

Densities, Conductivities, and Aggregation Numbers of Aqueous Solutions of Quaternary Ammonium Surfactants with Hydroxyethyl Substituents in the Headgroups

Zhiguo Zhang,[†] Huanhuan Wang,[†] and Weiguo Shen^{*,†,‡}

[†]School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China [‡]Department of Chemistry, Lanzhou University, Lanzhou, Gansu 730000, China

ABSTRACT: The aggregation behaviors of two cationic surfactants, namely, N-dodecyl-N-2-hydroxyethyl-N,N-dimethyl ammonium bromide (C12HDAB) and N-dodecyl-N,N-2dihydroxyethyl-N-methyl ammonium bromide (C_{12} DHAB), were studied by measurements of density, conductivity, and steady-state fluorescence quenching. The aggregation number, the volumetric properties, and the standard Gibbs energy ($\Delta G_{\rm mic}^0$) of micellization were obtained, and the surface area (A_{mic}) of the surfactant headgroups and the radius (r) of the micelles were estimated. It was found that substituting the methyl group with the hydroxyethyl group in the head of the surfactant led to the increase of the volume change of micellization and the decreases of the critical micelle concentration, association degree of the counterion, and the value of $\Delta G^0_{
m mic}$ while the aggregation number of those surfactants in



aqueous solutions was little affected by introducing the hydroxyethyl group. It was also found that the values of $A_{\rm mic}$ and r increase with the hydroxyethyl group.

INTRODUCTION

Alkyltrimethylammonium bromide surfactants such as dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB) are widely applied in practical fields as antimicrobial agents, fabric softeners, corrosion inhibitors, and catalysts.¹⁻⁴ Recently, it was found that by substituting the methyl group with the hydroxylalkyl group in the head of those surfactants can greatly enhance their efficiency of catalysis, which was attributed to the formation of the hydrogen bonds duo to introduction of the hydroxylalkyl groups.^{4,5} The micellization of the hydroethyl group substituted surfactants has been studied using isothermal titration calorimetry (ITC); however more experimental measurements are required for understanding the role of the hydroxylalkyl groups in the physicochemical properties and aggregation behaviors of these surfactants in aqueous solutions.

In this paper, the micellization properties of two DTAB derivatives, namely, N-dodecyl-N-2-hydroxyethyl-N,N-dimethyl ammonium bromide (C12HDAB) and N-dodecyl-N,N-2-dihydroxyethyl-N-methyl ammonium bromide (C₁₂DHAB), which have the same tails with DTAB but one or two hydroxyethyl substituent groups in the head, respectively, as shown in Figure 1, are studied by measurements of density, conductivity, and steady-state fluorescence. The critical micelle concentration CMC, the volumetric property, the dissociation degree of the counterions at the micellar state, and the aggregation number of the micelle are determined. The results are analyzed to obtain the Gibbs free energy of the micellization and to investigate the role of the hydroxylethyl group in the self-aggregation of the surfactants.



Figure 1. Chemical structures of the surfactants studied: a: DTAB, b: C₁₂HDAB, c: C₁₂DHAB.

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Table 1. Sources and Purities of the Chemicals

chemicals	source	initial mass fraction purity	purification method	final mass fraction purity	analysis method
dodecyltrimethylammonium bromide	J&K Chemical Ltd.	0.99	none		
cetylpyridinium bromide	Sinopharm Chemical Reagent Co.	0.98	none		
1-bromododecane	Sinopharm Chemical Reagent Co.	0.98	none		
N,N-dimethylethanolamine	Aladdin Chemistry Reagent Co.	0.98	none		
N-methyldiethanolamine	Aladdin Chemistry Reagent Co.	0.98	none		
N-dodecyl-N-2-hydroxyethyl-N,N- dimethylammonium bromide	synthesis		recrystallization	0.998	element analysis
N-dodecyl-N,N-2-dihydroxyethyl-N- methylammonium bromide	synthesis		recrystallization	0.998	element analysis

EXPERIMENTAL SECTION

Chemicals. The chemicals used in this work as well as their purities and suppliers are listed in Table 1, all of which were used without further purification; double-distilled water was used in preparation of all of the surfactant solutions.

Synthesis of *N*-Dodecyl-*N*-2-hydroxyethyl-*N*,*N*-dimethyl Ammonium Bromide (C_{12} HDAB). C_{12} HDAB was synthesized using the method reported by Tong et al.⁶ A sample of 7.5 g of 1-bromododecane and 3.2 g of *N*,*N*-dimethylethanolamine were refluxed with 60 mL of acetone at 70 °C for 8 h. After the reaction was completed, the mixture was cooled to -20 °C, and a white crystal appeared which was recrystallized in acetone at least four times; the product was then dried in an evacuated desiccator for 24 h. A white solid was obtained in 80 % yield. ¹H NMR (CDCl₃, 400 MHz) δ : 0.89 (t, *J* = 6.8 Hz, 3H), 1.27–1.37 (m, 18H), 1.73–1.79 (m, 2H), 3.38 (s, 6H), 3.54 (t, *J* = 8.4 Hz, 2H), 3.71 (t, *J* = 4.6 Hz, 2H), 4.10–4.17 (m, 2H); element analysis (% in mass): calculated C, 56.79; H, 10.72; N, 4.14; found C, 56.70; H, 10.59; N, 4.15.

Synthesis of *N*-Dodecyl-*N*,*N*-2-dihydroxyethyl-*N*methyl Ammonium Bromide (C_{12} DHAB). C_{12} DHAB was synthesized by refluxing 10 g of 1-bromododecane and 5.7 g of *N*,*N*-dimethylethanolamine in 60 mL of acetone at 70 °C for 8 h; the purification was the same as that of C_{12} HDAB which gave a white solid in 78 % yield. ¹H NMR (CDCl₃, 400 MHz) δ : 0.90 (t, *J* = 6.8 Hz, 3H), 1.27–1.38 (m, 18H), 1.75–1.78 (m, 2H), 3.35 (s, 3H), 3.55 (t, *J* = 8.4 Hz, 2H), 3.71–3.82 (m, 4H), 4.15–4.22 (m, 4H); element analysis (% in mass): Calculated: C, 55.43; N, 3.80; H, 10.40, found: C, 55.48; N, 3.73; H, 10.42.

Density Measurement. The measurements of the densities were carried out using a DMA 5000 M vibrating tube densimeter from Anton Paar.⁷ The apparatus consists of a U-shaped borosilicate glass tube with a platinum resistance thermometer inside the thermostatic jacket. The precisions in measurements of the density and the temperature given by the manufacturer were $\pm 10^{-6}$ g·cm⁻³ and ± 0.001 K, respectively. At the beginning of every set of experiments the apparatus was calibrated using dry air and double-distilled water. The accuracy in the density measurements was stated by the manufacturer to be $\pm 5 \cdot 10^{-6}$ g·cm⁻³. Surfactant solutions with the concentration being about 60 mmol·kg¹⁻ were prepared by weighing and then diluted to a series of dilute solutions for density measurements. The uncertainties of the concentrations were estimated to be about 0.05 % of the values.

Conductivity Measurement. Conductivity measurements were performed with a CON500 type conductometer from First Clean Co. using a dip-type cell with a cell constant of 0.893

cm^{-1.8} The conductivities of surfactant solutions at various concentrations were determined using a titration method. A certain amount of water was weighed into the dip-type cell, which was placed in a water bath where the temperature was controlled within \pm 0.1 K. A surfactant solution with the concentration being about 210.0 mmol·kg¹⁻ was prepared by weighing and titrated into cell using a microsyringe; after each titration, the cell was shaken and then kept undisturbed for thermal equilibrium before the conductivity measurement. The relative standard uncertainties in determinations of the conductivity and the concentration were about \pm 0.5 % and 2 %, respectively.

Steady-State Fluorescence Quenching. The steady-state fluorescence measurements were taken using a fluorimetry (model FLS 920) supplied by Edinburge Instrument. The fluorimetry was equipped with a 450 mW Xe arc lamp and a R928P Hamamatsu PMT detector. The temperature of the sample for the fluorescence measurement was controlled within \pm 0.2 K using a water circulating bath which pumped water into the sample hold in the fluoremeter. The aggregation number of the micelle was determined by fluorescence measurement using pyrene as the probe and cetylpyridinium bromide (CPB) as the quencher.⁹ The samples for steady-state quenching were prepared as follows: a surfactant/pyrene aqueous solution with the concentrations of the surfactant and the pyrene being 50.0 $mmol \cdot kg^{-1}$ and $6 \cdot 10^{-7} mol \cdot kg^{-1}$ respectively was prepared first. A proper amount of CPB/ethanol solution with the concentration of CPB being 20 mmol·kg⁻¹ was then transferred into a flask; after removing the solvent ethanol, it was dissolved by the surfactant/pyrene aqeuous solution to obtain a surfactant/ pyrene/CPB solution with the required concentration of CPB. In this way, a series of aqueous solutions with the concentrations of the quencher being from $(1.0 \times 10^{-5} \text{ to } 4.5 \times 10^{-4}) \text{ mol·kg}^{-1}$ were prepared for steady-state fluorescence measurements. During the fluorescence measurements the excitation wavelength was set at 337 nm, and the emission spectra were scanned from 360 to 480 nm with a step of 1 nm. The intensities at the first peak (373 nm) in the absence and presence of the quencher were measured and used to calculate the aggregation number.

