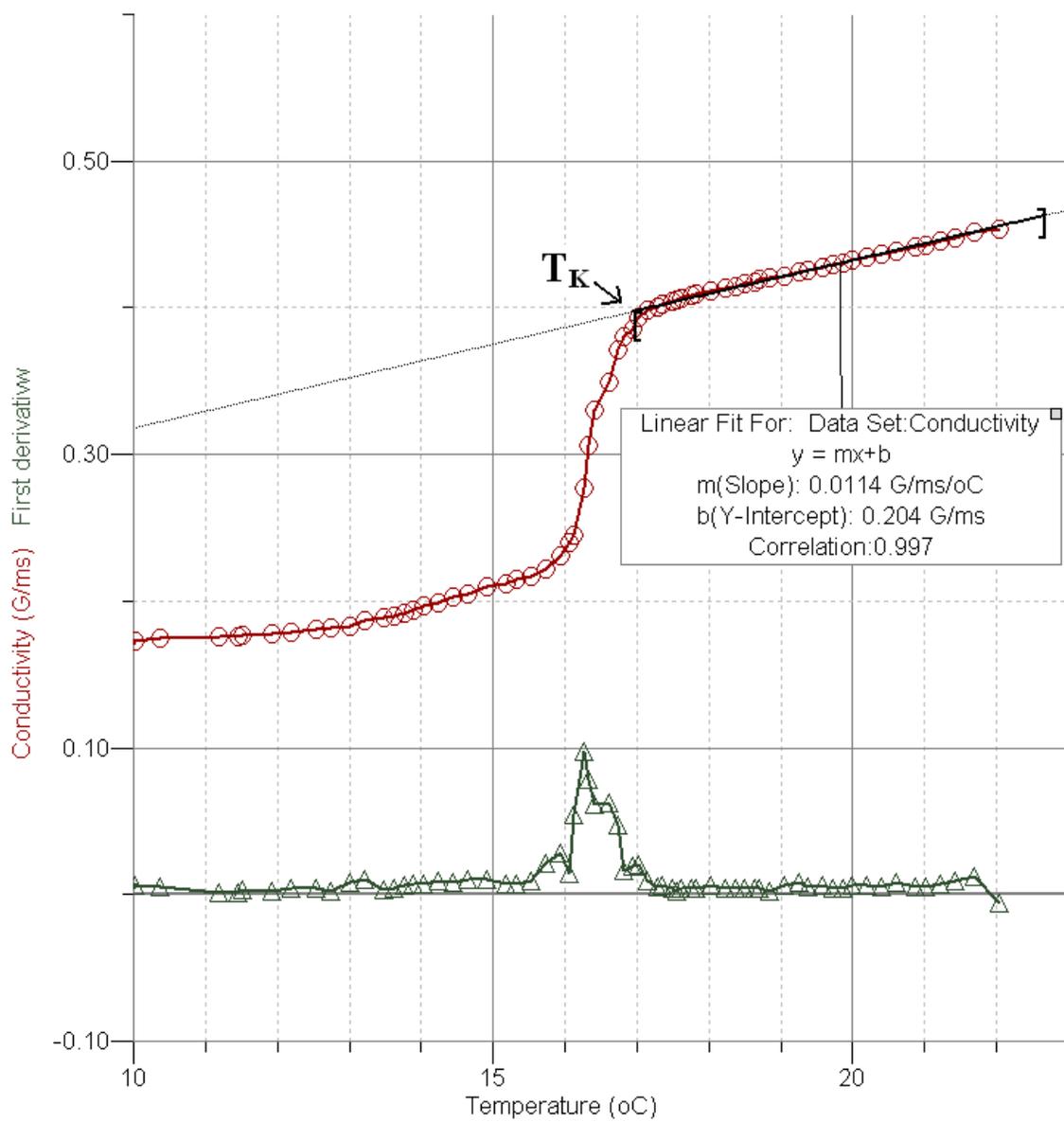


Figure 3.4. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.015 mol/L) in water.

