Both KCl and Na_2SO_4 have been studied between 100° and 165° C. by Soldano (*3-5*, *11*) and co-workers as well as in the range up to 45° C. Figures 2 and 3 show a plot of R *vs.* T between 25° and 165° C. for KCl and Na_2SO_4, respectively. Figure 3 shows the reported uncertainties associated with the data at each temperature. These plots of direct experimental ratios (involving no assumption about ϕ's for the reference salt, NaCl) show no sign of a discontinuity in the suspected range between 45° and 60° C. On the other hand, it is difficult to see how transitions from the low temperature legs of these curves can be made to the corresponding high temperature sections without multiple inflections or distinct discontinuities. These apparent inconsistencies are within the admitted uncertainty of the data above 120° C. (±1%). [Through private communication the authors of the 165° C. data (*11*) reported a typographical error changing their reported uncertainty from ±0.1% to ±1.0%.] Whatever the outcome of the higher temperature questions may be, the authors' work indicates that if there is unusual behavior in the intermediate range it occurs above 60° C.

ACKNOWLEDGMENT

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Apparent Molal Volumes of Aqueous Monovalent Salt Solutions at Various Temperatures

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A precision magnetic float densitometer has been used to measure the densities of 0.1 molal LiCl, NaCl, KCl, RbCl, CsCl, NaF, KBr, KI, and KNO_3 aqueous salt solutions at one-degree intervals from 20° to 40° C. The densities have been fit to an equation of the form, $d_{soln} = A + Bt + Ct^2 + Dt^3$ with a maximum root-mean-square deviation of 4 p.p.m. The apparent molal volume, ϕ_V, and the apparent molal expansibility, ϕ_E, have been calculated for these solutions from the density data. The values obtained agree very well with those from the literature. The apparent molal expansibilities for these solutions, ϕ_E, have been equated to the infinite dilution values—i.e., $\phi_E = \bar{E}^\circ$. The contributions to $\bar{E}^\circ$ (salt) have been divided into ionic contributions. The expansibilities for the cations decrease in the order $Na^+ > K^+ > Rb \sim Cs^+ > H^+ > Li^+$ and the expansibilities for the anions increase in the order $F^- < Cl^- \sim Br^- < I^- < NO_3^-$.

FEW STUDIES have been made on the various properties of aqueous solutions at closely spaced temperature intervals; furthermore, there seems to be a complete absence of reliable systematic data. For this reason, the authors have initiated a program of measuring various properties of aqueous solutions (such as partial molal volumes, compressibilities, viscosities, and conductivities) at closely spaced temperature intervals. The present paper describes the results of precision density measurements of a number of dilute salt solutions (LiCl, NaCl, KCl, RbCl, CsCl, NaF, KBr, KI, and KNO_3). The thermal expansion coefficients (at 25° C.), α_{soln}; apparent molal volumes, ϕ_V; and apparent molal expansibilities, ϕ_E, have been calculated from the density data.

EXPERIMENTAL

All the salts used (except RbCl and CsCl obtained from Chemical Procurement Laboratories, Inc.) were reagent grade Baker Analyzed chemicals and were used without further purification. The salts were dried for a day at 120° C. and stored in a desiccator before being used. The solutions were made by weight with doubly distilled water. Prior to making up the solutions, the water was freshly boiled to remove the dissolved gases and prevent the formation of bubbles on the magnetic float during a run.

The magnetic float densitometer used to make the density measurements and a review of the development of the magnetic float method has been described (*10*). The authors have made some changes to allow the apparatus to be used over a wide range of temperatures without disassembling. This results in a reduced sensitivity, since a large magnetic interaction constant must be used (*10*). A sketch of the densitometer is shown in Figure 1. The densitometer consists of a 110-ml. (glass) solution container (A) which fits into a brass support (E) containing two solenoids. The support is attached to a platform used to level the system on the botton of a constant temperature bath. The float

