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Apparent Molal Volumes of Some Organic Electrolytes in a Dilute Aqueous Solution at 5, 25, and 45 °C

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The apparent molal volumes, ϕ_v, of five series of homologous organic salts of the $H(CH_2)_nCOONa$ (n=0—6), $(CH_2)_n(COONa)_2$ (n=0,2,3,4,6,8), $H(CH_2)_nNH_3Cl$ (n=0,2,6), $(CH_2)_n(NH_3Cl)_2$ (n=2,3,6), and $H(CH_2)_nSO_3Na$ (n=1,2) types in a dilute aqueous solution have been measured by means of a float method as a function of the concentration and the temperature. The coefficients of the deviation of ϕ_v from the Debye-Hückel limiting law, b_v, are negative for most organic electrolytes. The large positive b_v values observed for the sodium oxalate and sodium succinate solutions at 5 °C have been attributed to ion-pair formation. The partial molal expansibility of organic ions has been evaluated and interpreted on the basis of the multilayer hydration model proposed by Frank and Wen. The estimation of volume increments per CH_2 group suggests that the influences of ammonium ions on the hydrophobic hydration around CH_2 groups differ significantly from those of carboxylate ions. The volume change accompanying the substitution of a terminal hydrogen atom with an ionic group has been calculated, and discussed in connection with the overlapping effect of electrostriction in bolaform electrolytes.

Our previous short communication¹⁾ has pointed out that the volumetric behavior of polyelectrolytes in an aqueous solution appears to be complicated by the fact that the interactions between ionic groups or hydrophobic groups on a polymer chain do not disappear even at an infinite dilution. In order to elucidate the complicated behavior of the polyelectrolytes, reliable volumetric information on various organic salts must be established.

It is well known that the concentration and temperature dependence of the apparent molal volumes, ϕ_v, of tetraalkylammonium halides (n-R_4NX) in water are abnormal compared to the case of simple electrolytes.²⁻⁷⁾ For example, the concentration dependence of the ϕ_v of n-Bu_4NBr exhibits both a maximum and a minimum, and the limiting partial molal volumes of the R_4NX do not go through a maximum when plotted against the temperature. This anomalous volumetric behavior of the R_4NX has been interpreted in terms of the enhancement or stabilization of the hydrogen-bonded structure of water in the vicinity of the nonpolar hydrocarbon portion of the R_4N^+ ions (hydrophobic hydration).

In the studies of the R_4NX solutions, the electrostriction of water molecules by the R_4N^+ ions has been considered to be almost negligible, since the central charges are completely masked by the large hydrocarbon groups. For more common organic electrolytes, there have been some careful examinations of the concentration dependence of ϕ_v at 25 °C in the cases of mono-, di-, and trisubstituted aliphatic ammonium salts,⁸⁻¹⁰⁾ cyclic ammonium

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1) M. Sakurai, T. Nakajima, T. Komatsu, and T. Nakagawa, *Chem. Lett.*, **1972**, 355.

2) W.-Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964); *ibid.*, **69**, 3569 (1965).

3) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).

4) F. Franks and H. T. Smith, *ibid.*, **63**, 2586 (1967).

5) F. J. Millero and W. Drost-Hansen, *J. Phys. Chem.*, **72**, 1758 (1968).

6) G. Gopal and M. A. Siddiqi, *ibid.*, **72**, 1814 (1968).

7) F. J. Millero, *Chem. Rev.*, **71**, 147 (1971); "Structure and Transport Processes in Water and Aqueous Solutions," ed. by R. A. Horne, Wiley-Interscience, New York, N. Y. (1971), Chapter 13.

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

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

10) L. H. Laliberté and B. E. Conway, *ibid.*, **74**, 4116 (1970).

salts,[11] sodium carboxylates,[12] and sodium alkylsulfates.[13,14]

This report will describe the results of precision-density measurements of the dilute aqueous solutions of several organic salts of the 1–1 and 2–1 (bolaform) types at 5, 25, and 45° C. The apparent molal volumes and the partial molal expansibilities have been calculated from these density data.

Experimental

Materials. The *n*-alkylamine hydrochlorides and sodium salts of formic, acetic, and propionic acids were reagent grade materials and were recrystallized from ethanol, acetone, or water. The dihydrochlorides of ethylenediamine, trimethylenediamine, and hexamethylenediamine were precipitated from ethanol solutions of the amines by the addition of an equivalent amount of hydrochloric acid, and were then washed with ethanol and acetone. All the other salts were prepared by the neutralization of the corresponding carboxylic acids or alkylsulfonic acids with sodium hydroxide, and were purified by crystallization from water-ethanol or water-acetone mixtures. Each salt was dried under a vacuum for at least 3 days before use. Deionized water was distilled using an quartz still.

