
Determination of enthalpy and entropy of micellization for Brij-35 and the Effect of salts on critical micellar concentration

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Abstract:

In this study the thermodynamic parameters of micelle formation for Brij-35 (the nonionic polyoxyethylene ether surfactants Brij 35 ($C_{12}E_{23}$ *i.e.* $CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH$) will be determined from kinetics data. The reaction used is the reduction of m-chloroperbenzoic acid by iodide. The initial concentrations of peracid and iodide were 4×10^{-6} M and 1.5×10^{-3} M respectively. Reactions were carried out in 0.003 M nitric acid and in presence of sodium sulphate and sodium perchlorate. The results show that, the Hydrophilic "salting out" sulphate ions increase the rate constant of the reaction in the micelle and reduce the critical micellar concentration (CMC); whereas hydrophobic "salting in" ions perchlorate decrease the rate constant and have much less effect on the CMC. In all different conditions investigated the temperature seems to increase the rate and decrease the critical micelle concentrations.

Introduction

When surfactant molecules adsorb at an interface they provide an expanding force and cause the interfacial tension to decrease (at least up to the CMC). This is illustrated by the general Gibbs adsorption equation, from which the surface excess concentration of a surfactant in a monolayer and the area

per adsorbed molecule can be calculated. Numerous examples are given by Rosen¹. The micelle formation thermodynamics are based on the Gibbs equation $\Delta G = \Delta H - T\Delta S$. The process of micelle formation at room temperature is assumed to be characterized by small positive values

of enthalpy, and high positive values of entropy, which is considered to be the main driving force for the process. This high positive value of ΔS is in contrast to the aggregation process in which the system become more ordered as one single entity (micelle) is formed from many monomers, and should result in negative contribution to entropy as the formation of micelle leads to order of surfactant monomer. Also, ΔH should be larger since hydrocarbon groups have very little solubility in water and hence a high enthalpy of solution.

The larger entropy increase of micellization in aqueous medium has been explained in two ways^{2, 3}. The first is based on the structure of water during the formation of micelle, and as the hydrophobic residues aggregate the highly structured water around each chain collapses back to bulk water, which accounts for the large gain in entropy of micellization. The second factor is the increased movement of hydrocarbon chains in the non-polar interior of the micelle compared to the aqueous phase^{2,3}.

The surface tension of an aqueous solution shows little change when the concentration of surfactant exceeds the

CMC. This well-known behavior suggests that micelles can be approximated as a phase since the chemical potential is kept nearly constant, irrespective of the amount of the material¹.

There are two models which are used to describe the micelle formation: one is called the mass action model in which the micelle and monomers are in equilibrium, and the other is the phase separation model in which the micelle is considered to constitute a new phase in the system at and above the CMC. These two models are well documented in literature and have been explained by Engberts⁴.

The process of micelle formation can be described as equilibrium between surfactant monomer and micelles, which in the case of non-ionic surfactants can be expressed by Equation 1 below⁵:



Where n is the number of molecules of surfactants S, associating with micelle S_n , and the equilibrium between micelle and monomers is assumed with corresponding equilibrium constant K_m :

$$K_m = \frac{[S_n]}{[S]^n}$$

The brackets indicate the concentration and n, the number of monomers in the micelle, aggregation number.

From Equation 2, the standard free energy of micellization per mole of micelle is given by:

$$\Delta G_m^o = -RT \ln K_m = -RT \ln S_n + nRT \ln S \quad 3$$

The standard free energy change per mole of monomer can be obtained by dividing the previous equation by n (aggregation number) which is assumed to be about 100 times larger for many micellar systems. It is also assumed that S is approximately equal to S_n at the CMC. Thus, the first term in the right hand of the equation can be ignored and the free energy of micellization per mole of surfactant becomes as shown in Equation 4, assuming S is approximately equal to S_n at the CMC^{5,6}.

$$\Delta G_m^o = RT \ln CMC \quad 4$$

2. Experimental section

2.1 Materials

Meta-chloroperbenzoic acid (MCPBA, it is molecular formula C₇H₅Cl O₃) was purchased from Sigma Chemical Company with purity of 80%, the main impurity is the parent acid, metachlorobenzoic acid. Potassium iodide (Analar reagent, 99.5%), sulphuric acid with minimum assay of (95%), were obtained from Aldrich. Sodium thiosulphate and perchlorate (99%) were purchased from Fisher Chemical Company and nitric acid which obtained from Aldrich. The reactants and reagents were prepared in distilled water.

