typical relative error being about 1%. By the method of propagation of errors, the largest uncertainty in α_0 was estimated to be about 0.8%, and the overall precision in the determination of the K_s's ranged from 0.9–4.5%. No complications were encountered from a potential association between the ions of the title electrolytes and those of LiCl. That there is no appreciable association between Li⁺ and Pi⁻ ions in ethanol–water solvents was reported from this laboratory earlier (6). In the present study, conductance measurements have shown that also Ph₄As Cl and Ph₄P Cl are completely dissociated in ethanol–water solvents.

NOMENCLATURE

A_{DH} = Debye-Hückel limiting slope
A_1, A_2, A_3 = empirical coefficients of power terms of $I^{1/2}$ in Equation 6
$a_\pm$ = mean ionic activity, mol/l.
C = concentration of electrolyte, mol/l.
C_0 = solubility in pure solvent, mol/l.
C_I = solubility in presence of added salt at ionic strength I, mol/l.
d_0 = density of solvent, g/ml
D = dielectric constant of solvent
$f_\pm$ = mean ionic activity coefficient of electrolyte referred to infinite dilution in given solvent as standard state
$f_{\pm,0}$ = mean ionic activity coefficient in absence of added salt
$f_{\pm,I}$ = mean ionic activity coefficient in presence of added salt at ionic strength I
I = ionic strength, mol/l.
k_0 = specific conductance of solvent, mho/cm
K_A = ion-pair association constant, l./mol
K_s = solubility product of an electrolyte, mol²/l.⁻²
M = mol/l. of solution
S = Onsager coefficient, $\alpha\Lambda_0 + \beta$ where

$$\alpha = \frac{0.8204 \times 10^6}{(DT)^{3/2}} \text{ and } \beta = \frac{82.501}{\eta(DT)^{1/2}} \text{ where } \eta$$
is viscosity in poises
$S_{(z)}$ = Shedlovsky function $\{z/2 + [1 + (z/2)^2]^{1/2}\}^2$, where $z = S\Lambda_0^{-3/2}(C\Lambda)^{1/2}$
w = wt % ethanol in mixture with water

GREEK LETTERS

α = degree of dissociation into ions
α_0 = degree of dissociation into ions in pure solvent
α_I = degree of dissociation in presence of added salt at an ionic strength I
Λ = equivalent conductance at finite concentration, mho l./cm mol
Λ_0 = limiting equivalent conductance, mho l./mol⁻¹ cm⁻¹

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Isopiestic Studies of Some Aqueous Electrolyte Solutions at 80°C

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Isopiestic ratios to NaCl of KCl, LiCl, BaCl₂, and Na₂SO₄ in water at 80.22°C are reported. Empirical equations for R and ϕ as functions of molality are given which reproduce the results within the experimental uncertainty of better than 0.001 for the range of molality covered by the measurements.

A previous paper (2) described an apparatus and procedure that yielded isopiestic data at 60°C of quality comparable to the best at 25°C and showed promise of extension to higher temperatures. This paper describes modifications of the former system that have proved equally successful at 80°C. Earlier work had raised questions about the consistency of data at temperatures below and above this point. Data at 80°C are reported for KCl, LiCl, BaCl₂, and Na₂SO₄ over a range of concentrations. These results are evaluated briefly with

respect to their relationship to our previous measurements at lower temperatures and the literature data at higher temperatures.

EXPERIMENTAL

The apparatus and procedure used were essentially the same as those developed previously (2). Minor modifications were made in apparatus and procedure to overcome difficulties attending the increase in temperature. Triethylene glycol was substituted for ethylene glycol as bath liquid because of its

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lower volatility. Brass pins in the lid-holder and Teflon-coated steel guide posts were both replaced with solid Teflon posts to prevent binding. The Teflon drive screw, which tended to warp at high temperature, was stiffened by forcing a steel rod into a channel bored through its center. The desiccator was fitted with a stainless steel band to which were welded handles to facilitate maneuvering at the higher temperature.

