Table III. Enthalpy of Solution of $NH_4HPO_3NH_2$ in 4.030*m* HCl + Stoichiometric H_2O + Stoichiometric H_3PO_4 at 25° C

Sample Wt., Grams	Solvent Wt., Grams	Corr. Temp. Rise, ° C	Enthalpy of Soln., −Cal/Sample	$-\Delta H$, Cal/Mole	Δ
9.03748	902.0304	1.1574	933.92	11784.8	−5.3
9.38211	901.3658	1.2009	969.16	11780.3	0.8
9.42745	901.3487	1.2089	974.55	11788.8	9.3
9.43190	901.4408	1.2051	973.33	11768.5	−11.0
9.46471	901.7051	1.2087	977.39	11776.7	−2.8
9.51416	901.5680	1.2157	982.39	11775.4	−4.1
9.51861	901.3247	1.2167	983.34	11781.2	1.7
9.53206	901.9604	1.2172	983.69	11768.8	−10.7
9.53890	901.6901	1.2224	986.24	11790.9	11.4
9.42749	901.6038		Av.	11779.5	± 2.7

of water. The enthalpy of solution of 0.12644 gram (0.00702 mole) of H_2O in 3.1674 moles of 4.030*m* HCl,

$$3.1674\ (HCl \cdot 13.7767\ H_2O) + 0.0070\ H_2O = 3.1674\ (HCl \cdot 13.7789\ H_2O) \quad (7)$$

calculated from a cubic equation fitted to the enthalpy-of-dilution data for HCl (*5*), is −68.57 cal per mole, the difference between the enthalpies of formation of the two concentrations of HCl. The enthalpy of solution of the stoichiometric amount of $H_3PO_4 \cdot 0.9151\ H_2O$ in 4.030*m* HCl to which the stoichiometric amount of H_2O had been added was calculated from Equation 6 to be −1853.03 cal per mole of $H_3PO_4 \cdot 0.9151\ H_2O$.

Substitution in Equation 1 of the measured enthalpies of solution gives −25,441 ± 6 cal for the enthalpy of reaction. The standard enthalpies of formation from the elements at 25° C (*5*) are: H_2O(liq), −68.315 ± 0.01; $NH_4H_2PO_4$(c), −345.38 ± 0.1; and $H_3PO_4 \cdot 0.9151\ H_2O$(liq), −304.58 ± 0.1 kcal per mole. The published value for $H_3PO_4 \cdot H_2O$ (*5*) was adjusted to the concentration $H_3PO_4 \cdot 0.9151\ H_2O$ by the heat-of-dilution data of Egan and Luff (*1*). The uncertainty intervals are the standard deviation of measured values. The values taken from NBS 270-3 (*5*) are used with uncertainty intervals of 10 in the last figure given. Substitution of these values in Equation 1 gives −292.42 ± 0.22 kcal per mole for the standard enthalpy of formation of $NH_4HPO_3NH_2$ at 25° C.

LITERATURE CITED

(1) Egan, E.P., Jr., Luff, B.B., *J. Phys. Chem.* **65**, 523 (1961).
(2) Egan, E.P., Jr., Wakefield, Z.T., Elmore, K.L., *J. Amer. Chem. Soc.* **78**, 1811 (1956).
(3) Herzog, A.H., Nielsen, M.L., *Anal. Chem.* **30**, 1490 (1958).
(4) McClellan, G.H., Waerstad, K.J., TVA, unpublished data.
(5) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Tech. Note **270-3** (1968).

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Apparent Molal Volumes of Aqueous Sodium Tetraphenylboron Solutions from 0° to 60° C

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The concentration and temperature behavior of the apparent molal volumes, ϕ_V's, of electrolytes that contain nonpolar hydrocarbon groups is abnormal compared to the more common electrolytes (*2-6, 10-15, 18, 21, 25, 26-28, 31, 34-38*). For example, the ϕ_V's of the Bu_4N^- halides have larger negative deviations from the limiting law, which become less negative at higher temperatures; at higher concentrations the ϕ_V's of the Bu_4N^- halides go through a minimum and the ϕ_V's increase with increasing concentration. At infinite dilution, the partial molal volumes of the Bu_4N^- halides do not appear to go through a maximum as a function of temperature—i.e., $\partial^2 \bar{V}_2^\circ / \partial T^2$ is positive. The anomalous concentration dependence of the ϕ_V's of the Bu_4N^- halides has been attributed to ion-pairing (*18, 21, 37*), "hydrophobic bonding" (*10*), "iceberg" effects (*9, 31, 36*), micelle formation (*37*), "salting-in" effects (*3-5, 34*), and induced cation-cation interactions (*2, 11, 14, 15, 35, 36*). The abnormal temperature behavior of the $\bar{V}_2^\circ$'s of the Bu_4N^- halides has been attributed to the ability of the nonpolar hydrocarbon portion of the Bu_4N^+ ion to increase or enforce the structure of water (*8, 9, 11*) and the release of the water with increasing temperature (*2, 13, 14, 15, 27, 31*).