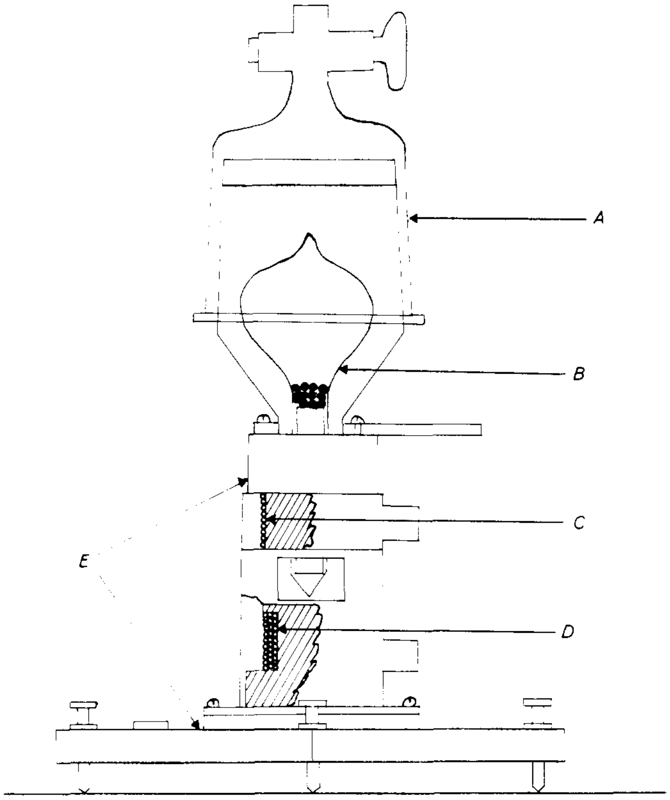

Figure 1. Schematic drawing of magnetic float densitometer (*10*)

(*B*) is made of borosilicate glass and contains a magnet. The volume of the float at 25° C. is 32.3786 ml. The pull-down solenoid (*C*) is used to bring the magnetic float to the bottom of the solution container into the field of the main solenoid (*D*). The main solenoid is made of about 700 turns of No. 28 Cu wire.

The procedure for making a run is as follows: The solution is allowed to come to equilibrium at the temperature of interest (about 40 minutes). A current is applied through the main solenoid and the magnetic float is pulled to the bottom by using the pull-down solenoid. The current through the main solenoid is slowly decreased until the float just leaves the bottom. This process is repeated until the "hold-down" (equilibrium) current is reproducible. The system is calibrated with water by measuring the hold-down current for the float with various platinum weights. The density of the solution at temperature t is equal to:

$$d^t_{\text{soln}} = \frac{W + w + f\,i}{V^t + w/d^t_{\text{Pt}}} \tag{1}$$

where W is the weight of the magnetic float, w is the weight of Pt on the float, f is the force exerted by the interaction of the magnetic float and the main solenoid (grams per ampere), i is the hold-down current, V^t is the volume of the float at temperature t; $V^t = V^{25}\,[1 + \alpha_{\text{float}}\,(t - 25)]$, and d^t_{Pt} is the density of Pt at temperature t; $d^t_{\text{Pt}} = d^{25}_{\text{Pt}}/[1 + \alpha_{\text{Pt}}\,(t - 25)]$.

The values of f and V^t were determined by measuring the hold-down current in water at various temperatures. With f equal to 3.5308 grams per ampere and V^{25} is equal to 32.3786 ml., Equation 1 represented the density data of water (*16*) to ±2 p.p.m. from 20 to 40° C. The system was recalibrated with water before and after each run to assure the absence of drift in f or V^t, and also to assure that the density of the water used was constant.

The entire densitometer is placed on the bottom of a constant temperature bath, controlled to ±0.001° C. with a Hallikainen regulator. The temperature of the bath was initially set and subsequently read to within ±0.002° C. with a Melabs platinum resistance thermometer.

RESULTS AND CALCULATIONS

The densities of the various solutions have been measured at one-degree intervals from 20° to 40° C. The densities of the salt solution were fit to equations of the form:

$$d_{\text{soln}} = A + Bt + Ct^2 + Dt^3 \tag{2}$$

The constants for this equation are listed in Table I along with the root-mean-square deviations. Figure 2 shows the errors in parts per million of the calculated density at one-degree intervals from 20° to 40° C. Table I also lists the temperatures of maximum density calculated by differentiating Equation 2 and solving for t_{max}. The values obtained in this study for the temperature maximum density are significantly lower than those obtained by Beattie (*1*). However, values in the present study were obtained by an extensive extrapolation (about 20° C.), and the values obtained should be used merely as a guide to indicate the relative accuracy of the proposed fit.