RESULTS AND DISCUSSION

Volumetric Properties. The densities of series of the DTAB, C_{12} HDAB, and C_{12} DHAB aqueous solutions at temperatures between 293.15 K and 318.15 K in a 5 K interval were measured, and their values are listed in column 2 of Table 2 for DTAB, Table 3 for C_{12} HDAB, and Table 4 for C_{12} DHAB, respectively. The values of the density measured for DTAB solutions in this work were in good agreement with that reported Table 2. Density ρ , Apparent Molar Volume V_{Φ} , Partial Molar Volume \overline{V} , and Isobaric Thermal Expansion Coefficient α_p for DTAB at Different Molalities *m* under Temperature T = (293.15 to 318.15) K and Pressure $p = 0.1 \text{ MPa}^a$

		2 .	-	-	
T/K	$m/\text{mmol}\cdot\text{kg}^{-1}$	$ ho/ extrm{g}\cdot extrm{cm}^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_P \cdot 10^3 / \mathrm{K}^{-1}$
293.15	0	0.998208			
	6.08	0.998345	286.3 ± 0.3	286.4 ± 0.3	0.2173
	7.07	0.998368	286.2 ± 0.2	286.3 ± 0.2	0.2176
	7.96	0.998388	286.2 ± 0.2	286.4 ± 0.2	0.2179
	8.97	0.998411	286.1 ± 0.2	286.4 ± 0.2	0.2182
	9.99	0.998434	286.1 ± 0.2	286.6 ± 0.2	0.2185
	10.96	0.998456	286.1 ± 0.2	286.9 ± 0.2	0.2188
	11.99	0.998480	286.1 ± 0.2	287.2 ± 0.2	0.2193
	12.99	0.998503	286.0 ± 0.2	287.6 ± 0.2	0.2197
	13.98	0.998524	286.1 ± 0.1	288.3 ± 0.1	0.2199
	15.03	0.998543	286.4 ± 0.1	289.2 ± 0.1	0.2198
	15.96	0.998556	286.9 ± 0.1	290.1 ± 0.1	0.2195
	18.02	0.998592	$28/.4 \pm 0.1$	291.6 ± 0.1	0.2205
	20.01	0.998622	288.0 ± 0.1	292.8 ± 0.1	0.2208
	24.94	0.998695	289.2 ± 0.1	294.2 ± 0.1	0.2218
	29.94	0.998773	269.7 ± 0.1	294.1 ± 0.1	0.2229
	33.01	0.998830	290.5 ± 0.1	294.1 ± 0.1	0.2241
	39.95	0.998918	290.9 ± 0.1 291.2 ± 0.1	294.1 ± 0.1 293.8 ± 0.1	0.2249
	49.73	0.998991	291.2 ± 0.1 291.4 ± 0.1	293.3 ± 0.1	0.2257
	54.98	0.999145	291.4 ± 0.1 291.5 ± 0.1	293.5 ± 0.1 293.1 ± 0.1	0.2200
	60.01	0.999217	291.5 ± 0.1 291.7 ± 0.1	293.5 ± 0.1	0.2277
298.15	0	0.997047	2)1./ <u>+</u> 0.1	275.5 <u>+</u> 0.1	0.2200
2,0110	6.08	0.997176	287.9 + 0.3	288.0 + 0.3	0.2598
	7.07	0.997197	287.9 + 0.2	288.1 + 0.2	0.2601
	7.96	0.997216	287.9 ± 0.2	288.1 ± 0.2	0.2604
	8.97	0.997237	287.9 ± 0.2	288.2 ± 0.2	0.2607
	9.99	0.997259	287.9 ± 0.2	288.3 ± 0.2	0.2610
	10.96	0.997280	287.8 ± 0.2	288.5 ± 0.2	0.2613
	11.99	0.997302	287.8 ± 0.2	288.8 ± 0.2	0.2617
	12.99	0.997324	287.7 ± 0.2	289.1 ± 0.2	0.2621
	13.98	0.997343	287.9 ± 0.1	289.8 ± 0.1	0.2623
	15.03	0.997363	288.0 ± 0.1	290.5 ± 0.1	0.2623
	15.96	0.997376	288.4 ± 0.1	291.4 ± 0.1	0.2621
	18.02	0.997408	289.0 ± 0.1	292.9 ± 0.1	0.2629
	20.01	0.997435	289.6 ± 0.1	294.1 ± 0.1	0.2632
	24.94	0.997505	290.7 ± 0.1	295.5 ± 0.1	0.2640
	29.94	0.997580	291.2 ± 0.1	295.5 ± 0.1	0.2650
	35.01	0.997647	291.9 ± 0.1	295.6 ± 0.1	0.2661
	39.95	0.997712	292.3 ± 0.1	295.5 ± 0.1	0.2668
	45.05	0.997780	292.7 ± 0.1	295.1 ± 0.1	0.2676
	49.73	0.997845	292.9 ± 0.1	294.6 ± 0.1	0.2685
	54.98	0.997923	293.0 ± 0.1	294.4 ± 0.1	0.2695
202.15	60.01	0.997992	293.1 ± 0.1	294.7 ± 0.1	0.2703
303.15	0	0.995649	200.1 + 0.2	200.2 + 0.2	0.3025
	6.08	0.995770	290.1 ± 0.3	290.2 ± 0.3	0.3028
	7.07	0.995790	290.0 ± 0.2	290.1 ± 0.2	0.3031
	/.90	0.995807	290.0 ± 0.2	290.2 ± 0.2	0.3034
	0.97	0.993827	290.0 ± 0.2	290.2 ± 0.2	0.3037
	9.99	0.993847	289.9 ± 0.2	290.3 ± 0.2	0.3040
	11.90	0.995886	289.9 ± 0.2	290.3 ± 0.2	0.3047
	12.99	0.995905	239.9 ± 0.2 290.0 ± 0.2	290.3 ± 0.2 291.1 ± 0.2	0.3049
	13.98	0.995923	290.0 ± 0.2 290.1 ± 0.1	291.6 ± 0.2	0.3050
	15.03	0.995942	290.1 ± 0.1	292.2 + 0.1	0.3049
	15.96	0.995956	290.4 + 0.1	292.8 + 0.1	0.3054
	18.02	0.995986	290.9 ± 0.1	294.1 ± 0.1	0.3057
	20.01	0.996013	291.4 ± 0.1	295.2 ± 0.1	0.3065
	24.94	0.996077	292.4 ± 0.1	296.6 ± 0.1	0.3074
	29.94	0.996147	292.9 ± 0.1	296.7 ± 0.1	0.3082

