Apparent Molal Volumes of *n*-Alkylammonium Chlorides and Sodium *n*-Alkanecarboxylates in Dilute Aqueous Solutions

Masao Sakurai, Tsuyoshi Komatsu, and Tsurutaro Nakagawa

Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 2, 1975)

The densities of dilute aqueous solutions of two homologous organic salts, RNH_3Cl and RCOONa, where R varies from H to *n*-octyl, have been measured at 5, 25, and 45 °C using a buoyancy technique. The apparent molal volumes, ϕ_v, of the salts and the limiting partial molal volumes, $\bar{V}°$, of the individual ions have been evaluated. The contributions of a methylene group to the partial molal volume, $\bar{V}°(CH_2)$, as estimated from the $\bar{V}°$ data for longer-chain salts, are nearly the same for both series: approximately 15.3, 15.9, and 16.5 ml/mol at 5, 25, and 45 °C respectively. Compared to these values, on the other hand, the $\bar{V}°(CH_2)$ estimated for shorter-chain RNH_3Cl is larger and that for shorter-chain RCOONa is smaller. The second derivative of the $\bar{V}°$ with respect to the temperature, $\partial^2\bar{V}°/\partial T^2$, which is often regarded as a useful measure of structural effects, is almost independent of the chain length for longer-chain homologues. The concentration dependence of ϕ_v does not always vary in a regular manner with the chain length. The present results suggest that the volumetric behavior of aqueous organic electrolyte solutions is more complicated than has previously been believed.

A careful examination of the volumetric properties of aqueous solutions can provide useful information about the nature of solute–water and solute–solute interactions. Although the partial molal volumes of simple electrolytes and alkylammonium halides have been extensively investigated,[1] little attention has been paid to other organic salts.

It is known that the hydrogen-bonded structure of water is enhanced by the introduction of a nonpolar solute molecule. Such a solute–water interaction is often called "iceberg formation,"[2] "hydrophobic hydration,"[3] or "hydration of a second kind."[4] The nature of this interaction is, however, not yet clearly understood. Furthermore, little is known about the contributions of polar groups to the structural effect. Previously we reported that the effects of NH_3^+ and COO^- groups on the hydrophobic hydration are quite different from one another.[5,6] The purpose of this paper is to supplement the earlier study[5] by presenting data on the apparent molal volumes of the organic salts recently measured in our laboratory.

Experimental

The *n*-alkylammonium chlorides, $H(CH_2)_nNH_3Cl$, and sodium *n*-alkanecarboxylates, $H(CH_2)_nCOONa$, were prepared by the neutralization of the corresponding amines and carboxylic acids with hydrochloric acid and sodium hydroxide respectively. The salts were recrystallized twice from ethanol for shorter-chain homologues and from ethanol-benzene mixtures for longer-chain salts. Each sample was then dried under vacuum at room temperature. The water used in all the measurements was deionized and further distilled using a quartz still.

The float densitometer (with a precision of 2 ppm) and the experimental procedure were previously described.[5]

The apparent molal volume, ϕ_v, was calculated by means of this equation:

$$\phi_v = \frac{1000(d_0-d)}{mdd_0} + \frac{M}{d} \tag{1}$$

where d and d_0 are the densities of the solutions and the water respectively, M is the molecular weight of the salts, and m is the molality.

Results and Discussion

The limiting partial molal volumes, $\bar{V}°(=\phi_v^\circ)$, were obtained from this equation:

$$\phi_v = \phi_v^\circ + S_v\sqrt{c} + b_v c \tag{2}$$

where S_v is the Debye-Hückel limiting slope, b_v is a deviation constant, and c is the molarity calculated from the observed density. The S_v values for the 1–1 electrolyte at 5, 25, and 45 °C are 1.529, 1.868, and 2.234 respectively.[7]

A few typical examples of the plots of $\phi_v - S_v\sqrt{c}$ *vs.* c are shown in Fig. 1. Good linearities were obtained over the concentration range studied, except for the octylammonium and octanecarboxylate salts (Figs. 5 and 6), which will be discussed later. The $\bar{V}°$ values estimated from these figures are summarized in Table

