Effects of long-chain alcohols on the micellar properties of anionic surfactants in non-aqueous solutions by titration microcalorimetry

Y. Li · G. Fei · Z. Honglin · L. Zhen · Z. Liqiang · L. Ganzuo

Abstract The power–time curves of micellar formation of two anionic surfactants, sodium laurate (SLA) and sodium dodecyl sulfate (SDS), in N,N-dimethyl acetamide (DMA) in the presence of various long-chain alcohols (1-heptanol, 1-octanol, 1-nonanol and 1-decanol) were measured by titration microcalorimetry at 298 K. The critical micelle concentrations (CMCs) of SLA and SDS under various conditions at 298 K were obtained based on the power–time curves. Thermodynamic parameters ($\Delta H^\circ_{\mathrm{mic}}$, $\Delta S^\circ_{\mathrm{mic}}$ and $\Delta G^\circ_{\mathrm{mic}}$) for micellar systems at 298 K were evaluated according to the power–time curves and the mass action model. The influences of the number of carbon-atom and the concentration of alcohol were investigated. Moreover, combined the thermodynamic parameters at 303, 308 and 313 K in our previous work and those of 298 K in the present work for SLA and SDS in DMA in the presence of long-chain alcohols, an enthalpy–entropy compensation effect was observed. The values of the enthalpy of micellization calculated by direct and indirect methods were made a comparison.

Keywords Long-chain alcohols · Anionic surfactant · Micellar properties · DMA · Microcalorimetry

Y. Li (✉) · G. Fei · L. Zhen · Z. Liqiang · L. Ganzuo
Ministry of Education, Key Lab for Colloid and Interface
Chemistry of Shandong University, Jinan 250100,
People's Republic of China
e-mail: ylmlt@sdu.edu.cn

Z. Honglin
College of Chemical Science, Qufu Normal University,
Qufu Shandong 273165, People's Republic of China

Introduction

The micelle formation in the aqueous solution is known to be affected by organic additives, and there have been many studies on the effect of organic additives on the CMC of the surfactants [1–5]. Recently, increasing attention has been devoted to the studies of the effects of the organic additives, on the micellization processes in the non-aqueous solutions [5–8]. Especially, increasing interest is being concentrated on the studies of the incorporation or solubilization of alcohols, which play a very important role in the preparation of microemulsions [1–3]. In addition to the importance of the theoretical study, researches on the effects of alcohol on the CMC and thermodynamic parameters of surfactants in non-aqueous solutions also have some industrial applications [9, 10]. For example, some new highly effective pesticides cannot dissolve in water or non-polar solvents. They have to be made as dusting or wettable powders which lower the killing efficiency and also harm the environment. In order to improve the efficiency, high security and environmentally friendly property, at first these technical materials must be dissolved in a polar solvent, and then form an oil in water microemulsion. Polar organic solvents resembling water in properties, such as ethylene glycol, glycerol, formamide, and N,N-dimethyl acetamide (DMA), have been widely investigated. These solvents share three physical properties [11]: high cohesive energy, high dielectric constant, and hydrogen bonding. However, it has been proposed that the ability for a solvent to form hydrogen bonds is the key condition for micellization [12].

The purpose of our work is to study the effects of some long-chain alcohols on the formation of micelles of anionic surfactants, sodium laurate (SLA) and sodium dodecyl sulfate (SDS) in N,N-dimethyl acetamide (DMA) by

titration microcalorimetric method. Our work essentially involves the determination of the CMCs of the surfactants and the thermodynamic parameters ($\Delta H^{\circ}_{\text{mic}}$, $\Delta G^{\circ}_{\text{mic}}$ and $\Delta S^{\circ}_{\text{mic}}$) of the micellization in DMA/long-chain alcohol and the acquirement of the relationship between these parameters and the number of carbon atoms, the concentration of alcohols and the temperature.

Experimental

Materials

Analytical grade reagent (>99%) DMA was purchased from Tianjin Kermel chemical reagents development center of China. The surfactants (SLA and SDS) and long-chain alcohols (1-heptanol, 1-octanol, 1-nonanol and 1-decanol) (analytical grade, >99%) used in the present work obtained from Shanghai chemical reagents plant of China.