A new turntable mechanism, designed to hold two equilibration vessels simultaneously and driven by a gear mechanism, was used. The belt-driven system gives a great deal of trouble in a hot glycol bath.

The temperature of the bath liquid was controlled by a Sargent Thermonitor, model ST. Checks with an Atkins electronic thermometer indicated a temperature at 80.22°C, confirmed by use of a Beckman thermometer to be constant to better than ±0.01°C.

The only significant change in procedure involved drying and preheating the air admitted when a run was terminated; even dried air caused condensation unless brought up to system temperature beforehand.

RESULTS

Sixty-nine isopiestic runs were used in generating these data. In each of these runs from two to four different salts were involved and the data on at least one salt, and in a majority of cases all salts, were of acceptable quality. A replicate set of at least three and in some cases as many as six samples of each salt was used. Most numbers represent the average of a set of four. Average molalities were subjected to a standard error analysis. After any statistically rejected replicates were removed, the standard deviation for each replicate set was computed using the formula,

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

where d_i is the deviation of a replicate molality from the average value and N is the total number of replicates in that set.

These σ's are informative only when compared at common molalities. To compare performance at different molalities, the "relative standard deviation," σ' defined as σ/m, was used.

The average percent deviation of a replicate from the mean for all salts in all the runs was 0.06% and the average σ' was 0.00092. Statistically, this σ' performance means that the odds are 2 to 1 that any individual isopiestic measurement selected at random from those reported will fall within 0.09% of the average reported. The performance of the system and the precision of the resulting data are comparable to the 60°C work in every respect.

Average isopiestic molalities of reference and subject salts are listed (in Table I by run numbers) in order to present the experimental results free of any smoothing errors or assumptions concerning reference data. The precision of each run is indicated as run-average relative standard deviation.

TREATMENT OF DATA

A polynomial regression program was used with an IBM 1130 system to fit the experimental isopiestic ratios, calculated from the molalities in Table I, to the molality for each salt. These equations are listed below along with the standard deviation of the experimental points from each line.

LiCl
R = −0.000399 m^3 + 0.003048 m^2 +
    0.030939 m + 1.01582   1.3 ≤ m ≤ 4.8   (1)
                                  σ = 0.00089