The present work on the ϕ_V's of sodium tetraphenylboron ($NaBPh_4$) solutions was undertaken to obtain accurate ϕ_V data as a function of concentration and temperature for an electrolyte that contains a nonpolar hydrocarbon group on a large anion. By comparing the ϕ_V results for this large anion with the large cation, Bu_4N^+, we can hopefully obtain a better understanding of the ion-ion and ion-water interactions of electrolytes with nonpolar hydrocarbon groups. Recently (*33*), the partial molal heat capacities at infinite dilution were shown to behave abnormally between 40° and 80°; thus, the results of this study may possibly be useful in explaining this behavior [since there appears to be a parallism between the partial molal volumes and the partial molal heat capacities of electrolytes as a function of temperature (*19*)].

Precision density measurements were made on dilute aqueous solutions of sodium tetraphenylboron as a function of concentration (0.001 to 0.1*m*) and temperature (0° to 60° C). The apparent and partial molal volumes for these solutions were calculated from these density data. The Debye-Hückel theoretical limiting law slope for ϕ_V as a function of the square root of molar concentration is approached at all the temperatures studied. The deviations from the limiting law are negative at all the temperatures studied and become less negative as the temperature is increased. The effect of temperature on the partial molal volumes of sodium tetraphenylboron at infinite dilution is similar to other common electrolytes—i.e., $\bar{V}_2^\circ$ appears to go through a maximum or $\partial \bar{E}_2^\circ/\partial T$ is negative. The ion-ion and ion-water interactions responsible for the observed behavior of the ϕ_V's as a function of temperature and concentration are briefly discussed.

EXPERIMENTAL

The $NaBPh_4$ used in this study was obtained from the Fisher Scientific Co. (99.9%) and purified by the methods of Skinner and Fuoss (*32*). All the solutions were made by weight with triply distilled water. The water was degassed before use, to prevent the formation of bubbles on the magnetic float during an experiment. To minimize the effects of differences in the isotopic content of the distilled water, all the solutions were made up with the same batch of water used in the calibration runs.

The density measurements were made with a magnetic float densitometer that has been described in detail (*22*, *24*). The densitometer has been shown to have a precision of 0.3 ppm and an accuracy of about 1 ppm (*24*). The deviations of the ϕ_V's in the lowest concentrations studied (0.001*m*) represent an error in density of ±0.4 ppm. The densitometer was calibrated with triply distilled water, using the densities tabulated by Kell (*20*). The density measurements were made by a weight dilution technique and on single stock solutions. Both methods agreed to within 1 ppm in density. The weight dilution technique consisted of adding weighed amounts of stock solution to pure water or adding weighed amounts of water to stock solutions. Fresh solutions were made for all the experimental runs, since the solutions turned brown with setting, especially at temperatures above 30° [probably because of decomposition (*1*)].

The temperature of the bath containing the densitometer was set to ±0.01° C with Brooklyn calorimeter thermometers and a Hewlett-Packard quartz crystal thermometer. Both thermometers were calibrated with a platinum resistance thermometer (calibrated by the National Bureau of Standards) and G-2 Mueller bridge. The bath was regulated with a Hallikainen Thermotrol and found to vary less than ±0.001° C over the entire temperature range (using the quartz crystal thermometer).

RESULTS AND CALCULATIONS

The densities of dilute aqueous solutions (0.001 to 0.1*m*) of $NaBPh_4$ have been determined at various temperatures from 0° to 60°, using a magnetic float densitometer (*24*). The results of the differences, Δd, between the density of water, d°, and the density of the solutions, d, at 0°, 25°, and 50° are given in Table I. The apparent molal volumes, ϕ_V's, for these solutions were calculated from the equation

$$\phi_V = 1000(d^\circ - d)/d\, d^\circ\, m + M/d \qquad (1)$$

where *m* is the molality and *M* is the molecular weight of $NaBPh_4$ (342.23). Figure 1 shows the ϕ_V's of these solutions as a function of the square root of the molar concentration at 0°, 25°, and 50°.

