

Conductance Study of the Thermodynamics of Micellization of 1-Hexadecylpyridinium Bromide in Mixed Solvents Containing Dilute Electrolyte Solutions

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The critical micelle concentration (CMC) of hexadecylpyridinium bromide (HDPB) is determined conductometrically in binary mixtures of water + cosolvent at various temperatures and at low concentrations of sodium bromide, ranging from 0 to 2.4×10^{-2} M. Dimethylsulfoxide (DMSO) and acetonitrile (AN) were used as cosolvents added to water. The ability of NaBr to lower the CMC of HDPB in water is inhibited by DMSO and AN. Thermodynamic parameters of micellization ΔH_m° , ΔS_m° , and ΔG_m° are evaluated according to the pseudo-phase model. The contribution of DMSO and AN in the micellization process of HDPB in aqueous electrolyte solutions are discussed in terms of the observed thermodynamic properties.

Keywords: Micellization, Dimethylsulfoxide, Acetonitrile, Counter ion

INTRODUCTION

In aqueous solution, the presence of electrolytes causes a decrease in the critical micelle concentration (CMC) of most surfactants, with the greatest effect being found for ionic surfactants [1-3]. The observed depression of the CMC value is primarily due to a reduction in the electrostatic repulsions between head groups in the presence of the excess counter ions from the electrolyte. The repulsion between head groups of surfactants is one of the main factors opposing micellization [4].

On the other hand, the addition of non-electrolytes to solutions of ionic surfactants is well known to influence their micellar properties by changing the structure of the solvent and the surfactant aggregates [1,5-7]. In a previous paper [7], micellization of hexadecylpyridinium bromide (HDPB) in various water-cosolvent mixtures was investigated. In all solvent mixtures studied, the CMC of HDPB increased with

respect to pure water. Previous studies show that the inhibitory effect of the cosolvent on micelle formation is due to the dielectric constant (ϵ) of the cosolvent and its hydrophobic character [6,8-12]. A decreased dielectric constant of the solvent mixture results in an easier denaturation of the micelles. Moreover, organic cosolvents with large hydrophobic surfaces break the micelles effectively. Acetonitrile (AN), because of its large hydrophobic character, has a strong effect on the HDPB micellization equilibrium.

In the present work, we report the effect of the presence of DMSO and AN as cosolvents added to water on the micellization process of HDPB at low concentrations of NaBr, ranging from 0 to 2.4×10^{-2} M. The formation of micelles was conductometrically followed at 25, 35, 45 and 55 °C.

EXPERIMENTAL

Triple-distilled deionized water was used throughout. HDPB (BDH-Sigma) was recrystallized four times from water and dried under reduced pressure over P_2O_5 . Reagent grade

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DMSO and AN (both from Merck) were used to prepare the different water-cosolvent mixtures by weight. Sodium bromide (Merck) was used without further treatment.

Conductance measurements were carried out with a Metrohm 712 conductivity meter using a dip-type cell made of platinum black. In all experiments, the cell was thermostated at the desired temperature ± 0.1 °C using an MLW thermostat. The reproducibility of the conductance measurements was estimated to be $\pm 0.5\%$.

RESULTS AND DISCUSSION

The CMC values of HDPB in different water-DMSO and water-AN mixtures were measured conductometrically in the presence of different concentrations of NaBr. Figure 1 shows typical plots of specific conductance (k) against the molar concentration of HDPB. The intersection of the two straight lines in each plot corresponds to the CMC. In water, the addition of NaBr lowers the CMC of HDPB continuously, as is obvious from Figs. 1 and 2. The excess of bromide ions in the micellar solution reduces the repulsion between pyridinium head groups, which favors the micellization and reduces the CMC.

On the other hand, cosolvents such as DMSO and AN when added to water increase the CMC value of HDPB, as was observed previously [7,8,10]. The increase in CMC values with cosolvent mass fraction can be explained by the decrease in polarity of water with the addition of cosolvent, which increases the solubility of the hydrocarbon chain of the surfactant monomer, thus, decreasing the driving force for monomer aggregation.

The results show that cosolvents have a greater effect than NaBr on the micellization of HDPB. In other words, DMSO and AN inhibit the formation of micelles even in the presence of NaBr. Typical plots are given in Fig. 3. All results are summarized in Tables 1 and 2. In the solvent mixture of AN + H₂O, shown in Fig. 3b, the CMC reducing effect of NaBr is greatly inhibited.

