

M.A. Morini
R.M. Minardi
P.C. Schulz
J.E. Puig
J.L. Rodriguez

Partial molar volume of dodecyltrimethylammonium hydroxide in water and NaOH aqueous solutions

Received: 27 October 1997
Accepted: 4 March 1998

M.A. Morini · R.M. Minardi
P.C. Schulz (✉) · J.L. Rodriguez
Departamento de Química e Ingeniería
Universidad Nacional del Sur
Avda. Alem 1253
8000 Bahía Blanca
Argentina

J.E. Puig
Departamento de Ingeniería Química
Universidad de Guadalajara
Jal. México

Abstract The partial molar volume of dodecyltrimethylammonium hydroxide in water and aqueous NaOH solutions was measured. The addition of NaOH did not affect either the micellized or the unmicellized molecules. The expansion on micellization is much larger than in dodecyltrimethylammonium bromide systems, which reflects the stronger ionization of the hydroxide surfactant micelles, when compared with that of the bromide amphiphile.

Key words Hydroxide surfactants – micelles – partial molar volume – Dodecyltrimethylammonium hydroxide

Introduction

Alkyltrimethylammonium hydroxides (RTAOH) are scarcely studied surfactants with some striking properties [1–3]. Much of the literature data is contradictory. The properties of DTAOH are of theoretical and practical interest, mainly in the interpretation of micellar catalysis [4].

In this laboratory, we studied some physicochemical properties of the dodecyltrimethylammonium hydroxide (DTAOH) aqueous solutions, and partial molar volume measurements gave valuable information about micelle structure and the interaction between surfactant and solvent.

Theory

The partial molar volume of the solute species at the critical micelle concentration (cmc) was computed with the

equation [5, 6]

$$\bar{V}_i = \frac{1}{\delta_{\text{cmc}}} \left[M - V \frac{\partial \delta}{\partial C} \right], \quad (1)$$

where the subscript i is m for the micellized surfactant and s for the single dispersed one. M is the molar mass of the surfactant ($245.45 \text{ g mol}^{-1}$), $\partial \delta / \partial C$ is the slope of the density-surfactant concentration curve below (for s) and above the cmc (for m), δ_{cmc} is the density at the cmc, and V is the volume of solution having 1000 cm^3 of water:

$$V = \frac{1000 + CM}{\delta} \quad (2)$$

Equation (1) assumes that the behaviour of the solvent is ideal. This is not strictly true, but we assumed approximately ideal behaviour of water based on water vapour pressure measurements in the system Aerosol OT–water, which indicated that the activity of water in dilute surfactant solutions is very close to that of pure water [7].

The partial molar volume of amphiphiles may be computed by the addition of the contributions of the polar

head $((\text{CH}_3)_3\text{N}^+)$, V_{ph} , the n_{C} methylene groups of the chain (V_{CH_2}) and the counterion V_{ci} [8]. The contributions of methylene groups are independent of the polar head nature [6, 8, 9], but the four methylene groups which are adjacent to the polar head have contributions to the whole partial molar volume which are different to that of the other methylene groups of the tail [9]. The methylene and polar head group contributions are also different in the micellized and single dispersed states of the surfactant molecules. In Table 1 we have collected these contributions from the literature. We computed the contribution of the polar head group with these data by the equation

$$\bar{V} = (n_{\text{C}} - 4)\bar{V}_{\text{CH}_2} + 4\bar{V}_{\text{CH}_2}^* + \bar{V}_{\text{ph}} + \bar{V}_{\text{ci}}, \quad (3)$$

where the asterisk indicates the contribution of the four methylene groups which are adjacent to the polar head group. The contribution of the hydrocarbon tail to the molar partial volume was computed as $189.5 \pm 1.6 \text{ cm}^3 \text{ mol}^{-1}$ for the unmicellised surfactant and $200 \pm 4 \text{ cm}^3 \text{ mol}^{-1}$ for the micellised one by using Eq. (3).

