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ORIGINAL CONTRIBUTION

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Enthalpy-entropy compensation in micellization of sodium dodecyl sulphate in water/methanol, water/ethylene glycol and water/glycerol binary mixtures

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Abstract The enthalpy-entropy compensation in micellization of sodium dodecyl sulphate (SDS) in binary mixtures of water/methanol (MeOH), water/ethylene glycol (EG) and water/glycerol (GL) over a temperature range of 10–60 °C was examined. When the cosolvent concentration was low, the critical micelle concentration (CMC) depended only on the total amount of the hydroxyl group added. When the cosolvent concentration was high, the increase in CMC followed the sequence: MeOH > EG > GL. Enthalpy and entropy changes were evaluated from which the compensation temperature was determined. Both enthalpy and entropy changes decreased on the addition of the cosolvents, indicating a lowering of solution hydrophobicity. The compensation temperature was found as a constant over the cosolvent concentration range, as a result, was not a good index for characterizing the solute/solvent interactions. The two reference temperatures at which the enthalpy or entropy change respectively became zero were strongly influenced by the cosolvent addition, therefore could serve as a proper index for solution hydrophobicity.

Key words Enthalpy-entropy compensation – cosolvent effects – critical micelle concentration – reference temperature – temperature effects

Introduction

Hydrophobicity plays an important role in the thermodynamics of surfactant micellization [1, 2]. ΔH versus ΔS plot (the compensation plot) in micellization process usually exhibits a linear character and the slope has a dimension of temperature which is referred as the compensation temperature T_c [3–7]. The compensation temperature is proposed as a characteristic of solute-solute and solute-solvent interactions [6, 7].

Recently, based on experiments over a wide range of temperature, many workers had re-examined the nature of the hydrophobic effect (e.g., see refs. [8–16]). Two reference temperatures, T^* (= 112 °C) and T_H, at which the entropy and enthalpy change for each hydrophobic compound in a series were respectively a common value, were found to be essential in hydrophobicity [13]. Murphy [16] has proposed that the compensation temperature is a combined effect of the two reference temperatures. Similar conclusion has been drawn in ionic micellization process [17]. Although the existence of a region of highly structured water (the iceberg) around a nonpolar solute molecule had been criticized [9], the water molecules close to the hydrophobic surface are still not the same as those in the bulk water. The assembly of these "anomalous" water molecules which may exist surrounding the hydrophobic tail of the surfactant monomer (in aqueous phase) was referred as the "hydration layer" in the present work (The differences between the iceberg concept and the hydration layer mentioned here could be found in [10]).

The effects of addition of organic cosolvents on micelle formation had been studied extensively [18–47]. When a cosolvent was added into the solution, CMC might increase or decrease, depending on whether the cosolvent will penetrate into the micelle, the strength of interactions between cosolvent molecules and water molecules around the hydrophobic tail of the surfactant monomer, or others (a discussion can be found in Hunter [2]).

In a study by Emerson and Holtzer [21], the CMC data for SDS or DTAB in water/MeOH, water/EG and water/GL mixtures were determined at 25 °C. When adding fixed amount of MeOH, EG or GL, the CMC values will increase and the magnitude of increase follows the sequence: GL > EG > MeOH. The addition of one mole of MeOH, EG or GL is equivalent to addition of one, two or three moles of hydroxyl groups into the solution. Notably the CMC data in ref. 21 with MeOH, EG or GL cosolvents will be close if the molarity of the hydroxyl group rather than the molarity of the cosolvent is fixed.

In this study, the CMCs of SDS in water/MeOH, water/EG, and water/GL binary mixtures over a temperature range of 10–60 °C were determined conductometrically. The role of these cosolvents on the enthalpy-entropy compensation in micellization was discussed based on phase separation model. The effects of these organic cosolvents on the two reference temperatures T^* and T_H, and the associated heat capacity changes were also examined.