The relationship between $\ln(\text{CMC})$ and $\ln([\text{NaBr}] + \text{CMC})$, well-known as Corrin-Harkins plots, are shown in Fig. 4. As is obvious, in the absence of the cosolvents, the CMC of HDPB decreases as the total concentration of the counter ion in the solution increases; the slope of the resultant line corresponds

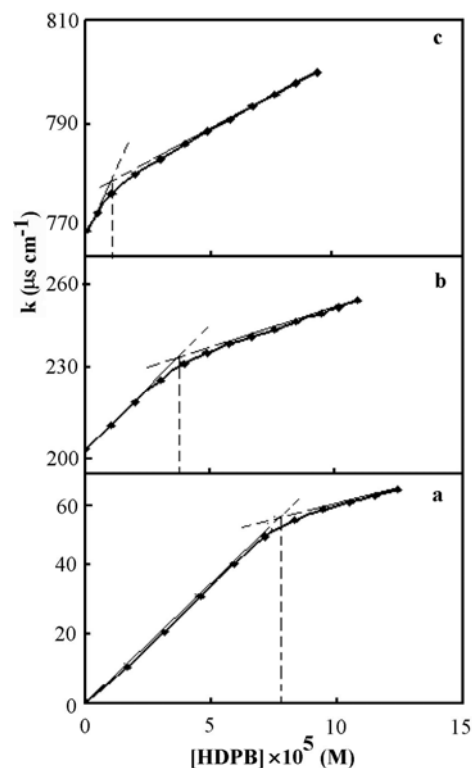


Fig. 1. Specific conductivity against HDPB concentration in water in the presence of NaBr concentrations of: (a) 0.0 M, (b) 2.0×10^{-3} M, (c) 8.0×10^{-3} M.

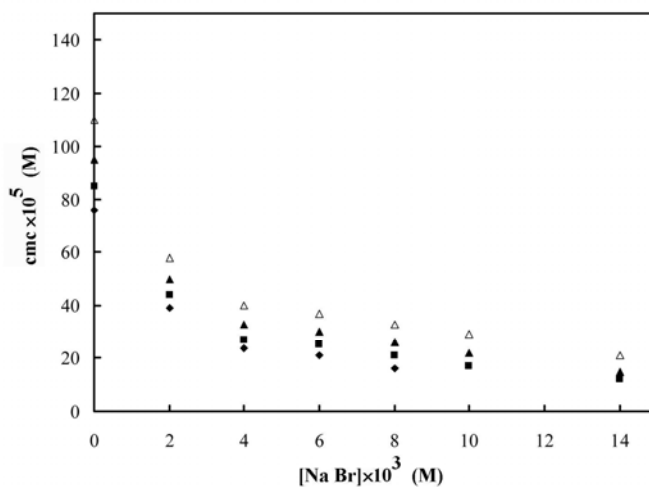


Fig. 2. Effect of NaBr concentration on CMC of HDPB in pure water at different temperatures 25 (◆), 35 (■), 45 (▲) and 55 °C (Δ).

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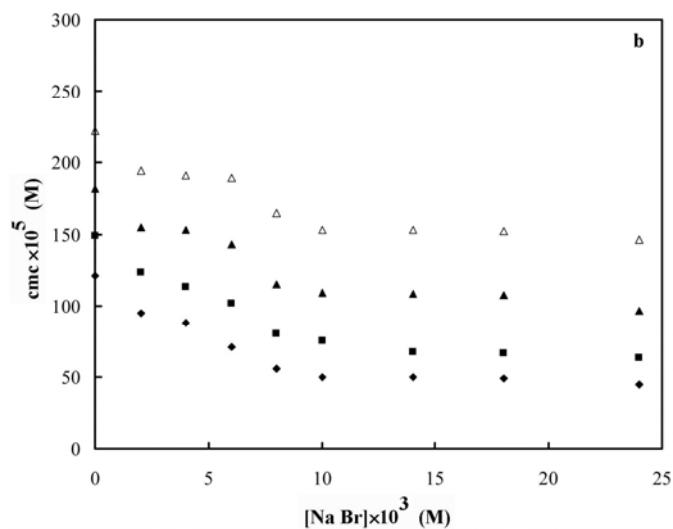
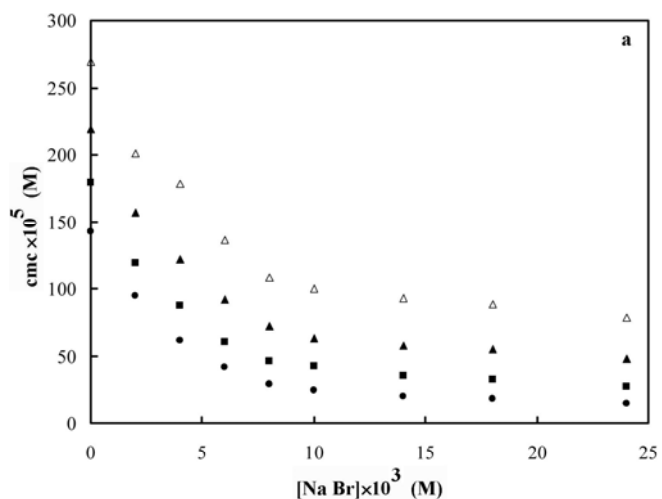