It was observed that amphiphile molar partial volumes are almost independent of concentration [8, 13–15], and they may be considered as the infinite dilution values (V_0). The radius r_i of the polar head group and the electrostric-

tion effect may be computed with the equation of Hapler [16, 17]:

$$\bar{V}_{0,i} - \bar{V}_{0,\text{H}^+} = \alpha_i r_i^3 - \frac{\beta_i Z_i^2}{r_i}, \quad (4)$$

where Z_i is the valence of the ion i , whose partial molar volume at infinite dilution is $V_{0,i}$, and α_i and β_i are constants equal to $5.3 \text{ cm}^3 \text{ mol}^{-1} \text{ \AA}^{-3}$ and $4.7 \text{ cm}^3 \text{ \AA} \text{ mol}^{-1}$ for cations and $4.6 \text{ cm}^3 \text{ mol}^{-1} \text{ \AA}^{-3}$ and $19 \text{ cm}^3 \text{ \AA} \text{ mol}^{-1}$ for anions. V_{0,H^+} is the partial molar volume of H^+ ions at infinite dilution, taken as $-4.5 \text{ cm}^3 \text{ mol}^{-1}$ [12]. The first term on the right-hand side of Eq. (4) is interpreted as the volume of the cavity formed in the solvent by the ion i , and the second term as the electrostriction effect.

Experimental

The preparation of DTAOH was reported in a preceding paper [18]. A concentrated solution of DTAOH was employed to prepare five series of dilutions with fixed NaOH concentrations: 0–0.0001–0.01–0.05 and 0.1 mol dm^{-3} . In all samples double-distilled, CO_2 -free water was employed. Precautions were employed to avoid CO_2 contamination of the solutions in the preparation and measurements, working in a CO_2 -free atmosphere [18]. Density measurements were made with a Chainomatic density balance at $20.0 \pm 0.1^\circ\text{C}$, using double-distilled water as reference.

Confidence intervals were taken with a confidence level of 0.90, using the Student's "t" distribution. Weighted averages were computed by the minimum variance unbiased linear estimation method [19].

Results

The density vs. concentration plots were linear with a break at the critical micelle concentration (cmc). Figure 1 shows that of DTAOH without added NaOH, the plots for the other systems being similar. Table 2 shows the data of density vs. concentration straight lines. The cmc values are similar to that previously determined with other methods [18]. The computed molar partial volumes are shown in Table 3.

Discussion

Table 3 shows that the partial molar volume of DTAOH was independent of the NaOH concentration. This situation has been found in other surfactant systems [20].

Table 1 Collected data for the contribution of components of the surfactant molecule to the partial molar volume

Group	Contribution [$\text{cm}^3 \text{ mol}^{-1}$]	Observations	Reference
–CH ₂ –	15.60 ± 0.69	a, m	[9]
	15.9	a, s	[9]
	$16.1 - 15.7 - 15.5$		
	– 15.8	b, s	[9]
	$15.5 - 15.4$	b, s	[8]
Average	15.70 ± 0.55	b, s	[6]
	15.66 ± 0.20	b, s	
	$17.4 - 17.2 - 17.3$	b, m	[9]
Average	17.28 ± 0.17	b, m	[6]
	17.18 ± 0.16	b, m	
–(CH ₃) ₃ N ⁺	$70.6 - 69.8 - 69.5$		
	– 68.6 – 68.3	s	[8]
	61.1	s	[10]
Average	68.0 ± 3.1	s	
	$67.3 - 67.6$	m	[8]
	74.2	m	[11]
	73.3	m	[11]
	70.8	m	[8]
Average:	70.6 ± 3.4	m	
OH [–]	– 1.1		[12]
Br [–]	29.2		[12]
Cl [–]	22.3		[12]

s: unmicellized, m: micellized, a: first four methylene groups adjacent to the polar head, b: other methylene groups.