2.2. Methods:

2.2.1. Solutions preparation

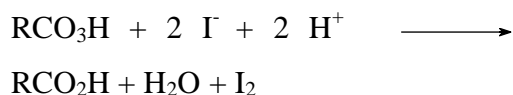
Solutions of meta-chloroperbenzoic acid were prepared normally by adding the required amount to distilled water and stirring for about an hour using a magnetic stirrer. The solution was filtered with a Duran Buchner funnel, 75 ml, with sintered disc 45 mm and pore diameter 16-40 micrometer. The concentration of MCPBA was determined iodometrically as described below. The required concentration for the working solution was obtained by further dilution in distilled water. The stock solutions of the MCPBA

required regular standardisation due to their decomposition.

2.2.2. Metachloroperbenzoic acid determination

The general method is as follows.

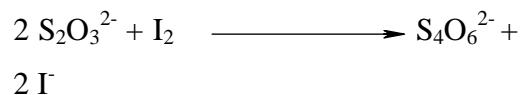
About 5 ml of 0.03 M potassium iodide and 10 ml of 2 M sulphuric acid were mixed in a 250 ml conical flask and 5.0 ml of the peracid was added by pipette and the mixture mixed thoroughly. The liberated iodine was titrated with the standard solution of sodium thiosulphate, 0.01 M, a small amount of iodine indicator was added toward the end of the titration. The end point is determined by the change of colour from pale blue to colourless.



2.3. Stopped flow method

A SX-17MV Stopped Flow Reaction Analyser from Applied Photophysics was used to measure the rate of the reaction between iodide and meta-chloroperbenzoic acid, this reaction is known to be very fast so a stopped-flow is required.

Calibration of the stopped flow is carried out before every experiment using distilled water in both syringes. Following that, the syringes are filled



It can be seen from the equations above that

$$2\text{I}^- \equiv 2\text{S}_2\text{O}_3^{2-} \equiv \text{RCO}_3\text{H}$$

Therefore the strength of metachloroperbenzoic acid can be calculated by the following equation.

$$[\text{MCPBA}] = \text{V of Na}_2\text{S}_2\text{O}_3 \times .01 \text{ M} / 2 \times \text{volume of MCPBA}$$

$$[\text{MCPBA}] = 0.01 \times \text{titre} / 10$$

So the measured volume of Na₂S₂O₃ in cm³ is directly equal to the concentration of MCPBA in 10⁻³ mol dm⁻³

with the relevant solutions. Air bubbles are removed before the runs by flushing backward and forward between the drive syringes and the reservoir syringes many times.

The kinetic run and the depression of the two reactants from syringes into the reactor chamber is done automatically, this forces the unreacted solution into the flow cell and also forces the reacted solution out of the

cell. The concentration of triiodide formed is measured by mean of its

absorption of ultra violet light.

3. Results and Discussion

3.1. Critical micelle concentration

Figure 1 illustrates three typical sets of results to determine Brij-35 surfactant CMC values under different experimental conditions. It shows the change in the observed pseudo first order rate constant, k_{obs} , at low surfactant concentrations. Arrows indicate breaks in the plots, which correspond to the CMC. The slight maxima in the gradients of the plots below the break are characteristic of all data sets.