The expansion coefficient,

$$\alpha_{\text{soln}} = -\frac{1}{d_{\text{soln}}}\left(\frac{\partial d_{\text{soln}}}{\partial t}\right)$$

of the solutions can be calculated from the equation;

$$\alpha_{\text{soln}} = -(B + 2Ct + 3Dt^2)/d_{\text{soln}} \tag{3}$$

The results of α_{soln} calculated from this equation agree within the experimental error with those compiled by Harned and Owen (*8*) for LiCl, NaCl, and KCl and 25° C.

The apparent molal volumes listed in Table II were calculated from the equation;

$$\phi_V = \frac{M}{d_{\text{soln}}} - \frac{1000\Delta d}{d_{\text{soln}}\,d_{\text{H}_2\text{O}}\,m} \tag{4}$$

The densities of H_2O used in these calculations were taken from Tilton and Taylor's work (*16*). The expansibilities of these solutions, $\phi_E = (\partial\phi_V/\partial_T)$, can be calculated from the partial molal values. The average values of ϕ_E calculated on the basis of the data at 20° to 30° C. are compiled in Table III. Also listed are the infinite dilution expansibilities for some of these salts at 25° C. compiled by Harned and Owen (*8*) and Noyes (*13*).

DISCUSSION OF RESULTS

The apparent molal volumes for the various salts cannot be directly compared with literature values since reliable values have been reported only at 25° C., and the present study was carried out at only one concentration. It is possible, however, to estimate the infinite dilution value from these data by using the equation;

$$\phi_V = \phi^\circ_V + S_V[c]^{1/2} + bc \tag{5}$$

where c is the concentration in moles per liter of solution, S_V is the theoretical limiting slope (*15*) (1.86 at 25° C.), and b is a constant that is determined from the experimental data. Since b is not known for all the salts studied in this paper and is normally small, the authors have assumed it to be zero in order to be able to compare the results with the literature values at 25° C. (*17*). The results (Table IV) agree well with the literature values at infinite dilution (*4, 5, 11, 14, 17*). Redlich and Meyer (*15*) have also calcu-

Table I. Constants for Density Equation and t_{max}

Salt	A, G./Ml.	$B \times 10^6$, G./Ml.-Deg.	$-C \times 10^6$, G./Ml.-Deg.^{2}	$D \times 10^6$, G./Ml.-Deg.^{3}	RMS, P.P.M.	t_{max}, °C.
LiCl	1.003169	19.202	6.4732	2.3584	1.34	1.5
NaCl	1.004806	43.453	7.4171	3.2848	1.72	2.9
KCl	1.005907	1.284_6	6.0180	1.8771	1.18	0.1
RbCl	1.009348	-8.676_4	5.6075	1.3732	2.00	-0.8
CsCl	1.013470	13.587	6.4353	2.3359	3.73	1.1
NaF	1.004587	25.758	6.7713	2.6845	1.94	1.9
KBr	1.009127	17.572	6.4946	2.3149	1.49	1.4
KI	1.012662	3.029_4	6.1981	2.0893	3.28	0.2
KNO_3	1.007037	2.329_8	6.2123	2.0805	2.96	0.2

Table II. Apparent Molal Volumes of Aqueous Salt Solutions at Various Temperatures

