W = first adsorption constant, temperature-dependent
Z = compressibility factor
a = constant in heat capacity equation, cal./g. mole-° K.-atm.
b = coefficient in Langmuir adsorption model, p.s.i.a.$^{-1}$
b_0 = volume of Eucken and Meyer, cc./g. mole
k = Boltzmann constant
l = total number of expansions
t^* = parameter in Stockmayer model, $\mu^{*2}/(8)^{1/2}$

Greek Letters

α = fraction of dimers
ϵ/k
and
σ = Stockmayer force constants
μ^* = reduced dipole moment, $\mu/(\epsilon\sigma^3)^{1/2}$
μ = dipole moment
ω = acentric factor of Pitzer

Subscripts

a = ambient conditions
i = integer indicating number of expansion
j = integer indicating number of expansion
r = variable divided by critical value

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RECEIVED for review September 25, 1967. Accepted March 15, 1968. Material supplementary to this article has been deposited as Document 10026 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $2.50 for photoprints or $1.75 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Osmotic Properties of Some Aqueous Electrolytes at 60° C.

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A modified isopiestic apparatus is described that performs satisfactorily at temperatures below 100° C. Isopiestic ratios to NaCl are reported for KBr, KCl, and Na_2SO_4 in H_2O at 60° C. over a wide concentration range. The ratios for KCl and KBr agree well with published data. Plots of *R* vs. *T* for KCl and Na_2SO_4 show agreement with lower temperature data, but reveal significant inconsistencies with data at higher temperatures.

AN attempt was made to extend the isopiestic method into the range between ambient and 100° C. (*2*). That attempt was modestly successful at 45° C. (*2*), but the apparatus and procedures were clearly not adequate for higher temperatures.

The purpose of this paper is to describe a modified apparatus and procedure, which appear to be highly satisfactory at least up to 80° C., and to report the osmotic properties of aqueous KCl, KBr, and Na_2SO_4 solutions over a wide concentration range at 60° C.

EXPERIMENTAL

A 3/8-inch Plexiglass plate, *1*, holding Teflon lids, *2*, (nylon lids varied widely in "dry weight" after equilibration) is connected by a threaded Teflon collar, *3*, to a nylon drive screw, *4*, that runs to the bottom of a 250-mm. Kimax vacuum desiccator, *5* (Figure 1). A similar Plexiglass plate, *6*, rests on a 2-inch thick gold-plated copper block, *7*, and serves to hold 1-inch diameter gold-plated silver cups, *8*, in place. The cups rest directly upon the copper block. A lever arm, *9*, with a Teflon-coated horseshoe magnet, *10*, at each end is located at the top of the drive screw. To lower the lids, one rotates the lever arm counterclockwise using a magnet so that the lid holder will move down the drive screw. Three Teflon-coated steel rods, *11*, mounted in the copper block guide the lid holder downward and prevent it from turning with the screw. The holes in the lid holder are larger than the diameter of a cup. As each lid comes into contact with its cup, the lid holder con-