In this section firstly the CMC of the studied surfactant, the Brij-35, will be measured in presence of different salt concentrations, and the reaction of iodide and peracid will be used in Brij-35 to determine the CMC. It can be seen that there are differences between the values of CMC found in literature^{7,8} and the values observed in this study for non-ionic surfactant (brij-35) (determined from kinetic measurement. These differences are most probably explained by the fact that literature values were measured by means of the surface tension method; this method is a surface phenomenon

and is highly sensitive to surface-active impurities in the surfactant solution, which often significantly reduce the CMC of surfactants,

In general, non-ionic surfactants show much lower CMC values than ionic ones, whose hydrophobic chains are of the same length, due to the absence of electrical repulsion between ionised groups¹. The critical micelle concentration of non-ionic surfactants is lowered by the addition of salt, but the lowering is always much smaller than that of ionic surfactants^{1,9}. In this study the effect of perchlorate and sulfate is shown in Figure 2, which plots CMC versus salt concentration. The data listed in Table 1 and 2 it is clear that the CMC is lowered as the concentration of sulphate increases. However, the effect of perchlorate is not clear and the CMC might have an effect but to a lesser extent than sulfate. Ray¹⁰ and colleagues have investigated the effect of inorganic salts (which include sulfate and perchlorate) on the CMC of p-tert-Octylphenoxy (polyethoxy) ethanol,

OPE₃₀ and OPE₉₋₁₀ in aqueous solution at 25°C. Their findings show that the CMC is lowered by all salts except Lithium iodide, which increases the CMC. By plotting CMC versus salt concentration it was found that the sulphate is the ion most effective at lowering the CMC and has the steepest slope, while the perchlorate has less of an effect than the sulphate. Ray¹⁰ concluded that the reduction in the CMC was due to the salting out or in

of the hydrocarbon moiety of the detergent.

The CMC is essentially independent of sodium perchlorate concentration, whereas for sodium sulfate it drops linearly, as shown in Figure 2. However, in general the CMC values in the presence of perchlorate is higher than in its absence, while the opposite is true for sulphate. This indicates the salting in and out effect of perchlorate and sulfate respectively.