	Apparent Molal Volumes, Ml./Mole								
Temp., °C.	LiCl 0.11715m	NaCl 0.11425m	KCl 0.11528m	RbCl 0.09958m	CsCl 0.10231m	NaF 0.10001m	KBr 0.10457m	KI 0.10154m	KNO_3 0.10451m
20	17.442	16.864	27.178	32.144	39.434	-1.808	34.147	45.443	38.324
21	17.449	16.911	27.260	32.172	39.445	-1.777	34.212	45.526	38.462
22	17.490	17.002	27.308	32.270	39.493	-1.698	34.306	45.627	38.572
23	17.505	17.049	27.399	32.277	39.531	-1.688	34.371	45.718	38.710
24	17.555	17.149	27.481	32.384	39.637	-1.619	34.426	45.759	38.829
25	17.596	17.195	27.555	32.461	39.653	-1.580	34.471	45.928	38.929
26	17.637	17.259	27.593	32.537	39.688	-1.492	34.515	46.085	39.038
27	17.669	17.420	27.666	32.592	39.860	-1.444	34.598	46.115	39.196
28	17.685	17.457	27.739	32.637	39.884	-1.386	34.641	46.242	39.305
29	17.743	17.547	27.786	32.681	39.986	-1.349	34.694	46.310	39.414
30	17.766	17.646	27.868	32.705	40.009	-1.292	34.747	46.367	39.551
31	17.773	17.727	27.923	32.748	40.031	-1.276	34.808	46.483	39.679
32	17.814	17.816	27.970	32.781	40.042	-1.220	34.870	46.549	39.797
33	17.837	17.897	28.016	32.834	40.073	-1.214	34.950	46.545	39.868
34	17.878	17.969	28.071	32.896	40.102	-1.128	35.020	46.659	39.919
35	17.893	18.093	28.135	32.958	40.161	-1.052	35.109	46.803	40.037
36	17.917	18.191	28.190	33.010	40.218	-0.987	35.150	46.857	40.213
37	17.957	18.281	28.262	33.071	40.266	-0.993	35.210	46.920	40.303
38	17.972	18.406	28.317	33.112	40.302	-0.959	35.269	47.033	40.479
39	18.013	18.451	28.380	33.183	40.358	-0.894	35.318	47.085	40.578
40	18.045	18.513	28.391	33.263	40.394	-0.891	35.387	47.146	40.628

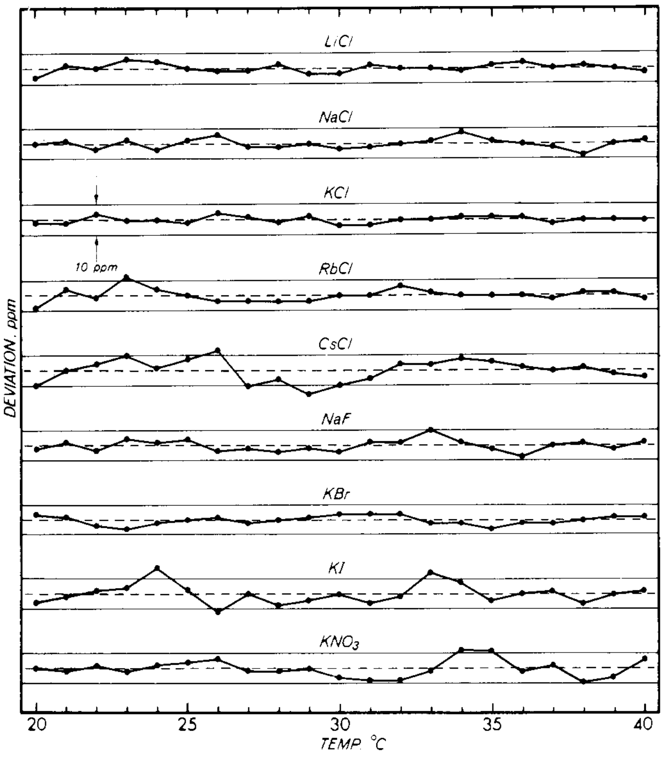

Figure 2. Deviation plots from density equation at various temperatures

Deviations in parts per million, see text for details

Table III. Apparent Expansibility of Salt Solutions at 25° C.