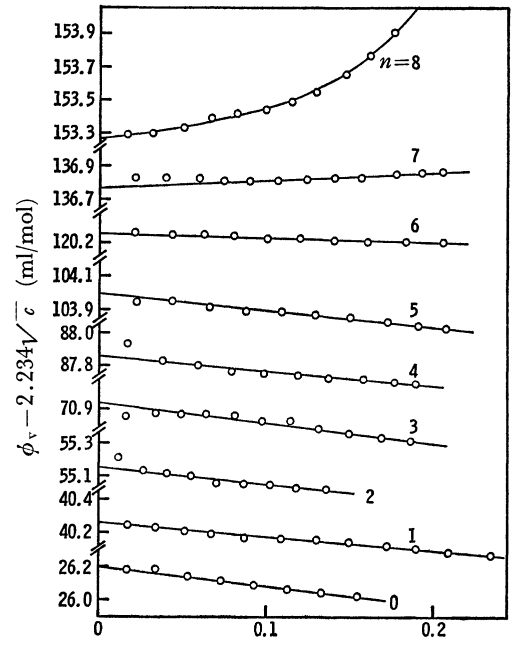

Fig. 1. Apparent molal volumes of sodium *n*-alkanecarboxylates, $H(CH_2)_nCOONa$, in water at 45 °C.

Table 1. Values of $\bar{V}^\circ$ and b_V at 5, 25, and 45 °C

n	$\bar{V}^\circ$ (ml/mol)			b_V (1 ml/mol^2)		
	5 °C	25 °C	45°C	5 °C	25 °C	45 °C
			$H(CH_2)_nNH_3Cl$			
0	34.51[a]	35.78[a]	36.03[a]	0.4[a]	−0.5[a]	−1.0[a]
1	52.52	53.93	54.39	0.04	−0.59	−0.89
2	70.13[a]	71.23[a]	71.86[a]	−0.7[a]	−0.8[a]	−1.3[a]
3	85.99	87.33	88.14	−1.24	−1.30	−1.56
4	101.69	103.36	104.60	−1.84	−1.79	−1.83
6	132.55[a]	135.26[a]	137.50[a]	−3.1[a]	−2.8[a]	−2.3[a]
7	147.72	151.02	153.86	−3.06	−2.33	−1.55
8	163.04	166.93	170.34	−3.91	−2.7	−1.4
			$H(CH_2)_nCOONa$			
0	22.53[a]	25.15[a]	26.20[a]	0.6[a]	0.0[a]	−1.1[a]
1	37.03	39.31[a]	40.26	0.72	0.0[a]	−0.80
2	51.19[a]	53.71[a]	55.15[a]	0.8[a]	0.0[a]	−1.0[a]
3	66.42	69.32[a]	70.93	0.48	−0.2[a]	−1.13
4	82.16	85.69	87.86	0.09	−0.81	−0.88
5	97.45	101.36	103.99	−0.28	−0.77	−0.96
6	112.59	117.05	120.25	−0.57	−0.57	−0.23
7	127.85	133.00	136.76	−0.37	−0.46	0.54
8	143.01	148.73	153.26	1.3	0.14	1.92

a) Ref. 5.

1. We could not obtain reasonable ϕ_V data for pentylammonium chloride; the value obtained by us was in disagreement with that calculated from the data of pentylammonium bromide[8] at 25 °C, and, furthermore, if the value was used in the calculation of $\bar{V}^\circ(CH_2)$ described below, Fig. 2a gave an anomalous maximum and minimum. It was also found that our earlier ϕ_V values[5] for butane-, pentane-, and hexanecarboxylate salts were too small compared to the present results.