Procedure. The solution densities were evaluated to six decimal places by means of a float method similar to that described by Desnoyers and Arel.[8] The float, with a volume of about 200 ml, was suspended to the pan of a Mettler balance (Model H20T) by a thin nylon thread (0.11 mm dia.). The volume of the float was calculated by weighing it in air and in pure water at a constant temperature. The temperature inside the cell was controlled to ±0.001 °C by circulating water from a well-insulated bath. The densities of pure water were taken as 0.999992, 0.997075, and 0.990244 g/ml at 5, 25, and 45 °C respectively.[15] The water was degassed to prevent the formation of bubbles on the float during the experiment. The effect of the surface tension at the nylon-solution interface was neglected. The reproducibility of the density measurements was found to be better than 2×10^{-6} g/ml.

The solutions were prepared by adding weighed amounts of the concentrated stock solutions into a cell containing a known amount of pure water. Only for sodium oxalate was dry solid salt added because of its low solubility in water.

The apparent molal volumes were calculated from the density measurements using this equation:

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

where d_0 is the density of water; d, that of the solution; M, the molecular weight of the salt, and m, its molality.

Results

The concentration dependence of the apparent molal volumes of the electrolytes can be fitted to the equation of Redlich and Meyer:[16]

$$\phi_V = \phi_V{}^\circ + S_V\sqrt{c} + b_Vc \tag{2}$$

where $\phi_V{}^\circ$ is the limiting apparent molal volume; S_V, the theoretical limiting slope; b_V, an empirical constant determined from the experimental results, and c, the molar concentration converted from the known density. The limiting slope can be derived from the Debye-Hückel limiting law; hence, it depends on the temperature, the physical properties of the solvent, and the valence factor of the electrolytes. The values of S_V for 1–1 and 2–1 electrolytes at 5, 25, and 45 °C were calculated from the table in Ref. 16.

A few typical examples of the plots of $\phi_V - S_V\sqrt{c}$ *vs.* c are shown in Figs. 1 and 2. From these figures, the values of the $\phi_V{}^\circ$ (equal to the limiting partial molal volume, $\bar{V}^\circ$) and the b_V slope were calculated for all the electrolytes studied. The results are given in Table 1. The $\bar{V}^\circ$ values of sodium formate, sodium acetate, and sodium butyrate at 25°C are in good agreement with the data reported by King.[12]

Discussion

Deviations from the Limiting Law. As is shown in Table 1, most of the b_V values are more or less negative, like those of simple electrolytes, except at lower temperatures. The negative deviation from the limiting law is expected if the equation for the concentration dependence of ϕ_V is derived from the extended Debye-Hückel law, including the ion-size parameter, a (Owen-Brinkley equation).[7] The extremely large negative b_V values observed for bolaform electrolytes may be accounted for qualitatively by this equation. Since the increase in the chain length is equivalent to the increase in a, very nega-

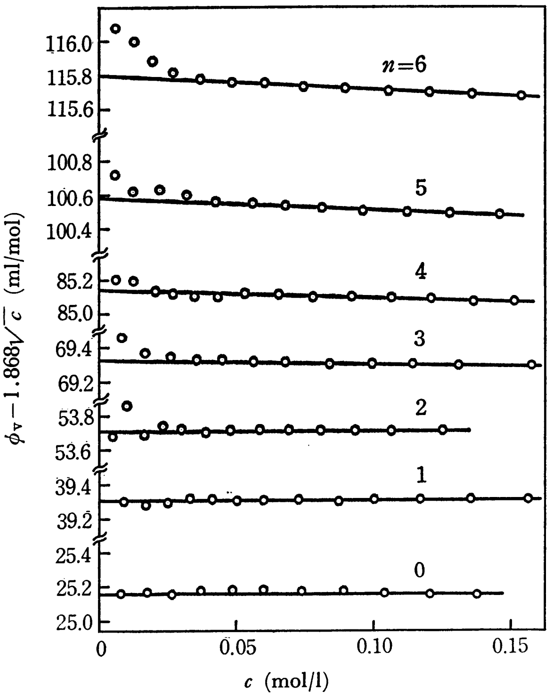

Fig. 1. Apparent molal volumes of sodium carboxylates, $H(CH_2)_nCOONa$, in water at 25 °C.