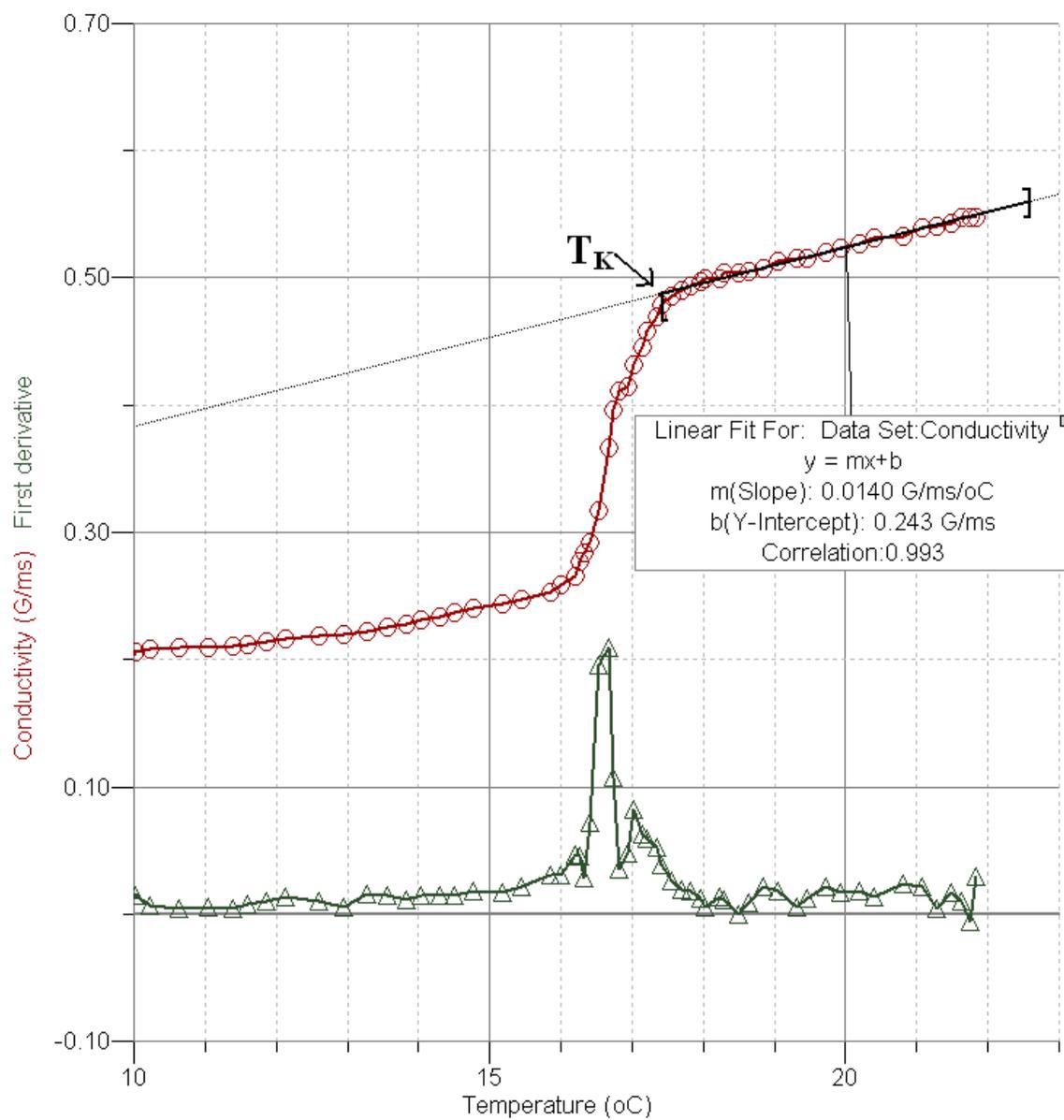


Figure 3.5. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.020 mol/L) in water.

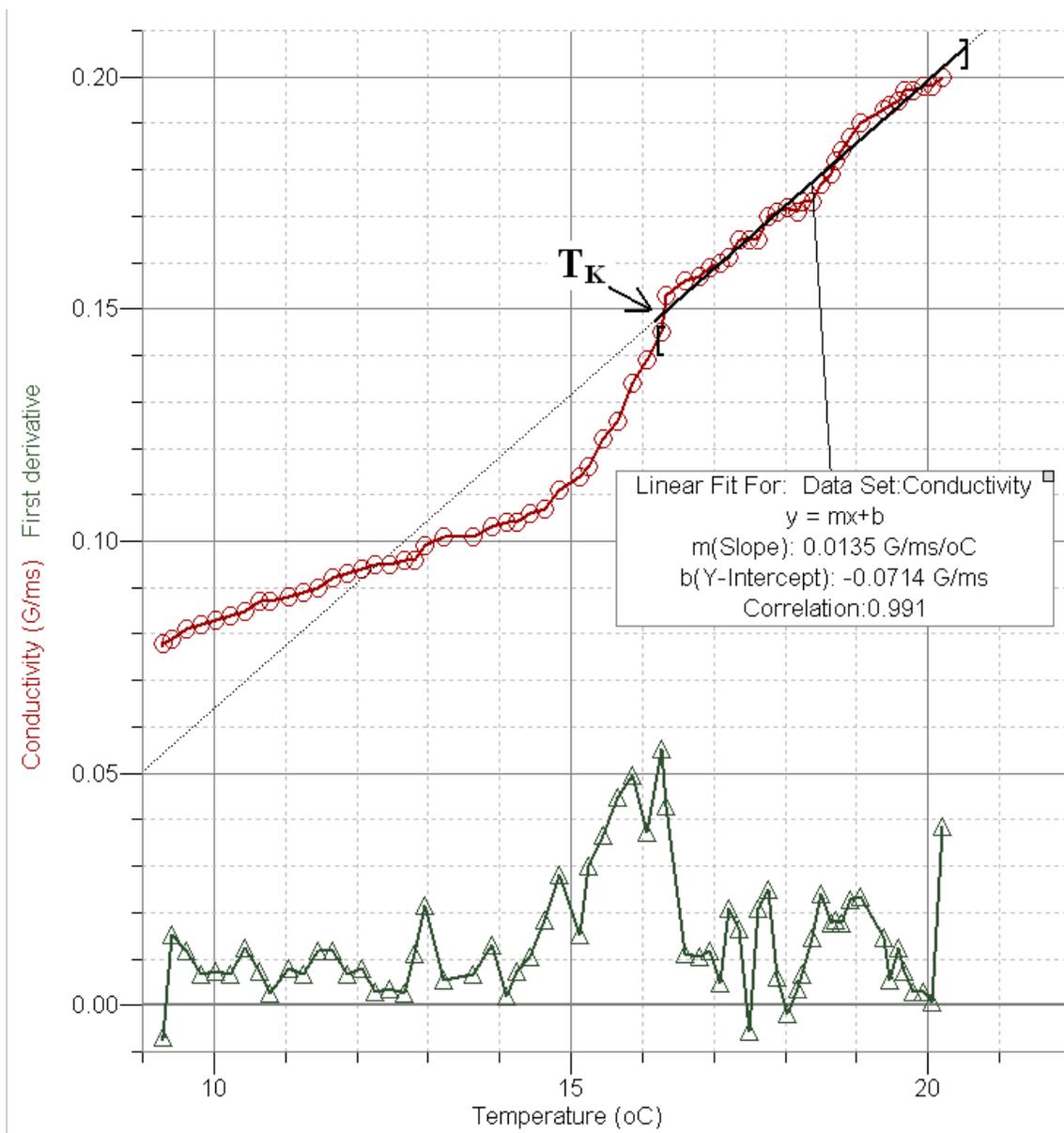


Figure 3.6. Temperature versus conductivity graph for SDS (0.100 mol/L) in 10% ethylene glycol.