Partial Molal Volume of a Methylene Group. The $\bar{V}^\circ$ increment per methylene group, $\bar{V}^\circ(CH_2)$, was calculated as:

$$\bar{V}^\circ(\mathrm{CH_2}) = \frac{\bar{V}^\circ(n_i)-\bar{V}^\circ(n_j)}{n_i-n_j} \tag{3}$$

where n_i and n_j are the number of methylene groups in the homologous pairs considered. Figure 2 shows the $\bar{V}^\circ(CH_2)$ as a function of $(n_i+n_j)/2$. It appears to converge toward a common $\bar{V}^\circ(CH_2)$ value as the chain length increases; approximately 15.3, 15.9, and 16.5 ml/mol at 5, 25, and 45 °C respectively. These values are in good agreement with our previous results obtained with the *n*-alcohol series: 15.5, 15.9, and 16.4 ml/mol at the above temperatures.[9]* These values represent the limiting partial molal volumes of the methylene group free from the influences of the polar groups.

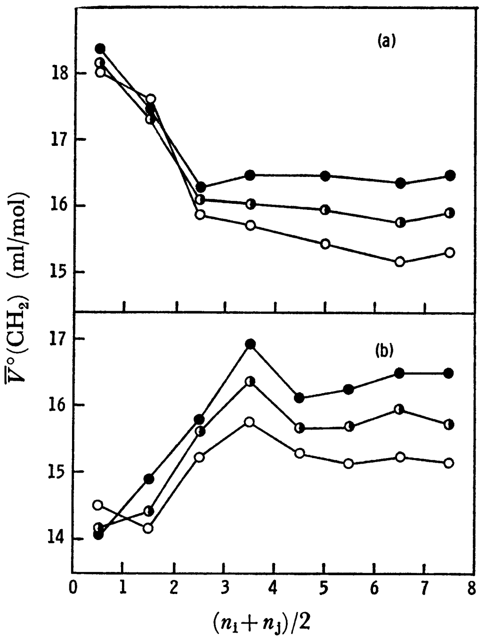

Fig. 2. Partial molal volume of a methylene group calculated from the data of *n*-alkylammonium chlorides (a) and sodium *n*-alkanecarboxylates (b).
○: 5 °C, ◐: 25 °C, ●: 45 °C.

With shorter-chain homologues, on the contrary, deviations from the common $\bar{V}^\circ(CH_2)$ value are apparent: a positive deviation was found for alkylammonium and a negative deviation for alkanecarboxylate salts. It seems likely that the deviations can be ascribed primarily to the influences of the polar groups on the hydrophobic hydration of the methylene group. This explanation may be supported by the fact that the $\bar{V}^\circ$ of branched isomers of butylammonium and butanecarboxylate salts, in which polar groups exist very

---

* Misleading errata are, unfortunately, present in Ref. 9. Readers interested in this paper are kindly asked to request a corrected copy from the authors.

near to the CH_2 groups, can be well predicted on the basis of the additivity of the $\bar{V}^\circ(CH_2)$ values.[6] The good agreement between predicted and experimental values suggests that the distance between the nonpolar part and the polar group in a solute molecule is a significant factor in determining the volumetric behavior of the organic salts. The effects of polar groups on the hydrophobic hydration have been discussed by Krishnan and Friedman[10] on the basis of their studies of the solvation enthalpies of various solutes.

Particularly to be noted in Fig. 2a is the fact that the $\bar{V}^\circ(CH_2)$ estimated from the $\bar{V}^\circ$ data of $MeNH_3Cl$ and $EtNH_3Cl$ at 5 °C is larger than that estimated at 25 or 45 °C. A similar phenomenon was observed with the $\bar{V}^\circ(CH_2)$ estimated from the data of HCOONa and MeCOONa (Fig. 2b). The former is closely related to the negative expansibility of the *tert*-butylammonium ion.[6] Quite similar behavior has been accounted for[6] in the case of the negative expansibilities of *tert*-butanol[11] and the methylene group estimated from methanol and ethanol.[9] These results suggest that the negative expansibility is mainly attributable to the influence of the polar group on the hydrophobic hydration; further details have been described in a previous paper.[6]

Temperature Dependence of Partial Molal Volume. For the study of ion–water interactions, it is necessary to divide the $\bar{V}^\circ$ values of salts into those of ions. Using $\bar{V}^\circ(H^+) = -5.1$, -5.4, and -5.8 ml/mol at 5, 25, and 45 °C respectively,[1] and also using the $\bar{V}^\circ$ data for HCl[12] and NaCl,[13] we calculated the ionic partial molal volumes of the organic ions under consideration.