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

12) E. J. King, *ibid.*, **73**, 1220 (1969).

13) F. Franks and H. T. Smith, *ibid.*, **68**, 3581 (1964).

14) F. Franks, M. J. Quickenden, R. R. Ravenhill, and H. T. Smith, *ibid.*, **72**, 2668 (1968).

15) G. S. Kell, *J. Chem. Eng. Data*, **12**, 66 (1967).

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

Table 1. Values of $\bar{V}^\circ$ $(=\phi_v{}^\circ)$ and b_v at 5, 25, and 45 °C

n	$\bar{V}^\circ$ (ml/mol) 5 °C	25 °C	45 °C	b_v (l ml/mol^2) 5 °C	25 °C	45 °C
			$H(CH_2)_nCOONa$			
0	22.53	25.15	26.20	0.6	0.0	−1.1
1		39.31			0.0	
2	51.19	53.71	55.15	0.8	0.0	−1.0
3		69.32			−0.2	
4		85.14			−0.4	
5		100.58			−0.7	
6	111.55	115.80	119.48	−0.3	−0.8	−0.7
			$(CH_2)_n(COONa)_2$			
0	22.56	28.08	30.08	5.6	−2.2	−6.5
2	48.85	54.10	55.82	1.7	−3.5	−7.1
3		69.98			−4.0	
4		86.24			−5.6	
6		117.61			−4.4	
8		148.91			−4.2	
			$H(CH_2)_nNH_3Cl$			
0	34.51	35.78	36.03	0.4	−0.5	−1.0
2	70.13	71.23	71.86	−0.7	−0.8	−1.3
6	132.55	135.26	137.50	−3.1	−2.8	−2.3
			$(CH_2)_n(NH_3Cl)_2$			
2	76.95	80.10	80.72	−1.1	−5.5	−8.2
3		99.58			−5.1	
6		152.04			−9.4	
			$H(CH_2)_nSO_3Na$			
1		53.88			0.0	
2	68.66	71.56	73.14	0.7	−0.1	−1.5

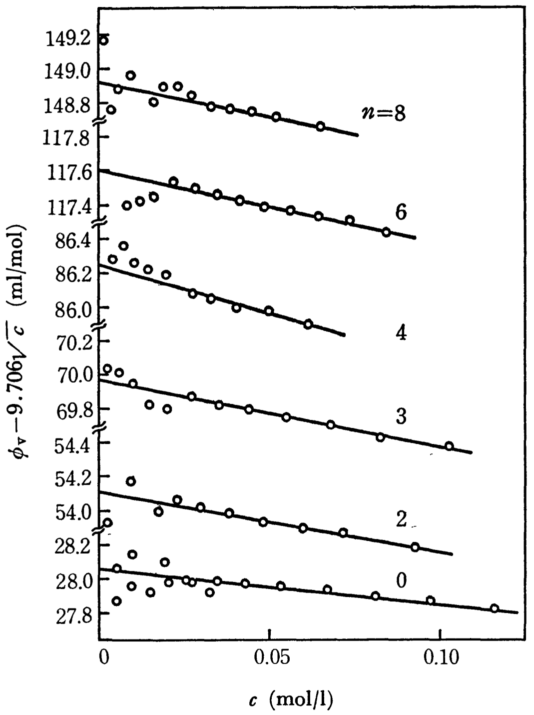

Fig. 2. Apparent molal volumes of sodium dicarboxylates, $(CH_2)_n(COONa)_2$, in water at 25 °C.

tive b_v values should be observed for larger bolaform electrolytes,

However, the Owen-Brinkley equation cannot give a reasonable interpretation of the positive b_v values observed for some electrolytes at 5°C, or of the change in b_v values with the increase in the chain length in the case of the 1–1 type homologous series, in which the a values are all the same.[8,17] From these points of view, the study of the b_v as a function of the size, the charge, and the temperature is assumed to provide useful information about ion-ion interactions.