Table I. Density of Aqueous Sodium Tetraphenylboron Solutions as a Function of Concentration and Temperature

0° C		25° C		50° C	
Molality	−1000Δd	Molality	−1000Δd	Molality	−1000Δd
0.0020506	0.1543	0.0017765	0.1178	0.0013587	0.0831
0.0022817	0.1715	0.0019798	0.1316	0.0018072	0.1105
0.0025715	0.1934	0.0022356	0.1489	0.0025971	0.1586
0.0029456	0.2213	0.0025673	0.1711	0.0029863	0.1821
0.0041545	0.3109	0.0036507	0.2425	0.0033557	0.2049
0.0046826	0.3509	0.0036896	0.2437	0.0036783	0.2245
0.0053649	0.4025	0.0038110	0.2530	0.0038266	0.2344
0.0062802	0.4712	0.0040635	0.2698	0.0044559	0.2719
0.0067579	0.5068	0.0045816	0.3032	0.0050493	0.3079
0.0073887	0.5548	0.0052511	0.3486	0.0058250	0.3551
0.0082030	0.6148	0.0061496	0.4063	0.0068822	0.4199
0.0092190	0.6900	0.0068578	0.4552	0.0071094	0.4330
0.010522	0.7868	0.0074192	0.4896	0.0083271	0.5052
0.012041	0.9011	0.0092145	0.6440	0.0083843	0.5099
0.012255	0.9148	0.012271	0.8123	0.0094961	0.5771
0.013975	1.0455	0.012408	0.8203	0.010948	0.6662
0.014196	1.0616	0.014145	0.9328	0.011659	0.7105
0.014676	1.0949	0.014604	0.9651	0.011987	0.7306
0.015857	1.1823	0.014670	0.9642	0.012469	0.7602
0.016121	1.2010	0.016039	1.0613	0.013399	0.8158
0.017849	1.3327	0.017735	1.1681	0.014112	0.8593
0.019409	1.4460	0.019263	1.2685	0.014480	0.8807
0.020826	1.5533	0.020647	1.3603	0.016004	0.9722
0.021700	1.6185	0.021905	1.4420	0.017698	1.0712
0.022849	1.7009	0.023055	1.5183	0.019225	1.1611
0.026885	1.9935	0.025045	1.6543	0.020607	1.2462
0.029850	2.2128	0.027007	1.7747	0.021865	1.3210
0.031593	2.3409	0.029490	1.9349	0.023015	1.3899
0.033551	2.4867	0.033447	2.1870	0.027008	1.6375
0.035768	2.6525	0.036794	2.4202	0.030819	1.8689
0.038299	2.8376	0.036993	2.4222	0.032761	1.9841
0.041215	3.0547	0.039734	2.6080	0.034694	2.1035
0.044611	3.3010	0.040188	2.6271	0.037174	2.2503
0.046836	3.4629	0.041587	2.7272	0.040035	2.4213
0.049294	3.6413	0.043082	2.8163	0.043373	2.6183
0.050025	3.6927	0.043621	2.8645	0.045377	2.7319
0.052025	3.8443	0.045716	2.9938	0.047575	2.8626
0.055076	4.0672	0.045865	3.0054	0.049997	3.0090
0.058507	4.3295	0.048123	3.1522	0.052678	3.1671
0.062393	4.6021	0.048352	3.1659	0.055664	3.3343
0.066833	4.9457	0.050024	3.2624	0.059008	3.5332
0.077931	5.7366	0.050331	3.2994	0.062780	3.7523
0.101634	7.4319	0.051124	3.3582	0.067067	4.0089
		0.054233	3.5530	0.071982	4.2951
		0.057745	3.7752	0.077675	4.6288
		0.061743	4.0446		
		0.066336	4.3519		
		0.071668	4.6743		
		0.077931	5.0726		
		0.101634	6.5665		