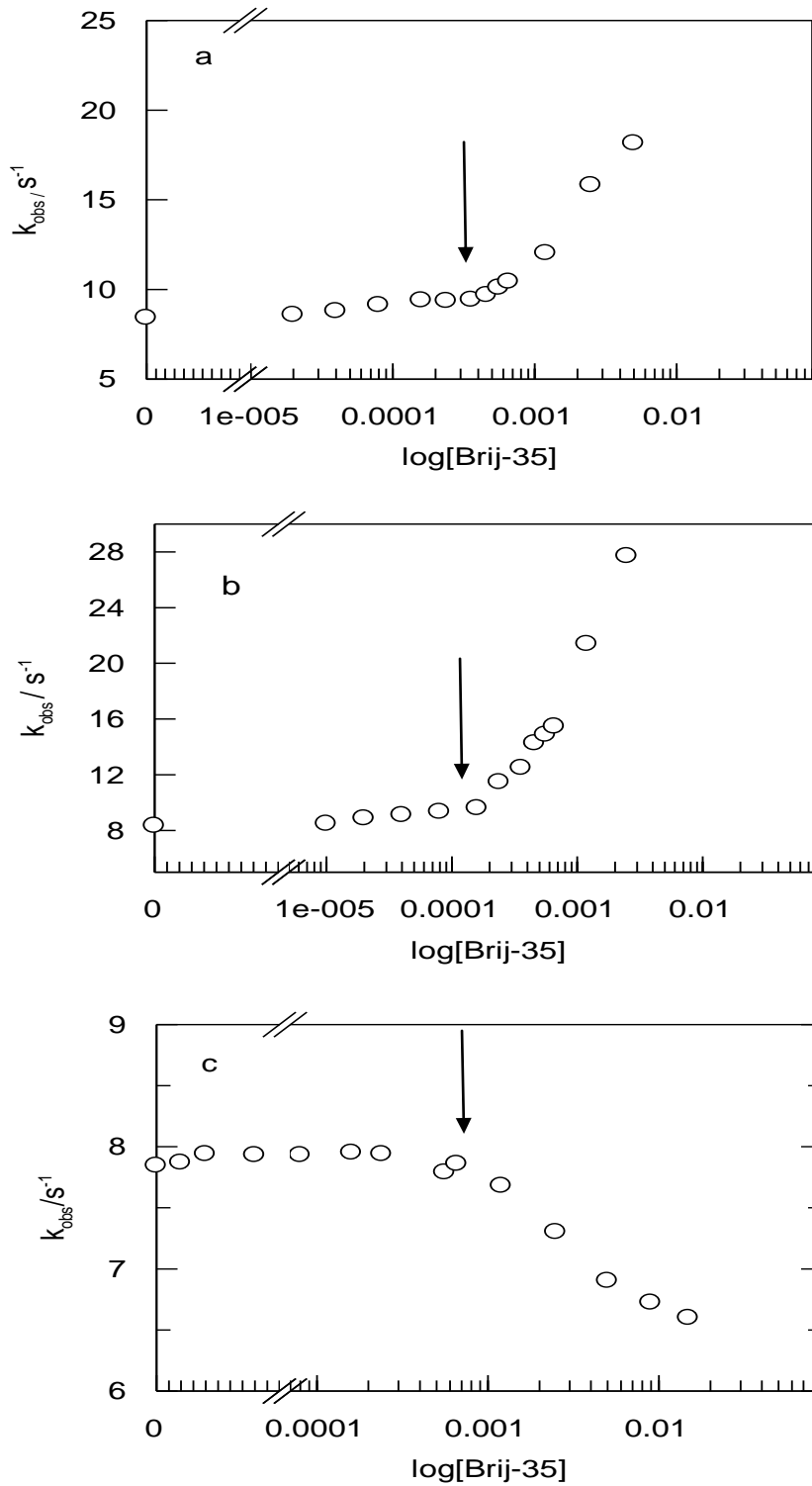


Figure 1: Observed rate constant versus logarithm of Brij-35 concentration for the reaction in water (a), 0.35 M sulfate (b), and 1 M perchlorate (c) at 25°C.

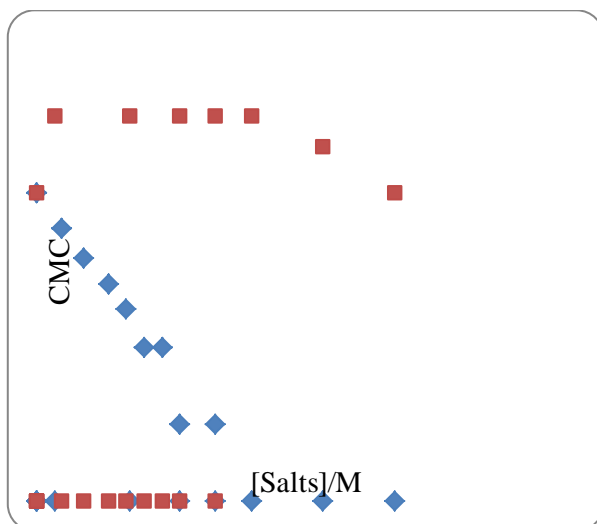


Figure 2: Critical micellar concentrations at different added salt concentrations. Squares represent perchlorate and diamonds represent sulfate.

Table 1: Effect of sodium sulfate on the CMC for the reaction of *ca.* 4×10^{-6} M MCPBA and 1.5×10^{-3} M iodide in 3.0×10^{-3} M nitric acid at 25°C.

[Na ₂ SO ₄], M	(<i>k</i> _{obs}) _o , s ⁻¹	CMC, 10 ⁻⁴ M
0.07	8.7	3.6
0.13	8.4	3.2
0.20	8.4	2.8
0.25	8.3	2.5
0.30	8.7	2.0
0.35	8.3	2.0
0.40	8.8	1.6
0.50	8.9	1.0

Table 2: Effect of sodium perchlorate on the CMC for the reaction of *ca.* 4×10^{-6} M MCPBA and 1.5×10^{-3} M iodide in 3.0×10^{-3} M nitric acid at 25°C.