Table I. Average Isopiestic Molalities at 80°C

Run[a]	NaCl	KCl	LiCl	BaCl₂	Na₂SO₄	Av, σ'[b]
37-F	0.6750	...	...	0.4986	...	0.0010
40-D	0.7754	0.7988	...	0.5697	...	0.0017
37-E	0.7819	...	...	0.5728	0.7042	0.0014
37-D	0.9270	...	...	0.6748	0.8525	0.0012
40-C	0.9960	1.0336	...	0.7231	0.9217	0.0013
37-C	1.0819	...	...	0.7802	1.0156	0.0009
37-B	1.1911	1.2458	...	0.8553	...	0.0016
39-C	1.2008	1.2523	...	0.8628	1.1360	0.0012
40-B	1.2271	1.2853	...	0.8812	1.1714	0.0013
37-A	1.3626	1.4286	...	0.9705	1.3193	0.0012
30-C	1.3774	1.4452	1.2982	0.9820	...	0.0006
40-A	1.3826	1.4532	...	0.9845	1.3408	0.0008
39-B	1.4535	...	...	1.0321	1.4190	0.0006
36-D	1.4597	...	...	1.0357	1.4243	0.0017
36-C	1.5738	...	...	1.1100	1.5510	0.0011
22-A	1.5851	...	...	...	1.5658	0.0002
39-A	1.5938	1.6877	...	1.1257	1.5784	0.0010
44-B	1.6069	1.6994	...	1.1332	1.5899	0.0008
30-B	1.6199	1.7116	1.5166	1.1404	...	0.0006
24-B	1.6588	...	...	1.1678	...	0.0007
36-B	1.7580	1.8664	...	1.2354	1.7636	0.0012
38-B	1.7822	1.8916	...	1.2497	1.7862	0.0014
44-A	1.8434	1.9597	...	1.2878	1.8569	0.0008
30-A	1.8543	1.9723	1.7247	1.2940	...	0.0011
35-B	1.9302	...	...	1.3444	...	0.0013
38-A	1.9777	2.1113	...	1.3766	2.0109	0.0011
36-A	2.0033	2.1410	...	1.3947	2.0450	0.0009
41-G	2.0165	2.1531	...	1.4006	...	0.0012
16-A	2.0286	2.1692	...	...	...	0.0014
33-B	2.1000	2.2517	...	1.4562	2.1515	0.0009
43-F	2.1092	2.2627	...	1.4626	2.1525	0.0006
41-F	2.1518	2.3087	...	1.4867	...	0.0011
43-E	2.2502	2.4190	...	1.5527	2.3128	0.0006
24-A	2.2515	2.4223	2.0662	1.5538	...	0.0006
43-D	2.4128	2.6048	...	1.6579	2.4970	0.0007
18-A	2.4150	2.6094	...	...	...	0.0014
41-E	2.4223	2.6138	...	1.6626	...	0.0010
34-B	2.4657	2.6628	...	...	2.5594	0.0012
34-A	2.5560	...	...	...	2.6651	0.0003
42-D	2.5795	2.7889	...	1.7641	...	0.0008
43-C	2.5852	2.8060	...	1.7692	2.6950	0.0005
32-B	2.6121	2.8333	...	...	...	0.0013
42-C	2.6152	2.8300	...	1.7859	...	0.0006
28-A	2.6274	...	2.3851	...	...	0.0006
23-E	2.6790	2.9127	...	...	...	0.0010
41-D	2.7053	2.9405	...	1.8464	...	0.0007
43-B	2.7258	2.9644	...	1.8584	2.8557	0.0007
42-B	2.7371	2.9715	...	1.8643	2.8632	0.0010
41-C	2.7703	3.0120	...	1.8847	...	0.0008
33-A	2.8224	3.0818	...	1.9216	2.9664	0.0011
43-A	2.8315	3.0840	...	1.9256	2.9749[c]	0.0006
29-G	2.8548	3.1136	...	...	...	0.0007
32-A	2.8667	3.1286	...	1.9473	...	0.0011
42-A	2.8970	3.1584	...	1.9667	...	0.0007
31-D	2.9542	3.2237	...	2.0045	...	0.0012
41-B	3.0406	3.3246	...	2.0602	...	0.0006
23-D	3.1180	3.4183	2.7943	...	...	0.0004
31-C	3.1915	...	...	2.1586	...	0.0011
41-A	3.2600	3.5900	...	2.2073[c]	...	0.0006
29-F	3.3856	3.7370	3.0037	...	...	0.0008
31-B	3.5411	3.9171	...	...	...	0.0002
29-E	3.6608	4.0655	3.2276	...	...	0.0007
31-A	3.6916	4.0976	3.2500	...	...	0.0005
29-D	3.9727	4.4418	3.4751	...	...	0.0008
29-C	4.3604	4.9159	3.7768	...	...	0.0005
23-B	4.6260	5.2459	3.9837	...	...	0.0003
23-A	5.0470	5.7735	...	...	...	0.0006
29-B	5.4126	6.2400	4.5760	...	...	0.0006
29-A	5.7342	6.6560	4.8132	...	...	0.0008