Fig. 3. Effect of NaBr concentration on CMC of HDPB in binary mixtures DMSO + H₂O (a) and AN + H₂O (b), at temperatures 25 (●), 35 (■), 45 (▲) and 55 °C (Δ). The mass fraction of DMSO and AN in the mixtures is 0.20.

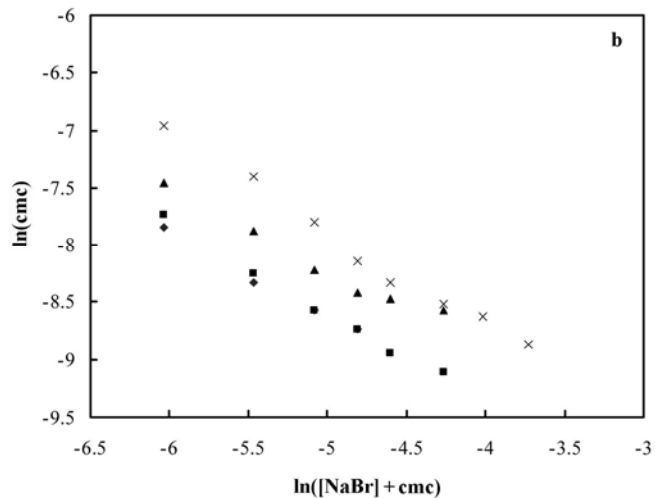
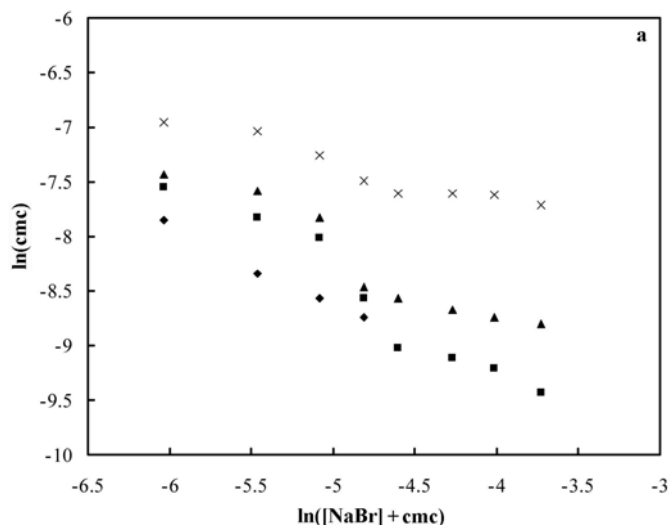


Fig. 4. LnCMC against ln([NaBr] + CMC) for solvent mixtures AN + H₂O (a) and DMSO + H₂O (b) at 25 °C. The mass fraction of the cosolvents are 0.00 (◆), 0.05 (■), 0.10 (▲) and 0.20 (×).

to the degree of counter ion binding to the micellar surface, β [13]. In the presence of the cosolvents, β decreases, which is related to the decrease in charge density of the Stern layer of the micelles formed, thereby decreasing the number of bromide ions bound to micelles [14].

In order to have a better understanding, the thermodynamic

parameters of micellization, ΔH_m° , ΔS_m° , and ΔG_m° , were evaluated according to the pseudo-phase model [15]. The corresponding equations are:

$$\Delta G_m^\circ = (2 - \alpha) RT \ln X_{CMC} \quad (1)$$

Table 1. Calculated CMC Valuse of HDPB in the Presence of Different Concentration of NaBr in Different DMSO + H₂O Mixtures at Various Temperatures (°C)