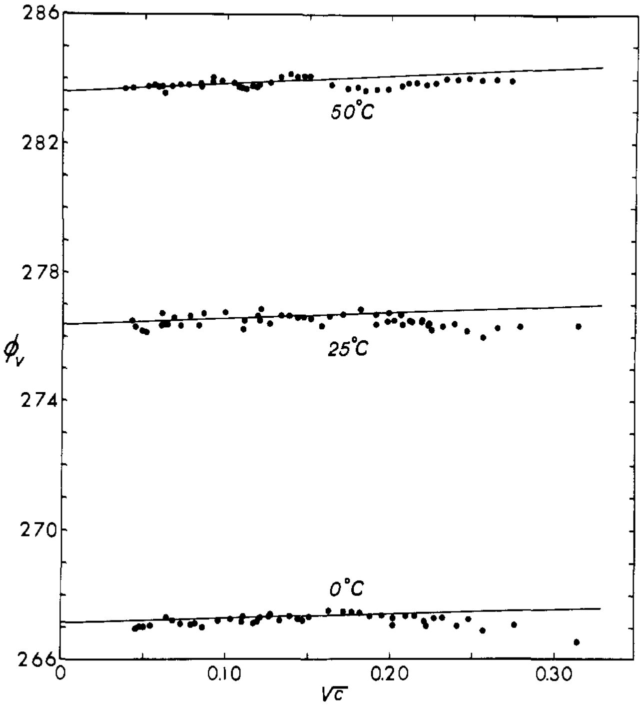

Figure 1. Apparent molal volumes of aqueous $NaBPh_4$ solutions as a function of square root of molal concentration at 0°, 25°, and 50° C

— Debye-Hückel limiting law

The ϕ_V's as a function of concentration at each temperature were fitted to the Redlich equation (*29*) by a least-squares best fit

$$\phi_V = \phi_V{}^\circ + S_V(c)^{1/2} + b_V c \qquad (2)$$

where $\phi_V{}^\circ$ is the apparent molal volume at infinite dilution (equal to the partial molal volume, $\overline{V}_2^\circ$), S_V is the Debye-Hückel limiting law slope (*29*), b_V is the deviation constant, and c is the molar concentration, $c = m\, d^\circ\, 1000/(1000 + m\, \phi_V d^\circ)$. As shown in Figure 1, the Debye-Hückel limiting slope is approached at all the temperatures studied. Table II lists the $\overline{V}_2^\circ$'s of $NaBPh_4$, the deviation constants, b_V, at various temperatures, and root mean square deviations. The $\overline{V}_2^\circ$ of $NaBPh_4$ at 25° agrees very well with the value (277.0 ml per mole) determined by Gilkerson and Stewart (*12*).

To examine the effect of temperature on the $\overline{V}_2^\circ$'s of $NaBPh_4$ solutions at closely spaced temperatures, we also made a number of ϕ_V determinations for some dilute solutions at 5° intervals from 0° to 60°. The $\overline{V}_2^\circ$'s were determined from these ϕ_V's by subtracting the limiting law slope contributions $[S_V\ (c)^{1/2}]$ and the deviation contributions $(b_V c)$—i.e., $\phi_V{}^\circ = \phi_V - S_V(c)^{1/2} - b_V c$. The S_V's used in these calculations were taken from the work of Redlich and Meyer (*29*) and the b_V's were interpolated from the values at 0°, 25°, and 50° given in Table II (fitted to the equation, $b_V = -7.38 - 1.88 \times 10^{-2}t + 1.456 \times 10^{-3}t^2$). The resulting $\overline{V}_2^\circ$'s are given in Table II and plotted against temperature in Figure 2. The largest correction needed to estimate $\overline{V}_2^\circ$ from the ϕ_V data was 0.4 ml per mole, which is about double the standard deviation of 0.2 ml per mole over the entire temperature range. The $\overline{V}_2^\circ$'s of $NaBPh_4$ given in Table II have been fitted to the equation

$$\overline{V}_2^\circ = 267.14 + 0.419\,t - 2.3943 \times 10^{-3}\,t^2 + 2.8369 \times 10^{-5}\,t^3 - 3.3237 \times 10^{-7}\,t^4 \qquad (3)$$

Table II. Partial Molal Volume, $\overline{V}_2^\circ$, and Expansibility, $\overline{E}_2^\circ$, of $NaBPh_4$ in Water and Deviation Constant, b_V, from Limiting Law at Various Temperatures[a]