The b_v values observed for 1–1 electrolytes become more negative with the increase in the number of CH_2 groups; this is analogous to the results obtained for *n*-alkylamine hydrobromides by Desnoyers and Arel.[8]

In aqueous solutions, as is well recognized, hydrophobic solutes enhance or stabilize the hydrogen-bonded structure of water in the vicinity of the nonpolar groups. Such a nonpolar group-water interaction is sometimes called "hydrophobic hydration" to distinguish it from normal hydration. Experimental evidence has confirmed a net contraction in volume when hydrophobic hydration takes place, although there has been no general agreement on the exact nature of the structure of water in this hydration layer.[18] At present it seems most reasonable to interpret the volumetric behavior of nonpolar solutes

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17) J. E. Desnoyers, M. Arel, and P. A. Leduc, *Can. J. Chem.* **47**, 547 (1969).

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

in water in terms of the formation of "quasi-clathrate cages."[2,4]

As the concentration increases, the overlap of these cage systems results in a more efficient contraction in volume as a result of the co-operative stabilization of the hydrogen-bonded structure. Consequently, larger negative b_V values should be observed for the 1–1 organic salts with larger hydrocarbon portions.

Millero has pointed out that an examination of the temperature dependence of b_V can reveal the nature of the ion-ion interactions.[19,20] Table 1 shows that the effects of the temperature on the b_V are similar to the cases of more common electrolytes such as NaCl, in that $\partial b_V/\partial T$ is negative for all the organic salts except for the *n*-hexylamine hydrochloride solution, in which $\partial b_V/\partial T$ is positive as in *n*-Bu_4NBr. The latter behavior may be interpreted on the basis of the assumption that the volume contraction caused by the overlap of the hydrophobic hydration with the increase in concentration is more pronounced at lower temperatures, since the hydrogen-bonded structure of water is stabilized at low temperatures.

For the bolaform electrolytes, the $\partial b_V/\partial T$ values are much more negative. In contrast with the effect of hydrophobic hydration, the negative contribution of the electrostriction to the ϕ_V is more pronounced at higher temperatures, according to the Drude-Nernst equation.[7] Therefore, the negative $\partial b_V/\partial T$ value can be interpreted in terms of the overlap of the highly-electrostricted regions caused by charges in the like sign of the divalent bolaform ions.

It is noteworthy that the b_V values for sodium oxalate and sodium succinate are large and positive at 5°C. The positive b_V value has been interpreted in terms of the cation-anion interactions[21] or the ion-pair formation.[19] The ion-pair formation may be regarded as the limiting case of the cation-anion attraction. Thus, one can predict an ion-pairing in aqueous solutions of the bolaform electrolytes such as sodium oxalate at very low temperatures.

Partial Molal Volumes and Expansibilities of Ions. The study of the limiting partial molal volume, $\bar{V}^\circ$, and the limiting partial molal expansibility, $\bar{E}^\circ = \partial\bar{V}^\circ/\partial T$, may be a useful tool for elucidating ion-water interactions. It has been well established that the $\bar{V}^\circ$ of an electrolyte is equal to the sum of its ionic components: $\bar{V}^\circ = \bar{V}^\circ(\text{cation}) + \bar{V}^\circ(\text{anion})$.[21] Many workers have attempted to determine the individual ionic volume by means of various methods, and many different values of the partial molal volume of a proton, $\bar{V}^\circ(H^+)$, have been reported.[7]

In the present analysis, we have utilized the equation for the temperature dependence of the $\bar{V}^\circ(H^+)$ proposed by Millero:[7]

$$\bar{V}^\circ(H^+) = -5.1 - 0.008\,T - 1.7 \times 10^{-4}T^2 \qquad (3)$$

Table 2. Values of $\bar{V}^\circ$ (ion) at 5, 25, and 45 °C, and $\bar{E}^\circ$ (ion) at 15 and 35 °C

n	$\bar{V}^\circ$(ion) (ml/mol)			$\bar{E}^\circ$(ion) (ml/mol deg)	
	5 °C	25 °C	45 °C	15 °C	35 °C
H^+	−5.1	−5.4	−5.8	−0.015	−0.020
Cl^-	21.8	23.2	24.2	0.070	0.050
Na^+	−7.6	−6.6	−6.6	0.050	0,000
$H(CH_2)_nCOO^-$					
0	30.1	31.8	32.8	0.085	0.050
2	58.8	60.3	61.8	0.075	0.075
6	119.2	122.4	126.1	0.160	0.185
$^-OOC(CH_2)_nCOO^-$					
0	37.8	41.3	43.3	0.175	0.100
2	64.1	67.3	69.0	0.160	0.085
$H(CH_2)_nNH_3^+$					
0	12.7	12.6	11.8	−0.005	−0.040
2	48.3	48.0	47.7	−0.015	−0.015
6	110.8	112.1	113.3	0.015	0.060
$^+H_3N(CH_2)_nNH_3^+$					
2	33.4	33.7	32.3	0.015	−0.070
$H(CH_2)_nSO_3^-$					
2	76.3	78.2	79.7	0.095	0.075