[NaBr] × 10 ³ (M)	CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)			
	25	35	45	55	25	35	45	55	25	35	45	55	25	35	45	55
	0 wt.% DMSO				5 wt.% DMSO				10% DMSO				20% DMSO			
0	76	85	95	110	85	93	104	115	109	125	144	170	142	179	219	269
2	39	44	50	58	44	53	64	81	60	72	87	107	95	119	157	201
4	24	27	33	40	25	33	42	57	40	50	64	79	61	87	122	178
6	21	25	30	37	19	24	34	44	30	40	54	70	41	60	92	136
8	16	21	26	33	17	22	29	38	22	32	45	65	29	46	72	108
10		17	22	29	13	18	25	32	21	30	44	63	24	42	63	100
14		12	15	21	11	15	22	29	19	29	43	62	20	35	58	93
18						13	19	26		25	39	57	18	32	55	88
24							15	22		21	32	51	14	27	48	78

Table 2. Calculated CMC Valuse of HDPB in the Presence of Different Concentration of NaBr in Different AN + H₂O Mixtures at Various Temperatures (°C)

[NaBr] × 10 ³ (M)	CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)				CMC × 10 ⁵ (M)			
	25	35	45	55	25	35	45	55	25	35	45	55	25	35	45	55
	0 wt.% AN				5 wt.% AN				10% AN				20% AN			
0	76	85	95	110	82	98	118	134	130	140	150	158	131	150	175	205
2	39	44	50	58	34	42	54	65	61	74	94	110	103	123	153	192
4	24	27	33	40	26	32	42	52	33	42	54	76	88	113	153	191
6	21	25	30	37	22	27	35	45	28	38	52	70	71	101	143	189
8	16	21	26	33	19	24	33	43	22	31	42	60	56	80	115	165
10		17	22	29	12	17	23	30	20	29	40	56	50	75	109	153
14		12	15	21	11	16	22	30	17	26	36	51	50	68	108	153
18					10	15	22	30	16	25	34	50	49	67	107	152
24					8	12	17	25	15	23	32	49	45	63	96	146

$$\Delta H_m^\circ = -(2 - \alpha) RT^2 d(\ln X_{CMC})/dT \quad (2)$$

$$\Delta G_m^\circ = \Delta H_m^\circ - T \Delta S_m^\circ \quad (3)$$

In these equations, α is the degree of dissociation of the micelle, which is obtained from the ratio of the slopes of the

straight line segments of post- and pre-micellar regions of the plots of specific conductance (k) vs. the molar concentration of HDPB (Fig. 1). X_{CMC} is the mole fraction of the surfactant at the CMC. All the calculated thermodynamic parameters are listed in Tables 3 and 4. For comparison, the experimental data in the previous study [7] (α and CMC for micellization of

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Table 3. Thermodynamic Parameters of Micellization of HDPB in the Presence of Various Concentrations of NaBr in Different DMSO + H₂O Mixtures at 25 °C

[NaBr] × 10 ³ (M)	0% DMSO			5% DMSO			10% DMSO			20% DMSO		
	ΔH _m ^{oa}	ΔS _m ^{ob}	ΔG _m ^{oc}	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o
0	-15.5	108	-47.7	-16.5	103	-47.2	-19.0	93	-46.6	-26.0	57	-42.8
0 ^d	-15.9	106	-47.8									
2	-17.1	115	-51.4	-24.6	88	-50.8	-27.4	77	-50.4	-33.3	49	-47.9
4	-22.0	102	-52.6	-29.4	77	-52.4	-34.5	60	-52.4	-44.7	10	-47.6
6	-29.0	90	-55.8	-36.2	59	-53.8	-43.2	29	-51.8	-52.2	-5	-50.8
8	-31.1	82	-55.6	-42.9	64	-62.0	-47.6	24	-54.8	-58.0	-16	-53.1
10				-35.8	52	-51.3	-48.1	21	-54.3	-65.5	-28	-57.2
14				-40.9	45	-54.5	-46.6	10	-49.6	-70.0	-44	-56.8
18										-69.1	-48	-54.6
24										-79.5	-68	-59.3

^akJ mol⁻¹. ^bJ mol⁻¹ K⁻¹. ^ckJ mol⁻¹ (estimated uncertainties are ±0.2 kJ mol⁻¹ in ΔH_m^o, ±2 J mol⁻¹ K⁻¹ in ΔS_m^o and ±0.1 kJ mol⁻¹ in ΔG_m^o). ^dCalculated from the data given in Ref. [7].