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Table 2. continued

T/K	$m/mmol \cdot kg^{-1}$	$ ho/ m g\cdot cm^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_p \cdot 10^3 / \mathrm{K}^{-1}$
	35.01	0.996212	293.4 ± 0.1	296.8 ± 0.1	0.3089
	39.95	0.996271	293.9 ± 0.1	296.8 ± 0.1	0.3097
	45.05	0.996336	294.2 ± 0.1	296.4 ± 0.1	0.3105
	49.73	0.996396	294.4 ± 0.1	295.9 ± 0.1	0.3115
	54.98	0.996470	294.4 ± 0.1	295.7 ± 0.1	0.3122
	60.01	0.996535	294.6 ± 0.1	295.9 ± 0.1	0.3025
308.15	0	0.994034			
	6.08	0.994144	292.2 ± 0.3	292.2 ± 0.3	0.3453
	7.07	0.994162	292.1 ± 0.2	292.1 ± 0.2	0.3456
	7.96	0.994178	292.1 ± 0.2	292.1 ± 0.2	0.3459
	8.97	0.994196	292.1 ± 0.2	292.1 ± 0.2	0.3462
	9.99	0.994214	292.1 ± 0.2	292.2 ± 0.2	0.3466
	10.96	0.994232	292.0 ± 0.2	292.3 ± 0.2	0.3468
	11.99	0.994250	292.1 ± 0.2	292.5 ± 0.2	0.3472
	12.99	0.994268	292.1 ± 0.2	292.8 ± 0.2	0.3475
	13.98	0.994286	292.0 ± 0.1	293.1 ± 0.1	0.3477
	15.03	0.994304	292.1 ± 0.1	293.6 ± 0.1	0.3479
	15.96	0.994320	292.1 ± 0.1	294.0 ± 0.1	0.3478
	18.02	0.994345	292.8 ± 0.1	295.5 ± 0.1	0.3481
	20.01	0.994370	293.2 ± 0.1	296.5 ± 0.1	0.3484
	24.94	0.994432	294.0 ± 0.1	297.8 ± 0.1	0.3491
	29.94	0.994498	294.4 ± 0.1	298.0 ± 0.1	0.3499
	35.01	0.994557	295.0 ± 0.1	298.1 ± 0.1	0.3506
	39.95	0.994615	295.4 ± 0.1	297.9 ± 0.1	0.3512
	45.05	0.994675	295.7 ± 0.1	297.6 ± 0.1	0.3520
	49.73	0.994733	295.8 ± 0.1	297.3 ± 0.1	0.3527
	54.98	0.994801	295.9 ± 0.1	297.2 ± 0.1	0.3537
212.15	60.01	0.994860	296.1 ± 0.1	297.5 ± 0.1	0.3543
313.15	0	0.992216	201.1 + 0.2	2012 . 02	0.2004
	6.08	0.992319	294.4 ± 0.3	294.3 ± 0.3	0.3884
	7.07	0.992336	294.2 ± 0.2	294.1 ± 0.2	0.3887
	/.96	0.992350	294.3 ± 0.2	294.2 ± 0.2	0.3890
	8.97	0.992307	294.2 ± 0.2	294.1 ± 0.2	0.3893
	9.99	0.992303	294.5 ± 0.2	294.5 ± 0.2	0.3890
	10.90	0.992399	294.2 ± 0.2	294.3 ± 0.2	0.3899
	12.99	0.992410	294.2 ± 0.2	294.4 ± 0.2	0.3902
	12.99	0.992432	294.2 ± 0.2	294.0 ± 0.2	0.3903
	15.03	0.992466	294.1 ± 0.1	295.1 ± 0.1	0.3910
	15.96	0.992480	2942 ± 01	295.5 ± 0.1	0.3910
	18.02	0.992506	294.6 ± 0.1	296.6 ± 0.1	0.3911
	20.01	0.992532	294.9 ± 0.1	297.5 ± 0.1	0.3913
	24.94	0.992587	295.8 ± 0.1	299.1 + 0.1	0.3919
	29.94	0.992647	296.2 ± 0.1	299.3 ± 0.1	0.3927
	35.01	0.992706	296.6 ± 0.1	299.2 ± 0.1	0.3931
	39.95	0.992760	296.9 ± 0.1	299.1 ± 0.1	0.3938
	45.05	0.992817	297.1 ± 0.1	298.9 ± 0.1	0.3945
	49.73	0.992871	297.3 ± 0.1	298.5 ± 0.1	0.3951
	54.98	0.992935	297.4 ± 0.1	298.3 ± 0.1	0.3961
	60.01	0.992993	297.5 ± 0.1	298.5 ± 0.1	0.3966
318.15	0	0.990212			
	6.08	0.990306	296.1 ± 0.3	296.1 ± 0.3	0.4317
	7.07	0.990321	296.1 ± 0.2	296.1 ± 0.2	0.4320
	7.96	0.990334	296.1 ± 0.2	296.1 ± 0.2	0.4323
	8.97	0.990349	296.1 ± 0.2	296.1 ± 0.2	0.4326
	9.99	0.990364	296.1 ± 0.2	296.2 ± 0.2	0.4329
	10.96	0.990379	296.1 ± 0.2	296.2 ± 0.2	0.4332
	11.99	0.990394	296.1 ± 0.2	296.3 ± 0.2	0.4335
	12.99	0.990409	296.1 ± 0.2	296.4 ± 0.2	0.4338
	13.98	0.990424	296.1 ± 0.1	296.6 ± 0.1	0.4340
	15.03	0.990440	296.1 ± 0.1	296.8 ± 0.1	0.4343

Table 2. continued

T/K	$m/\text{mmol·kg}^{-1}$	$ ho/{ m g\cdot cm^{-3}}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_{P} \cdot 10^{3}/\mathrm{K}^{-1}$
	15.96	0.990454	296.1 ± 0.1	297.0 ± 0.1	0.4344
	18.02	0.990480	296.3 ± 0.1	297.8 ± 0.1	0.4343
	20.01	0.990503	296.6 ± 0.1	298.6 ± 0.1	0.4344
	24.94	0.990558	297.3 ± 0.1	299.9 ± 0.1	0.4350
	29.94	0.990616	297.6 ± 0.1	300.3 ± 0.1	0.4357
	35.01	0.990671	298.0 ± 0.1	300.5 ± 0.1	0.4359
	39.95	0.990721	298.3 ± 0.1	300.6 ± 0.1	0.4366
	45.05	0.990774	298.6 ± 0.1	300.4 ± 0.1	0.4372
	49.73	0.990824	298.7 ± 0.1	300.0 ± 0.1	0.4378
	54.98	0.990883	298.8 ± 0.1	299.8 ± 0.1	0.4387
	60.01	0.990938	298.9 ± 0.1	299.9 ± 0.1	0.4392

^{*a*}The relative standard uncertainty u_r of *m* is $u_r(m) = 0.0006$; the standard uncertainties *u* are $u(\rho) = 5 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$, u(T) = 0.01 K, $u(\alpha_p) = 5 \cdot 10^{-7} \text{ K}^{-1}$, and u(p) = 10 kPa.

in the literature.¹⁰ The measured density data were used to calculate the apparent molar volumes (V_{Φ}) by:¹¹

$$V_{\Phi} = \frac{M}{\rho} + \frac{10^{3}(\rho_{0} - \rho)}{m\rho_{0}\rho}$$
(1)

where *M* and *m* are the molar mass and the molality of the surfactant with the units being $g \cdot mol^{-1}$ and $mol \cdot kg^{-1}$, respectively; ρ_0 and ρ are the densities of the pure water and the surfactant solution with the unit being $g \cdot cm^{-3}$. The values of V_{Φ} are listed in column 3 of Table 2, Table 3, and Table 4, respectively, and they are plotted against the reciprocal molality in Figure 2a for DTAB, b for C₁₂HDAB, and c for C₁₂DHAB. From each of the figures one can see that, in the low surfactant concentration region, the value of V_{Φ} remains almost constant; when the surfactant concentration reaches a certain value it increases rapidly with the surfactant concentration.

According to the pseudophase separation mode, below the CMC, all of the surfactant molecules exist in the monomer state, and thus the apparent molar volume of the surfactant is that of the monomer

$$V_{\Phi} = V_{\Phi}^{\text{mon}} \qquad m \le \text{CMC}$$
 (2a)

while above the CMC, the total volume occupied by the surfactant is the sum of the contributions of the monomer and the micelle; hence the apparent molar volume V_{Φ} can be expressed as:

$$V_{\Phi} = V_{\Phi}^{\text{mic}} + \frac{\text{CMC}}{m} (V_{\Phi}^{\text{mon}} - V_{\Phi}^{\text{mic}}) \qquad m > \text{CMC}$$
(2b)

where V_{Φ}^{mon} and V_{Φ}^{mic} are the apparent molar volumes at the monomer and micellar states, respectively. As can be seen in Figure 2, the experimental apparent molar volumes for each of the systems at each of the temperatures are well fitted by two straight lines; the right horizontal one represents eq 2a, and the left is described by eq 2b. By least-squares fitting the experimental data, the slopes and the intercepts of the two straight lines were obtained, and their intersection was determined as the CMC. The values of CMC are listed and compared with the reference values^{10,12} in Table 5, which are in good agreement within the experimental uncertainties. The values of the slope CMC ($V_{\Phi}^{\text{mon}} - V_{\Phi}^{\text{mic}}$), the intercept V_{Φ}^{mic} , and the CMC allowed us to calculate V_{Φ}^{mon} for each of the systems at various temperatures; the values of V_{Φ}^{mic} and V_{Φ}^{mon} are listed in Table 6.

As can be seen from Table 6, the apparent molar volumes at the micelle state are larger than those at the monomer state for surfactants at all temperatures studied, which can be attributed to the release of the structured water molecules around the surfactants to the less ordered bulk water during the micellization processes, since the structured water molecules pack more tightly than the bulk ones.