Since the structural effect is considered to show characteristic temperature behavior, it is very useful to examine the partial molal expansibility, $\partial\bar{V}^\circ/\partial T$, and especially its temperature dependence, $\partial^2\bar{V}^\circ/\partial T^2$.[5,9,14–16] Figure 3 shows the $\partial\bar{V}^\circ/\partial T$ values at 15 and 35 °C as a function of the chain length. For both the homologous ions, the expansibilities seem to increase linearly with the increase in chain length when $n>3$ or 4. Therefore, it appears that the ionic hydration caused by NH_3^+ or COO^- ions affects the hydrophobic hydration up to the β- or γ-CH_2 groups. This is consistent with the results of the chain-length dependence of $\bar{V}^\circ(CH_2)$ shown in Fig. 2.

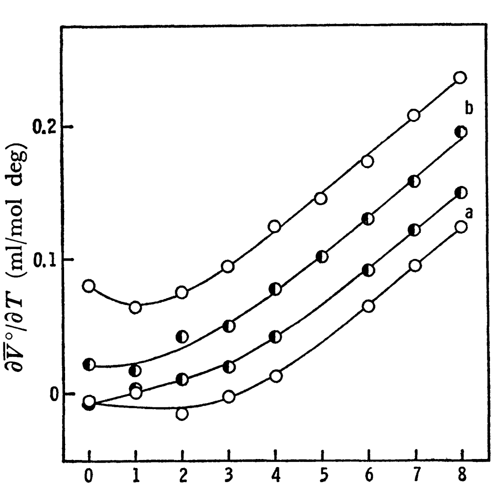

Fig. 3. Partial molal expansibilities of *n*-alkylammonium ions (a) and *n*-alkanecarboxylate ions (b).
○: 15°C, ◐: 35 °C.

On the basis of the thermodynamic relation, $\partial(\bar{C}^\circ_p/\partial P)_T = -T(\partial^2\bar{V}^\circ/\partial T^2)_p$, Hepler[14] proposed that structure-making solutes are accompanied by positive $\partial^2\bar{V}^\circ/\partial T^2$ values, and structure-breaking solutes, by negative values. His proposal has been supported by the experimental results with tetraalkylammonium halides[15] and various nonelectrolytes.[16] Recently we have reported that, in the case of the homologous *n*-alcohol series, the $\partial^2\bar{V}^\circ/\partial T^2$ values increase linearly with the chain length;[9] this may imply that the hydrophobic hydration becomes more significant with the increase in the chain length. It is apparent from Fig. 4 that, for the alkylammonium and alkanecarboxylate salts, on the other hand, the $\partial^2\bar{V}^\circ/\partial T^2$ values are almost independent of the chain length, with the exception of the shorter-chain homologues. This fact may suggest either that the saturation of the hydrophobic hydration takes place with an increase in the chain length,[17] or that the $\partial^2\bar{V}^\circ/\partial T^2$ value is governed primarily by the influence of the polar group on the hydrophobic hydration. At present, the second interpretation seems to us more likely, although the molecular aspect of the effect of the polar group is less understood. As was mentioned in the preceding section and in a previous paper,[6] we consider that the anomalous temperature behavior of the nonpolar groups, especially that of the *tert*-butyl group, which has been believed to be evidence of the hydrophobic hydration, can be mainly ascribed to the effect of the polar group.