		Ml./Mole-Degree		
Salt	Molality	This work	Infinite dilution value	Ref.
LiCl	0.11715	0.032	0.025	(*8*)
NaCl	0.11425	0.078	0.093	(*8*)
KCl	0.11528_5	0.069	0.085	(*8*)
RbCl	0.09957_8	0.062	0.070	(*13*)
CsCl	0.10231	0.058	0.070	(*13*)
NaF	0.10000_9	0.067	. . .	. . .
KBr	0.10457_5	0.060	0.093	(*13*)
KI	0.10153_5	0.092	0.127	(*13*)
KNO_3	0.10451	0.123	. . .	. . .
HCl	. . .	. . .	0.034	(*8*)

lated the limiting slope, S_V, at other temperatures; however, until more is known about the constant b, similar calculations at other temperatures may be meaningless.

The expansibilities listed for the various salts in Table III agree within experimental error (±0.01 ml. per mole degree) with the available data. Since ϕ_E is not strongly dependent upon concentration (*8*), without significant error, the authors' value can be equated with, $\phi_E^\circ = \bar{E}^\circ$—i.e., the partial molal expansibility at infinite dilution.

Recently, many workers (*3, 7, 9, 12*) have attempted to divide the partial molal volume of ions at infinite dilution into two contributions

Table IV. Apparent Molal Volumes at Infinite Dilution of Monovalent Salts at 25° C.

Salt	$\phi_V - 1.86\,[C]^{1/2}$	ϕ°_V, Lit.	Ref.
LiCl	16.96 ml./mole	16.99	(*17*)
NaCl	16.57	16.63	(*17*)
KCl	26.93	26.89	(*17*)
RbCl	31.87	31.94	(*17*)
CsCl	39.09	39.15	(*17*)
NaF	−2.17	−2.29	(*11*)
KI	45.34	45.30	(*14*)
KBr	33.87	33.73	(*4*)
KNO_3[a]	38.34	38.05	(*5*)

[a] $\bar{V}^\circ$ (KNO_3) does not obey the Debye-Hückel limiting law in this concentration region and *b* is very large ~2.0 (*5*). If one makes this correction, the difference between the authors' value and the literature value is only 0.09 ml. per mole.

$$\bar{V}^\circ\ (\text{ion}) = \bar{V}^\circ\ (\text{int}) + \bar{V}^\circ\ (\text{elect}) \qquad (6)$$

where $\bar{V}^\circ$ (int) is the intrinsic volume of the ion plus the volume due to void space and where $\bar{V}^\circ$ (elect) is the decrease in volume due to electrostriction. If this equation is differentiated with respect to temperature, one obtains;

$$\bar{E}^\circ\ (\text{ion}) = \bar{E}^\circ\ (\text{int}) + \bar{E}^\circ\ (\text{elect}) \qquad (7)$$

where $\bar{E}^\circ$ (int) is the expansibility due to the volume occupied by the ion and $\bar{E}^\circ$ (elect) is the expansibility due to electrostriction—i.e. solute-solvent interactions. Since $\bar{V}^\circ$ (ions) are additive within experimental error, the temperature derivatives—i.e. $\bar{E}^\circ$ (ion)—should also be additive. The problem of dividing E° (salt) into ionic contributions is similar to the division of $\bar{V}^\circ$ (salts) (*3, 7, 9, 12*). As a first approximation, the authors assumed that $\bar{E}^\circ$ (H^-) is zero. The results of this division are shown in Figure 3 where $\bar{E}^\circ$ (ion) is plotted *vs.* $\bar{V}^\circ$ (int) calculated from $\bar{V}^\circ$ (int) $= 2.51\ (r + 0.55)^3$ where *r* is the crystal radius in A. units (*7*). The values for $\bar{E}^\circ$ (ion) are obtained using the results listed in Table III. The expansibilities of the monovalent cations decrease from Na^+ to Cs^+ and the expansibility of the monovalent anions increase from F^- to I^-. This trend was discussed by Fajans and Johnson (*6*). Another possible explanation can be developed by discussing the effects of the components, $\bar{E}^\circ$ (int) and $\bar{E}^\circ$ (elect) in Equation 8. For small ions, $\bar{E}^\circ$ (int) $\cong 0$ and $\bar{E}^\circ$ (elect) is the important contribution, decreasing by $1/r$; [$\bar{E}^\circ$ (elect) $\propto : Z^2/r$]. For larger ions (Cl^- to I^-), $\bar{E}^\circ$ (int) becomes important and eventually predominates [$\bar{E}^\circ$ (elect) $\cong 0$]. The point of transition between these two opposing effects is near $\bar{V}^\circ = 18$ ml. per mole or $\bar{V}^\circ$ (H_2O). Apparently, [$\bar{E}^\circ$ (int) $\propto$ $\bar{V}^\circ$ (int) $-$ $\bar{V}^\circ$ (H_2O)]. This is what one would expect since "void space" effects have been shown to be important only for ions with $r > r$ (H_2O) (*7*). The expansibility for Li^+, H^-, and NO_3^- ions seem to be anomalous. The $\bar{E}^\circ$ of Li^+ and H^+ are apparently low (or negative) due to their ability to act as "structure formers." Their "ice-like" hydrated structures have a negative expansibility similar to H_2O below 4° (or ice becoming a liquid at 0° C.). The $\bar{E}^\circ$ (NO_3^-) may be out of line due to specific solvation effects.