Table 4. Thermodynamic Parameters of Micellization of HDPB in the Presence of Various Concentrations of NaBr in Different AN + H₂O Mixtures at 25 °C

[NaBr] × 10 ³ (M)	0% AN			5% AN			10% AN			20% AN		
	ΔH _m ^{oa}	ΔS _m ^{ob}	ΔG _m ^{oc}	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o	ΔH _m ^o	ΔS _m ^o	ΔG _m ^o
0	-15.5	108	-47.7	-18.9	78	-42.3	-17.4	58	-34.9	-19.4	49	-34.0
2	-17.1	115	-51.4	-23.3	88	-49.6	-23.8	57	-40.7	-25.5	45	-39.0
4	-22.0	102	-52.6	-26.6	85	-52.0	-29.8	53	-45.6	-28.4	37	-39.4
6	-28.8	90	-55.8	-28.4	78	-51.7	-41.6	37	-52.6	-36.2	16	-41.1
8	-28.8	90	-55.8	-36.8	64	-55.9	-42.4	29	-51.1	-39.3	7	-41.5
10				-35.1	50	-50.2	-45.5	25	-53.3	-41.6	4	-42.8
14				-38.1	41	-50.3	-44.3	23	-51.1	-46.0	0.75	-46.5
18				-47.8	32	-57.4	-42.3	20	-48.2	-44.3	-0.57	-44.1
24				-30.6	20	-36.5	-44.0	15	-48.4	-46.8	-3.03	-45.9

^akJ mol⁻¹. ^bJ mol⁻¹ K⁻¹. ^ckJ mol⁻¹ (estimated uncertainties are ±0.2 kJ mol⁻¹ in ΔH_m^o, ±2 J mol⁻¹ K⁻¹ in ΔS_m^o and ±0.1 kJ mol⁻¹ in ΔG_m^o).

HDPB in pure water) were used to evaluate the thermodynamic parameters according to Eqs. (1-3), with satisfactory results (Table 3). The magnitude and sign of the ΔH_m^o and ΔS_m^o values are in accord with the destruction of hydrophobic hydration in the process of micellization [1,16-

22]. Micelle formation in water is both enthalpically and entropically stabilized. The micelle formation in the NaBr solution is energetically more favorable because of a decrease in repulsions between head groups. The entropy loss is due to the formation of larger micelles in electrolyte solutions

compared to that of water [14,23-24].

On the other hand, the presence of the cosolvents inhibits micellization and reduces the effect of the presence of NaBr. AN is more effective than DMSO in this regard. The values of ΔH_m° and ΔS_m° reveal that the inhibitory effect of AN has an enthalpic origin, mainly because the value of ΔH_m° in the presence of AN is less negative compared to that in the presence of DMSO (Tables 3 and 4). This observation is reasonable due to the lower polarity of AN ($\epsilon = 38$) compared to that of DMSO ($\epsilon = 45$), which increases the solubility of the hydrocarbon chains of the surfactant monomers and hence reduces the tendency of monomers to aggregate. On the other hand, one of the main factors in determining ΔH_m° is the repulsion between head groups at the micellar surface. This repulsion is reduced by electrostatic attraction between head groups of the surfactants and counter ions from the solution. The addition of DMSO or AN to water inhibits the binding of counter ions to the micelles. In the case of AN as a cosolvent, the association of bromide ions with micelles is almost completely inhibited (Figs. 4a and 5), with the consequence of a greater repulsion between pyridinium head groups and thus a greater enthalpic loss.

The data given in Tables 3 and 4 reveal that the micellization process in all cosolvent + H₂O mixtures is associated with an entropic loss compared to that of pure water (due to preferential solvation of the surfactant tail by the cosolvent molecules). Looking at the values of ΔG_m° reveals that the Gibbs free energy changes are almost constant over the entire concentration range of NaBr as well as mass fractions of cosolvents in solution, a correlation that is known as enthalpy-entropy compensation. Actually, there is a fairly good linear correlation between the ΔH_m° and $T\Delta S_m^\circ$ values (Fig. 6) with the regression equation:

$$\Delta H_m^\circ = \Delta H_{0m}^\circ + bT\Delta S_m^\circ \quad (4)$$

in which $\Delta H_{0m}^\circ = -53 \text{ kJ mol}^{-1}$ and $b = 0.80$ are the intercept and slope of the ΔH_m° against $T\Delta S_m^\circ$ plot, respectively, obtained with a regression coefficient of 0.92. Equation 4 suggests that the enthalpic change consists of two components. The first component (ΔH_{0m}°) is independent of the entropy change and the second one ($bT\Delta S_m^\circ$) is proportional to it. The proportionality factor, b , is a quantitative measure of the