By using this equation and the additivity principle, one can calculate the values of $\bar{V}^\circ(Cl^-)$ and $\bar{V}^\circ(Na^+)$ from the $\bar{V}^\circ$ data for HCl[22] and NaCl,[19] and hence those of the $\bar{V}^\circ$(ion) for the organic ions from our $\bar{V}^\circ$ data. The results are given in Table 2, together with the $\bar{E}^\circ$(ion) values at 15 and 35 °C.

The $\bar{V}^\circ$(ion) and $\bar{E}^\circ$(ion) can be divided into four major components on the basis of the multilayer hydration model proposed by Frank and Wen:[23]

$$\bar{V}^\circ(\text{ion}) = \bar{V}^\circ(\text{cryst}) + \bar{V}^\circ(\text{elect}) + \bar{V}^\circ(\text{disord}) + \bar{V}^\circ(\text{str}) \qquad (4)$$

$$\bar{E}^\circ(\text{iron}) = \bar{E}^\circ(\text{cryst}) + \bar{E}^\circ(\text{elect}) + \bar{E}^\circ(\text{disord}) + \bar{E}^\circ(\text{str}) \qquad (5)$$

where (cryst) means the crystal partial molal component; (elect), the contribution of the electrostrictional effect; (disord), that of the disordered or void space-packing effect, and (str), that of hydrophobic hydration. A detailed discussion of the natures of these components has been given by Millero.[7]

Table 2 shows that the $\bar{E}^\circ$(ion) values for the alkylammonium ions are much smaller than those for the carboxylate ions with the same hydrocarbon chains. As has been mentioned above, the volume decrease due to the electrostriction is, as a first approximation, more pronounced at higher temperature. Therefore, this finding may be attributed to the larger contribution of the $\bar{E}^\circ$(elect) for the NH_3^+ group than for the COO^- group, because of a low charge density on the

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[19] F. J. Millero, *J. Phys. Chem.*, **74**, 356 (1970).

[20] F. J. Millero, *J. Chem. Eng. Data*, **15**, 562 (1970); *ibid.*, **16**, 229 (1971).

[21] J. E. Desnoyers, M. Arel, G. Perron, and C. Jolicoeur, *J. Phys. Chem.*, **73**, 3346 (1969).

[22] G. Akerlöf and J. W. Teare, *J. Amer. Chem. Soc.*, **60**, 1226 (1938).

[23] H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).

COO^- group due to electron delocalization.[12] This also appears to fit well the findings on the volume changes for ionization reactions reported by Kauzmann *et al*; the volume decrease accompanying the ionization of carboxylic acids is only one half that of alkylamines.[24] It should, however, be noted that there remains some uncertainty as to the above conclusion because of an ambiguity in the determination of the absolute $\overline{V}^\circ(H^+)$ values.

It is of interest to examine the temperature dependence of the $\overline{E}^\circ$(ion) in connection with the hydrocarbon-chain length. Table 2 apparently shows that the $\partial\overline{E}^\circ(\text{ion})/\partial T$ value is negative for the $n=0$ compounds, nearly zero for $n=2$, and positive for $n=6$ in the series of both *n*-alkylammonium ions and carboxylate ions. The positive temperature dependence of the $\overline{E}^\circ$, which has been found for R_4NX or hydrophobic nonelectrolytes, implies that the $\overline{V}^\circ$-temperature plot does not go through a maximum; in this it is unlike the simple inorganic ions. This behavior can be ascribed to the effect of the hydrophobic hydration around the long hydrocarbon chains, since the hydrogen-bonded structure of water is sensitive to the temperature and, hence, the negative contribution of $\overline{V}^\circ$(str) to the $\overline{V}^\circ$(ion) should become less important as the temperature is increased. A similar discussion has been made by Hepler in relation to the pressure dependence of the partial molal heat capacity.[25]