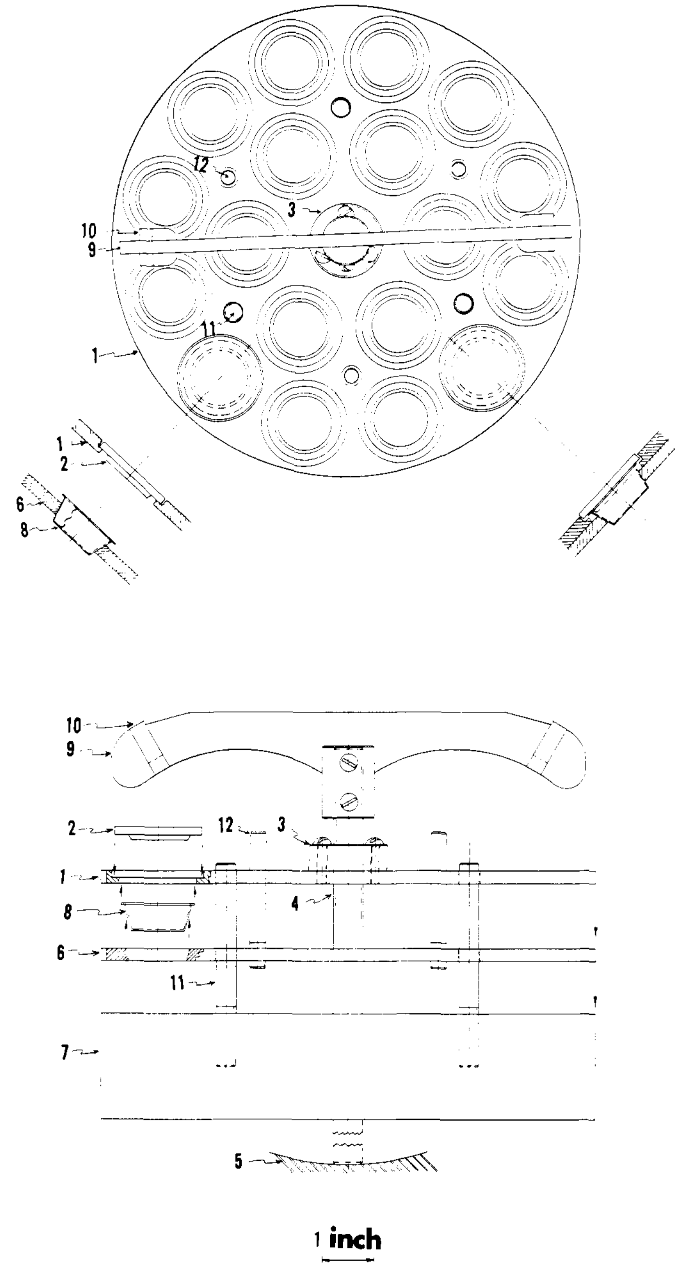

Figure 1. Lid lowering mechanism

tinues downward around the cup. The cups, with lids in place, can then be removed from the desiccator by lifting three brass bolts, *12*, attached only to the cup holder and running freely through the lid holder. This arrangement allows each individual cup to be removed from the holder assembly with its lid still in place.

The external sleeve stopcock on the desiccator was cemented in an open position with a special epoxy formulation (H. V. Hardman Co., Inc., Belleville, N. J.), because it tended to work loose and leak upon thermal expansion of the glass. Vacuum tubing was permanently attached to the tubulature, and closure was made with a pinch clamp.

Reagent grade salts were dried to constant weight and weighed directly into the cups as anhydrous salts without further purification. Freshly boiled water was added to the cups to obtain a solution of approximately the final molality desired. Cups and lids were placed in their respective holders, and the entire mechanism was loaded with a 100-ml. reservoir solution of sodium chloride in the bottom of the desiccator. The lid was sealed with a minimum amount of Dow Corning high vacuum grease. The system was evacuated, in approximately 10 pumping cycles using a ballast bulb technique (*7*), to the vapor pressure of water at room temperature.

The sealed desiccator was placed in a bath controlled at 59.98° ± 0.01° C. as indicated on a calibrated thermometer. Ethylene glycol was used as bath liquid, since water evaporates too rapidly at this temperature, and minute contamination by water-insoluble oils is very detrimental to isopiestic equilibration. The equilibrating system was rotated at 12 r.p.m. for 2 days for solutions above 1 molal and for 3 days at lower concentrations. At the end of the equilibration time, the lids were lowered onto the cups and dry air was admitted to the desiccator through a P_2O_5 drying tower, while the entire system was still under vacuum and still immersed in the bath. Cloth-lined Neoprene gloves were employed to remove the desiccator from the bath. The entire cup and lid holder assembly was removed and placed on a brass plate to begin cooling. Each cup and lid unit was then removed from the holder as quickly as possible and placed on another cool brass plate in preparation for final weighing.

RESULTS

Twenty-five runs were made in which three or four samples each of KCl, KBr, and Na_2SO_4 solutions were simultaneously equilibrated with four samples of NaCl solution. Of the 80 sets of replicates, 26 showed a precision of better than 0.03% average deviation from the mean; 25 sets fell between 0.03 and 0.05%; 18 between 0.06 and 0.10%; and 11 from 0.11 to 0.17%. The over-all average deviation of all runs included in this work was 0.05%. Reliability of the measurements is also indicated by relative σ values, which are recorded in Table I with the isopiestic molalities. Isopiestic ratios for each salt to NaCl were calculated from

Table I. Average Isopiestic Molalities at 60° C.