Experimental

SDS, MeOH, EG and GL were all of GR grade (Merck Taiwan Ltd.) and were used as supplied. Conductometric measurements were made with a Suntax Model SC-17A conductivity meter. Other experimental details could be found elsewhere [17]. CMC was determined by least-square fitting the conductivity-SDS concentration data above and below the transition point with a correlation coefficient greater than 0.9999.

The weight percents for MeOH tests were fixed at 4.8, 9.1 or 16.7% w/w; for EG tests, 4.7, 8.9 or 16.3% w/w; while for GL, 4.6, 8.8 or 16.1% w/w, respectively. The molarity of hydroxyl groups could thereby be kept at three fixed levels: 1.57, 3.21 or 6.42 m. These cosolvent

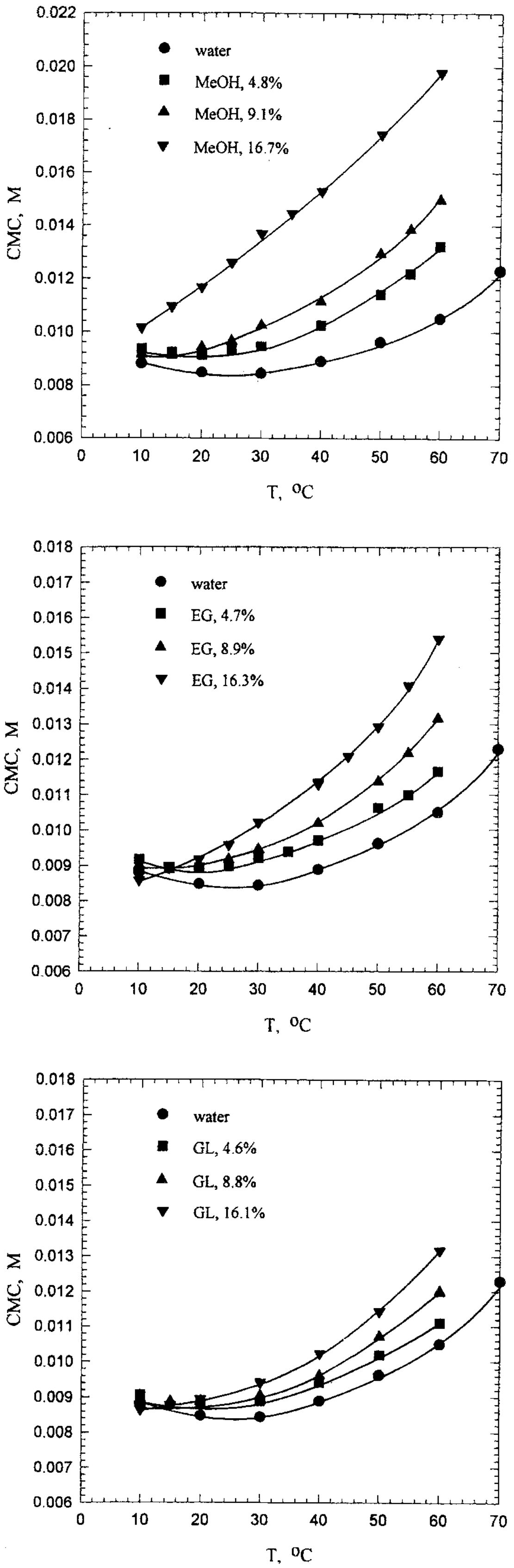

Fig. 1 CMC data versus temperature. (a) water/methanol mixtures (b) water/ethylene glycol mixtures (c) water/glycerol mixtures

concentrations were well below the proposed micelle breakdown limit [38, 39].

At least three runs were conducted for each condition to check the data reproducibility. In most cases, the maximum errors in CMC determination were below 4%. However, due to the less obvious transition of the conductivity-SDS concentration curve when the temperature and/or the cosolvent concentration were high, larger uncertainty existed in these tests.

Results and discussion

The experimental results are summarized in Figs. 1(a)–(c). The CMC data for pure water tests are also shown in these figures for comparison [17, 48, 49]. The data fit very well with those available in literature.