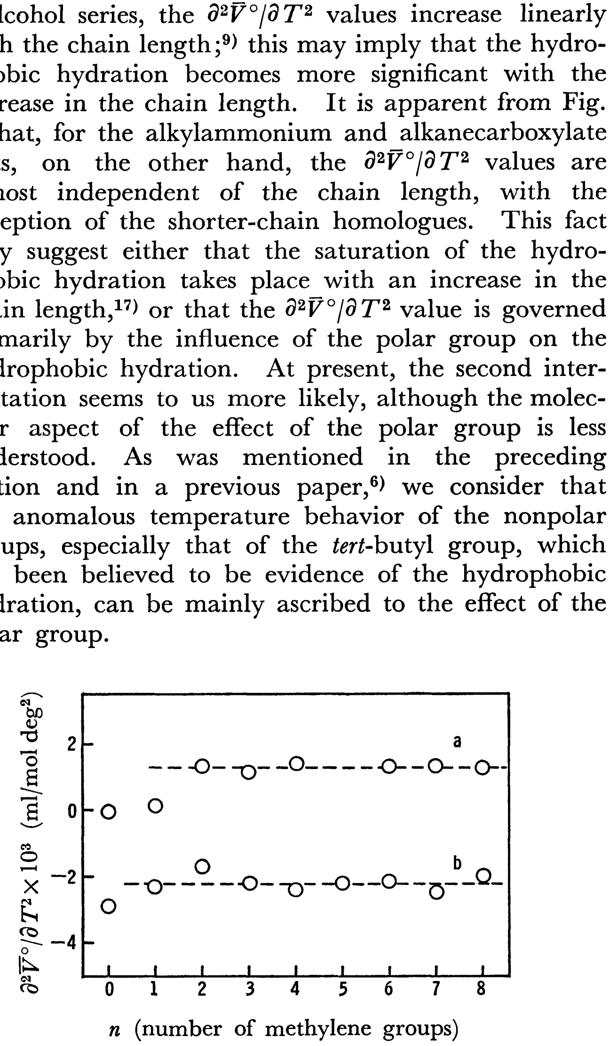

Fig. 4. The $\partial^2\bar{V}^\circ/\partial T^2$ values of *n*-alkylammonium ions (a) and *n*-alkanecarboxylate ions (b).

It is interesting that the $\partial^2\bar{V}^\circ/\partial T^2$ values for RNH_3^+ are positive, while those for $RCOO^-$ are negative. Based on the classification of the structural effect of solutes proposed by Hepler,[14] it may be concluded that the alkylammonium is a structure-maker, and the alkanecarboxylate ion, a breaker. In this connection we should note another classification of the solutes presented recently by Tamaki *et al.*[18] on the basis of viscosity measurements; the carboxylate ion is an "electrostrictive structure maker," while the ammonium ion is a "structure breaker." The apparent contradiction of the two classifications mentioned above may not be surprising, because it is known that the features of the structural effect vary from property to property.

Concentration Dependence of Apparent Molal Volume. We can obtain information on solute-solute interactions from a careful examination of the concentration dependence of the apparent molal volume. The b_V value in Eq. (2) reflects the solute–solute interactions other than the Coulombic force expected from the Debye-Hückel theory. A number of investigators have discussed the b_V values,[19] but, in our opinion, there still appears to be no satisfactory explanation. For the most of the alkylammonium salts,[8,20–23] the b_V values have been reported to be more or less negative; this is also the case in our study, as can be seen from Table 1. It has been known that the concentration dependence of the apparent molal volume, $\partial\phi_V/\partial m$, is negative for hydrophobic nonelectrolytes, such as alcohols[9,24] or amines,[24] and positive for hydrophilic solutes, such as glycol or urea.[16] Furthermore, it has been known that the b_V or $\partial\phi_V/\partial m$ value becomes more negative as the alkyl-chain length increases.[5,8,9,20,21] On the basis of these experimental results, the negative b_V value has been interpreted in terms of the overlap of the hydrophobic hydration accompanying the increase in concentration.

At present, however, there are two contradictory explanations for the overlapping effect: (1) the overlap results in a more efficient hydrophobic hydration because of co-operative stabilization,[5,25] and (2) the total increase in the hydrophobic hydration caused by the two solutes is less than twice that caused by the first solute alone.[8,9] The discrepancy in the above two explanations may be related in part to the model used for the explanation of the volume change associated with the mixing of water and organic solutes. Many authors believe that the hydrophobic hydration is accompanied by a net volume contraction.[8] On the other hand, some workers[9,26] have attributed the negative excess volume of mixing observed in aqueous systems to the ability of the small water molecules to fill in the free space between larger solute molecules. They have, therefore, concluded that the hydrophobic hydration results in an increase in the volume as a result of the increase in the bulky icelike structure of water.