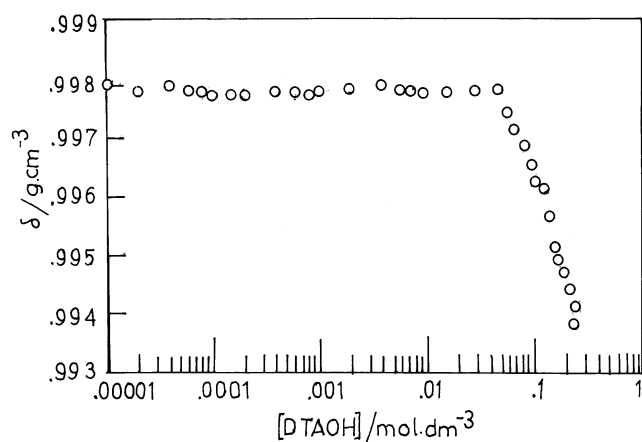


Fig. 1 Density of DTAOH aqueous solutions vs. the molar concentration

Table 2 Data for the density vs. concentration curves (density in g cm^{-3} , concentration in mol dm^{-3})

[NaOH]	Pre-cmc		Post-cmc		cmc
	Intercept	Slope	Intercept	Slope	
0	0.99782	-0.001	0.9983	-0.0186	0.026
0.0001	0.99823	0.004	0.99839	-0.024	0.006
0.01	0.99813	0.004	0.9986	-0.018	0.02
0.05	0.99840	0.010	0.99860	-0.0145	0.013
0.1	0.9976	0.000	0.9980	-0.019	0.029

Table 3 Partial molar volume of micellized and unmixed DTAOH at different concentration of added NaOH

[NaOH] [mol dm ⁻³]	Partial molar volume ($\text{cm}^3 \text{mol}^{-1}$)		Change on micellization
	micellized	unmicellized	
0	264.80 ± 0.76	246.9 ± 2.3	17.9 ± 3.0
0.0001	269.7 ± 1.6	242 ± 11	28 ± 13
0.01	264.1 ± 1.1	242 ± 11	22 ± 13
0.05	260.41 ± 0.38	236 ± 6.7	24.4 ± 7.1
0.1	265.5 ± 3.6	250 ± 21	15 ± 25

Table 4 Contribution of different parts of the molecule to the partial molar volume of DTAOH

[NaOH] [mol dm ⁻³]	$V_{\text{DTA}^+,s}$ [$\text{cm}^3 \text{mol}^{-1}$]	$V_{\text{DTA}^+,m}$ [$\text{cm}^3 \text{mol}^{-1}$]	$V_{(\text{CH}_3)_3\text{N}^+,s}$ [$\text{cm}^3 \text{mol}^{-1}$]	$V_{(\text{CH}_3)_3\text{N}^+,m}$ [$\text{cm}^3 \text{mol}^{-1}$]
0	248.0 ± 2.3	265.9 ± 0.76	59.1 ± 0.7	66.1 ± 3.3
0.0001	243 ± 11	270.8 ± 1.6	54.2 ± 9.4	71.0 ± 2.4
0.01	243 ± 11	265.2 ± 1.1	54.2 ± 9.4	65.4 ± 2.9
0.05	237.1 ± 6.7	261.51 ± 0.38	48.2 ± 5.1	61.7 ± 3.7
0.1	251.1 ± 2.1	266.6 ± 3.6	62 ± 19	66.8 ± 0.4
Average	246.6 ± 2.1	262.98 ± 0.32	58.8 ± 0.7	66.8 ± 30.4

The average value of the unmicellized surfactant was $V_{\text{DTA}^+,s} = 245.5 \pm 2.1 \text{ cm}^3 \text{mol}^{-1}$. From Eq. (3) the partial molar volume of the trimethylammonium group $V_{(\text{CH}_3)_3\text{N}^+,s}$ was computed as being $58.8 \pm 0.7 \text{ cm}^3 \text{mol}^{-1}$. This value significantly differs from that of literature (68.0 ± 3.1) (Table 1). We also computed the contribution of the micellized surfactant ion ($V_{\text{DTA}^+,m}$) and the polar head group ($V_{(\text{CH}_3)_3\text{N}^+,m}$) by Eq. (3). Results are shown in Table 4.