5.0×10^{-3} mol dm^{-3} anionic surfactant (SLA or SDS) solution in DMA was prepared by mass using a Mettler AE 200 balance with a precision of ±0.0001 g in the presence of 0.10, 0.50, 1.0, 1.5 mol dm^{-3} alcohol.

Instruments

The calorimetric system was a 2277-Thermal Activity Monitor (Made in Sweden). 4 cm^3 stainless steel titration ampoule units are inserted into the thermostats. The titration ampoule units are equipped with a stirrer at the desired speed (0–120 rpm). The performance of the calorimeter was periodically calibrated electrically and verified by measuring the dilution enthalpies of concentrated sucrose solution [13, 14].

Methods

In this experiment, a 4 cm^3 stainless steel titration ampoule microcalorimetric unit was used. A titrating tube was used to pump 0.5 cm^3 solution (see the components above) into DMA in the ampoule. The operator rotated the stirrer shaft at the desired speed 120 rpm. Control experiments included the titration of 5.0×10^{-3} mol dm^{-3} anionic surfactant (SLA or SDS) solution into 2 cm^3 DMA and alcohol into DMA and the latter experiment were done for each alcohol concentration. All experiments were repeated twice at each temperature, and the reproducibility was within ±1%. The heat flow in or out of the ampoule per injection and the corresponding enthalpy changes per mole of the added surfactant were obtained using Microcal Origin software. Corrected data refer to experimental data after subtraction of the anionic surfactant into DMA and alcohol into DMA control data. The uncertainties of the thermal

powers determined was 0.3% and the uncertainties of the CMC and thermodynamic parameters of micellar processes were less than 1.5%.

Results and discussion

At 298 K the effect of the concentration and the number of carbon-atom of alcohol on the CMCs of surfactants

The power–time curves of the micelle formation process were determined for anionic surfactants (SLA and SDS) in DMA in the presence of some long-chain alcohols with various concentration (0.10, 0.50, 1.0 and 1.5) mol dm^{-3} at 298 K. It should be noted that the enthalpies of dilution of surfactant and alcohol must be deducted from the total enthalpic effect of the micelle formation process and the remaining is the real micelle formation of the thermal effect. Partial curves after handling are shown in Fig. 1. As is well known, a decrease in the molar conductivity or surface tension is observed at a certain concentration, and the change is sharp enough to determine the CMC as described in the literatures [6–8]. Some literatures [15, 16] also determined the CMC value from the first-order differential curve of the ITC curve. In contrast to the above method to obtain the value of CMC, according to our previous work [17], the turning point, namely, the lowest point of the power–time curves have been investigated and the corresponding concentration can be calculated according to the volume of the solution injected into the ampoule. And this concentration is the CMC of surfactant under the certain condition.
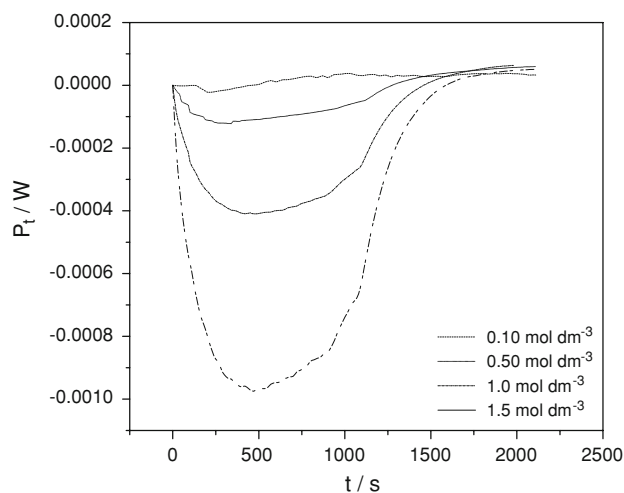

Fig. 1 The power–time curves of the micelle formation processes for 0.010 mol dm^{-3} SDS in DMA in the presence of various concentration of 1-nonanol at 298 K

The CMC values obtained on the basis of the above method have been reported in Table 1. For all the long-chain alcohols investigated, anionic surfactants SLA and SDS give similar behavior, namely, CMC increases with increasing concentration and decreasing number of carbon-atom of the alcohol in DMA. It is known that the major factor that determines the inter-micellar solubility of long-chain alcohols is the change in hydrophilic balance of the micelle during the inclusion of alcohol [18]. So the above phenomenon can be ascribed to the increased solubility of the long-chain alcohol into the interface of the micelle in the non-aqueous medium.