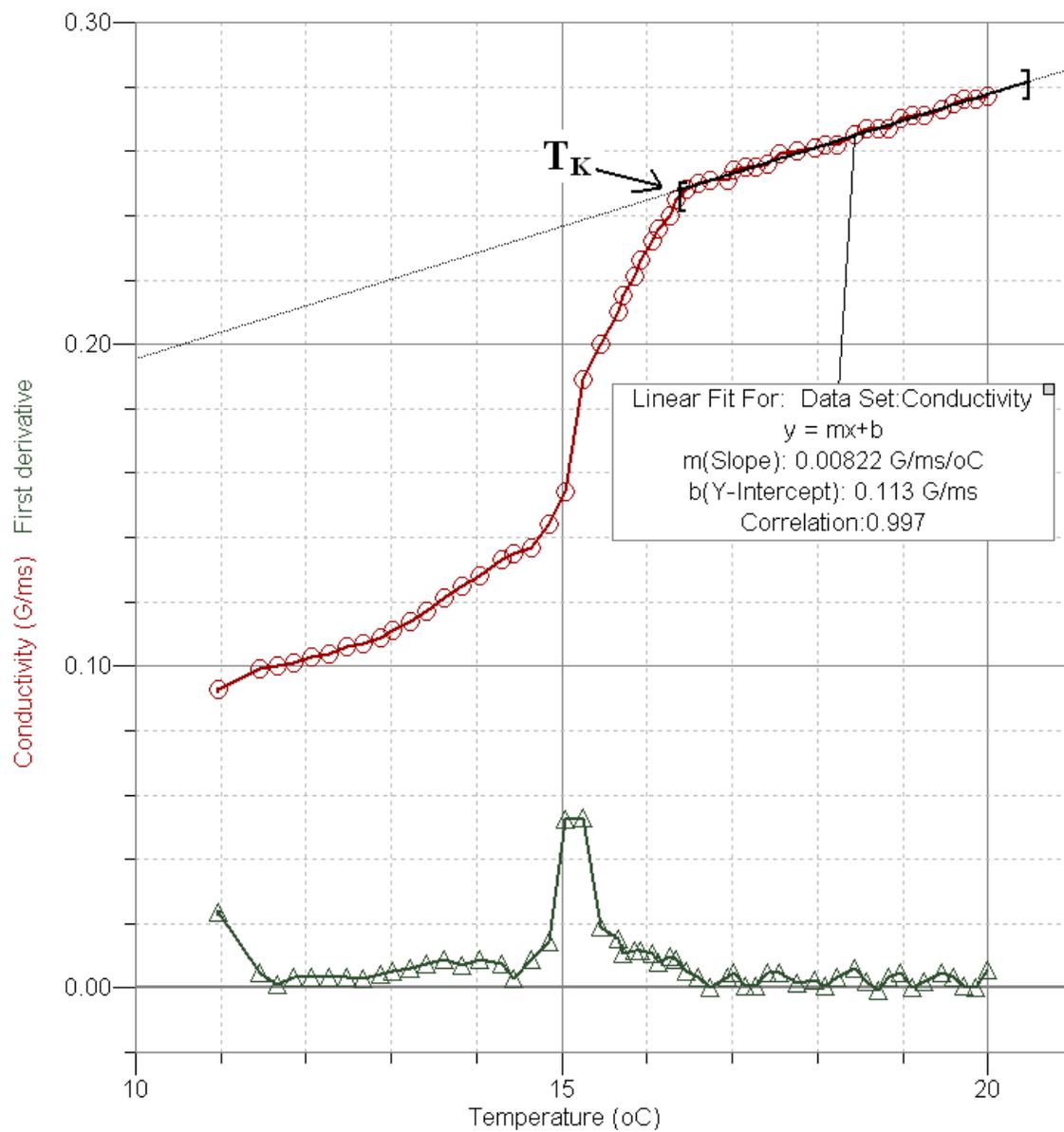


Figure 3.7. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.005 mol/L) in 10% ethylene glycol.