The finding that the hydrophobic hydration predominantly contributes to the ion-water interactions for the ions with $n>2$ is consistent with the findings on the heat of transfer from H_2O to D_2O for sodium carboxylates reported by Snell and Greyson[26] and on that for *n*-alkylamine hydrobromides reported by Desnoyers *et al.*[27]

Particular attention should be given to the fact that the $\overline{E}^\circ$(ion) values of the ammonium ion and the ethylammonium ion are negative, while $\overline{E}^\circ(Na^+)$ is positive. At least the tendency that $\overline{E}^\circ(Na^+)>\overline{E}^\circ(NH_4^+)$ or $\overline{E}^\circ(EtNH_3^+)$ is not affected by any choice of the $\overline{V}^\circ(H^+)$ values. Millero *et al.*[5] have accounted for the low $\overline{E}^\circ$ of the NH_4Cl in terms of the ability of NH_4^+ to form an "icelike" structure. Their proposal, however, could not interpret the negative $\partial\overline{E}^\circ(NH_4^+)/\partial T$ value. Although we have no clear explanation of this finding at present, it might be correlated with the unknown nature of the $\overline{V}^\circ$(disord) or $\overline{E}^\circ$(disord) terms for organic ions. Furthermore, it should be kept in mind that the last three components in Eqs. (4) and (5) are inseparable from each other as a result of their overlapping or competing effects, as will be described in the following section.

Partial Molal Volume of a CH_2 Group. The difference in the $\overline{V}^\circ$ for the successive homologous salts is taken as the contribution of a methylene group, $\overline{V}^\circ(CH_2)$, to the limiting partial molal volume of the organic ion in water. This quantity may be affected by the changes in the overlapping or competing effects between $\overline{V}^\circ$(elect), $\overline{V}^\circ$(disord), and $\overline{V}^\circ$(str). The $\overline{V}^\circ(CH_2)$ values are shown in Fig. 3 as a function of the chain length, and are compared with similar data obtained for other homologous organic salts.[3,8,11]

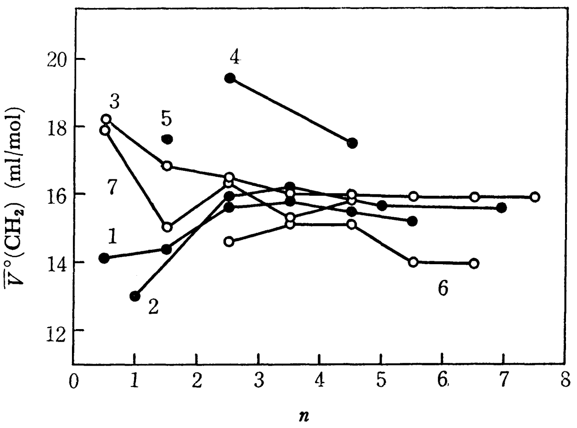

Fig. 3. The values of $\overline{V}^\circ(CH_2)$ as a function of chain length, calculated from the $\overline{V}^\circ$ data of homologous salts. 1: $H(CH_2)_nCOONa$, 2: $(CH_2)_n(COONa)_2$, 3: $H(CH_2)_nNH_3Br$,[8] 4: $(CH_2)_n(NH_3Cl)_2$, 5: $H(CH_2)_nSO_3Na$, 6: $(CH_2)_nNH_2Cl$,[11] 7: $[H(CH_2)_n]_4NBr$.[3,8]

It appears that the values of $\overline{V}^\circ(CH_2)$ approach about 16 ml/mol at 25 °C as the chain length increases. This value is quite similar to those obtained for sodium alkyl sulfates[14] and alcohols.[28] The methylene groups far apart from ionic groups may promote the structure of water in their vicinity without any disturbance by the ionic groups. Therefore, it can be stated that the partial molal volume of a CH_2 group in water is about 16 ml/mol at 25 °C when such a "normal" hydrophobic hydration takes place.

On the other hand, the deviations of the $\overline{V}^\circ(CH_2)$ values from the value of 16 ml/mol can be predicted for the electrolytes with shorter hydrocarbon chains as a result of the influences of the ionic groups. As Fig. 3 clearly shows, in fact, positive deviations are found for ammonium salts and sulfonates, and negative deviations for carboxylates. These results suggest that the influence of the COO^- group on the hydrophobic hydration surrounding CH_2 groups is significantly different from that of the NH_3^+ or SO_3^- groups.

For cyclic ammonium salts,[11] the $\overline{V}^\circ(CH_2)$ values deviate from the 16 ml/mol value even for longer-chain salts; this may indicate that the partial molal volume of a CH_2 group in a cyclic structure differs from that in an open chain.