Decrease in the CMC on addition of alcohol may result from the penetration of alcohol molecules into the micelle. As the length of the hydrocarbon chain of the alcohol increases, the shielding interaction of the alcohol to the ionic charges of the surfactants enhances and the repulsive interaction between the ionic charges weakens. Thus the micelle is easier to form. On the other hand, the hydrophobic effect, which is associated with the length of the alkyl chain of alcohol molecules also favors micellization and increases as the length of the hydrocarbon chain of the alcohol increases [6]. This can explain why the CMCs of SLA and SDS in DMA in the presence of alcohol decrease as the number of carbon atom increases.

Because the polarity of DMA is greater than the long-chain alcohol, the polarity of the system will decrease with increase in the concentration of alcohol and the electric repulsive force of the ion group will strengthen. Thus the formation of the micelle is difficult. As a result, CMC

Table 1 The CMCs and the thermodynamic parameters ΔH_{mic}°, ΔG_{mic}°, ΔS_{mic}° of SLA and SDS in DMA in the presence of alcohols with different concentration at 298 K

Surfactant	Alcohol	Parameter	0.10 mol dm^{-3}	0.50 mol dm^{-3}	1.0 mol dm^{-3}	1.5 mol dm^{-3}
SLA	1-heptanol	10^4 CMC (mol dm^{-3})	5.55	7.77	9.10	9.99
		ΔH_{mic}° (kJ mol^{-1})	−2.88	−6.18	−12.09	−21.22
		ΔG_{mic}° (kJ mol^{-1})	−48.94	−47.28	−46.5	−46.04
		ΔS_{mic}° (J k^{-1} mol^{-1})	154.6	137.9	115.5	83.29
	1-octanol	10^4 CMC (mol dm^{-3})	5.11	7.10	8.44	9.32
		ΔH_{mic}° (kJ mol^{-1})	−3.91	−9.01	−18.25	−32.40
		ΔG_{mic}° (kJ mol^{-1})	−49.36	−47.72	−46.86	−46.38
		ΔS_{mic}° (J k^{-1} mol^{-1})	152.5	129.9	96.01	46.91
	1-nonanol	10^4 CMC (mol dm^{-3})	4.88	6.22	7.99	8.88
		ΔH_{mic}° (kJ mol^{-1})	−4.92	−12.86	−26.03	−43.70
		ΔG_{mic}° (kJ mol^{-1})	−49.58	−48.38	−47.14	−46.62
		ΔS_{mic}° (J k^{-1} mol^{-1})	149.9	119.2	70.84	9.799
	1-decanol	10^4 CMC (mol dm^{-3})	4.44	5.77	7.33	8.44
		ΔH_{mic}° (kJ mol^{-1})	−6.76	−17.37	−38.75	−64.22
		ΔG_{mic}° (kJ mol^{-1})	−50.02	−48.76	−47.56	−46.86
		ΔS_{mic}° (J k^{-1} mol^{-1})	145.2	105.3	29.56	−58.26
SDS	1-heptanol	10^4 CMC (mol dm^{-3})	5.10	6.66	8.44	9.99
		ΔH_{mic}° (kJ mol^{-1})	−8.14	−11.11	−17.77	−27.11
		ΔG_{mic}° (kJ mol^{-1})	−49.36	−48.04	−46.86	−46.04
		ΔS_{mic}° (J k^{-1} mol^{-1})	138.3	123.9	97.61	63.52
	1-octanol	10^4 CMC (mol dm^{-3})	4.42	6.22	7.99	9.55
		ΔH_{mic}° (kJ mol^{-1})	−9.96	−14.87	−30.04	−49.22
		ΔG_{mic}° (kJ mol^{-1})	−50.08	−48.36	−47.14	−46.26
		ΔS_{mic}° (J k^{-1} mol^{-1})	134.6	112.4	57.38	−9.933
	1-nonanol	10^4 CMC (mol dm^{-3})	4.04	5.77	7.10	9.10
		ΔH_{mic}° (kJ mol^{-1})	−12.87	−20.10	−43.66	−75.82
		ΔG_{mic}° (kJ mol^{-1})	−50.52	−48.76	−47.72	−46.5
		ΔS_{mic}° (J k^{-1} mol^{-1})	126.3	96.17	13.62	−98.39
	1-decanol	10^4 CMC (mol dm^{-3})	3.62	5.33	6.66	8.66
		ΔH_{mic}° (kJ mol^{-1})	−15.53	−31.14	−60.06	−100.46.
		ΔG_{mic}° (kJ mol^{-1})	−51.06	−49.14	−48.04	−46.74
		ΔS_{mic}° (J k^{-1} mol^{-1})	119.2	60.40	−40.34	−180.3