[NaClO ₄], M	(<i>k</i> _{obs}) _o , s ⁻¹	CMC, 10 ⁻⁴ M
0.05	8.5	5.0
0.26	8.2	5.0
0.40	7.9	5.0
0.50	8.0	4.5
0.60	8.1	4.5
0.80	8.1	4.0
1.00	7.8	4.0

3.2. Effect of temperature on the micelle formation

It has been observed that for non-ionic surfactants, CMC decreases with an increase in temperature due to an increase in hydrophobicity caused by the destruction of hydrogen bonds between water molecules and hydrophilic groups. The plot of $\log c_{mc}$ against $1/T$ is almost linear, and as the process of micellization is one of the most important characteristics of a surfactant solution⁴, this plot is used to derive the thermodynamics of micelle formation, which can help us to understand the nature of thermodynamics and the driving force behind micelle formation.

From Table 3 to 5 it is clear that temperature induces micellization in the absence and presence of sulphate salt. Also, the data show that the CMC is lowered by increasing the temperature, which is a well documented finding¹. Megure¹¹ has extensively reviewed the effect of temperature on the CMC of non-ionic surfactants and has compiled CMC dependent temperatures for several non-ionic surfactants of the type ($C_n E_m$), in which n is the number of carbon in the alkyl chain and m is the number of oxyethylene groups in the

surfactant. All the CMC temperature data (with temperature ranging from 15°C to 40°C) in his review show that CMC is decreased as temperature is raised, which is a similar finding to what we have observed.

The variation of CMC with temperature can be used to calculate the enthalpy and entropy of micellization, as shown in Figure 3a which plots the natural logarithm of CMC as a function $1/T$ for the reaction in water, 0.35 M sulfate and 1 M perchlorate respectively. From the slope and intercept of this plot the enthalpy and entropy of micellization was calculated. The entropy of micellization, ΔS_m^0 , versus the enthalpy of micellization, ΔH_m^0 , is shown in Figure 3b. This plot shows that the micellization process exhibits compensation phenomena, as stated in^{12,13} in which an increase in the entropy ΔS_m^0 is compensated by a decrease in enthalpy, the reaction in presence of sulphate which has the highest entropy of micellization due to an increase in the disorder of the system. On the other hand, perchlorate decreases the entropy of micellization even it break structure of water. From Figure 3b it

can be seen that the micellization associated with enthalpy-entropy compensation is a universal phenomenon that can be seen in most chemical and biological processes^{12,13}. Plots of enthalpy against entropy, or vice versa, are a common approach to displaying thermodynamic data obtained for rate and equilibria processes where structural or solvent effects are being investigated

The calculated thermodynamic parameters of standard free energy and the enthalpy and entropy of micellization in three conditions (in water, 0.35 M sulfate and 1 M perchlorate) are shown in Table 6 with other thermodynamic parameters. These will be discussed in the following sections. The value of standard free energy for Brij-35 in water and sulphate and perchlorate shows that micellization is more spontaneous for all the investigated systems and are similar while the enthalpy and entropy are different.

The significance of these standard values (enthalpy, entropy and free energy of micellization) is that they give an insight into the force driving the micelle formation. From Table 6 it can be seen that the free energy is large

and negative, while enthalpy of micellization is positive, indicating that the micelle formation is an endothermic process. In addition, entropy is large and positive, which suggests that the micellization process results in an increase in entropy. Also, Table 6 shows that the value of free energy for the three studied systems is about -20 kJ/mol^{-1} which accounts for the compensation effect illustrated in Figure 3b.