Run Number[a]	NaCl, Ref.	KBr	KCl	Na_2SO_4	Av. σ'[b]
5,C	0.9838	1.0075	1.0294	0.9086	0.0012
4,D	1.1765	...	1.2325	1.1164	0.0011
4,C	1.6410	1.7061	1.7444	1.6237	0.0014
4,A	1.8455	1.9269	1.9679	1.8478	0.0012
1,C	2.0334	2.1309	2.1795	2.0594	0.0011
4,B	2.1937	2.3072	...	2.2338	0.0012
1,B	2.5490	2.7037	2.7723	2.6264	0.0009
3,F	2.7396	2.9159	2.9895	2.8330	0.0009
2,D	2.9383	3.1320	3.2179	3.0337	0.0015
3,E	3.0423	3.2576	3.3456	3.1531	0.0006
1,A	3.0707	3.2964	3.3792	3.1795	0.0007
2,C	3.2333	3.4769	3.5752	3.3496	0.0010
3,C	3.2388	3.4854	3.5729	...	0.0004
3,D	3.3152	3.5748	3.6721	3.4397	0.0007
6,H	3.6397	3.9464	4.0640	[c]	0.0004
6,G	4.0028	4.3757	4.5127		0.0004
3,B	4.0639	4.4580	4.5803		0.0006
3,A	4.0722	4.4637	4.5884		0.0004
6,A	4.4132	4.8807	5.0173		0.0006
6,F	4.7872	5.3285	5.5009		0.0007
6,D	5.2090	5.8503	6.0512		0.0014
6,E	5.2396	5.8967	6.0894		0.0010
6,B	5.4957	6.2241	6.3983		0.0008
6,C	6.2301[c]	7.1519	[c]		0.0006

[a] Numbers refer to series (common salt samples) and letters to individual equilibration. [b] Standard deviations expressed as relative values, to average them for the three salts.

$$\sigma = \left[\sum \frac{(d_i^2)}{(N-1)}\right]^{1/2} \quad \text{and} \quad \sigma' = \frac{\sigma}{m}$$

Column 6 is average of σ' values calculated for each set of salt samples. [c] Saturation.

the equilibrium molalities in Table I. Equations for R *vs.* m for each salt were then fit by an IBM 1130 computer, using a polynomial regression program. These equations, listed below, reproduce the experimental R values within ± 0.001 unit.

KBr

$$R = 0.00033m^2 - 0.02039m + 0.99631 \qquad 1.0 \le m \le 7.1$$

KCl

$$R = 0.00029m^2 - 0.02069m + 0.97600 \qquad 1.0 \le m \le 6.4$$

Na_2SO_4

$$R = -0.01181m^3 + 0.09004m^2 - 0.2419m + 0.87791 \qquad 1.0 \le m \le 3.5$$

These equations are valid within the ranges of the experimental molalities and must not be used outside these limits.

EVALUATION OF APPARATUS AND PROCEDURE

The performance of the apparatus and procedure, as indicated by the data collected at 60° C., is satisfactory in every respect. Sample and run "casualties" are rare. Measurements above 1.0 molal can be consistently reproduced within 0.001 unit in R. Furthermore, block temperature *vs.* time studies indicate that, with the stirring provided and with judicious choice of reservoir molalities, equilibration times could be appreciably shortened without seriously affecting the quality of the data. In short, the system gives precision at 60° C. comparable with that commonly reported at 25° C. but with speed approaching that observed at 100° C. and higher (*3-5*) when stirring is not provided.

The authors have run stability tests up to 90° C. on the grease and epoxy formulations used to seal the system. No problems are indicated with either up to that temperature. On the other hand, ethylene glycol is too volatile to serve as a suitable bath liquid above 60° C. Triethylene glycol was tested and was satisfactory. Work is now underway, using only slightly modified procedures, at the higher temperatures and will be reported in a subsequent paper.

DISCUSSION

Osmotic data on NaCl and KBr between 60° and 100° C. are available from the boiling point elevation studies by Smith (*8-10*). The osmotic coefficients of both salts below 45° C. do not seem to fit smoothly with their higher temperature values (*1*). The authors' isopiestic ratios have been used to check the internal consistency of Smith's NaCl and KBr osmotic coefficients at 60° C. and to indicate the course of the osmotic behavior of all three salts relative to NaCl through the range where the apparent discontinuities in the data occur. Table II shows a comparison between the authors' measured R values (WTH) at 60° C. and those calculated from Smith's ϕ's for the two salts. Some of the discrepancies are larger than the standard deviations of the ratios but are probably within the combined uncertainties of the authors' and Smith's experiments. This result confirms only the internal consistency of Smith's values on the two salts and does not give an absolute check on either; therefore, if one is high, as the figures in reference (*1*) suggest, then both are.