values increase with increasing concentration of long-chain alcohol used in DMA. In addition, as the literature reported [19], benzyl alcohol solubilisation is probably localized in the palisade layer. When the benzyl alcohol content approximates to $x = 0.77$, benzyl alcohol may go predominantly to the centre of the micellar interior core. So the micellar size increases and consequently the CMC values increases. The CMC values for the SLA and SDS increase with increasing concentration of alcohols used in DMA due to the above two effects.

The thermodynamic parameters of micellization at 298 K

Based on the power–time curves, the heat effect (Q), which is the area of the power–time curve for the titration process, can be obtained. The standard enthalpy change (($\Delta H^{\circ}_{\text{mic}}$)) of micelle formation in DMA/alcohol mixtures was obtained in connection with the heat effect of the micellization process. According to the mass action model of micellization, the standard Gibbs free energy ($\Delta G^{\circ}_{\text{mic}}$) and the entropy of micelle formation ($\Delta S^{\circ}_{\text{mic}}$) of an ionic surfactant can be obtained using the relationship [20].

$$\Delta G^{\circ}_{\text{mic}} = 2RT \ln X_{\text{CMC}} \tag{1}$$

$$\Delta S^{\circ}_{\text{mic}} = (\Delta H^{\circ}_{\text{mic}} - \Delta G^{\circ}_{\text{mic}})/T \tag{2}$$

where X_{CMC} stands for the mole fraction of surfactant in DMA solution at CMC.

The thermodynamic parameters for SLA and SDS in DMA in the presence of different long-chain alcohols at 298 K were calculated and listed in Table 1. All values of $\Delta H^{\circ}_{\text{mic}}$ are negative, which demonstrates that the micellization processes for SLA and SDS under the circumstance studied are exothermic. The micelle formation in DMA in the presence of long-chain alcohol could be due to the effects like ion-solvent interactions, hydrogen bonding and dispersion forces [6]. Since DMA has a strong tendency to form hydrogen bonding, positive values are generally attributed to the disruption of the ice-berg structure surrounding the hydrocarbon chains of the monomeric surfactants [21]. Orientation of the opposite end of the solvent dipole can cause ion-solvent interaction during the micelle formation process in DMA and the nitrogen of DMA molecule can participate in resonance with the carbonyl group [6]. The dispersion forces also exist among the alkyl chains of the surfactant ions. The negative values of enthalpy, suggests the importance of the London-dispersion interactions as an attractive force for micellization [22]. In this sense, it seems clear that during the micellization processes in the presence of long-chain alcohol in DMA, London dispersion interactions play a predominant role. Obviously, the enthalpies of micellization strongly

decrease with the increasing of the alcohol concentration, which suggests that alcohol molecules can play an important role in creating of micelles and may stabilize them through creating of the hydrogen bonds.