The CMC-temperature curve for each binary mixture exhibits a local minimum as that for the pure water test. The temperature and CMC values of the minimum point can be determined by fitting the experimental data with a fourth-order polynomial and by interpolation, as suggested in [49]. In some high cosolvent concentration tests the minimum point has shifted outside the experimental range. In these cases the minimum point is determined by a slight extrapolation of the best-fitted polynomial. The obtained CMC (CMC_0) and the temperature (T_0) data of the minimum point are listed in Table 1. Clearly the increase in cosolvent concentration shifts the minimum point toward the region of lower temperature. The data for 16.7 w/w water/MeOH test is excluded from Table 1 since the minimum point is rather hard to determine.

Table 1 CMC_0, T_0, T_C, T^* and ΔC_P for various binary water/cosolvent mixtures. SDS

System	CMC_0 10^{-3} M	T_0 °C	T_C °C	T^* °C	ΔC_P J/mol-K
water	8.2	25	32	112	−620
MEOH, 4.8%	9.0	21	35	104	−480
MEOH, 9.1%	9.0	13	32	99	−420
EG, 4.7%	8.9	20	36	105	−470
EG, 8.9%	9.0	15	35	101	−400
EG, 16.3%	8.4	4	31	97	−360
GL, 4.6%	8.7	22	43	109	−490
GL, 8.8%	8.7	15	44	107	−420
GL, 16.1%	8.6	8	32	98	−490