The ratios for KCl are compared with Robinson's (*6*) work in the range between 1 and 4 molal (Table III).

Table II. Comparison with Smith's KBr Data

m_{KBr}	Smith, R	WTH, R	ΔR^a
1.0	0.974	0.976	-0.002
1.2	0.970	0.972	-0.002
1.4	0.967	0.967	0.000
1.6	0.964	0.964	0.000
1.8	0.961	0.961	0.000
2.0	0.957	0.957	0.000
2.5	0.949	0.948	+0.001
3.0	0.941	0.938	+0.003
3.5	0.932	0.929	+0.003

[a] $\Delta R = R_{Smith} - R_{WTH}$.

Table III. Comparison with Robinson's KCl Data

m_{KCl}	Robinson, R	WTH, R	ΔR^a
1.04	0.958	0.955	+0.003
1.26	0.952	0.951	+0.001
1.48	0.948	0.946	+0.002
1.70	0.942	0.942	0.000
1.92	0.937	0.938	-0.001
2.15	0.932	0.933	-0.001
2.37	0.927	0.928	-0.001
2.60	0.922	0.924	-0.002
2.72	0.919	0.922	-0.003
2.83	0.917	0.920	-0.003
3.06	0.912	0.915	-0.003
3.30	0.908	0.911	-0.003
3.54	0.903	0.906	-0.003
3.91	0.896	0.899	-0.003

[a] $\Delta R = R_{Robinson} - R_{WTH}$.

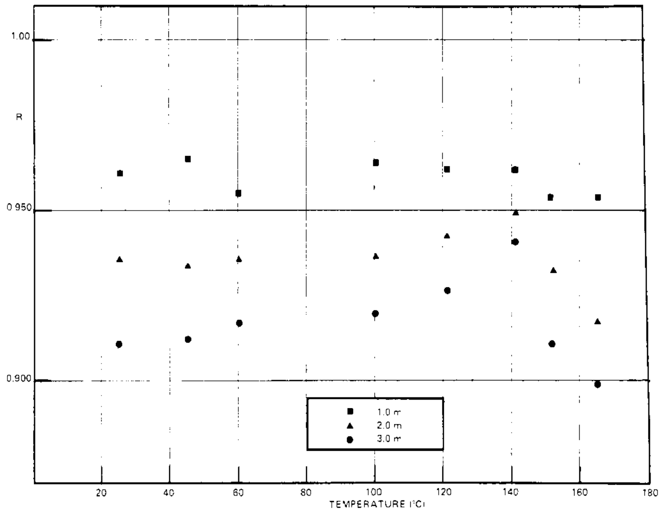

Figure 2. R *vs.* temperature for KCl

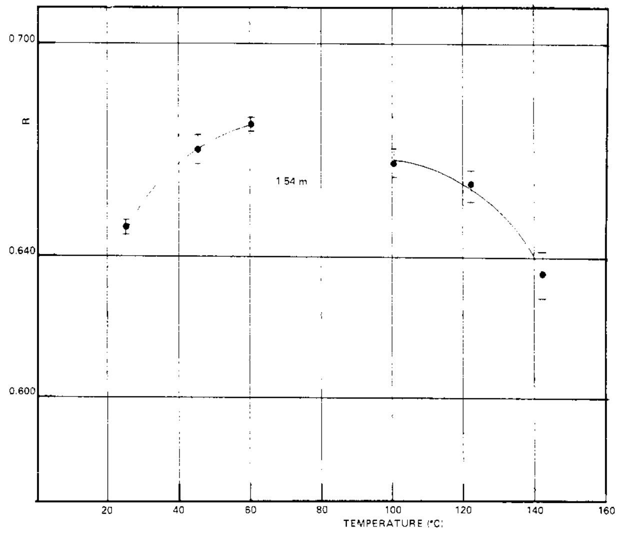

Figure 3. R *vs.* temperature for Na_2SO_4

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

The authors thank B. A. Soldano and the Oak Ridge National Laboratory Reactor Chemistry Division for some apparatus used in the work and J. D. Warren of the Greenville Technical Education Center for his help in constructing the closing mechanism.

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Received for review October 5, 1967. Accepted March 7, 1968.

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