In Table 1, the standard entropy of micellization $\Delta S^{\circ}_{\text{mic}}$ is positive firstly and then it becomes less positive in the presence of alcohols with longer carbon chain and higher concentration. The positive entropy change indicates that in these systems entropy is dominating over the micellization process, particularly when the entropy change is high. The positive $\Delta S^{\circ}_{\text{mic}}$ is due to the melting of "icebergs" around the hydrocarbon tails of the surfactant monomers and the increased randomness of the hydrocarbon chains in the micellar core [23]. As observed in Table 1, with the increase of the concentration and number of carbon-atom of the alcohol, the lower magnitudes of $\Delta S^{\circ}_{\text{mic}}$ suggest that these additives still control the three-dimensional DMA matrix.

As shown in Table 1, $\Delta G^{\circ}_{\text{mic}}$ becomes less negative as the alcohol concentration increases, which can be attributed to the steric inhibition of micellization. And at a fixed solvent composition, $\Delta G^{\circ}_{\text{mic}}$ undergoes small variations and more negative with the increase of the carbon atoms of alcohol, which indicates that SLA and SDS can form micelles more easily in DMA in the presence of the longer-chain alcohol. In general, the micelle formation processes for SLA and SDS in the medium studied become less favorable as the concentration of alcohol increases in the solvent system, but more favorable as the alkyl chain of alcohol lengthens. Obviously, the driving force for the micellization processes of SLA and SDS in DMA/long-chain alcohol is the entropy from the beginning and then change to the enthalpy with the increasing concentration and alkyl chain of the alcohols. In this situation, the micelle formation process for SLA and SDS in DMA is enthalpy-driven and this presents a striking contrast to the micelle formation of surfactants in aqueous solution, which is totally driven by entropy [16, 24].

Enthalpy-entropy compensation phenomenon for micelle formation in the temperature range from 298 to 313 K

The power–time curves of the micelle formation of SLA and SDS in DMA in the presence of 1.0 mol dm^{-3} alcohols at 303, 308 and 313 K have also been determined. The CMCs and thermodynamic parameters for SLA and SDS under these conditions are reported in our previous work [25].

As is well known to all, the so-called enthalpy-entropy compensation phenomenon has been observed in several processes, including the micellization of surfactants [26]. In general, the compensation phenomenon is expressed by a linear relationship in the form

$$\Delta H_{mic}^{\circ} = \Delta H_{m}^{*} + T_{c}\Delta S_{mic}^{\circ} \qquad (3)$$

where ΔH_{mic}° is the enthalpy change, ΔS_{mic}° is the entropy change. The slope of the compensation plot, T_{c}, is known as the compensation temperature and ΔH_{m}^{*} is the interception of the compensation line. According to the viewpoint of Lumry and Rafender [27] for the compensation phenomenon, the micellization can be described as a process consisting of two-part: (a) the "desolvation" part, i.e., the dehydration of the hydrocarbon tail of surfactant molecules, and (b) the "chemical" part, i.e., aggregation of the hydrocarbon tails of surfactant molecules to form a micelle. T_{c} provides a measure of the "solvation" part in the micellization process. ΔH_{m}^{*} is considered as an index of the "chemical" part of the micelle formation.

A good linear relationship has been obtained in all compensation plots based on the values of ΔH_{mic}° and ΔS_{mic}° in Table 1 of this work and those of our previous work [25]. This proves that there exist enthalpy-entropy compensation effects for SLA and SDS in DMA in the presence of 1.0 mol dm^{-3} long-chain alcohol. It must be noted that the T_{c} value we have found (around 300 K) falls into the suggested range of 270–300 K for water systems [27]. This fact indicates that, in relation to the solvation part, the micellization of SLA or SDS in DMA in the presence of long-chain alcohols takes place under the similar structural conditions to water.

Comparison of the values of the enthalpy of micellization calculated by two methods in the temperature range from 298 to 313 K

In the temperature range from 298 to 313 K, the average ΔH_{mic}° values obtained by the direct method on the basis of the power–time curves, are reported in Table 2.