The average value of $V_{\text{DTA}^+,s}$ was $246.6 \pm 2.1 \text{ cm}^3 \text{mol}^{-1}$. The value derived from DTAB solutions by Guvelli et al. [10] is $248.9 \text{ cm}^3 \text{mol}^{-1}$. We also estimated this value with Eq. (3) and the literature data shown in Table 1, obtaining $V_{\text{DTA}^+,s} = 258 \pm 2 \text{ cm}^3 \text{mol}^{-1}$. The values of $V_{\text{DTA}^+,m}$ in the literature are 266.3 [8] and 255.9 [10] from DTAB, and 273.2 $\text{cm}^3 \text{mol}^{-1}$ from DTAC + 0.1 mol dm^{-3} NaCl [11], similar to our values in Table 4. These data show an expansion on micellization which was also seen in other surfactant systems [8, 21]. This expansion may be due to the release of water molecules from the hydrophobic hydration shell of the chains in the unmicellized state (these water molecules are highly structured) to the intermicellar solution. Another possible explanation is that there is a high interfacial energy between tail and water in unmicellized surfactant, which tends to reduce the interface and compress the hydrocarbon chains. When micellization occurs, the hydrocarbon-water contact is strongly reduced and the chains are free to expand. This is reflected in the contribution of methylene groups on the molar volume of liquid alkanes ($16.7 \text{ cm}^3 \text{mol}^{-1}$) compared with the contribution in micelles ($17.3 \text{ cm}^3 \text{mol}^{-1}$).

The average expansion on micellization in DTAOH systems is $\Delta V_{s \rightarrow m} = 18.6 \pm 1.0 \text{ cm}^3 \text{mol}^{-1}$. Literature data are $7.8 \pm 0.5 \text{ cm}^3 \text{mol}^{-1}$ in DTAB, from apparent molar volumes [13] and 8.5 (DTAB, from partial molar volumes) [9]. This difference may be due to the structure of DTAOH micelles. There is much evidence in the literature [1, 18] which indicates that RTAB micelles are almost fully ionized at the cmc. This causes an increased repulsion among the head groups. This may be interpreted as a negative pressure which expands the micelle core. The much less ionized RTAB micelles are less expanded. The point of

Table 5 Radius of the $-(\text{CH}_3)_3\text{N}^+$ group

[NaOH] [mol dm ⁻³]	r [Å] (Eq. (4))		r [Å] (from $V_{(\text{CH}_3)_3\text{N}^+}$)	
	s	m	s	m
0	2.320 ± 0.069 ^{a)}	2.39	2.862 ± 0.050 ^{a)}	2.970 ± 0.086
0.0001	2.26		2.78	3.042 ± 0.093
0.01	2.26		2.78	2.960 ± 0.091
0.05	2.19		2.67	2.903 ± 0.083
01	2.36		2.91	2.98 ± 0.12
	2.278 ± 0.018 ^{a)}		2.800 ± 0.056 ^{a)}	2.960 ± 0.045 ^{a)}

^{a)} Average values.

m: micellized surfactant, s: unmicellized surfactant.

departure is the same, the unmicellized surfactant, so the $\Delta V_{s \rightarrow m}$ value must be larger in the most ionized micelles, provided the counterion contribution does not change on micellization and cancel itself. This phenomenon has also been observed when ΔV_m values for sodium dodecanoate ($11.6 \text{ cm}^3 \text{ mol}^{-1}$) and sodium perfluorooctanoate ($13.3 \text{ cm}^3 \text{ mol}^{-1}$) are compared [22]. It was also interpreted as the fluorinated surfactant gives less ordered micelles having a smaller aggregation number and higher degree of dissociation. The much higher value of ΔV_m for DTAOH reflects the extremely high degree of dissociation of its micelles.

The radius of the polar head group was computed by Eq. (4) by successive approximations (Newton's method) and the values are shown in Table 5. It may be seen that the radius of the micellized head group is slightly but significantly larger than that of the unmicellized amphiphile. This may be due to the reduction of the electrostriction when the polar head groups enter in the Stern layer of micelles. The concentration of electrolytes at the micelle surface must reduce the electrostriction effect [23, 24]. On the other hand, the radius computed from

$V_{(\text{CH}_3)_3\text{N}^+}$ is larger than that computed by Eq. (4) and must reflect the influence of the head group hydration, which is probably maintained on micellization [25].

Conclusions

- There is a stronger expansion on micellization in DTAOH micelles than in DTAB ones, which reflects the larger ionization of the former than the latter micelles.
- The electrostriction on the polar head group is reduced in the micelle Stern layer when compared with the unmicellized state.
- The addition of NaOH to DTAOH solutions does not modify the partial molar volume of both micellized and unmicellized surfactant molecules.