It should be noted that the $\overline{V}^\circ$ values of the R_4NBr series increase in a peculiar manner with the increase in the alkyl-chain length. This implies that one cannot obtain a linear relation between the $\overline{V}^\circ$ and

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[24] W. Kauzmann, A. Bodanszky, and J. Rasper, *J. Amer. Chem. Soc.*, **84**, 1777 (1962).

[25] L. G. Hepler, *Can. J. Chem.*, **47**, 4613 (1969).

[26] H. Snell and J. Greyson, *J. Phys. Chem.*, **74**, 2148 (1970).

[27] J. E. Desnoyers, R. Francescon, P. Picker, and C. Jolicoeur, *Can. J. Chem.*, **49**, 3460 (1971).

[28] T. Nakajima, to be published.

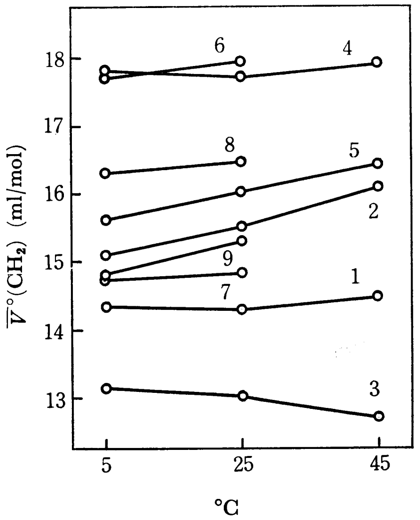

Fig. 4. Temperature dependence of the $\bar{V}^\circ(CH_2)$ evaluated from the difference in the $\bar{V}^\circ$ values of the salts with n= 0, 2 and 6; 1: $H(CH_2)_nCOONa$; (2−0), 2: $H(CH_2)_nCOONa$; (6−2), 3: $(CH_2)_n(COONa)_2$; (2−0), 4: $H(CH_2)_nNH_3Cl$; (2−0), 5: $H(CH_2)_nNH_3Cl$; (6−2), 6: $[H(CH_2)_n]_4NBr$; (1−0),[4,8] 7: $[H(CH_2)_n]_4NBr$; (2−1),[4] 8: $[H(CH_2)_n]_4NBr$; (3−2),[4] 9: $[H(CH_2)_n]_4NBr$; (4−3).[4]

the molecular weights of cations, though such a relationship was assumed by Conway *et al.*[3] in order to determine the ionic partial molal volume of the Br^- ion.

The effect of the temperature on the $\bar{V}^\circ(CH_2)$ value is shown in Fig. 4, together with the data for R_4NBr series.[4] The mean values of $\bar{V}^\circ(CH_2)$, evaluated from the difference in the $\bar{V}^\circ$ values of ethylamine and *n*-hexylamine hydrochloride, $\Delta\bar{V}^\circ(n=6-2)$, are in excellent agreement with the values calculated for alcohols[28] at all the temperatures studied. Therefore, these values may reflect the effect of "normal" hydrophobic hydration at all temperatures. The partial molal volume of a CH_2 group far apart from the ionic group for the sodium carboxylates is apparently smaller than that for the *n*-alkylamine hydrochlorides at all temperatures. In both series, however, the temperature dependence of the $\bar{V}^\circ(CH_2)$ is almost linear or slightly concave upward.

The mean values of $\bar{V}^\circ(CH_2)$ evaluated from $\Delta\bar{V}^\circ$ $(n=2-0)$ for both series exhibit less temperature dependence, while their absolute values differ greatly. Furthermore, the temperature dependence of the $\bar{V}^\circ(CH_2)$ calculated from the $\bar{V}^\circ$ values of sodium oxalate and succinate is obviously negative. Such a negative temperature dependence may be attributed to the strong influences of electrostriction on the $\bar{V}^\circ$, as was discussed in the preceding section.