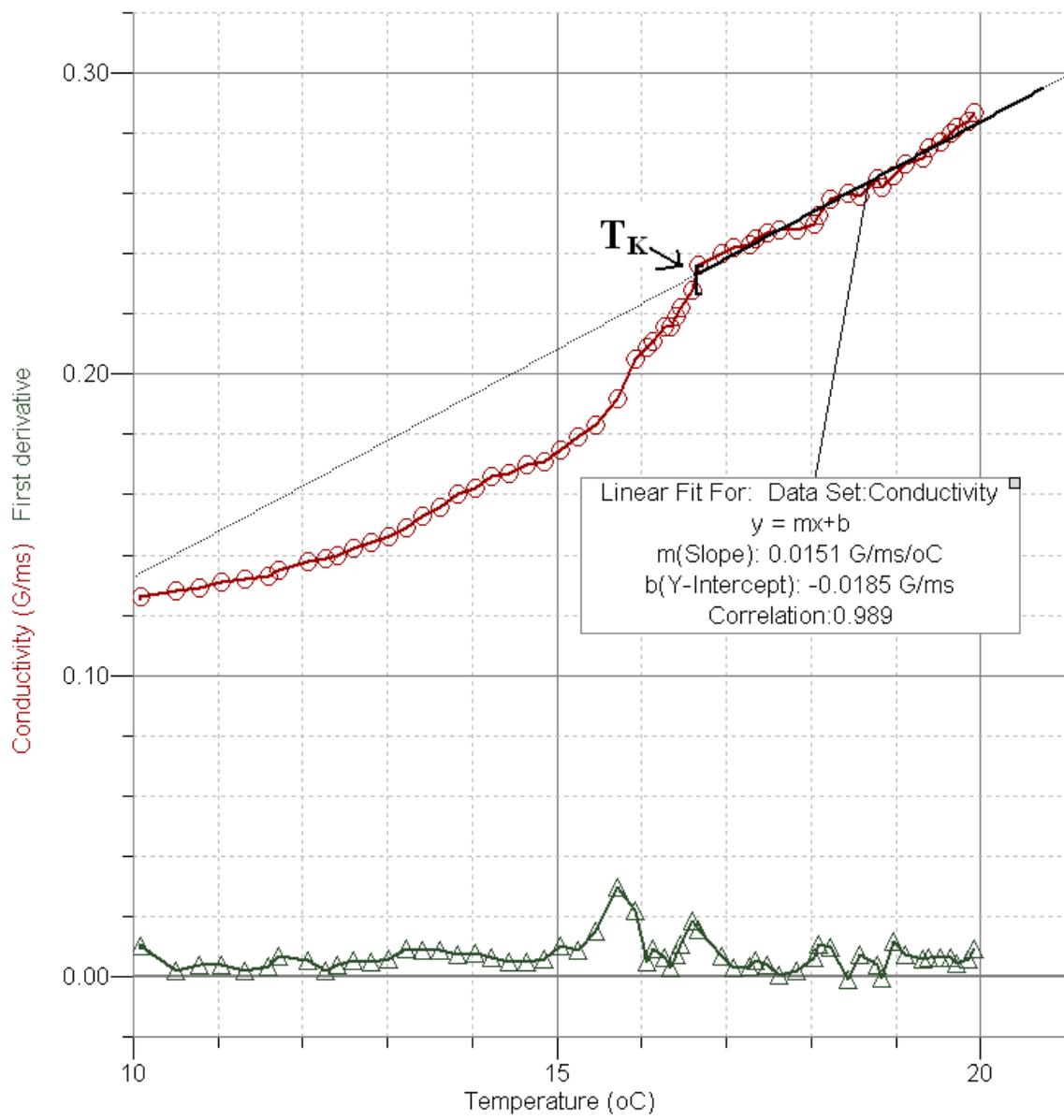


Figure 3.8. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.010 mol/L) in 10% ethylene glycol.

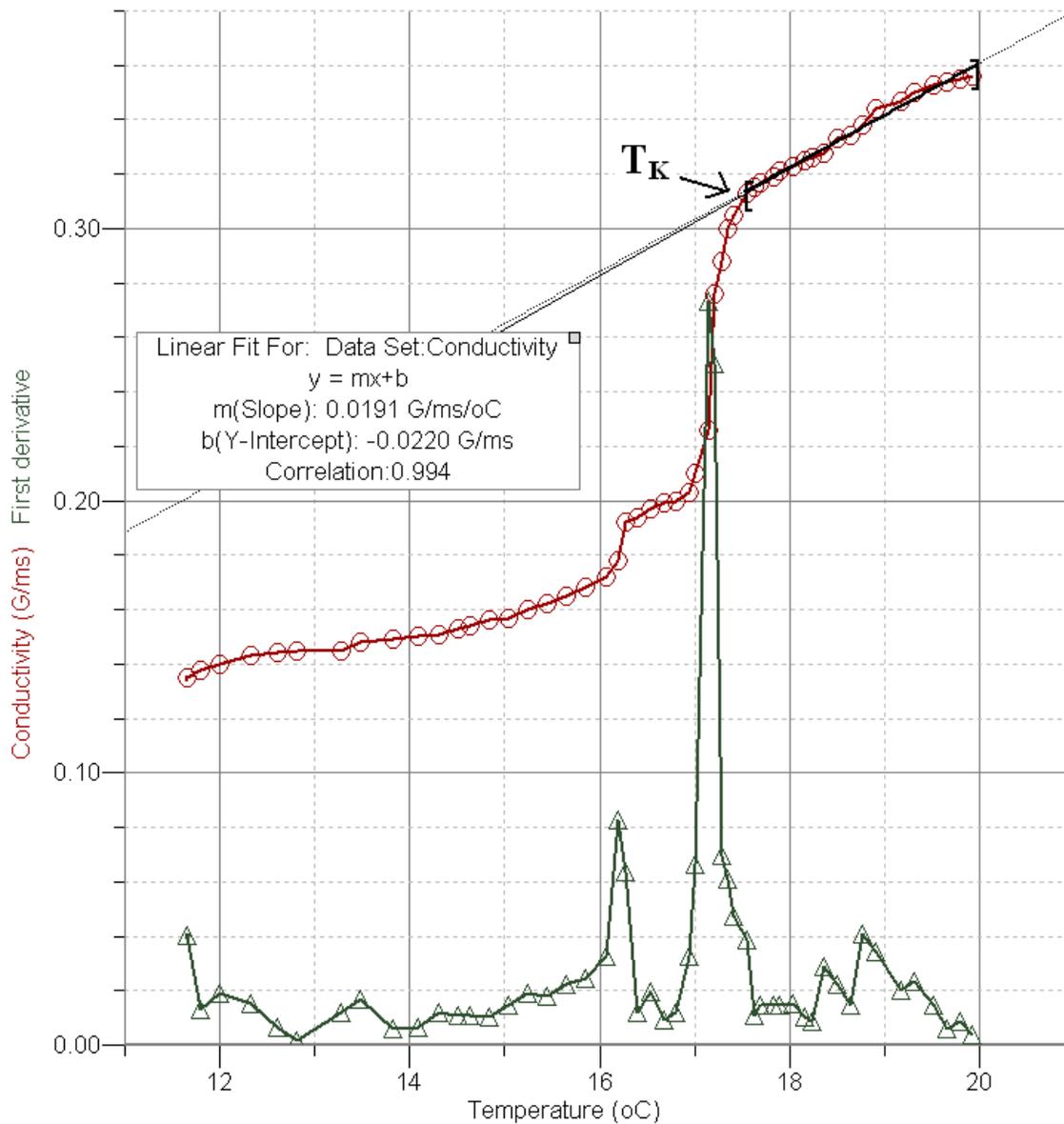


Figure 3.9. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.015 mol/L) in 10% ethylene glycol.