The large positive entropy ΔS_m^0 is considered to be primarily due to the disruption of the iceberg structure of water during the course of micellization, and the larger positive ΔS_m^0 in sulphate can be due to the contribution of sulphate to dehydration of polyoxyethylene head group of Brij-35. The addition of perchlorate reduces the entropy and this may be due to the fact that perchlorate increase the hydration of hydrophobic group of Brij-35 and thus reduce the number of available water in solution, and this lead to weaken of hydrophobic interaction, which are the important driving force for micelle formation. These ions prefer to bind to the zwitterionic micelle sulfobetaine, which may actually be happening here; thus, repulsion of the monomer causes

an increase in the CMC, compared to that which occurs in the absence and presence of sulfate.

Rakshit and co-worker¹⁴ conducted a thermodynamic study into the pure aqueous solution of Brij-35 and also in the presence of different concentrations of polyethylene glycol solvents. Their general conclusion was that CMC is decreased by increasing the temperature from 35 °C to 50° C in an aqueous system and in the presence of the additive PEG. The calculated thermodynamic parameters for the process of micellization show that micelle formation was exothermic in the presence of the additive but endothermic in the pure aqueous solution. Also, the entropy of micellization was positive in all cases. They attributed this high entropy change to phase change, and also to the breakdown of water structure on micellization.

In general, the results obtained in this study are similar to those of Rakshit and co-worker¹⁴, in which the CMC is lowered by increasing the temperature and the entropy and enthalpy of micellization are positive in all conditions. Tadros⁶ has shown that the

thermodynamic of non-ionic micelle formation can be calculated from a plot of log CMC versus 1/T. The results in this study show the same behavior and the micellization process is associated with positive standard enthalpy and large positive standard entropy (see Table 6). These positive values were attributed to an increase in the disorder of the system: even though the aggregation leads to entropy loss, the main reason behind the positive entropy is the desolvation of the ethylene oxide chain and a release of more water molecules. Another factor contributing to the large positive entropy upon micellization is the increase in flexibility of the hydrocarbon chain upon its transfer from the aqueous phase to hydrocarbon medium in the micelle core; thus the orientation of the organic chain is more restricted in the aqueous phase than in the organic phase⁶. Also, in a non-ionic micelle increasing the polyoxyethylene chain causes an increase in the CMC and decreases the micelle size¹. This gives the monomer more hydrophilic character and thus higher CMC.

The process of micelle formation has been described as an example of entropy that is driven by the

hydrophobic bond; when the micelle is formed the surfactant monomers come close to each other and produce one cavity (before, each monomer has its own cavity), which is smaller than the sum of the two separated cavities

accommodating each monomer. This contraction in the cavity is entropy driven and ΔS_m^0 become more positive as a result of the release of water and distribution of the solute –solute or solute-solvent interaction¹⁵.

Table 3: Effect of temperature in the absence of added salt: for the reaction of *ca.* 4×10^{-6} M MCPBA and 1.5×10^{-3} M iodide in 3.0×10^{-3} M nitric acid.

T, °C	$(k_{obs})_o, s^{-1}$	CMC, 10^{-4} M
15	5.1	5.0
20	6.5	4.3
25	8.4	4
30	10.3	3
35	12.9	2.0

Table 4: Effect of temperature in the presence of 0.35 M sodium sulfate: for the reaction of *ca.* 4×10^{-6} M MCPBA and 1.5×10^{-3} M iodide in 3.0×10^{-3} M nitric acid.

T, °C	$(k_{obs})_o, s^{-1}$	CMC, 10^{-4} M
15	5.3	4.5
20	6.8	4.0
25	8.3	2.0
30	10.8	1.6
35	13.1	1.0

Table 5: Effect of temperature in the presence of 1.0 M sodium perchlorate:, for the reaction of *ca.* 4×10^{-6} M MCPBA and 1.5×10^{-3} M iodide in 3.0×10^{-3} M nitric acid.

T, °C	$(k_{obs})_o, s^{-1}$	CMC, 10^{-4} M
15	4.77	5.4
20	6.2	4.8
25	7.9	4.0
30	9.9	3.8
35	12.4	3.4

Table 6: Calculated thermodynamic parameters for the reaction of 0.0015 M potassium iodide and 4×10^{-6} MCPBA in 0.003 M nitric acid.