Temp., °C	$\phi_V{}^\circ = \overline{V}_2^\circ$ Ml/Mole	$\phi_E{}^\circ = \overline{E}_2^\circ$ Ml/Mole Deg	b_V, Ml/Mole	R.M.S.[b], Ml/Mole
0.0	267.16	0.419	−7.38	0.14
5.0	(269.18)	0.397		0.2
10.0	(271.04)	0.378		0.2
15.0	(272.89)	0.361		0.2
20.0	(274.86)	0.346		0.2
25.0	276.41	0.332	−6.94	0.17
30.0	(278.17)	0.316		0.2
35.0	(279.57)	0.299		0.2
40.0	(280.85)	0.279		0.2
45.0	(282.31)	0.255		0.2
50.0	283.63	0.227	−4.68	0.13
55.0	(284.74)	0.193		0.2
60.0	(285.39)	0.153		0.2

[a] $\phi_V{}^\circ$ values in brackets estimated from ϕ_V data (at least two points at each temperature), using equation, $\phi_V^\circ = \phi_V - S_V(c)^{1/2} - b_V\, c$. $\overline{E}_2^\circ$ values calculated by differentiating Equation 3 with respect to temperature and solving for $\overline{E}_2^\circ$ at given temperatures. [b] Root mean square standard deviation. Deviation of ±0.2 ml per mole at concentration of 0.002m represents an error in density of ±0.4 ppm.

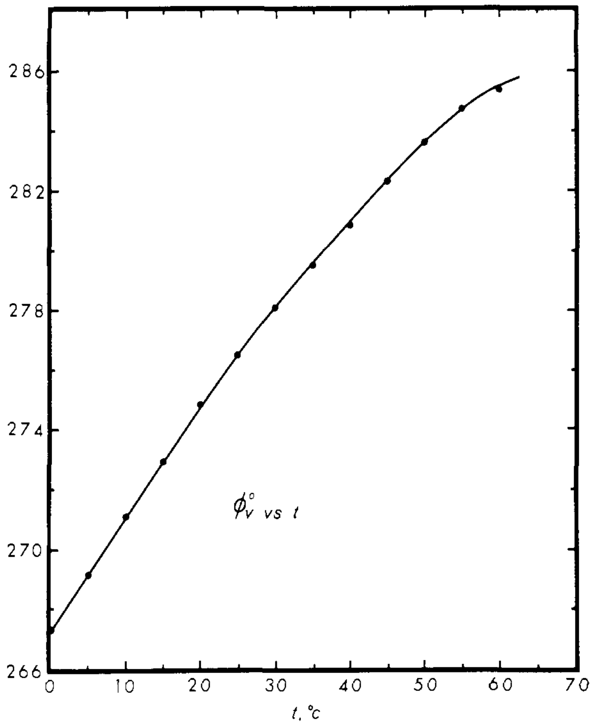

Figure 2. Partial molal volume of aqueous $NaBPh_4$ solutions at infinite dilution as a function of temperature

The partial molal expansibilities, $\overline{E}_2^\circ$'s, of the $NaBPh_4$ solutions calculated by differentiating Equation 3 with respect to temperature are given in Table II at 5° intervals from 0° to 60°. In Figure 3 we have plotted the $\overline{E}_2^\circ$'s of $NaBPh_4$ solutions *vs.* temperature; the $\overline{E}_2^\circ$'s of NaCl (*7, 23*) and Bu_4NCl (*24*) solutions are included for comparison. By extrapolating the $\overline{E}_2^\circ$'s of $NaBPh_4$ solutions *vs.* temperature to zero, it is possible to estimate the temperature at which $\overline{V}_2^\circ$ goes through a maximum. Depending upon the method of extrapolation, t_{max} occurs between 75° and 110°.

The $\phi_V{}^\circ$ and $\phi_E{}^\circ$ data for the $NaBPh_4$ solutions do not show any abnormal temperature behavior between 0° and