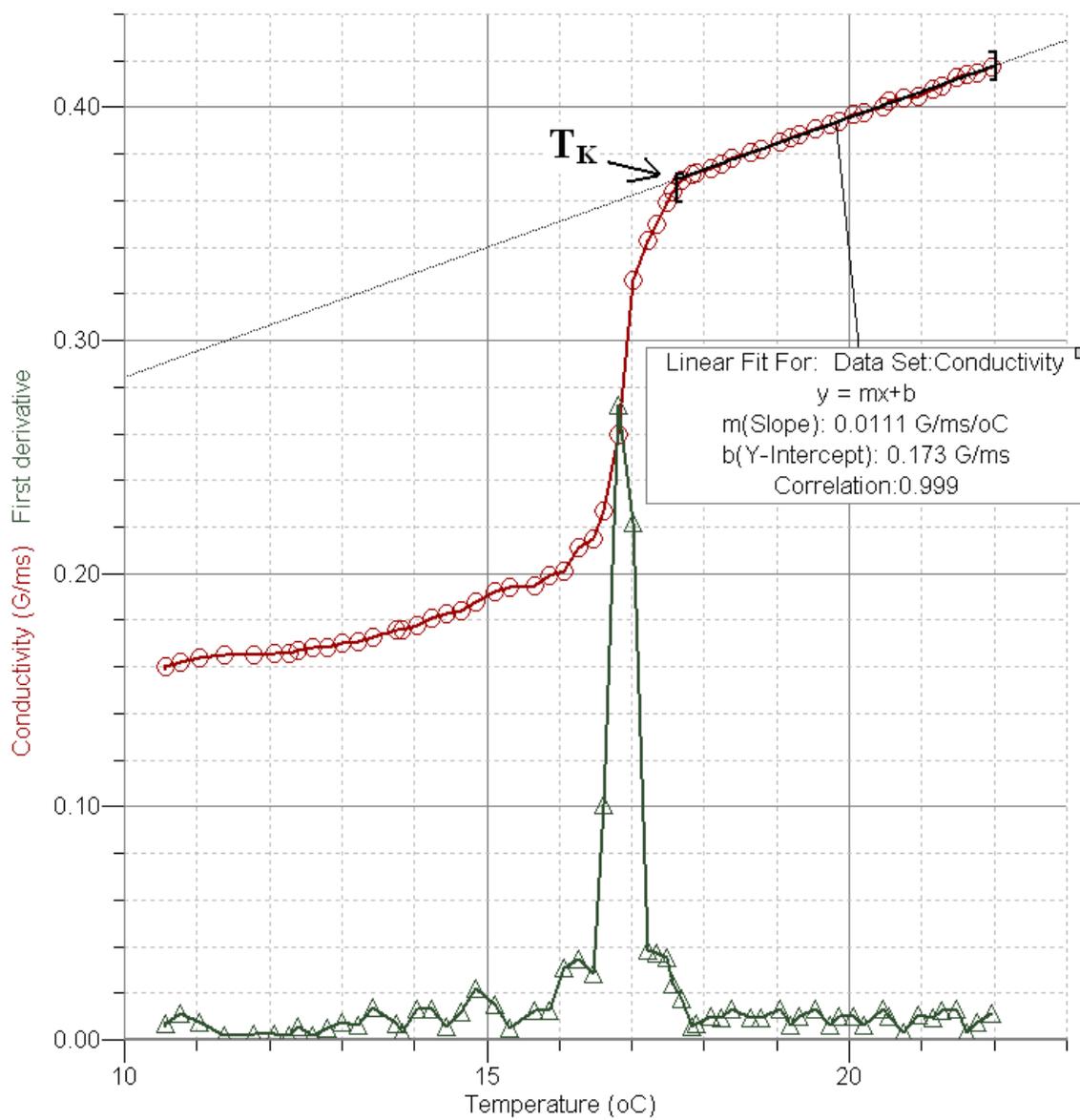


Figure 3.10. Temperature versus conductivity graph for SDS (0.100 mol/L) & NaCl (0.020 mol/L) in 10% ethylene glycol.

The Krafft temperature of the sodium dodecyl sulfate was increased in both water (Table 3.1.) and in 10% ethylene glycol (Table 3.2.) by increasing the concentration of counter ion. The concentration of the counter ion was increased by adding salt (NaCl) to the surfactant solution.

Even though the concentration of the counter ion is same for all the samples in water (Table 3.1.) and 10% ethylene glycol (Table 3.2.), the Krafft temperature of sodium dodecyl sulfate is higher in 10% ethylene glycol than in water.

Ethylene glycol is more polar and has higher cohesive energies, dielectric constants and hydrogen bonding ability than water.^{11, 17} Since hydrogen bonding ability is an important requirement for the formation of the micelles, Krafft temperatures were higher in 10% ethylene glycol than in water.

Table 3.1. Krafft temperatures of SDS in water at different counter ion concentrations.

Sample	C_t mol/L	C_{ad} mol/L	$F(C_t)$	$C_{aq} = F(C_t)$ $\{\alpha C_t + C_{ad}\}$ mol/L	T_k (°C) in Water	
					Trial I	Trial II
1	0.100	0.000	1.03	0.02678	15.66	15.70
2	0.100	0.005	1.03	0.03193	16.06	16.02
3	0.100	0.010	1.03	0.03708	16.35	16.41
4	0.100	0.015	1.03	0.04223	17.01	17.03
5	0.100	0.020	1.03	0.04738	17.59	17.53

Table 3.2. Krafft temperatures of SDS in 10% ethylene glycol at different counter ion concentrations.