Table 2 For the micellization processes of the surfactants studied in DMA in the presence of 1.0 mol dm^{-3} alcohol, the comparison between the enthalpies values of based on the power–time curves (ΔH_{mic}°) and those calculated according to the mass action model ($\Delta H_{mic}^{\circ}(*)$) in the temperature range from 298 to 313 K

Surfactant	Alcohol	ΔH_{mic}° (kJ mol^{-1})	$(\Delta H_{mic}^{\circ}(*))$ (kJ mol^{-1})
SLA	1-heptanol	−11.9	−16.2
	1-octanol	−17.7	−19.9
	1-nonanol	−24.9	−22.9
	1-decanol	−34.5	−25.2
SDS	1-heptanol	−16.9	−22.7
	1-octanol	−28.8	−24.8
	1-nonanol	−40.3	−30.2
	1-decanol	−56.4	−35.1

In addition, according to the mass action model of micellization, the enthalpy of micellization can be obtained by [20]:

$$\Delta H_{mic}^{\circ} = -2RT^{2}\mathrm{d}\ln X_{CMC}/\mathrm{d}T \qquad (4)$$

where ΔH_{mic}° is the enthalpy of micellization. The plot of $\ln X_{CMC}$ for the two ionic surfactants in the temperature range from 298 to 313 K against $1/T$ gives a good straight line with a negative slope, which shows that the micelle size does not change within the temperature range studied [6]. Based on the slope of the straight line, the values of enthalpy of micellization which has been expressed as $\Delta H_{mic}^{\circ}(*)$, as distinct from that obtained on the basis of the power–time curves, calculated by such an indirect method have also been listed in Table 2. As can be seen, in spite of the discrepancy of the two methods to obtain the enthalpy of micellization, the two sets of data are in agreement to a certain extent. The ΔH_{mic}° data obtained by microcalorimetry are considered to approximate the true enthalpies. According to the classical model of micellization, the approximation implies that the degrees of counterion binding of micelles and monomers are small and identical, the aggregation number is high, and the activities can be replaced by concentrations [26]. The difference between the direct method and indirect method show that the model can be expected to be further improved. As both ΔH_{mic}° and CMC can be obtained by microcalorimetry, this technique has been used as an ideal method by many authors in checking their models of micelle formation.

Conclusions

This work has studied the effects of long-chain alcohol and temperature on the micellization process of ionic surfactants (SLA and SDS) in DMA. The results show that there exists a rule similar to short-chain alcohol for CMCs and thermodynamic parameters. Enthalpy–entropy compensation phenomenon has also been observed in the processes. In contrast to the entropy-driven process in the aqueous solution, the driving force of micelle formation changes from entropy to enthalpy with the increment of the carbon chain length and the concentration of the long-chain alcohol. Comparison has been made of the enthalpy changes of micellization determined by calorimetry and from the temperature dependence of the CMC and the values of the enthalpy of micellization calculated by the direct and indirect methods are approximate. This work can enrich the knowledge about solvent and solute effects on surfactant aggregation.