	Added salt		
	None	0.35 M Na ₂ SO ₄	1.0 M NaClO ₄
$\Delta H^\ddagger(k_{\text{obs}})$, kJ mol ⁻¹	31.5 ± 0.65	30.7 ± 0.7	32.9 ± 0.2
$\Delta S^\ddagger(k_{\text{obs}}/s^{-1})$, J mol ⁻¹ K ⁻¹	-122 ± 2	-124 ± 2	-117.5 ± 0.6
$\Delta G^\ddagger(k_{\text{obs}})$, kJ mol ⁻¹	67.8 ± 2.1	67.6 ± 2	67.9 ± 0.63
ΔS_m^0 , kJ mol ⁻¹	25 ± 4	60 ± 7	17 ± 2
ΔH_m^0 , J mol ⁻¹ K ⁻¹	150 ± 10	270 ± 20	122 ± 5
ΔG_m^0 , kJ mol ⁻¹	-19.68 ± 4.8	-20 ± 5.3	-19.2 ± 2

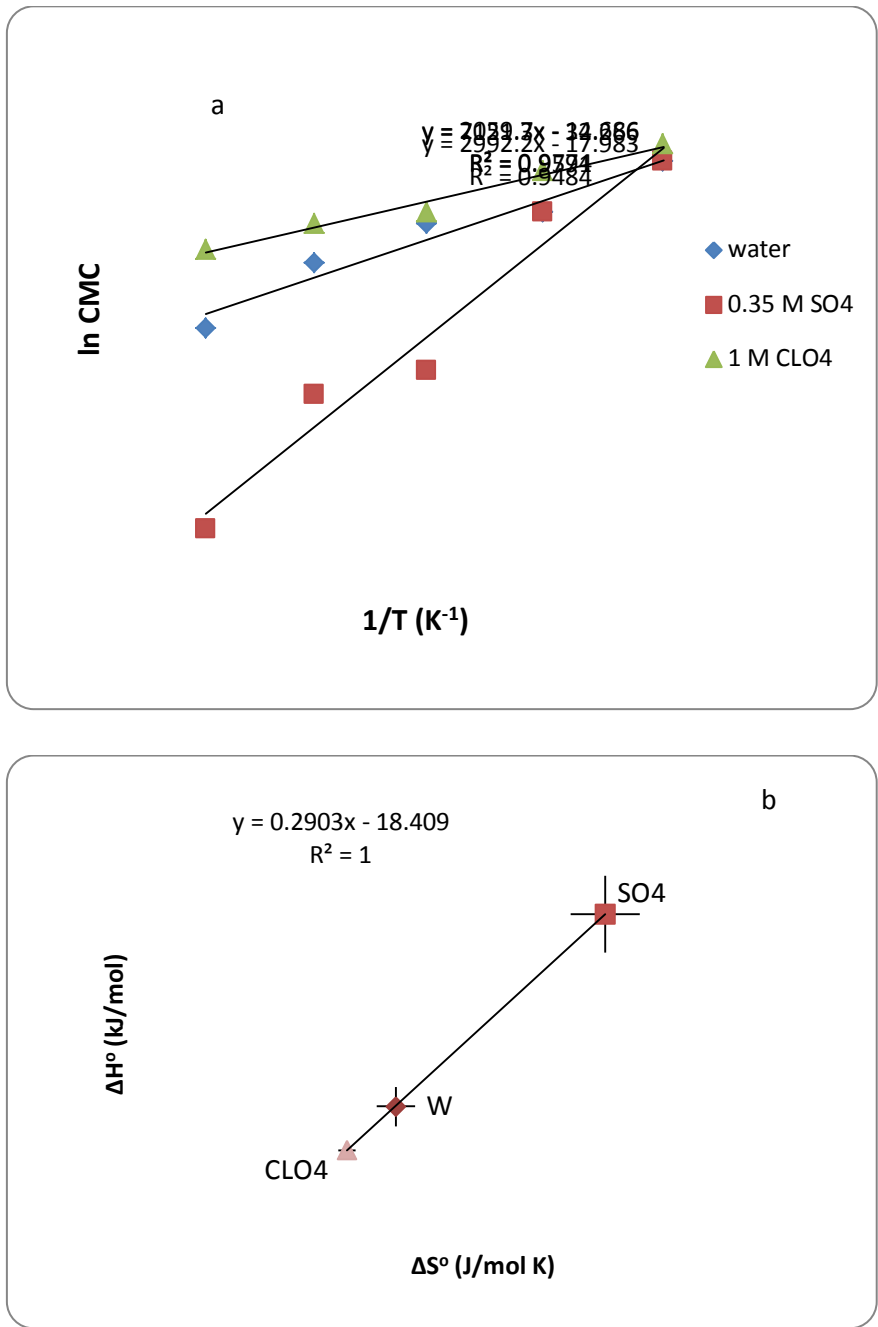


Figure 3.: Plot of reciprocal of temperature versus natural logarithm of the critical micelle concentration for the reaction of MCPBA 4×10^{-6} M with 0.0015 M potassium iodide in 0.003 M nitric acid in water, 0.35 M sulfate and 1 M perchlorate (a), (b) shows the enthalpy versus entropy of micellization data taken from Table 6. The isokinetic temperature is 290 K.

Conclusion

The critical micelle concentration (CMC) was determined kinetically under several different conditions. Increasing the temperature was found to cause a decrease in the CMC for the MCPBA-iodide reaction; an increase in the sulfate concentration was also found to decrease the CMC, though the presence of perchlorate has limited affect on the CMC. Plots of enthalpy against entropy, or vice versa, are common approaches to displaying thermodynamic data obtained for rate and equilibria processes where structural or solvent effects are being investigated

It was found that there was a very good linear relationship between entropy and enthalpy micellization