The volume change ΔV of the micellization at a certain temperature $(\Delta V = \Delta V_{\Phi}^{\text{mic}} - \Delta V_{\Phi}^{\text{mon}})$ follows the order of DTAB $< C_{12}HDAB < C_{12}DHAB$. It may be attributed to the different extent of the hydrogen bond formation between hydroxylethyl groups of the nearby heads at the micellar state which causes the release of water molecules from the hydration shell of the head groups to the bulk water. This is different from what was observed in the comparative studies of the micellizations of dodecyldimethylethylammonium bromide (DTEAB) and DTAB, where one of the methyl group is substituted by an ethyl group in the head of DTEAB and there is no hydrogen bond formation during micellization; hence the volume changes of the micellization are almost the same for both surfactants.¹³ It can also be seen from Table 6 that the values of ΔV for all surfactants decrease with temperature increasing, which may be attributed to the fact that the increase of temperature loosens the hydration shell of surfactants; thus the volume difference occupied by the structured water and the bulk water becomes smaller.

The partial molar volume (\overline{V}) was calculated by¹⁴

$$\overline{V} = V_{\Phi} + m \left(\frac{\partial V_{\Phi}}{\partial m}\right)_{T,P}$$
(3)

The values of $(\partial V_{\Phi}/\partial m)_{T,P}$ in eq 3 can be obtained by the numeric differential of the dependence of V_{Φ} on *m* determined by the experiment. The values of the partial molar volumes of DTAB, C₁₂HDAB, and C₁₂DHAB at different temperatures are listed in column 4 of Table 2, Table 3, and Table 4, respectively. The variation of the partial volume with the molality also showed the turning points, and the corresponding CMC values were in consistency with that obtained from the plots of the apparent molar volume against the reciprocal molarity.

Isobaric Thermal Expansion Coefficient. The isobaric thermal expansion coefficient (α_p) was defined as:

$$\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \tag{4}$$

Table 3. Density ρ , Apparent Molar Volume V_{Φ} , Partial Molar Volume \overline{V} , and Isobaric Thermal Expansion Coefficient α_p for C_{12} HDAB at Different Molalities *m* under Temperature T = (293.15 to 318.15) K and Pressure $p = 0.1 \text{ MPa}^a$

T/K	$m/mmol \cdot kg^{-1}$	$ ho/{ m g}{\cdot}{ m cm}^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_P \cdot 10^3 / \mathrm{K}^{-1}$
293.15	7.98	0.998500	302.2 ± 0.2	302.0 ± 0.2	0.2177
	9.00	0.998537	302.2 ± 0.2	302.0 ± 0.2	0.2180
	10.03	0.998574	302.2 ± 0.2	302.0 ± 0.2	0.2183
	10.99	0.998610	302.1 ± 0.2	302.1 ± 0.2	0.2188
	11.95	0.998646	302.1 ± 0.2	302.7 ± 0.2	0.2191
	13.00	0.998684	302.1 ± 0.2	304.1 ± 0.2	0.2195
	13.95	0.998716	302.3 ± 0.2	305.9 ± 0.2	0.2197
	14.98	0.998747	302.7 ± 0.1	307.8 ± 0.1	0.2196
	15.95	0.998774	303.2 ± 0.1	309.3 ± 0.1	0.2199
	17.93	0.998831	303.9 ± 0.1	310.7 ± 0.1	0.2204
	19.91	0.998886	304.6 ± 0.1	310.9 ± 0.1	0.2209
	24.89	0.999025	305.8 ± 0.1	311.2 ± 0.1	0.2215
	29.94	0.999159	306.8 ± 0.1	311.2 + 0.1	0.2224
	34.93	0.999299	307.3 ± 0.1	310.0 ± 0.1	0.2231
	39.90	0.999439	307.6 ± 0.1	309.8 ± 0.1	0.2245
	44.93	0.999582	307.9 ± 0.1	310.3 ± 0.1	0.2252
	49.82	0.999714	308.2 ± 0.1	310.6 ± 0.1	0.2257
	54.88	0.999856	308.3 ± 0.1	309.9 ± 0.1	0.2272
298.15	7.98	0.997328	303.9 ± 0.2	303.7 + 0.2	0.2603
	9.00	0.997364	303.8 ± 0.2	303.7 ± 0.2	0.2605
	10.03	0.997400	303.8 ± 0.2	303.7 ± 0.2	0.2608
	10.99	0.997434	303.8 ± 0.2	303.8 ± 0.2	0.2612
	11.95	0.997468	303.8 ± 0.2	304.4 ± 0.2	0.2615
	13.00	0.997503	304.0 ± 0.2	305.8 ± 0.2	0.2619
	13.95	0.997536	304.0 ± 0.2	3074 ± 0.2	0.2621
	14.98	0.997566	304.4 ± 0.1	309.6 ± 0.1	0.2621
	15.95	0.997591	304.9 ± 0.1	3110 ± 0.1	0.2622
	17.93	0.997647	305.5 ± 0.1	311.0 ± 0.1 311.9 ± 0.1	0.2622
	19.91	0.997700	306.2 ± 0.1	311.9 ± 0.1 311.9 ± 0.1	0.2630
	24.89	0.997835	307.3 ± 0.1	312.6 ± 0.1	0.2638
	29.94	0.997963	308.3 ± 0.1	312.5 ± 0.1 312.5 ± 0.1	0.2645
	34.93	0.998101	308.5 ± 0.1 308.7 ± 0.1	312.9 ± 0.1 310.9 ± 0.1	0.2652
	39.90	0.998235	309.1 ± 0.1	311.4 ± 0.1	0.2663
	44.93	0.998372	309.3 ± 0.1	311.7 ± 0.1	0.2670
	49.82	0.998500	309.6 ± 0.1	311.9 ± 0.1	0.2676
	54.88	0.998637	309.7 ± 0.1	311.0 ± 0.1 311.1 ± 0.1	0.2688
303 15	7 98	0.995920	305.9 ± 0.2	305.8 ± 0.2	0.3030
000110	9.00	0.995954	305.9 ± 0.2	305.9 ± 0.2	0.3033
	10.03	0.995989	305.8 ± 0.2	305.9 ± 0.2	0.3035
	10.99	0.996020	305.9 ± 0.2	306.2 ± 0.2	0.3039
	11.95	0.996053	305.9 ± 0.2	306.6 + 0.2	0.3042
	13.00	0.996087	306.0 + 0.2	307.6 + 0.2	0.3045
	13.95	0.996117	306.1 + 0.2	308.8 ± 0.2	0.3047
	14.98	0.996147	306.4 + 0.1	310.2 + 0.1	0.3047
	15.95	0.996174	306.7 ± 0.1	311.5 + 0.1	0.3047
	17.93	0.996226	307.4 ± 0.1	313.1 ± 0.1	0.3051
	19.91	0.996278	307.9 ± 0.1	313.4 ± 0.1	0.3053
	24.89	0.996408	309.0 ± 0.1	313.6 ± 0.1	0.3061
	29.94	0.996535	309.8 ± 0.1	313.4 + 0.1	0.3067
	34.93	0.996667	310.2 ± 0.1	312.8 ± 0.1	0.3074
	39.90	0.996795	310.6 ± 0.1	312.6 ± 0.1	0.3083
	44.93	0.996930	310.8 ± 0.1	312.5 ± 0.1	0.3090
	49.82	0.997055	311.0 + 0.1	313.1 + 0.1	0.3097
	54.88	0.997186	311.2 ± 0.1	313.0 ± 0.1	0.3106
308.15	7.98	0.994291	308.0 + 0.2	307.9 ± 0.2	0.3459
	9.00	0.994324	307.9 ± 0.2	307.8 ± 0.2	0.3462
	10.03	0.994356	308.0 ± 0.2	307.9 ± 0.2	0.3465
	10.99	0.994387	308.0 ± 0.2	307.9 ± 0.2	0.3467
	11.95	0.994418	307.9 ± 0.2	308.2 ± 0.2	0.3470
	13.00	0.994451	308.0 ± 0.2	308.9 ± 0.2	0.3472