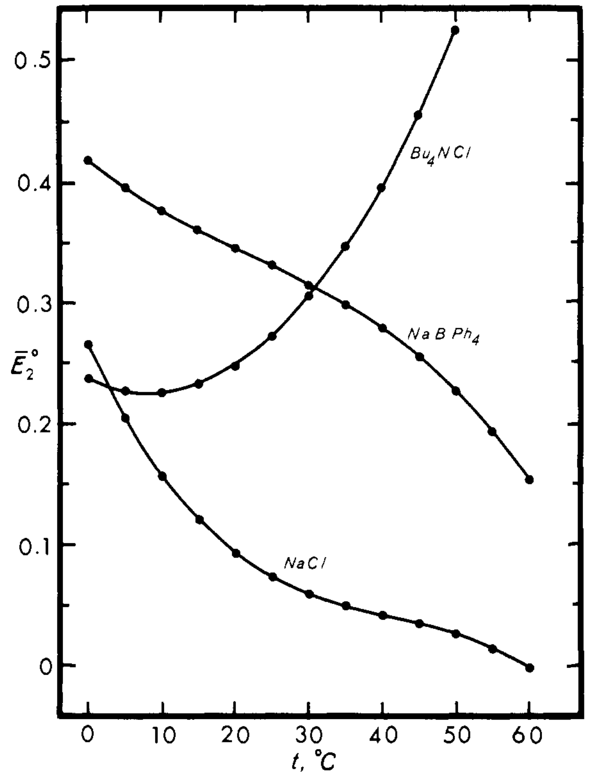

Figure 3. Partial molal expansibility of aqueous NaCl, $NaBPh_4$, and Bu_4NCl at infinite dilution as a function of temperature

60°—i.e., within the experimental error of ±0.2 ml per mole for $\bar{V}_2^\circ$ and ±0.02 ml per mole for $\bar{E}_2^\circ$. Thus, the $\phi_V{}^\circ$ data for $NaBPh_4$ do not show the abnormal temperature behavior observed by Subramanian and Ahluwalia (*33*) for the partial molal heat capacity. Since we were not able to extend our measurements to temperatures above 60° (because of limitations in the density of the magnetic float and the apparent decomposition of the solution with setting at high temperatures), we cannot speculate about the $\phi_V{}^\circ$ behavior between 60° and 80°.

DISCUSSION OF RESULTS

The deviations of the ϕ_V's for $NaBPh_4$ solutions from the limiting law—i.e., b_V—are large and negative. This ϕ_V behavior is similar to the large R_4NX's (*2, 4, 11, 36*). The effect of temperature on the deviation constant for $NaBPh_4$ solutions is also similar to the behavior for the large R_4NX's, in that $\partial b_V/\partial T$ is positive [for more common electrolytes like NaCl, $\partial b_V/\partial T$ is negative (*7, 23*)]. Because of the similarities in the deviations of $NaBPh_4$ and Bu_4NBr solutions, one might postulate that similar types of ion-ion interactions are responsible in both systems. From recent discussions, it appears that some type of cation-cation interaction (*2, 11, 13, 14, 15, 35*) is responsible for the large negative deviations of the R_4NX solutions; thus, by analogy one might attribute the negative deviations of the $NaBPh_4$ solutions to anion-anion ($BPh_4^- - BPh_4^-$) interactions. The role of the structure of water in the ion-ion interactions of the large R_4N^- halides is not clear. Since recent ϕ_V work (*14, 15, 28*) in nonaqueous solvents has shown that the deviations of the R_4NX's are also negative, the unique role of water structure may not be necessary to cause the observed ion-ion interactions. A more reasonable explanation for the negative deviations of large electrolytes appears to be related to some sort of packing effect (*14, 15*). Whether the packing effect is caused by mutual penetration of the hydrocarbon portion of these ions or the filling of the void space between the large ions is not known for certain. Further ϕ_V work on these large electrolytes in other solvents may clear up this issue.

The $\partial^2 \bar{V}^\circ/\partial T^2 = \partial \bar{E}^\circ/\partial T$ of the $NaBPh_4$ solutions (shown in Figure 3) indicate that the ion-water interactions for BPh_4^- are similar to the more common anion, Cl^-. The cause of the decrease of $\bar{E}^\circ$ with increasing temperature or the maximum in the $\bar{V}^\circ$ of common ions has been attributed to the decrease in volume due to the increase in electrostriction with increasing temperature—i.e., $\bar{V}^\circ$ (elect) and $\bar{E}^\circ$ (elect) (*23, 25, 26*). For common ions, this decrease in volume due to electrostriction is larger than the increase in volume due to the increase of the intrinsic size of the ion (including void space effects), while for the large R_4N^- ions, the electrostriction is very small and the intrinsic volume is the predominant effect (thus, the maximum does not occur).