process (enthalpy-entropy compensation). This can be attributed to that the enthalpic gain is offset, either partly or wholly by an entropic penalty, and vice versa, resulting in a smaller than expected, or negligible change to the overall free energy and this is illustrated by the nearly constant value of free energy as seen in Table 6. Finally, enthalpy-entropy compensation plots when applied to individual reaction, determined under the different conditions by the same method, enthalpy-entropy compensation plots are a useful tool for visualising thermodynamic data and showing differences between different systems and its occurrence may be indication of the presence of the same mechanism

تقدير المحتوى الحراري والانتروبييا لتكوين البوليمر (micelle) للمركب Brij-35

- ودراسة تأثير الأملاح على التركيز الحرج لتكوين البوليمر

سالم منصور موسى

كلية العلوم جامعة سبها قسم الكيمياء

في هذه الدراسة تم تحديد المحتوى الحراري والانتروبييا لتكوين البوليمر الغير قطبي (بولي اوكسي ايثيلين الايثر، Brij-35) وهو من المركبات الفعالة سطحيا. $(C_{12}E_{23} \text{ i.e. } CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH)$ من البيانات الحركية والتفاعل المستخدم هو اختزال m-Chloroperbenzoic acid باليود. يحدث التفاعل في وسط

حمضي من HCl بتركيز 0.003M في غياب وفي وجود كلا من كبريتات الصوديوم وبيركلورات الصوديوم عند درجات حرارة مختلفة. ويكون التركيز الابتدائي لليود والحمض هي $1.5 \times 10^{-3} M$ و $4 \times 10^{-6} M$ على التوالي. اظهرت النتائج ان ايون الكبريتات (وهو هيدروفيلك ايون تبعا لسلسلة هوفميسر) يزيد من معدل التفاعل ويعمل على خفض التركيز الحرج للبوليمر (CMC)، بينما بيركلورات (وهو هيدروفوبيك ايون تبعا لسلسلة هوفميسر) يعمل على تقليل معدل سرعة التفاعل وله تاثير قليل على (CMC). وكذلك اظهرت النتائج ان الزيادة في درجة الحرارة يصاحبها خفض في قيمة CMC للبوليمر.

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