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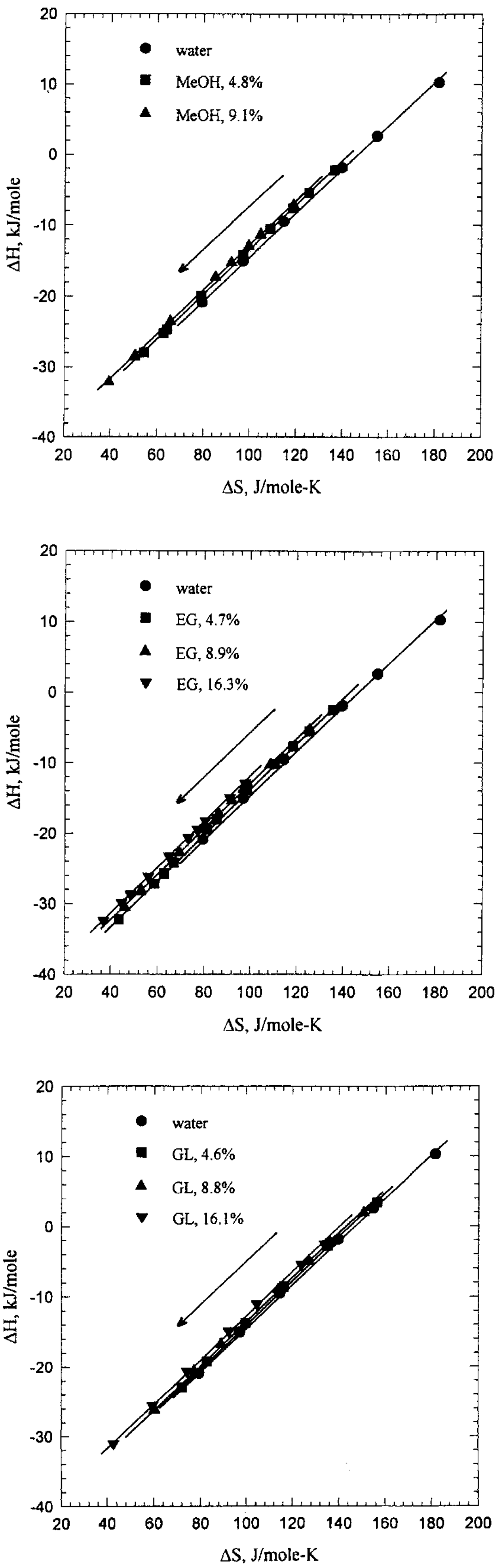
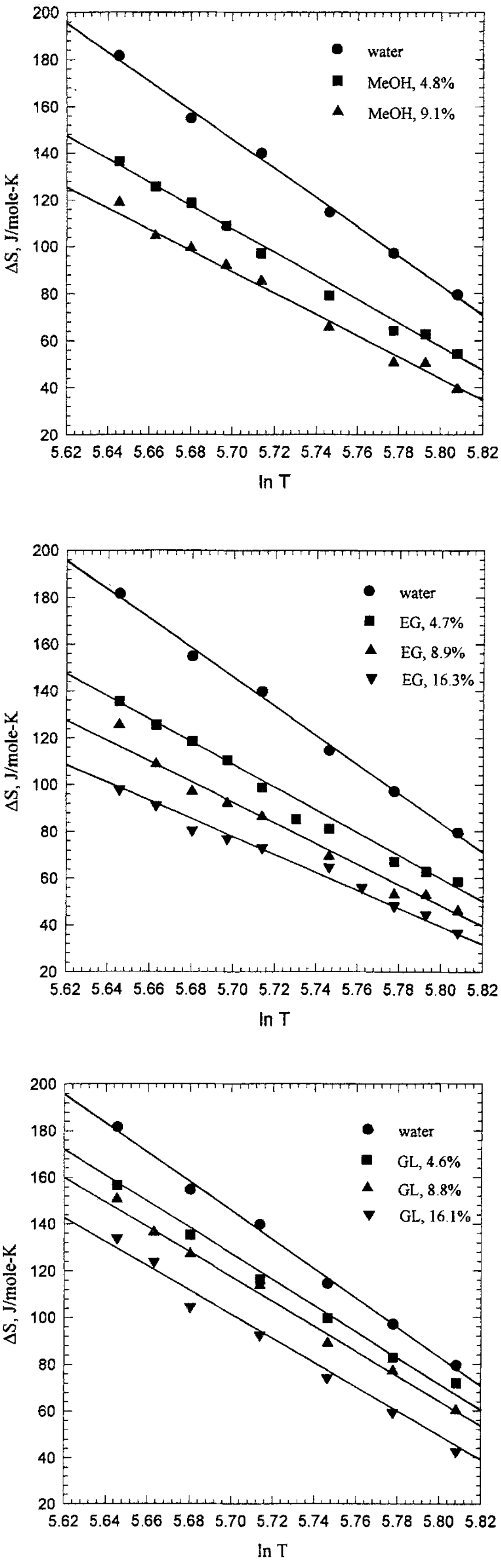


Fig. 2 ΔH versus ΔS. Arrow indicates the increase in temperature. (a) water/methanol mixtures (b) water/ethylene glycol mixtures (c) water/glycerol mixtures



For $T > T_0$ range, CMC increases with increasing cosolvent concentration, indicating that the presence of these organic cosolvent molecules is micelle formation unfavourable [21]. Notably the CMC data for low cosolvent concentration tests (MeOH, 4.8% w/w, EG, 4.7% w/w, GL, 4.6% w/w) are very close. Since the number of the C–OH groups (not the number of cosolvent molecules) in these solutions are the same, the CMC is therefore dependent on the total number of hydroxyl group added, but on the total number of the cosolvent molecules, which is consistent with the previous work at 25 °C [21]. When cosolvent concentration is increased, based on the same molarity of hydroxyl group addition, the increase in CMC follows the sequence: MeOH > EG > GL.

The Gibbs free energy is evaluated based on phase separation model as follows [17]:

$$\Delta G = 2RT \ln(\mathrm{CMC}) . \qquad (1)$$

The entropy and enthalpy changes can then be evaluated from the Gibbs free energy data and are demonstrated in Figs. 2(a)–(c), which are usually referred as the compensation plots. The arrows indicate the increase in temperature.