Table 3. continued

T/K	$m/mmol \cdot kg^{-1}$	$\rho/g \cdot cm^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_{\rm p} \cdot 10^3 / {\rm K}^{-1}$
,	13.05	0.004/81	308.0 ± 0.2	309.8 ± 0.2	0 3474
	13.95	0.994481	308.0 ± 0.2 308.2 ± 0.1	309.8 ± 0.2	0.3475
	15.05	0.994511	308.2 ± 0.1 308.4 ± 0.1	312.5 ± 0.1	0.3473
	13.95	0.994537	308.4 ± 0.1	312.3 ± 0.1	0.3473
	17.95	0.004627	309.1 ± 0.1	314.5 ± 0.1	0.3479
	19.91	0.994037	309.7 ± 0.1	314.7 ± 0.1	0.3478
	24.89	0.994/00	310.3 ± 0.1	314.0 ± 0.1	0.3487
	27.74	0.994000	311.5 ± 0.1	314.7 ± 0.1	0.3491
	20.00	0.995018	311.0 ± 0.1	313.9 ± 0.1	0.3498
	39.90	0.995142	512.0 ± 0.1	313.9 ± 0.1	0.5505
	44.93	0.9952/4	312.1 ± 0.1	313.7 ± 0.1	0.3512
	49.82	0.995395	312.4 ± 0.1	314.6 ± 0.1	0.3519
212.15	54.88	0.995520	312.6 ± 0.1	314.8 ± 0.1	0.3526
313.15	/.98	0.992462	310.3 ± 0.2	309.8 ± 0.2	0.3890
	9.00	0.992494	310.1 ± 0.2	309.6 ± 0.2	0.3893
	10.03	0.992525	310.1 ± 0.2	309.7 ± 0.2	0.3896
	10.99	0.992554	310.1 ± 0.2	309.7 ± 0.2	0.3898
	11.95	0.992584	310.0 ± 0.2	$309.8 \pm \pm 0.2$	0.3901
	13.00	0.992616	310.0 ± 0.2	310.3 ± 0.2	0.3902
	13.95	0.992644	310.1 ± 0.2	311.0 ± 0.2	0.3904
	14.98	0.992676	310.0 ± 0.1	312.0 ± 0.1	0.3905
	15.95	0.992701	310.3 ± 0.1	313.4 ± 0.1	0.3902
	17.93	0.992750	310.9 ± 0.1	315.4 ± 0.1	0.3905
	19.91	0.992800	311.3 ± 0.1	316.0 ± 0.1	0.3906
	24.89	0.992920	312.3 ± 0.1	316.2 ± 0.1	0.3916
	29.94	0.993043	312.9 ± 0.1	315.2 ± 0.1	0.3918
	34.93	0.993170	313.1 ± 0.1	315.0 ± 0.1	0.3924
	39.90	0.993291	313.4 ± 0.1	315.1 ± 0.1	0.3929
	44.93	0.993419	313.6 ± 0.1	315.0 ± 0.1	0.3936
	49.82	0.993537	313.8 ± 0.1	315.7 ± 0.1	0.3944
	54.88	0.993660	313.9 ± 0.1	315.6 ± 0.1	0.3947
318.15	7.98	0.990446	312.1 ± 0.2	311.8 ± 0.2	0.4324
	9.00	0.990476	312.1 ± 0.2	311.7 ± 0.2	0.4327
	10.03	0.990506	312.0 ± 0.2	311.6 ± 0.2	0.4330
	10.99	0.990534	312.0 ± 0.2	311.6 ± 0.2	0.4331
	11.95	0.990562	312.0 ± 0.2	311.6 ± 0.2	0.4334
	13.00	0.990593	311.9 ± 0.2	311.8 ± 0.2	0.4335
	13.95	0.990621	311.9 ± 0.2	312.1 ± 0.2	0.4337
	14.98	0.990650	312.0 ± 0.1	312.9 ± 0.1	0.4337
	15.95	0.990679	311.9 ± 0.1	313.7 ± 0.1	0.4333
	17.93	0.990727	312.4 ± 0.1	315.9 ± 0.1	0.4336
	19.91	0.990776	312.8 ± 0.1	316.9 ± 0.1	0.4336
	24.89	0.990893	313.7 ± 0.1	317.5 ± 0.1	0.4346
	29.94	0.991013	314.3 ± 0.1	316.5 ± 0.1	0.4347
	34.93	0.991136	314.5 ± 0.1	316.4 ± 0.1	0.4353
	39.90	0.991254	314.8 ± 0.1	316.4 ± 0.1	0.4356
	44.93	0.991378	314.9 ± 0.1	316.7 ± 0.1	0.4362
	49.82	0.991490	315.2 ± 0.1	317.0 ± 0.1	0.4371
	54.88	0.991613	315.3 ± 0.1	316.1 ± 0.1	0.4372
^a The relative stand	ard uncertainty $u_{\rm r}$ of m is $u_{\rm r}$	(m) = 0.0006; the stan	dard uncertainties u are $u(\rho$	$(v) = 5 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}, u(T) =$	0.01 K, $u(\alpha_p) = 5 \cdot 10^{-7}$

 K^{-1} , and u(p) = 10 kPa.

where *V* is the volume of the sample. Equation 4 can be rewritten as:

$$\alpha_{\rm p} = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_{\rm p} \tag{5}$$

The values of $(\partial \rho / \partial T)_p$ in eq 5 can be obtained by differential of the dependence of ρ on *T*, which was well-expressed by a quadratic form. The values of isobaric thermal expansion coefficients calculated by eq 5 for aqueous solutions of DTAB,

C₁₂HDAB, and C₁₂DHAB at six different temperatures are listed in column 5 of Table 2, Table 3, and Table 4, respectively; the uncertainty in determination of α_p was estimated to be about \pm $5 \cdot 10^{-7}$ K⁻¹. As an example, a typical plot of the isobaric thermal expansion coefficient against the molality of DTAB at 303.15 K is illustrated in Figure 3. It can be observed that α_p increases with the concentration of the surfactant, which may be interpreted by that increase of the amount of the surfactant in an aqueous solution results in the increase of the structured water molecules around the surfactant, hence in the increase of the amount of the Table 4. Density ρ , Apparent Molar Volume V_{Φ} , Partial Molar Volume \overline{V} , and Isobaric Thermal Expansion Coefficient α_p for C₁₂DHAB at Different Molalities *m* under Temperature T = (293.15 to 318.15) K and Pressure $p = 0.1 \text{ MPa}^a$

T/K	$m/mmol \cdot kg^{-1}$	$ ho/\text{g}\cdot\text{cm}^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\alpha_{P} \cdot 10^{3}/\mathrm{K}^{-1}$
293.15	4.97	0.998465	317.0 ± 0.3	317.5 ± 0.3	0.2172
	6.07	0.998521	317.2 ± 0.3	317.6 ± 0.3	0.2176
	6.98	0.998568	317.2 ± 0.3	317.5 ± 0.3	0.2180
	8.05	0.998622	317.3 ± 0.2	317.7 ± 0.2	0.2184
	9.09	0.998675	317.3 ± 0.2	318.1 ± 0.2	0.2187
	10.02	0.998722	317.4 ± 0.2	318.9 ± 0.2	0.2190
	11.09	0.998774	317.7 ± 0.2	320.2 ± 0.2	0.2192
	12.02	0.998818	317.9 ± 0.2	321.5 ± 0.2	0.2193
	13.06	0.998867	318.2 ± 0.2	323.2 ± 0.2	0.2195
	14.14	0.998915	318.7 ± 0.2	325.4 ± 0.2	0.2198
	15.05	0.998953	319.1 ± 0.1	327.0 ± 0.1	0.2197
	16.09	0.998993	319.8 ± 0.1	327.7 ± 0.1	0.2198
	18.15	0.999080	320.6 ± 0.1	326.9 ± 0.1	0.2205
	20.08	0.999160	321.2 ± 0.1	327.1 ± 0.1	0.2205
	25.18	0.999367	322.5 ± 0.1	327.9 ± 0.1	0.2214
	30.23	0.999571	323.4 ± 0.1	327.2 ± 0.1	0.2219
	35.25	0.999778	323.8 ± 0.1	326.7 ± 0.1	0.2233
	40.28	0.999983	324.2 ± 0.1	326.5 ± 0.1	0.2239
	45.12	1.000187	324.4 ± 0.1	325.9 ± 0.1	0.2248
	50.25	1.000398	324.6 ± 0.1	326.7 ± 0.1	0.2258
298.15	4.97	0.997294	319.4 ± 0.3	319.4 ± 0.3	0.2596
	6.07	0.997349	319.4 ± 0.3	319.4 ± 0.3	0.2600
	6.98	0.997394	319.4 ± 0.3	319.5 ± 0.3	0.2603
	8.05	0.997446	319.5 ± 0.2	319.5 ± 0.2	0.2607
	9.09	0.997498	319.4 ± 0.2	319.3 ± 0.2	0.2610
	10.02	0.997544	319.4 ± 0.2	319.6 ± 0.2	0.2613
	11.09	0.997597	319.4 ± 0.2	320.9 ± 0.2	0.2615
	12.02	0.997641	319.6 ± 0.2	322.8 ± 0.2	0.2617
	13.06	0.997686	320.1 ± 0.2	325.0 ± 0.2	0.2618
	14.14	0.097734	320.4 ± 0.2	326.7 ± 0.2	0.2620
	15.05	0.997//1	320.9 ± 0.1	328.0 ± 0.1	0.262
	10.09	0.007807	521.5 ± 0.1	328.4 ± 0.1	0.2021
	20.08	0.997976	322.1 ± 0.1 322.6 ± 0.1	327.7 ± 0.1 328.1 ± 0.1	0.2628
	25.18	0.998178	323.9 ± 0.1	329.0 ± 0.1	0.2635
	30.23	0.998380	324.7 ± 0.1	3284 ± 0.1	0.2641
	35.25	0.998580	325.2 ± 0.1	328.4 ± 0.1	0.2652
	40.28	0.998782	325.6 ± 0.1	327.4 ± 0.1	0.2658
	45.12	0.998981	325.7 ± 0.1	327.2 ± 0.1	0.2666
	50.25	0.999187	325.9 ± 0.1	328.1 ± 0.1	0.2675
303.15	4.97	0.995890	321.6 ± 0.3	321.8 ± 0.3	0.3022
	6.07	0.995942	321.7 ± 0.3	321.9 ± 0.3	0.3026
	6.98	0.995986	321.6 ± 0.3	321.7 ± 0.3	0.3029
	8.05	0.996036	321.7 ± 0.2	321.8 ± 0.2	0.3032
	9.09	0.996086	321.7 ± 0.2	321.8 ± 0.2	0.3035
	10.02	0.996130	321.7 ± 0.2	322.3 ± 0.2	0.3038
	11.09	0.996180	321.8 ± 0.2	323.2 ± 0.2	0.3040
	12.02	0.996222	322.0 ± 0.2	324.3 ± 0.2	0.3042
	13.06	0.996268	322.2 ± 0.2	325.5 ± 0.2	0.3043
	14.14	0.996315	322.5 ± 0.2	326.9 ± 0.2	0.3044
	15.05	0.996353	322.8 ± 0.1	328.1 ± 0.1	0.3044
	16.09	0.996394	323.2 ± 0.1	329.1 ± 0.1	0.3045
	18.15	0.996476	323.9 ± 0.1	329.4 ± 0.1	0.3049
	20.08	0.996554	324.4 ± 0.1	329.4 ± 0.1	0.3052
	25.18	0.996752	325.6 ± 0.1	330.2 ± 0.1	0.3058
	30.23	0.996950	326.3 ± 0.1	329.6 ± 0.1	0.3064
	33.23	0.007244	320.8 ± 0.1	329.0 ± 0.1	0.3072
	40.28	0.007520	$32/.1 \pm 0.1$	328.7 ± 0.1	0.30/8
	43.12	0.77/337	327.2 ± 0.1	320.5 ± 0.1 320.5 ± 0.1	0.3000
	50.25	0.77// TU	54/.T <u>1</u> 0.1	547.5 <u>1</u> 0.1	0.3073