Sample	C_t mol/L	C_{ad} mol/L	$F(C_t)$	$C_{aq} = F(C_t)$ { $\alpha C_t + C_{ad}$ } mol/L	T_k ($^{\circ}C$) in 10% Ethylene glycol	
					Trial I	Trial II
1	0.100	0.000	1.03	0.02678	16.34	16.30
2	0.100	0.005	1.03	0.03193	16.49	16.43
3	0.100	0.010	1.03	0.03708	16.68	16.74
4	0.100	0.015	1.03	0.04223	17.56	17.57
5	0.100	0.020	1.03	0.04738	17.69	17.63

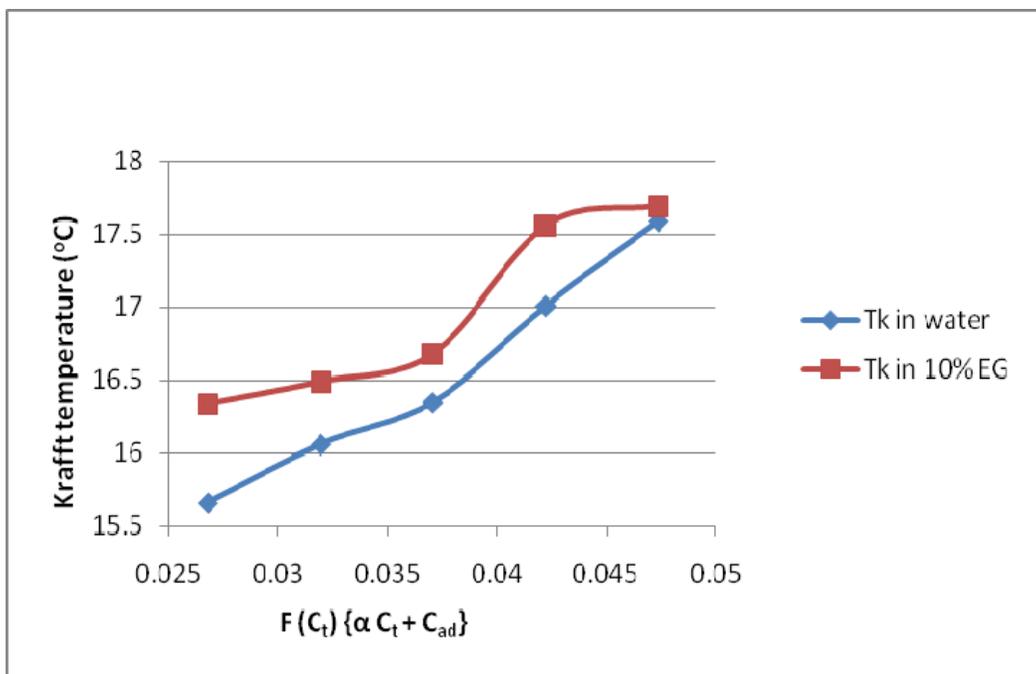


Figure 3.11. Krafft temperatures (T_k) versus counter ion concentrations.

The difference in Krafft temperatures in water and 10% ethylene glycol was observed to be less at higher counter ion concentration (Figure 3.11).

There was an unidentified problem in determining the Krafft temperature of sodium dodecyl sulfate at higher surfactant concentrations (0.175 mol/L). The abrupt change in slope of conductivity versus temperature graphs was not observed at higher surfactant concentrations to determine Krafft temperature as shown in figure 3.12.

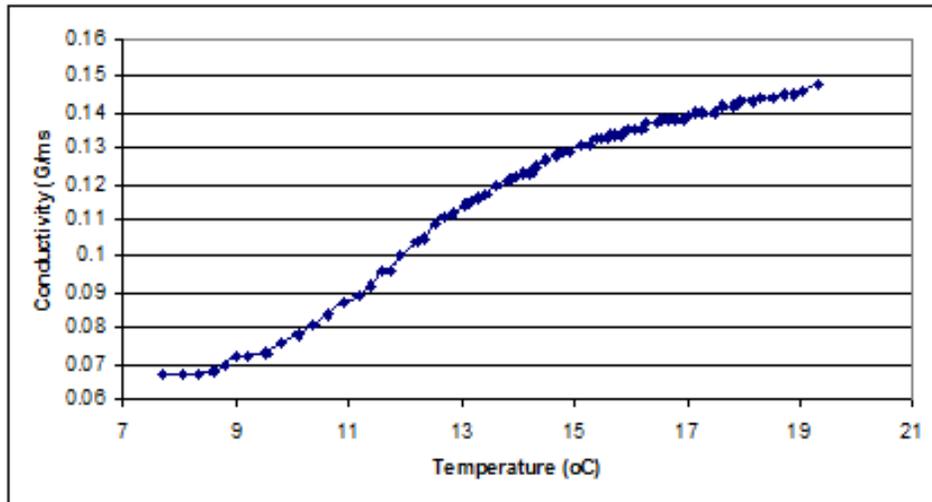


Figure 3.12. Temperature versus conductivity graph for SDS (0.175 mol/L)

The mean aggregation number did not show any pattern with increasing the salt concentration, moreover at higher surfactant concentrations the samples turns cloudy when quencher was added and could not be studied further.

The luminescence intensity was measured for sodium dodecyl sulfate (0.010M to 0.050M) in water without NaCl. The ratio of $\ln[I/I_0]$ was plotted against the concentration of sodium dodecyl sulfate (figure 3.13). Using equation (7) the mean aggregation number was found to be 100.