As shown in Fig. 2, the addition of cosolvent will lower both the entropy and enthalpy changes, which makes a shift of the curves to region of smaller entropy change and more negative enthalpy change. All compensation curves exhibit a similar slope (the compensation temperature), as listed in Table 1. Based on the compensation plot, therefore, the micellization of SDS in these binary mixture systems is still a compensation process as in the pure water [17], and the presence of cosolvent molecules has only a minor effect on the solute/solvent interactions.

However, the addition of these cosolvents does have a strong influence on the ΔS versus $\ln T$ plot, as demonstrated in Fig. 3. A linear relationship as that in the pure water test [17] still holds in all these binary mixtures (though finite scattering exists in some high concentration tests due to the uncertainty in CMC determination). The following basic equation can therefore be employed:

$$\Delta S = \Delta S^* + \Delta C_P \ln \frac{T}{T^*} \qquad (2)$$

where T^* is the reference temperature, ΔS^* the entropy change at $T = T^*$, and ΔC_P the heat capacity change. Take T^* as the temperature at which $\Delta S = 0$, the reference temperature T^* and the heat capacity change can be obtained by linear regression of experimental data with

Fig. 3 ΔS versus $\ln T$. (a) water/methanol mixtures (b) water/ethylene glycol mixtures (c) water/glycerol mixtures a correlation coefficient above 0.98. The results are also listed in Table 1. Since certain errors exist in some high concentration tests and these results should be considered as of a preliminary nature.

Note that the reference temperature T^* is no longer 112 °C as in the pure water test but decreases with increasing cosolvent concentration. Based on phase separation model the reference temperature T_H is equivalent to the minimum point temperature T_0, which is also decreased on the addition of cosolvent. The corresponding heat capacity change for micellization becomes less negative. On each carbon atom of the MeOH, EG or GL molecule there is a hydrophilic (hydroxyl) group, which makes these cosolvent molecules unable to penetrate into the micelle [38]. A possible candidate responsible for the reduction in reference temperatures and heat capacity change is the change in solute/solvent interactions.

The effects of addition of urea on heat capacity change of DTAB in water/urea mixture was found to depend essentially on the surfactant chain length but on the urea concentration [44]. Singh and Ahluwalia [43] also studied the effects of addition of urea on NTAB, SDS, CPB and CPC. Despite of the large uncertainties involved, the partial molar heat capacity of surfactant in micellar phase is shown to be independent of the surfactant species and the cosolvent molecules. The decrease in heat capacity change when urea is added was hence claimed as mainly contributed from the decrease in the partial molar heat capacity of surfactant in the aqueous phase.

We may therefore first assume the heat capacity change reduction found in Table 1 is contributed from the interactions between the cosolvent and the water molecules in the hydration layer surrounding the hydrophobic tail of the surfactant monomer. Since the increase in CMC is mainly determined by the total amount of hydroxyl group but on the cosolvent species when cosolvent concentration is low, it is the binary interactions between water/water and water/hydroxyl group in the hydration layer which dominate. When cosolvent concentration is high, ternary interactions appear and the effect of cosolvent species itself enters.

Clearly the introduction of foreign cosolvent molecules into the hydration layer will interrupt the H-bond networks which raises both the enthalpy and the entropy level of the hydration layer. If further assume the micellar phase is not influenced by the cosolvents as suggested in refs. 43 or 44, at a given temperature, the enthalpy change for micellization will become more negative, and the entropy change less positive. This naturally gives a lower reference temperature to make entropy or enthalpy change zero.

The compensation temperature has been proposed as a combined effect of T^* and T_H [16, 17]. As stated above, since both reference temperatures are reduced when cosolvent is added, the near constant compensation temperatures listed in Table 1 can be a 'compensation' result from the simultaneous reductions of both T^* and T_H. The interpretation based on the compensation plot might therefore be erroneous.

The presence of the cosolvent molecules in the present study reduces both the magnitude of the heat capacity change and the entropy change, or equivalently, the solution hydrophobicity. Since the compensation temperature is found rather insensitive to such a change the reference temperature T^* and T_H are proposed as a better index for solution hydrophobicity.

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