Table 4. continued

T/K	$m/\text{mmol}\cdot\text{kg}^{-1}$	$ ho/ ext{g}\cdot ext{cm}^{-3}$	$V_{\Phi}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$\overline{V}/\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$	$\alpha_{p} \cdot 10^{3} / \mathrm{K}^{-1}$
308.15	4.97	0.994266	323.7 ± 0.3	323.7 ± 0.3	0.3450
	6.07	0.994317	323.7 ± 0.3	323.7 ± 0.3	0.3453
	6.98	0.994359	323.7 ± 0.3	323.7 ± 0.3	0.3456
	8.05	0.994408	323.7 ± 0.2	323.7 ± 0.2	0.3459
	9.09	0.994456	323.7 ± 0.2	323.6 ± 0.2	0.3462
	10.02	0.994499	323.7 ± 0.2	323.7 ± 0.2	0.3465
	11.09	0.994548	323.7 ± 0.2	324.2 ± 0.2	0.3467
	12.02	0.994590	323.8 ± 0.2	325.0 ± 0.2	0.3469
	13.06	0.994637	323.8 ± 0.2	326.6 ± 0.2	0.3470
	14.14	0.994681	324.2 ± 0.2	328.8 ± 0.2	0.3471
	15.05	0.994719	324.4 ± 0.1	330.3 ± 0.1	0.3471
	16.09	0.994756	325.1 + 0.1	331.4 + 0.1	0.3472
	18.15	0.994837	325.7 + 0.1	330.8 ± 0.1	0.3474
	20.08	0.994913	326.1 ± 0.1	330.5 ± 0.1	0.3478
	25.18	0.995110	327.1 + 0.1	330.9 ± 0.1	0.3483
	30.23	0.995305	327.7 ± 0.1	330.9 ± 0.1	0.3488
	35.25	0.995497	328.2 ± 0.1	330.8 ± 0.1	0.3494
	40.28	0.995692	328.4 ± 0.1	329.7 ± 0.1	0.3500
	45.12	0.995884	328.5 ± 0.1	329.6 ± 0.1	0.3507
	50.25	0.996082	328.7 ± 0.1	330.6 ± 0.1	0.3513
313.15	4.97	0.992443	325.8 ± 0.3	325.9 ± 0.3	0.3880
515.15	4.97	0.992492	325.9 ± 0.3	325.9 ± 0.3	0.3883
	6.98	0.992533	325.9 ± 0.3 325.8 ± 0.3	325.9 ± 0.3	0.3885
	8.05	0.992580	325.9 ± 0.2	325.9 ± 0.9 326.1 ± 0.2	0.3887
	8.05	0.992580	325.9 ± 0.2	326.1 ± 0.2	0.3801
	9.09	0.992620	325.9 ± 0.2	326.2 ± 0.2	0.3894
	11.00	0.992007	323.9 ± 0.2	326.2 ± 0.2	0.3897
	11.09	0.992/14	320.0 ± 0.2	320.2 ± 0.2	0.3897
	12.02	0.992/33	320.0 ± 0.2	320.4 ± 0.2	0.3898
	13.00	0.992801	320.0 ± 0.2	327.1 ± 0.2	0.3898
	14.14	0.99284/	520.1 ± 0.2	326.7 ± 0.2	0.3899
	15.05	0.992884	320.5 ± 0.1	330.4 ± 0.1	0.3899
	10.09	0.992925	320.7 ± 0.1	331.9 ± 0.1	0.3900
	10.15	0.993001	327.4 ± 0.1	332.5 ± 0.1	0.3901
	20.08	0.993070	327.7 ± 0.1	332.1 ± 0.1	0.3900
	25.18	0.993207	328.7 ± 0.1	332.5 ± 0.1	0.3910
	30.23	0.993400	329.2 ± 0.1	331.0 ± 0.1	0.3910
	35.25	0.993649	329.7 ± 0.1	332.1 ± 0.1	0.3918
	40.28	0.993840	329.9 ± 0.1	331.3 ± 0.1	0.3925
	45.12	0.994027	330.0 ± 0.1	331.0 ± 0.1	0.3932
210.15	50.25	0.994223	330.1 ± 0.1	331.5 ± 0.1	0.3935
516.15	4.97	0.990430	327.8 ± 0.3	327.5 ± 0.3	0.4312
	6.07	0.990478	327.8 ± 0.3	327.5 ± 0.5	0.4315
	0.98	0.990318	327.7 ± 0.3	327.4 ± 0.3	0.4317
	8.05	0.990564	327.7 ± 0.2	327.6 ± 0.2	0.4319
	9.09	0.990609	327.7 ± 0.2	$32/.7 \pm 0.2$	0.4322
	10.02	0.990649	327.7 ± 0.2	327.8 ± 0.2	0.4325
	11.09	0.990695	327.7 ± 0.2	$32/.8 \pm 0.2$	0.4329
	12.02	0.990735	327.7 ± 0.2	328.0 ± 0.2	0.4330
	13.06	0.990780	327.7 ± 0.2	328.6 ± 0.2	0.4330
	14.14	0.990825	327.8 ± 0.2	329.9 ± 0.2	0.4330
	15.05	0.990862	328.0 ± 0.1	331.3 ± 0.1	0.4330
	16.09	0.990900	328.4 ± 0.1	332.5 ± 0.1	0.4331
	18.15	0.990980	328.8 ± 0.1	333.3 ± 0.1	0.4331
	20.08	0.991051	329.3 ± 0.1	333.7 ± 0.1	0.4336
	25.18	0.991242	330.1 ± 0.1	333.2 ± 0.1	0.4339
	30.23	0.991431	330.6 ± 0.1	332.9 ± 0.1	0.4345
	35.25	0.991620	330.9 ± 0.1	333.0 ± 0.1	0.435
	40.28	0.991807	331.2 ± 0.1	332.7 ± 0.1	0.4352
	45.12	0.991991	331.3 ± 0.1	332.1 ± 0.1	0.4358
	50.25	0.992184	331.4 ± 0.1	332.5 ± 0.1	0.4360

Table 4. continued

^aThe relative standard uncertainty u_r of m is $u_r(m) = 0.0006$; the standard uncertainties u are $u(\rho) = 5 \cdot 10^{-6}$ g·cm⁻³, u(T) = 0.01 K, $u(\alpha_p) = 5 \cdot 10^{-7}$ K^{-1} , and u(p) = 10 kPa.