In Table 1 we can find some interesting features of the variation of the b_V values with the solute species, with the chain length, and with the temperature. For both the homologous series, the b_V values decrease with the increase in the chain length. However, with longer-chain members, the opposite order was observed, especially in the cases of alkanecarboxylate salts and at higher temperatures. This unexpected trend for the salts with large alkyl residues has been also reported by Desnoyers *et al.*,[27,28] who proposed extra weak interactions between the solutes other than the hydrophobic hydration. Lindenbaum[29] pointed out that the positive b_V values for sodium carboxylates signify the structure-breaking effect of the salts and are, therefore, incompatible with the thermochemical results. Recently we reported that the b_V values are almost independent of the chain branching of alkyl residues,[6] although the chain branching causes some changes in the nature of the hydration layers, as can be expected from the $\bar{V}^\circ$ behavior. Considering these experimental results and the obscurity concerning the effect of the hydrophobic hydration on the volumetric behavior mentioned above, we cannot offer a plausible explanation of the concentration dependence of the apparent molal volume. Before we can do so it will be necessary to examine the b_V values as functions of various solute species, solvents, and temperatures.

Figures 5 and 6 show the concentration dependence of ϕ_V for the octylammonium and octanecarboxylate salts at 5, 25, and 45 °C. We can see upward deviations from the linearity of the $\phi_V - S_V\sqrt{c}$ *vs.* c plot. This is analogous to the sharp increase in ϕ_V at critical micelle concentration(CMC) in surfactant solutions.[28,30,31] Although the micellization is not sharp for the salts under consideration, the CMC seems to be about 0.15∼0.2 mol/l for both the salts; this is in agreement with the literature value.[32] It should be

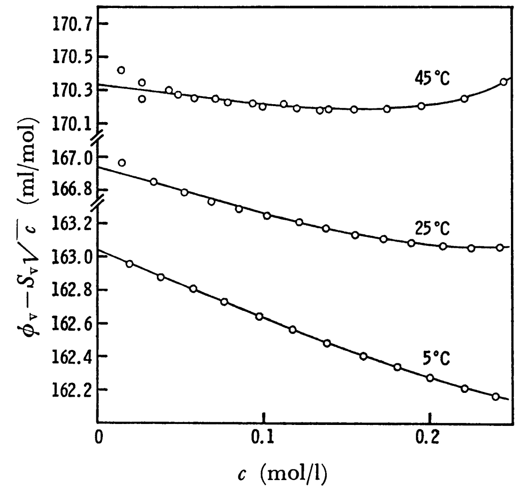

Fig. 5. Apparent molal volumes of *n*-octylammonium chloride.

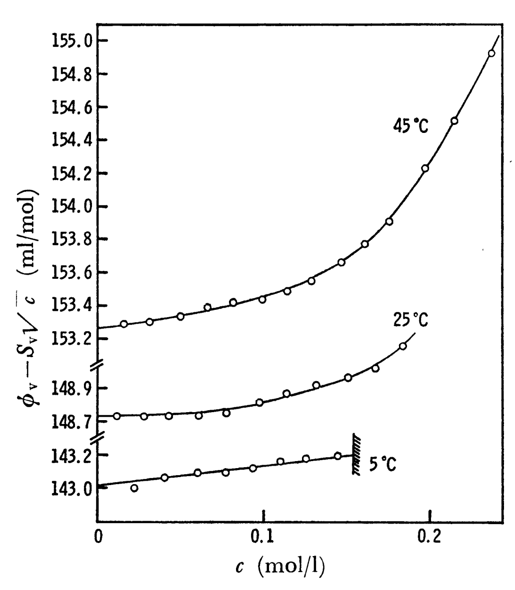

Fig. 6. Apparent molal volumes of sodium *n*-octanecarboxylate.

noted that the deviations are more remarkable at higher temperatures, whereas the CMC of typical surfactants goes through a minimum at room temperature.[28] The large increase in ϕ_v may be interpreted mainly in terms of the increase in free space associated with the micellization.[28,31]

We would like to thank Mr. Toshio Nakajima and Mr. Shigeharu Harada for their helpful discussions. The present work has been supported in part by a Grant for Scientific Research from the Ministry of Education.