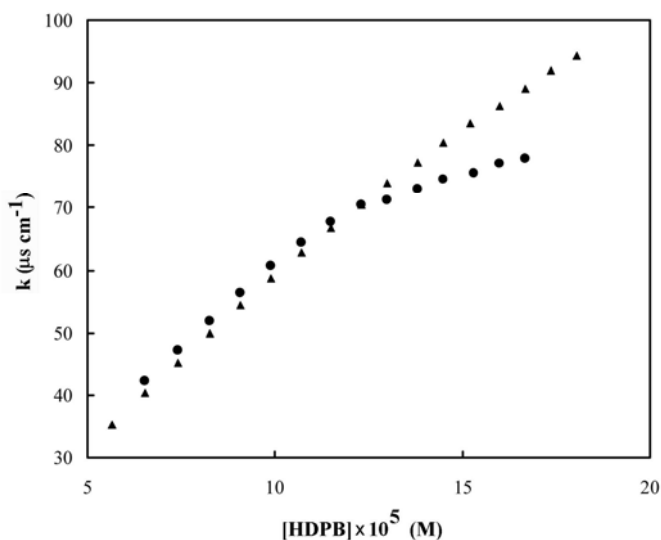


Fig. 5. Specific conductivity against HDPB concentration at 25 °C in DMSO + H₂O (●) and AN + H₂O (▲) mixtures. The mass fraction of DMSO or AN is 0.10.

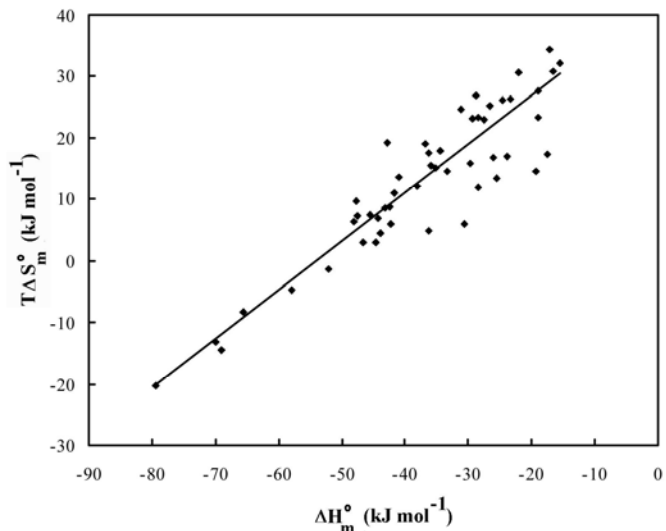


Fig. 6. $T\Delta S_m^\circ$ against ΔH_m° at 25 °C for the micellization of HDPB in various concentrations of NaBr in different solvent mixtures.

enthalpy-entropy compensation. The b value of 0.80 indicates that only 20% of the increase in $T\Delta S_m^\circ$ contributes to an increase in the micelle stability. The negative ΔH_{0m}° value of

-53 kJ mol⁻¹ (the intrinsic enthalpic gain) emphasizes that the micellization is favored even in the absence of any entropic gain. This relationship was observed previously [7,25-26].

The enthalpy-entropy compensation plot obtained in this work was compared with the analogous plot in the previous study [7]. In the previous study, the composition of the binary solvent mixture was varied, while in the present work the composition of the binary solvent mixtures as well as the amount of NaBr present in the solutions were varied. Because of the different solution compositions used, some differences between the slopes and intercepts of the lines was expected. However, a comparison of the results reveals that, although the slopes of the two lines are about the same, a relatively large difference in their intercepts (ΔH_{0m}°) exists. The greater ΔH_{0m}° (-53 kJ mol⁻¹ in this work compared to -42 kJ mol⁻¹ in Jalai *et al.*) may be due to the presence of NaBr, which lowers the repulsions between head groups and makes micelle formation more favorable.

CONCLUSIONS

We studied the effect of the simultaneous presence of an electrolyte (NaBr) and nonelectrolyte species (DMSO and AN) in aqueous solution on the micellization of HDPB. The presence of NaBr favors the micellization of HDPB mainly due to a decrease in repulsions between micelle head groups. Adding a cosolvent, such as DMSO or AN, to water inhibits the formation of micelles because of the increase in hydrophobic character of the mixed solvent, which increases the attraction of surfactant monomers toward the solvent. Changes in the thermodynamic parameters of micellization, ΔH_m° , ΔS_m° and ΔG_m° were related to the presence of NaBr and cosolvents.

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