Hepler (*17*) has recently developed a method of classifying solutes by considering the sign of $\partial \bar{E}_2^\circ/\partial T$ using the thermodynamic relation

$$(\partial \bar{C}_p^\circ/\partial P)_T = -T(\partial^2 \bar{V}^\circ/\partial T^2)_P = -T(\partial \bar{E}^\circ/\partial T)_P \tag{4}$$

where $\bar{C}_p^\circ$ is the partial molal heat capacity of the solute at infinite dilution. Hepler (*17*) reasons that $\partial \bar{C}_p^\circ/\partial T$ should be negative or $\partial \bar{E}^\circ/\partial T$ should be positive for a "structure-making" solute and $\partial \bar{C}_p^\circ/\partial P$ should be positive or $\partial \bar{E}^\circ/\partial T$ should be negative for a "structure-breaking" solute. To compare the ion-water interactions of the BPh_4^- anion and the Bu_4N^- cation on an absolute basis, it is necessary to separate the $\bar{V}^\circ$'s of the electrolytes into their ionic components. Using $\bar{V}^\circ(H^+)$ = −5.1, −5.4, and −5.9 ml per mole (*25*), respectively, at 0°, 25°, and 50°, we have calculated the absolute $\bar{V}^\circ$'s and $\bar{E}^\circ$'s of Bu_4N^- and BPh_4^- ions (Table III). Thus, using Hepler's reasoning (*20*), BPh_4^- would be considered a structure-breaking ion and Bu_4N^- would be considered a structure-making ion. Since the $\bar{V}^\circ$ (ion) consists of at least three major components (*22–27*),

$$\bar{V}^\circ \text{ (ion)} = \bar{V}^\circ \text{ (cryst)} + \bar{V}^\circ \text{ (elect)} + \bar{V}^\circ \text{ (disord)} \tag{5}$$

which all appear to be a function of temperature for the R_4N^- ions (*25, 26*), the division of ions into various categories by examining $\partial^2 \bar{V}^\circ/\partial T^2$ may be the resultant of many inseparable or competing effects. Another method (*25, 26*) that can be used to examine the major factors affecting ion-water interactions (that hopefully solves this problem) is to examine the sign of the quantity $\bar{V}^\circ$ (ion) − $\bar{V}^\circ$ (cryst) = $\bar{V}^\circ$ (ion) − 2.52 r^3, where r is the crystal radius in A units. If $\bar{V}^\circ$ (ion) − $\bar{V}^\circ$ (cryst) is positive, the ion is classified as a "negative-solvating" or a "structure-breaking" ion and if this quantity is negative, the ion is classified as a "positive-solvating" or "structure-making" ion. Using $r(Bu_4N^-)$ = 4.94 A (*30*) and $r(BPh_4^-)$ = 4.2 A (*16*), we obtain $\bar{V}^\circ(Bu_4N^-) - \bar{V}^\circ$ (cryst) = −33.4 ml per mole and $\bar{V}^\circ(BPh_4^-) - \bar{V}^\circ$ (cryst) = 96.3 ml per mole.

Table III. Partial Molal Volume and Expansibility at Infinite Dilution of BPh_4^- and Bu_4N^- Ions at Various Temperatures[a]

Ion	$\bar{V}^\circ$ (Ion), Ml/Mole		
	0° C	25° C	50° C
BPh_4^-	275.8	283.0	289.8
Bu_4N^-	266.0	270.3	279.1
	$\bar{E}^\circ$ (Ion), Ml/Mole Deg		
	12.5° C		37.5° C
BPh_4^-	0.288		0.272
Bu_4N^-	0.172		0.352

[a] Based on $\bar{V}^\circ$ data tabulated by Millero (*25*).

Thus, Bu_4N^- is a "positive hydrating" ion and PBh_4^- is a "negative-hydrating" ion, in agreement with Hepler's methods (*20*).

The differences between the ion-water interactions of electrolytes with an aromatic or an alkane hydrocarbon group may be due to the differences in the structure of the benzene ring compared to the alkane group—e.g., resonance effects—or to differences in the packing of water molecules around the benzene ring compared to the alkane group. For example, water molecules may be able to fill up or penetrate the void space around the Bu_4N^- ion, while for the BPh_4^- ion, this filling up or penetration may not be possible.

Since Gopal and Siddiqi (*14, 15*) have found that the $\bar{V}^\circ$'s of electrolytes (with and without a nonpolar hydrocarbon group) may or may not go through a maximum as a function of temperature in the solvents formamide and *N*-methylacetamide, the types of ion-solvent interactions causing (or not causing) the maximum are not confined to aqueous solutions or due to the unique structural properties of water. Thus, "structure-breaking or negative-solvating" and "structure-making or positive-solvating" effects of solutes determined from volume properties, using the methods of Hepler (*20*) or Millero (*25, 26*), occur in solvents other than water.