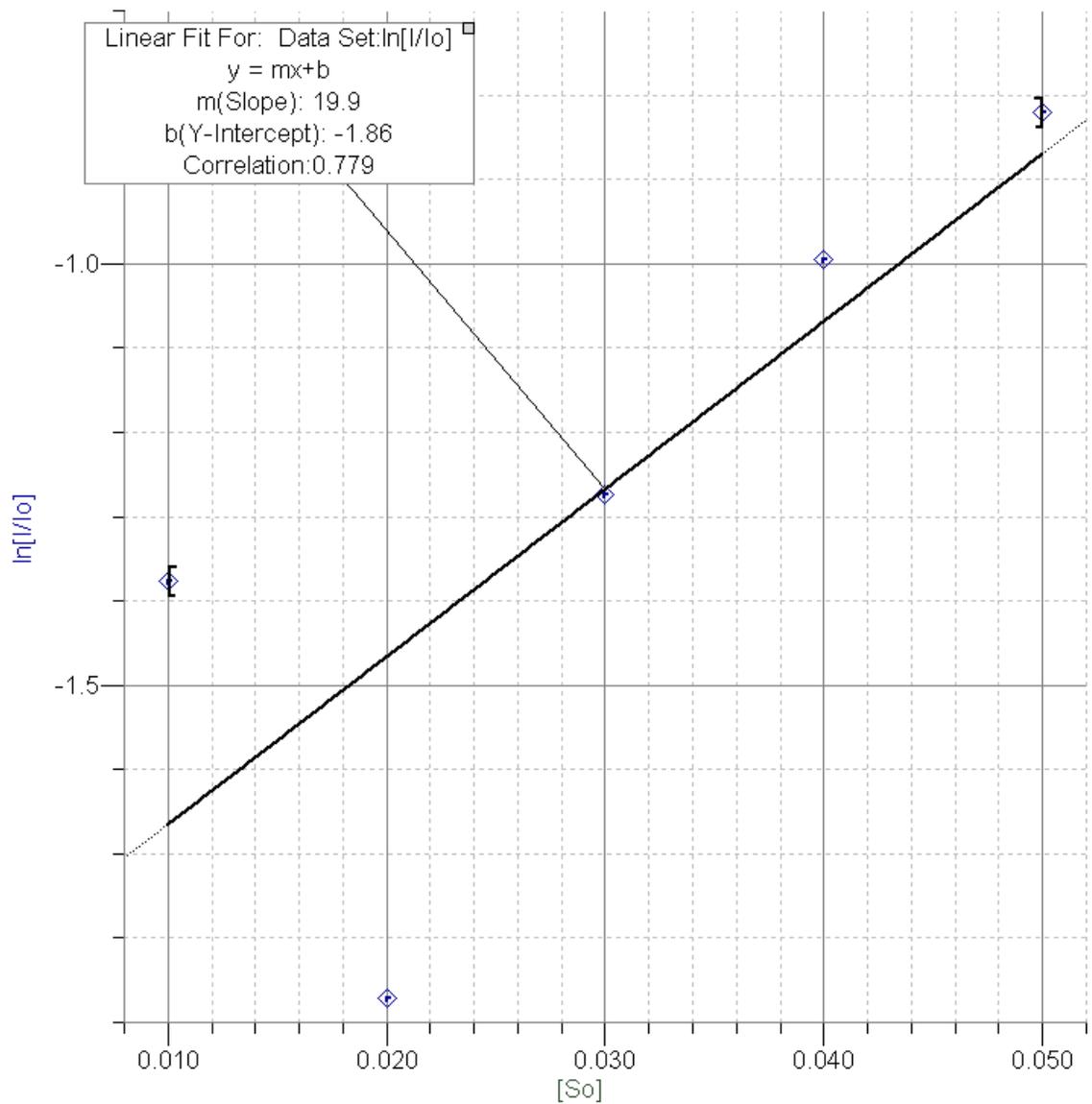


Figure 3.13. $\ln [I/I_0]$ vs concentration of sodium dodecyl sulfate in water

The luminescence intensity was measured for sodium dodecyl sulfate (0.010M to 0.050M) in water with NaCl (0.010M). The ratio of $\ln[I/I_0]$ was plotted against the concentration of sodium dodecyl sulfate (figure 3.14). Using equation (7) the mean aggregation number was found to be 41.