Figure 2. Dependence of the apparent molar volume on the reprocical molality of the surfactants: a, DTAB; b, C12HDAB; c, C12DHAB. The symbols represent the experimental data: \Rightarrow , 318.15 K; \bullet , 313.15 K; \triangle , 308.15 K; ▲, 303.15 K; O, 298.15 K; ■, 293.15 K; the lines are the results of the fits.

structured water being loosened due to increase of the temperature. There is a clear discontinuity in the plot of $\alpha_{\rm P}$ against the concentration as shown in Figure 3, where the

concentration coincides well with the CMC value for DTAB at 303.15 K. Similar discontinuities and the consistency in the CMC values were observed for aqueous solutions of C12HDAB, C12DHAB, and DTAB at all temperatures studied. After the micellization, the amount of the structured water around the surfactant significantly reduces; thus the discontinuities on the plots of $\alpha_{\rm P}$ against the concentration of the surfactant are expected.

The apparent thermal expansion coefficient α_p^i (i = monomer or micellar state) of the surfactant at the monomer state or the micellar state can be calculated through

$$\alpha_p^{i} = \frac{1}{V_{\Phi}^{i}} \left(\frac{\partial V_{\Phi}^{i}}{\partial T} \right)_p = -\frac{1}{\rho^{i}} \left(\frac{\partial \rho^{i}}{\partial T} \right)_p \tag{6}$$

The values of $(\partial_{\rho}^{i}/\partial T)_{p}$ in eq 6 can be obtained by differential of the dependences of ρ^{i} on T, which were well-described by linear forms for both monomer and micellar states of all systems we studied. Table 6 also lists the values of α_{P}^{i} from which one can see that at the micellar state $\alpha_p^{\rm mic}$ decreases with the increase of the hydroxyethyl substituent number, which may be attributed to the fact that the hydrogen bonding formation between hydroxyethyl groups disorders the structured water around the headgroups, which reduces the extent to further loosen their structure order during increasing the temperature; while at the monomer state, the distinction between C₁₂HDAB and C₁₂DHA in the isobaric thermal expansion α_p^{mon} is not obvious, because the hydrogen bonding between the headgroups hardly forms in the dilute surfactant monomer aqueous solutions.

Micellization Thermodynamics. The conductivity is plotted against the concentration for each of surfactant solutions and each of the temperatures in Figure 4a for C12HDAB and Figure 4b for C_{12} DHAB, respectively, from which one can clearly see a turning point for each of the curves. By least-squares fitting of the experiment data before and after the point, two straight lines can be obtained whose intersection was taken as the CMC. The values of the CMC obtained by the conductivity measurements are listed in row 6 for C12HDAB and row 10 for C12DHAB in Table 5. The CMC values detected by using the conductivity method were in good consistence with that determined by measurements of the density and agreed well

Fable 5. CMC Values of DTAI	B, C12HDAB, and C12DHAB at Temp	perature $T = (293.15 \text{ to } 318.15)$) K and Pressure <i>p</i> = 0.1 MPa ^a
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T/K	293.15	298.15	303.15	308.15	313.15	318.15
			DTAB			
CMC ^{dm} /mmol·kg ⁻¹	14.3 ± 0.3	14.7 ± 0.4	15.4 ± 0.4	15.9 ± 0.3	16.4 ± 0.4	17.6 ± 0.7
$\rm CMC^r/mmol\cdot L^{-1}$	14.3 ^b	14.6 ^b	15.1 ^b ,15.3 ^c	15.9 ^b	16.6 ^b	17.5 ^b
			C ₁₂ HDAB			
CMC ^{cm} /mmol·kg ⁻¹	13.1 ± 0.4	13.4 ± 0.7	13.5 ± 0.7	13.9 ± 0.6	14.2 ± 0.5	14.9 ± 0.8
CMC ^{dm} /mmol·kg ⁻¹	13.7 ± 0.3	13.9 ± 0.4	14.1 ± 0.4	14.5 ± 0.3	14.9 ± 0.3	15.6 ± 0.3
$\rm CMC^r/mmol\cdot L^{-1}$		13.20 ^d	13.43 ^d	13.92 ^d	14.22 ^d	14.83 ^d
			C ₁₂ DHAB			
CMC ^{cm} /mmol·kg ⁻¹	12.1 ± 0.3	12.3 ± 0.4	12.6 ± 0.5	13.0 ± 0.5	13.3 ± 0.7	13.8 ± 0.6
CMC ^{dm} /mmol·kg ⁻¹	12.1 ± 0.3	12.4 ± 0.4	12.6 ± 0.4	13.0 ± 0.2	13.5 ± 0.6	13.9 ± 0.4
CMC ^r /mmol·L ⁻¹		12.46 ^d	12.62^{d}	13.09 ^d	13.36 ^d	13.89 ^d

^aCMC^{cm}: determined by conductivity measurement in this work, CMC^{dm}: determined by density measurement in this work, CMC': from reference. The standard uncertainties u are u(T) = 0.01 K and u(p) = 10 kPa. ^bReference 10. ^cReference 12. ^dReference 6.

Table 6. Volumetric Properties of DTAB, C_{12} HDAB, and C_{12} DHAB at Monomer and Micellar States at Temperature T = (293.15 to 318.15) K and Pressure $p = 0.1 \text{ MPa}^a$

T/K	293.15	298.15	303.15	308.15	313.15	318.15
			DTAB			
$V_{\Phi}^{\mathrm{mon}}/\mathrm{cm}^{3}\cdot\mathrm{mol}^{-1}$	286.1 ± 0.1	287.9 ± 0.1 288.2^{b}	290.0 ± 0.1	292.1 ± 0.1 292.2^{b}	294.1 ± 0.1	296.1 ± 0.1
$V_{\Phi}^{ m mic}/ m cm^3 \cdot mol^{-1}$	293.4 ± 0.1	294.7 ± 0.2 294.8^{b}	296.3 ± 0.1	297.5 ± 0.1 297.5^{b}	298.7 ± 0.1	300.2 ± 0.1
$\Delta V/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	7.3 ± 0.2	6.8 ± 0.3 6.6^{b}	6.3 ± 0.2	5.4 ± 0.2 5.3^{b}	4.6 ± 0.2	4.1 ± 0.2
$\alpha^{\text{mon}} \cdot 10^3 / \text{K}^{-1}$	1.4086	1.3996	1.3899	1.3797	1.3702	1.3613
$\alpha^{\rm mic} \cdot 10^3/{\rm K}^{-1}$	0.9167	0.9127	0.9080	0.9042	0.9005	0.8961
			C ₁₂ HDAB			
$V_{\Phi}^{\rm mon}/{\rm cm}^3 \cdot {\rm mol}^{-1}$	302.1 ± 0.2	303.9 ± 0.2	305.9 ± 0.2	307.9 ± 0.1	310.0 ± 0.1	311.8 ± 0.1
$V_{\Phi}^{ m mic}/ m cm^3 \cdot mol^{-1}$	310.5 ± 0.1	311.8 ± 0.1	313.1 ± 0.1	314.2 ± 0.1	315.5 ± 0.1	316.7 ± 0.1
$\Delta V/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	8.4 ± 0.3	7.9 ± 0.3	7.2 ± 0.3	6.3 ± 0.2	5.5 ± 0.2	4.9 ± 0.2
$\alpha^{\text{mon}} \cdot 10^3 / \text{K}^{-1}$	1.3091	1.3012	1.2927	1.2841	1.2757	1.2680
$\alpha^{\rm mic} \cdot 10^3/{\rm K}^{-1}$	0.7948	0.7915	0.7883	0.7854	0.7824	0.7792
			C ₁₂ DHAB			
$V_{\Phi}^{\mathrm{mon}}/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	317.4 ± 0.1	319.3 ± 0.1	321.7 ± 0.1	323.7 ± 0.1	325.8 ± 0.1	327.6 ± 0.1
$V_{\Phi}^{ m mic}/ m cm^3 \cdot mol^{-1}$	327.1 ± 0.1	328.3 ± 0.1	329.4 ± 0.1	330.6 ± 0.1	331.9 ± 0.1	333.0 ± 0.1
$\Delta V/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	9.7 ± 0.2	9.0 ± 0.2	7.7 ± 0.2	6.9 ± 0.2	6.1 ± 0.2	5.4 ± 0.2
$\alpha_p^{\text{mon}} \cdot 10^3 / \text{K}^{-1}$	1.3104	1.3025	1.2929	1.2849	1.2766	1.2694
$\alpha_P^{ m mic} \cdot 10^3/ m K^{-1}$	0.7268	0.7241	0.7216	0.7190	0.7162	0.7139
	(i) -			b_{-}		

^aThe standard uncertainties u are $u(\alpha_P^i) = 5 \cdot 10^{-7} \text{ K}^{-1}$, u(T) = 0.01 K, and u(p) = 10 kPa. ^bReference 20.