In summary, the ϕ_V behavior of $NaBPh_4$ solutions indicates that this electrolyte behaves like the large R_4NCl's in its ion-ion interactions and like NaCl in its ion-water interactions. The dual nature of the ϕ_V behavior of $NaBPh_4$ electrolyte points out the necessity of using only infinite dilution thermodynamic data to discuss ion-solvent or solvent-solvent interactions.

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LITERATURE CITED

(1) Ahluwalia, J.C., personal communication, 1969.
(2) Broadwater, T.L., Evans, D.F., *J. Phys. Chem.* **73**, 164 (1969).
(3) Conway, B.E., Verrall, R.E., *Ibid.*, **70**, 1473, 3952 (1966).
(4) Conway, B.E., Verrall, R.E., Desnoyers, J.E., *Trans. Faraday Soc.* **62**, 2738 (1966); *Z. Physik Chem. (Leipzig)* **230**, 157 (1965).
(5) Desnoyers, J.E., Arel, M., *Can. J. Chem.* **45**, 359 (1967).
(6) Dunn, L.A., *Trans. Faraday Soc.* **64**, 1898 (1968).
(7) *Ibid.*, p. 2951.
(8) Frank, H.S., Evans, M.W., *J. Chem. Phys.* **13**, 507 (1945).
(9) Frank, H.S., Wen, W-Y., *Discuss. Faraday Soc.* **24**, 133 (1957).
(10) Franks, F., Smith, H.T., *J. Phys. Chem.* **68**, 3581 (1964).
(11) Franks, F., Smith, H.T., *Trans. Faraday Soc.* **63**, 2586 (1967).
(12) Gilkerson, W.R., Stewart, J.L., *J. Phys. Chem.* **65**, 1465 (1961).
(13) Gopal, G., Siddiqi, M.A., *Ibid.*, **72**, 1814 (1968).
(14) *Ibid.*, **73**, 3390 (1969).
(15) Gopal, G., Siddiqi, M.A., *Z. Physik. Chem.* **67**, 122 (1969).
(16) Grunwald, W., Baughman, G., Kohnstam, G., *J. Amer. Chem. Soc.*, **82**, 5801 (1960).
(17) Hepler, L.G., *Can. J. Chem.* **47**, 4613 (1969).
(18) Hepler, L.G., Stokes, J.M., Stokes, R.H., *Trans. Faraday Soc.* **61**, 20 (1965).
(19) Kaminsky, K., *Discuss. Faraday Soc.* **24**, 171 (1957).
(20) Kell, G.S., J. CHEM. ENG. DATA **12**, 66 (1967).
(21) Levien, B.J., *Aust. J. Chem.* **18**, 1161 (1965).
(22) Millero, F.J., *J. Phys. Chem.* **71**, 4567 (1967).
(23) *Ibid.*, **74**, 356 (1970).
(24) Millero, F.J., *Rev. Sci. Instr.* **38**, 1441 (1967).
(25) Millero, F.J., "Structure and Transport Processes in Water and Aqueous Solutions," Chap. 15, R.A. Horne, ed., Wiley, New York, 1970, in press.
(26) Millero, F.J., "Treatise on Skin," Chap. 11, H.R. Elden, ed., Wiley, New York, 1970, in press.
(27) Millero, F.J., Drost-Hansen, W., *J. Phys. Chem.* **72**, 1758 (1968).
(28) Padova, J., Abrahamer, I., *Ibid.*, **71**, 2112 (1967).
(29) Redlich, O., Meyer, D.M., *Chem. Rev.* **64**, 221 (1964).
(30) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," p. 125, Butterworths, London, 1959.
(31) Schiavo, S., Scrosati, B., Tommasini, A., *Ric. Sci.* **37**, 211 (1967).
(32) Skinner, J.F., Fuoss, R.M., *J. Phys. Chem.* **68**, 1882 (1964).
(33) Subramanian, S., Ahluwalia, J.C., *Ibid.*, **72**, 2525 (1968).
(34) Verrall, R.E., Conway, B.E., *Ibid.*, **70**, 3952 (1966).
(35) Wen, W-Y., Nara, K., *Ibid.*, **71**, 3907 (1967); **72**, 1137 (1968).
(36) Wen, W-Y., Saito, S., *Ibid.*, **68**, 2639 (1964); **69**, 3569 (1965).
(37) Wirth, H.E., *Ibid.*, **71**, 2922 (1967).
(38) Zana, R., Yeager, E., *Ibid.*, **71**, 4241 (1967).

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