Acknowledgements This work was supported by a Research Grant of the Universidad Nacional del Sur. Two of us (M.A.M. and R.M.M.) have fellowships from the Consejo Nacional de Investigaciones Científicas y Técnicas (Argentina) and one of us (J.L.R.) have a fellowship of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires.

References

1. Lianos P, Zana R (1983) *J Phys Chem* 87:1289
2. Ninham BW, Evans DF, Ewi GJ (1983) *J Phys Chem* 87:5020
3. Clancy SF, Steigter PH, Tammer DA, Thies M, Paradies HH, *J Phys Chem* (1944) 98(43):11143
4. (a) Germani R, Savelli G (1993) *Langmuir* 9:61; (b) Chaimovich H, Bonilla JBS, Politi MJ, Quina FH (1979) *J Phys Chem* 83(14):1851; (c) Bunton CA, Carrasco N, Huang SF, Paik CH, Romsted LS (1978) *J Am Chem Soc* 100:5420; (d) Bunton CA, Gan L-H, Mofatt JR, Romsted LS (1981) *J Phys Chem* 85:4118
5. Mysels KJ (1955) *J Colloid Sci* 10:507
6. Schulz PC (1981) *Anales Asoc Quím Argentina* 89:185
7. Schulz PC, Puig JE, Barreiro G, Torres LA (1994) *Thermochim Acta* 231:239
8. Tanaka M, Kaneshina S, Shin-No K, Okajima T, Tomida T (1974) *J Colloid Interface Sci* 46:132
9. Corkill JH, Goodman JF, Walker T (1967) *Trans Faraday Soc* 63:768
10. Guvelli DE, Kayes JG, Davis SS (1981) *J Colloid Interface Sci* 82:307
11. Mukerjee P (1969) *J Phys Chem* 73(6):2054
12. Mukerjee P (1961) *J Phys Chem* 65:740
13. Brun TS, Hoiland H, Vikingstad E (1978) *J Colloid Interface Sci* 63:89
14. Shinoda K, Soda T (1963) *J Phys Chem* 67:2072
15. Kodama M, Miura M (1972) *Bull Chem Soc Japan* 45:2265
16. Hapler LG (1953) *J Phys Chem* 61:426
17. Hapler LG, Stokes JM (1965) *Trans Faraday Soc* 61:29
18. Schulz PC, Morini MA, Minardi RM, Puig JE (1995) *Colloid Polym Sci* 273(10):959
19. Mandell J (1964) *The Statistical Analysis of Experimental Data*. Interscience, New York

-
20. Mukerjee P (1962) *J Phys Chem* 66:1733
21. (a) Corkill JM, Goodman JF, Robson P, Tate JR (1966) *Trans Faraday Soc* 62:987; (b) Fisher FH (1962) *J Phys Chem* 66:1607; (c) Hamman SD (1962) *J Phys Chem* 66:1359; (d) Hamman SD, Pearce PJ, Strauss W (1964) *J Phys Chem* 68:375; (e) Kushner LM, Duncan BC, Hoffman JT (1952) *J Res Natl Bur Std* 49:85; (f) Kushner LM, Hubbard WD, Parker RA (1957) *J Res Natl Bur Std* 59:113; (g) Osugi J, Sata M, Ifuku N (1966) *Nippon Kagaku Zasshi* 87:329; (h) Osugi J, Sata M, Ifuku N (1965) *Rev Phys Chem Japan* 35:32; (i) Shinoda K, Soda T (1963) *J Phys Chem* 67:2072
22. Milioto S, Crisantino R, De Lisi R, Inglese A (1995) *Langmuir* 11:718
23. Harned HS, Owen BB (1958) *The Physical Chemistry of Electrolyte Solutions*. Reinhold, New York
24. Mukerjee P (1962) *J Phys Chem* 66:943
25. (a) Stigter D, Overbeek JThG (1957) *Proc Int Congr Surface Activ*, 2nd 1957, 1:311; (b) Grahame DC (1955) *J Chem Phys* 23:1725; (c) Mukerjee P, Banerjee K (1964) *J Phys Chem* 68:3567; (d) Grahame DC (1958) *J Am Chem Soc* 80:420