Figure 3. Illustration of dependence of isobaric thermal expansion coefficients of the DTAB aqueous solutions on the concentration at 293.15 K.

with those reported in the literature.⁶ It can also be found that the values of CMC slightly increase with the temperature for all three surfactants. This phenomenon was commonly reported for the ionic surfactants and can be explained by that the hydrophobic interaction of the surfactant tails becomes weaker and the static repulsion between the headgroups is strengthened due to the decrease of the association degree of the counterion when temperature increases, both of which hinder the micelle formation. The CMC values of the three surfactants follow the order of DTAB > C_{12} HDAB > C_{12} DHAB at the same temperature. As mentioned above, the formation of hydrogen bonds between hydroxyethyl groups in micelles is enhanced by increase of the micellization at the relatively lower surfactant concentration.

The slopes of the plot of the conductivity against the concentration of the surfactant in the post-CMC region (k) and the pre-CMC region (k') in Figure 4 were used to calculate the dissociation degree (α) of the counterions by $\alpha = k/k'$, and the association degree (β) was obtained by $\beta = 1 - \alpha$, which is



Figure 4. Variation of the conductivity with the concentration of the surfactants in aqueous solutions: a, C_{12} HDAB; b, C_{12} DHAB. The symbols represent the experimental data: \Rightarrow , 318.15 K; \bigcirc , 313.15 K; \triangle , 308.15 K; \bigstar , 303.15 K; \bigcirc , 298.15 K; \blacksquare , 293.15 K, the lines are results of the fits.

listed in row 3 for C₁₂HDAB and row 7 for C₁₂DHAB of Table 7, respectively. As can be seen from Table 7, the values of β for both surfactants decrease with the increase of temperature, which is commonly observed for ionic surfactants and may be attributed to increase of the dissociation entropy of counterions with temperature. At a certain temperature the value of β decreases with the increase of the substituent hydroxyethyl group, which is in consistent with what was observed by Chatterjee et al. in their

T/K	293.15	298.15	303.15	308.15	313.15	318.15
			C ₁₂ HDAB			
β	0.766 ± 0.005	0.764 ± 0.005	0.761 ± 0.005	0.758 ± 0.005	0.756 ± 0.005	0.754 ± 0.005
$\Delta G_{ m mic}^0/{ m KJ}{ m \cdot mol}^{-1}$	-35.94 ± 0.44	-36.42 ± 0.48 -41.37^{b}	-36.91 ± 0.48 -41.97^{b}	-37.33 ± 0.47 -42.48 ^b	-37.78 ± 0.47 -43.06^{b}	-38.10 ± 0.50 -43.52^{b}
			C ₁₂ DHAB			
β	0.764 ± 0.005	0.758 ± 0.005	0.753 ± 0.005	0.748 ± 0.005	0.743 ± 0.005	0.740 ± 0.005
$\Delta G_{ m mic}^0/{ m KJ}{ m \cdot mol^{-1}}$	-36.24 ± 0.43	-36.65 ± 0.45 -41.65^{b}	-37.06 ± 0.46 -42.29^{b}	-37.40 ± 0.46 -42.80^{b}	-37.81 ± 0.50 -43.39^{b}	-38.17 ± 0.48 -43.87^{b}
am1 1 1			to ID bD C			

^{*a*}The standard uncertainties *u* are u(T) = 0.05 K and u(p) = 10 kPa. ^{*b*}Reference 6.

studies of the series of hydroxyethyl substituted cetylammonium bromide surfactants.¹⁵ This may be attributed to the fact that the volume of the hydroxyethyl group is larger than that of the methyl group which leads to the increase of the distance and hence the decrease of the positive charge density on the micelle interface; thus the binding ability of negatively charged counterions to the micelle surface is reduced.

The micellization of a one mole single tail ionic surfactant may be interpreted by that it reacts with β mole counterions. Thus the standard Gibbs free energy $\Delta G_{\rm mic}^0$ of micellization may be defined by the change of the Gibbs free energy in an ideal dilute surfactant solution with the surfactant concentration being 1 mol·kg⁻¹. The value of $\Delta G_{\rm mic}^0$ may be calculated by¹⁶

$$\Delta G_{\rm mic}^0 = (1+\beta)RT \ln({\rm CMC}/m^0) \tag{7}$$

where $m^0 = 1$ mol·kg⁻¹. The values of ΔG_{mic}^0 for C₁₂HDAB and C₁₂DHAB are listed in Table 7 and compared with those obtained by using the isothermal titration calorimetry reported by Tong et al.⁶ The differences were mainly resulted from the contributions of the association degree of the counterions at the micellar state, which were neglected by Tong et al.⁶ As it can be seen from eq 7 the absolute value of ΔG_{mic}^0 should decrease with β ; however it increases, and β decreases with the increase of temperature as shown in Table 7, which is in accordance with those reported in literature.^{17,18} It indicates that the temperature dependence of ΔG_{mic}^0 is dominated by CMC. It can also been seen from Table 7 that the values of ΔG_{mic}^0 slightly decrease with the increase of the number of the hydroxyethyl groups, which is resulted from the change of CMC with the increase of the number of hydroxyethyl groups in the head of the surfactant.

Aggregation Number. The aggregation numbers (N) of the micelle formed by C₁₂HDAB and C₁₂DHAB are determined by using the steady-state fluorescence. The aggregation numbers are obtained using the following relation:

$$\ln \frac{I_0}{I} = \frac{N[Q]}{C - CMC} \tag{8}$$

where I_0 and I are the fluorescence intensities at 373 nm in the absence and presence of the quencher, respectively; [Q] and C are the concentrations of the quencher and the surfactant with the units being mmol·kg⁻¹. The plots of $\ln(I_0/I)$ against [Q] are shown in Figure 5. Linear least-squares fits of the experimental data gave the slopes which together with known values of C and CMC were used to calculate the aggregation numbers N. The obtained values of N were 52 ± 2 for C_{12} HDAB and 51 ± 2 for C_{12} DHAB, respectively; the value of N for DTAB was reported to be 51 by the literature,¹⁹ and it seems that the hydroxyethyl substituent has little effect on the aggregation number of the micelle formed by this series of surfactants.



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Figure 5. Dependence of $\ln(I_0/I)$ on the concentration of the quencher. The symbols represent the experimental data: \blacksquare , C₁₂HDAB ($C = 50.0 \text{ mmol} \cdot \text{kg}^{-1}$); \bullet , C₁₂DHAB ($C = 50.0 \text{ mmol} \cdot \text{kg}^{-1}$); the lines are the results of the fits.

The radius (r) of the micelle formed by the surfactant can be calculated using the volumetric data and the aggregation number through a simple geometric model:

$$V_{\rm m} = \frac{4}{3}\pi r^3 = \frac{N(V_{\Phi}^{\rm mic} - \alpha V_{\rm Br})}{N_{\rm A}}$$
(9)

where $V_{\rm m}$ is the volume of a micelle, $N_{\rm A}$ is the Avogadro constant, and $V_{\rm Br^-}$ is the volume of Br⁻. The surface area $(A_{\rm mic})$ occupied by a surfactant molecule can be obtained though $A_{\rm mic} = 4\pi r^2/N$. The values of *r* and $A_{\rm mic}$ are listed and compared with that reported in the literature^{17,18} in Table 8, from which one can see

Table 8. Radius of the Micelle *r* and the Surface Area A_{mic} Occupied by a Surfactant Molecule in the Micellar State in Aqueous Solutions at Temperature *T* = 298.15 K and Pressure *p* = 0.1 MPa^{*a*}

	DTAB	C ₁₂ HDAB	C ₁₂ DHAB
r/nm	$1.80/1.8^{b}$	1.86 ± 0.02	1.87 ± 0.02
$A_{\rm mic}/\rm nm^2$	0.79/0.78 ^c	0.82 ± 0.01	0.86 ± 0.01
'The standard	uncertainties <i>u</i> are	u(T) = 0.05 K an	d $u(p) = 10$ kPa.
Reference 17	^c Reference 18		

that our results are in excellent agreement with the literature ones and they increase with the substituent number of the hydroethyl group in the headgroup. The increase of $A_{\rm mic}$ with the substituent number of the hydroethyl group is in consistence with what we proposed in above discussion of the association degree β of the counterion to the micelle, which was found to decrease with the increase of the substituent number of the hydroxyethyl group in the headgroup.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86 21 64250804. Fax: +86 21 64250804. E-mail: shenwg@ecust.edu.cn.

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