References

1) F. J. Millero, "Water and Aqueous Solutions," ed. by R. A. Horne, Wiley-Interscience, New York, N. Y. (1971), Chapter 13.

2) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

3) F. Franks, *Ann. New York Acad. Sci.*, **125**, 277 (1965).

4) E. Wicke, *Angew. Chem., Int. Ed.*, **5**, 106 (1966).

5) M. Sakurai, This Bulletin, **46**, 1596 (1973).

6) M. Sakurai, T. Komatsu, and T. Nakagawa, *J. Solution Chem.*, **4**, 511 (1975).

7) O. Redlich and D. M. Meyer, *Chem. Rev.*, **64**, 221 (1964).

8) J. E. Desnoyers and M. Arel, *Can. J. Chem.*, **45**, 359 (1967).

9) T. Nakajima, T. Komatsu, and T. Nakagawa, This Bulletin, **48**, 783 (1975).

10) C. V. Krishnan and H. L. Friedman, *J. Solution Chem.*, **2**, 37 (1973).

11) F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **64**, 2962 (1968).

12) F. J. Millero, E. V. Hoff, and L. Kahn, *J. Solution Chem.*, **1**, 309 (1972).

13) F. J. Millero, *J. Phys. Chem.*, **74**, 356 (1970).

14) L. G. Hepler, *Can. J. Chem.*, **47**, 4613 (1969).

15) F. J. Millero, *J. Chem. Eng. Data*, **15**, 562 (1970).

16) J. L. Neal and D. A. I. Goring, *J. Phys. Chem.*, **74**, 658 (1970).

17) C. V. Krishnan and H. L. Friedman, *ibid.*, **73**, 1572 (1969).

18) K. Tamaki, Y. Ohara, H. Kurachi, M. Akiyama, and H. Odaki, This Bulletin, **47**, 384 (1974).

19) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971).

20) R. E. Verrall and B. E. Conway, *J. Phys. Chem.*, **70**, 3961 (1966).

21) G. Perron and J. E. Desnoyers, *J. Chem. Eng. Data*, **17**, 136 (1972).

22) P. -A. Leduc, J. L. Fortier, and J. E. Desnoyers, *J. Phys. Chem.*, **78**, 1217 (1974).

23) S. Cabani, G. Conti, and L. Lepori, *ibid.*, **76**, 1343 (1972).

24) S. Cabani, G. Conti, and L. Lepori, *ibid.*, **78**, 1030 (1974).

25) F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **63**, 2586 (1967).

26) L. Bøje and A. Hvidt, *J. Chem. Thermodyn.*, **3**, 663 (1971); *Biopolymers*, **11**, 2357 (1972).

27) P. -A. Leduc and J. E. Desnoyers, *Can. J. Chem.*, **51**, 2993 (1973).

28) G. M. Musbally, G. Perron, and J. E. Desnoyers, *J. Colloid Interface Sci.*, **48**, 494 (1974).

29) S. Lindenbaum, *J. Chem. Thermodyn.*, **3**, 625 (1971).

30) F. Franks, M. J. Quickenden, J. R. Ravenhill, and H. T. Smith, *J. Phys. Chem.*, **72**, 2668 (1968).

31) S. Harada, T. Nakajima, T. Komatsu, and T. Nakagawa, *Chem. Lett.*, **1975**, 725.

32) "Handbook of Surfactants," ed. by E. Takahashi, Y. Namba, M. Koike, and M. Kobayashi, Kogakutosho, Tokyo (1972).