It should be noticed that we were unable to find any distinct difference in the temperature dependences of the $\bar{V}^\circ(CH_2)$ values between carboxylate ions and *n*-alkylammonium ions. On the other hand, the $\bar{V}^\circ$ (CH_2) values are considerably different in their dependences on the chain length. A similar situation is found in the results for the R_4NBr solutions (Fig. 4). If the marked difference in the $\bar{V}^\circ(CH_2)$ behavior were caused by any structural change of water, it would also cause a difference in the temperature dependence of the $\bar{V}^\circ(CH_2)$ value between carboxylate ions and *n*-alkylammonium ions. The experimental results, however, do not coincide with this prediction. Therefore, it may be concluded that the volume change caused by the overlapping or competing effects between $\bar{V}^\circ$(elect), $\bar{V}^\circ$(disord), and $\bar{V}^\circ$(str) is insensitive to the temperature. An alternative explanation is that the $\bar{V}^\circ$(ion) in Eq. (4) involves another additional component, whose nature is less temperature-sensitive. In this connection we wish to call attention to a calculation for the volume change on the mixing of hard spheres of different sizes.[29]

Volume Change for the Substitution with an Ionic Group. It is of interest to evaluate the volume change for the substitution of a terminal hydrogen atom on a hydrocarbon chain with an ionic group as follows:

$$H(CH_2)_nH \xrightarrow{\Delta\bar{V}_1^\circ} H(CH_2)_nCOO^-$$
$$\xrightarrow{\Delta\bar{V}_2^\circ} {}^-OOC(CH_2)_nCOO^-$$

TABLE 3. $\bar{V}^\circ$ OF HYDROCARBONS, $H(CH_2)_nH$, IN WATER AT 25 °C

n	1	2	3	4	5	6
$\bar{V}^\circ$ (ml/mol)	37.3[a]	51.2[a]	66.8[a]	82.7[b]	98.6[b]	114.5[b]

a) Ref. 30.
b) These values were evaluated by the addition of $\bar{V}^\circ(CH_2)=15.9$ ml/mol[8,28] to the $\bar{V}^\circ$ value of propane.

TABLE 4. THE VOLUME CHANGES FOR THE SUBSTITUTION OF H ATOM WITH IONIC GROUPS AT 25 °C

n	$\Delta\bar{V}_1^\circ$(ml/mol)	$\Delta\bar{V}_2^\circ$(ml/mol)
$H(CH_2)_nH \rightarrow H(CH_2)_nCOO^- \rightarrow {}^-OOC(CH_2)_nCOO^-$		
1	18.6	—
2	9.1	7.0
3	9.1	7.3
4	9.0	7.7
5	8.6	—
6	7.9	8.4
$H(CH_2)_nH \rightarrow H(CH_2)_nNH_3^+ \rightarrow {}^+H_3N(CH_2)_nNH_3^+$		
1	−6.6[a]	—
2	−3.2	−14.3
3	−2.7[a]	−10.9
4	−2.6[a]	—
5	−2.5[a]	—
6	−2.4	−6.5

a) These values were calculated from the $\bar{V}^\circ$ data of Desnoyers and Arel[8] for *n*-alkylamine hydrobromides assuming that $\bar{V}^\circ(Br^-)-\bar{V}^\circ(Cl^-)=6.9$ ml/mol[21] at 25 °C.

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29) P. Assarsson and F. R. Eirich, *J. Phys. Chem.*, **72**, 2710 (1968).

$$\mathrm{H(CH_2)_nH} \xrightarrow{\Delta\overline{V}_1{}^\circ} \mathrm{H(CH_2)_nNH_3{}^+}$$
$$\xrightarrow{\Delta\overline{V}_2{}^\circ} \mathrm{{}^+H_3N(CH_2)_nNH_3{}^+}$$

The partial molal volumes of methane, ethane and propane in water were taken from the data by Masterton;[30] they are listed in Table 3.

The results are given in Table 4. As the number of methylene groups is increased, the $\Delta\overline{V}_1{}^\circ$ values decrease for the carboxylate ions, whereas the opposite order was observed for the alkylammonium ions. This finding might be correlated with the difference in the $\overline{V}^\circ(\mathrm{CH_2})$ observed for these two homologous series.

It is noteworthy that the $\Delta\overline{V}_2{}^\circ$ values are much more negative than the $\Delta\overline{V}_1{}^\circ$ values in the case of substitution with the $NH_3{}^+$ group. This behavior may be interpreted in terms of the "reinforcing effect on the electrostriction,"[24] as a result of the overlap of the electrostricted regions around the two $NH_3{}^+$ groups on the bolaform ion. It seems that the reinforcing effects caused by the diammonium ions are more remarkable than in the case of the dicarboxylate ions.

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[30] W. L. Masterton, *J. Chem. Phys.*, **22**, 1830 (1954).