References

1. Baglioni P, Kevan L. Structural effects of alcohol addition to sodium dodecyl sulfate micelles studied by electron spin-echo modulation of 5-doxylstearic acid spin probe. J Phys Chem. 1987;91:1516–8.
2. Bravo C, Leis JR, Pena ME. Effect of alcohols on catalysis by dodecyl sulfate micelles. J Phys Chem. 1992;96:1957–61.
3. Forland GM, Sameth J, Hoiland H, Mortensen K. The effect of medium chain length alcohols on the micellar properties of sodium dodecyl sulfate in sodium chloride solutions. J Colloid Interface Sci. 1994;164:163–7.
4. Pablo ML, Juan MR, Gerardo P, Félix S. Surface tensions, critical micelle concentrations, and standard free energies of micellization of C8−lecithin at different pHs and electrolyte concentrations. J Chem Eng Data. 2002;47:1017–21.
5. Yogesh R, Sunil SB. CMC determination of an odd carbon chain surfactant (C13E20) mixed with other surfactants using a spectrophotometric technique. J Chem Eng Data. 2006;51:2026–31.
6. Akhter MS, Al-Alawi SM. The effect of organic additives on critical micelle concentration of non-aqueous micellar solutions. Colloids Surf A. 2000;175:311–20.
7. Evans DF, Miller DD. In: Friberg SE, Lindman B, editors. Organized solutions. New York: Marcel Dekker; 1992.
8. Chen D, Zhu JX, Yuan P, Yang SJ, Chen TH, He HP. Preparation and characterization of anion-cation surfactants modified montmorillonite. J Therm Anal Calorim. 2008;94:841–8.
9. Galán JJ, Del Castillo JL, González-Pérez A, Fuentes-Vázquez V, Rodríguez JR. Solubilization of butanol/pentanol/hexanol in dodecylpyridinium chloride. J Therm Anal Calorim. 2007;87:159–63.
10. González-Pérez A, Galán JJ, Rodríguez JR. The solubilization of alcohols in micellar solutions. J Therm Anal Calorim. 2003;72:471–9.
11. Sjoberg M, Henriksson U, Warnheim T. Deuteron nuclear magnetic relaxation of [1,1-2H] hexadecyltrimethylammonium bromide in micellar solutions of nonaqueous polar solvents and their mixtures with water. Langmuir. 1990;6:1205–11.
12. Beesley AH, Evans DF, Laughlin RG. Evidence for the essential role of hydrogen bonding in promoting amphiphilic self-assembly: measurements in 3-methylsydnone. J Phys Chem. 1988;92:791–3.
13. Honglin Z, Xiufang Y, Xiangyang L, Haitao S, Yi N, Lili W, et al. Microcalorimetric study of the oscillating extraction system. J Therm Anal Calorim. 2002;68:931–6.
14. Gucker FT, Pickard HB, Planck RW. A new micro-calorimeter: the heats of dilution of aqueous solutions of sucrose at 20 and 30° and their heat capacities at 25°. J Am Chem Soc. 1939;61:459–70.
15. Paula S, Süs W, Tuchtenhagen J, Blume A. Thermodynamics of micelle formation as a function of temperature: a high sensitivity titration calorimetry study. J Phys Chem. 1995;99:11742–51.
16. Dai S, Tam KC. Isothermal titration calorimetric studies of alkyl phenol ethoxylate surfactants in aqueous solutions. Colloids Surf A. 2003;229:157–68.
17. Yu XF, Wu LL, Zhang HL. Microcalorimetric study on the formation of reversed micelle in P204Li organic phase. Chin J Appl Chem. 2002;3:263–7.
18. Ralston AW, Eggenberger DW. The effect of organic non-electrolytes upon the conductivities of aqueous solutions of cationic colloidal electrolytes. J Am Chem Soc. 1948;70:983–7.
19. Li GZ, Lin Y, Guo R, Wang GT. High resolution NMR studies of the solubilised process of micellar solution. Acta Phys Chim Sin. 1986;2:183–9.
20. Philips JN. The energetic of micelle formation. Trans Faraday Soc. 1955;51:561−9.
21. Kresheck GC. Water: a comprehensive treatise. New York: Plenum Publications; 1995.
22. Nusselder JJH, Engberts JB. Toward a better understanding of the driving force for micelle formation and micellar growth. J Colloid Interface Sci. 1992;148:353–61.
23. Shaw DJ. Introduction to colloid and interface chemistry. 2nd ed. London: Butterworths; 1978.
24. Shimizu S, Augusto P, Pires R, Seoud AE. Thermodynamics of micellization of benzyl(2-acylaminoethyl)dimethylammonium chloride surfactants in aqueous solutions: a conductivity and titration calorimetry study. Langmuir. 2004;20:9551–9.
25. Zhang HL, Kong Z, Yan YM, Li GZ, Yu L, Li Z. Studies on the CMC and the thermodynamic function of the anionic surfactants in the DMA/long-chain alcohol systems using a microcalorimetric method. Acta Chim Sin. 2007;65:906–12.
26. Singh HN, Syed M, Saleem SM, Singh RP, Birdi KS. Micelle formation of ionic surfactants in polar nonaqueous solvents. J Phys Chem. 1980;84:2191–4.
27. Lumry R, Rafender S. Enthalpy-entropy compensation phenomena in water solutions of proteins and small molecules: a ubiquitous properly of water. Biopolymers. 1970;9:1125–7.