Noyes (*13*) has calculated the theoretical $\bar{E}^\circ$ (elect) from ∂V (elect)$/\partial t$ to be equal to $0.0274\ Z^2/r$, where *Z* is the charge on the ion and *r* is the crystal radius in A. units. Using this equation, he has calculated $\bar{E}^\circ$ (int) $= \bar{E}^\circ$ (ion) $-\bar{E}^\circ$ (elect), and by plotting $\bar{E}^\circ$ (int) *vs.* r^3, he obtained the best fit assuming $\bar{E}^\circ$ (H^+) $= -0.051$ to -0.038 ml. per atom mole degree. Using a similar treatment, the authors' values for $\bar{E}^\circ$ (ion) give $\bar{E}^\circ$ (H^+) $= -0.030$ ml. per mole degree. These numbers for $\bar{E}^\circ$ (H^+) may be meaningless since it appears that $\bar{E}^\circ$ (elect) is positive. Also Benson and Copeland (*2*) have explained the positive values of $\bar{E}^\circ$ (ion) by completely neglecting $\bar{E}^\circ$ (int) and attributing all the effects to $\bar{E}^\circ$ (elect). Until the partial molal volumes are measured for a number of divalent and other polyvalent ions over a wide range of temperatures, these explanations must be viewed with considerable skepticism.

The authors are now measuring the ϕ_V of electrolytes and nonelectrolytes as a function of concentration and temperature. Thus, in future work, the authors hope to obtain a better understanding of solute-solute interactions.

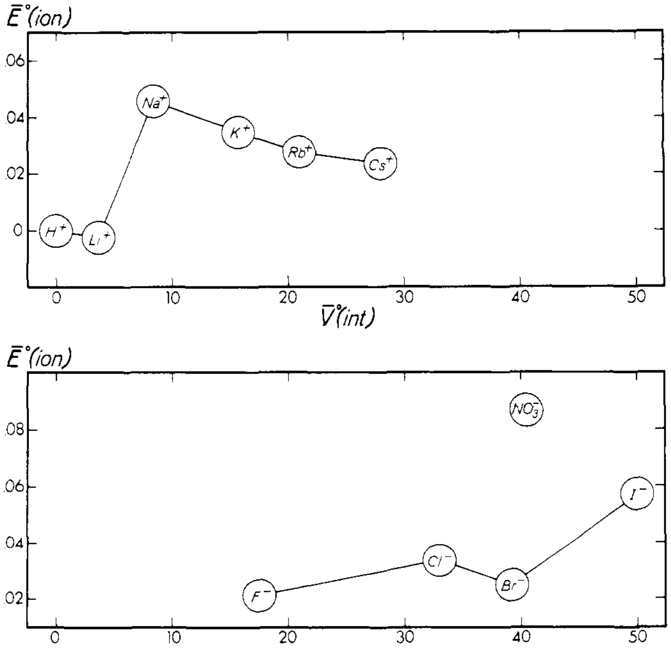

Figure 3. Ion expansibilities vs. intrinsic volume for cations and anions separately

ACKNOWLEDGMENT

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