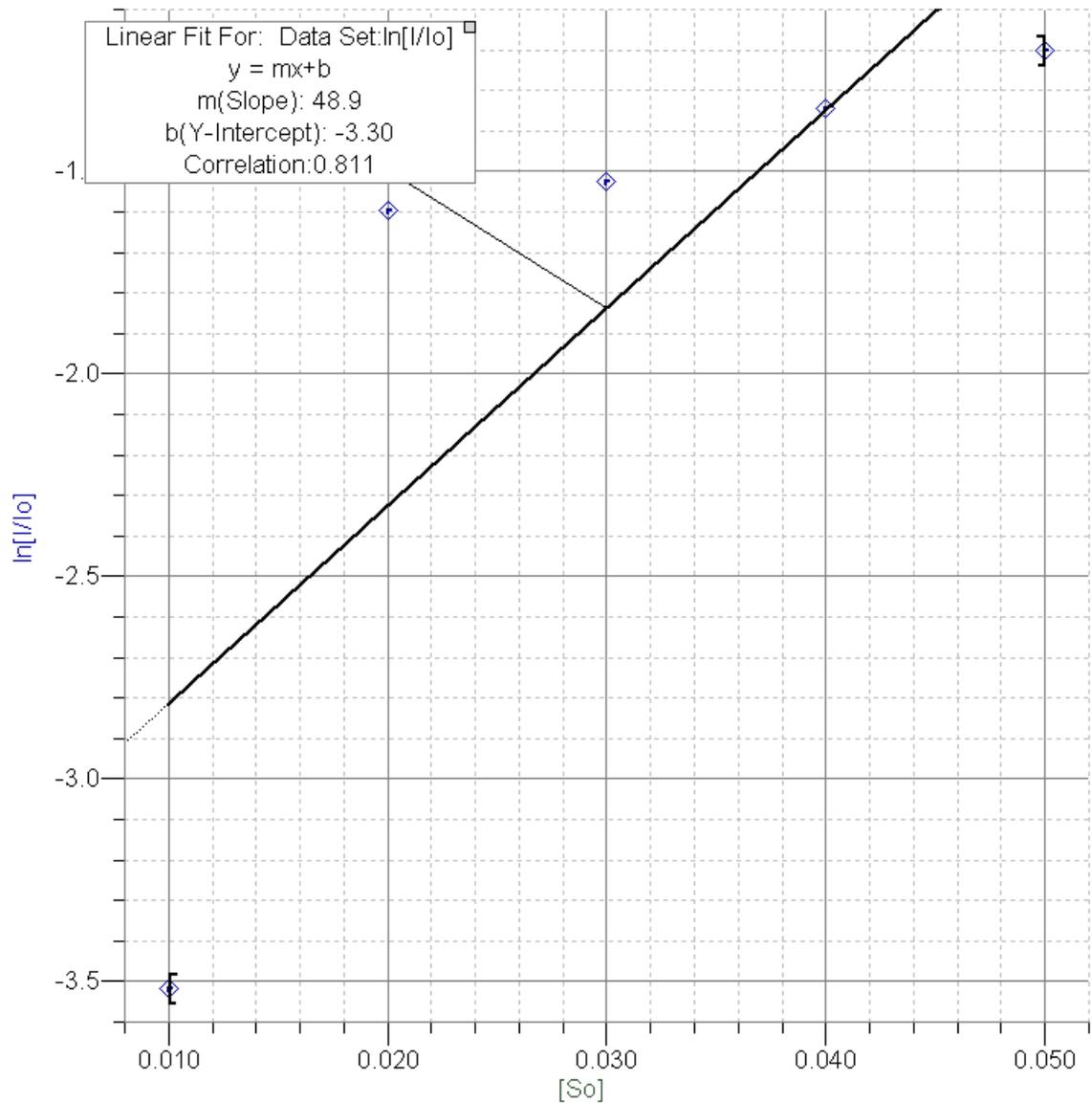


Figure 3.14. $\ln [I/I_0]$ vs concentration of sodium dodecyl sulfate in water with NaCl (0.010mol/L)

The luminescence intensity was measured for sodium dodecyl sulfate (0.010M to 0.050M) in water with NaCl (0.020M). The ratio of $\ln[I/I_0]$ was plotted against the concentration of sodium dodecyl sulfate (figure 3.15). Using equation (7) the mean aggregation number was found to be 55.

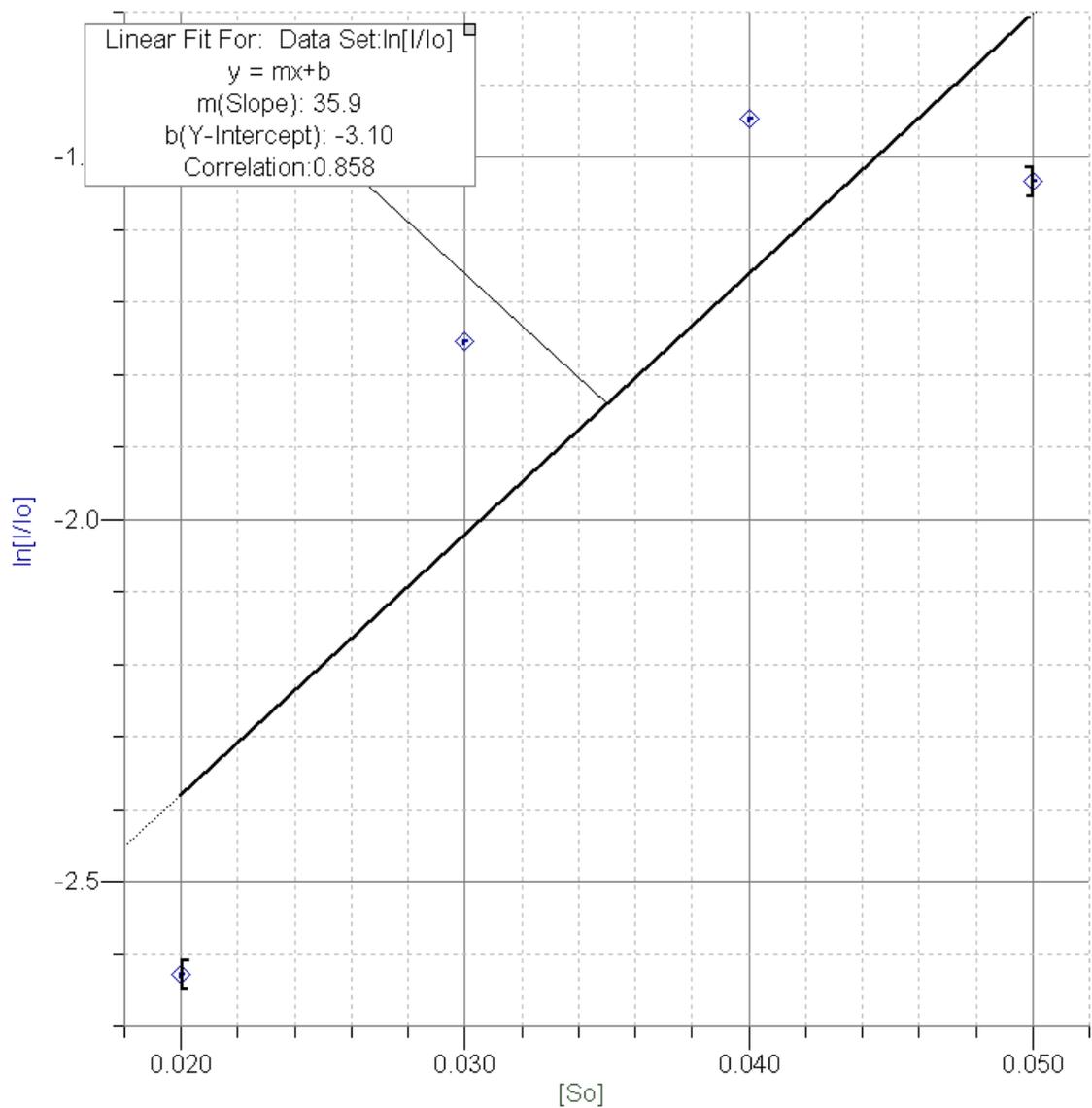


Figure 3.15. $\ln [I/I_0]$ vs concentration of sodium dodecyl sulfate in water with NaCl (0.020mol/L)

CHAPTER 4:

CONCLUSION

The Krafft temperature of sodium dodecyl sulfate increased in water by increasing the concentration of the counter ion (sodium) provided by both the surfactant and added salt. The Krafft temperature of sodium dodecyl sulfate increased in 10% ethylene glycol by increasing the concentration of the counter ion (sodium) provided by both the surfactant and added salt. Since 10% ethylene glycol is more polar and has higher cohesive energies, dielectric constants and hydrogen bonding ability than water, the Krafft temperature of the sodium dodecyl sulfate in 10% ethylene glycol is higher than the Krafft temperature of sodium dodecyl sulfate in water at the same counter ion concentration.

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