[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 salts. See text. The numbers are run averages of σ' values calculated for each set of salt samples. [c] Saturation.
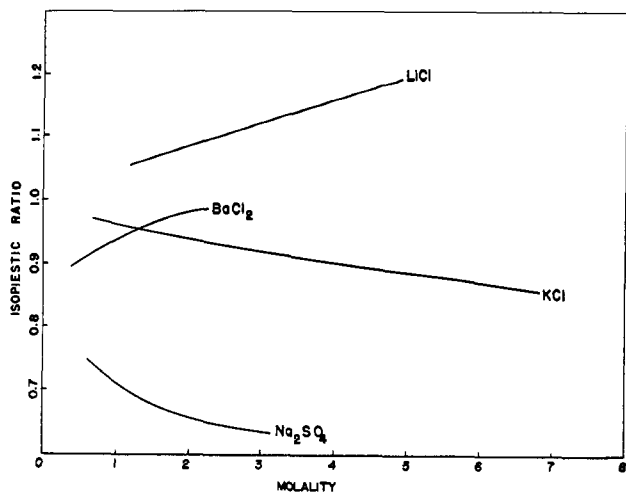
Figure 1. Experimental isopiestic ratios vs. molality at 80°C

Lines represent computer fit to data in Table I (Equations 1-4). Experimental points not shown since, on this scale, none deviates visibly from the lines as drawn
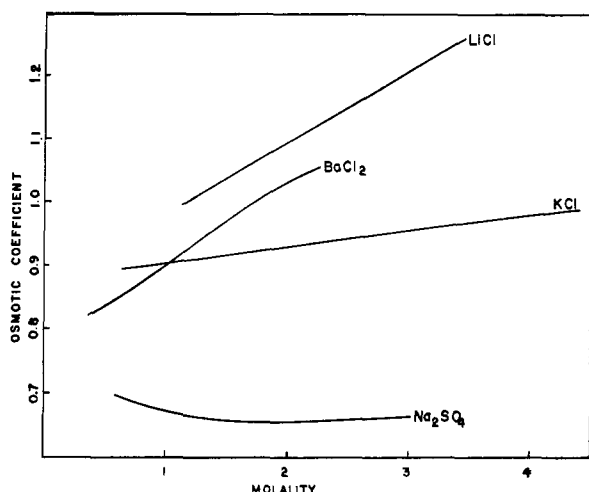

Figure 2. Calculated osmotic coefficients vs. molality at 80°C

Lines represent Equations 5-8 which are based upon the experimental isopiestic ratios and Smith's NaCl data taken as standard

BaCl₂
$$R = -0.003268 \; m^3 - 0.003646 \; m^2 +$$
$$0.078762 \; m + 0.86520 \qquad 0.57 \leq m \leq 2.2 \quad (2)$$
$$\sigma = 0.00089$$

KCl
$$R = -0.000235 \; m^3 + 0.003656 \; m^2 -$$
$$0.034026 \; m + 0.99456 \qquad 0.80 \leq m \leq 6.7 \quad (3)$$
$$\sigma = 0.00094$$

Na₂SO₄
$$R = -0.005451 \; m^3 + 0.049570 \; m^2 -$$
$$0.166586 \; m + 0.83505 \qquad 0.70 \leq m \leq 3.0 \quad (4)$$
$$\sigma = 0.00099$$

The computer was also used to generate osmotic coefficients at round molalities from the isopiestic ratios represented by the equations above and a similar equation fit to the ϕ vs. m data of Smith (4) and Smith and Hirtle (5) at 80°C combined with

the definitions $R = (\nu_{\text{NaCl}} m_{\text{NaCl}})/(\nu_x m_x) = \phi_x/\phi_{\text{NaCl}}$. The resulting ϕ vs. m equations are listed below:

LiCl
$$\phi = 0.000758 \; m^2 + 0.109796 \; m +$$
$$0.87171 \qquad 1.2 \leq m \leq 3.5 \quad (5)$$
$$\sigma = 0.00106$$

BaCl₂
$$\phi = -0.024375 \; m^3 + 0.088549 \; m^2 +$$
$$0.038152 \; m + 0.79661 \qquad 0.60 \leq m \leq 2.20 \quad (6)$$
$$\sigma = 0.00065$$

KCl
$$\phi = -0.000586 \; m^3 + 0.003766 \; m^2 +$$
$$0.019285 \; m + 0.87972 \qquad 0.8 \leq m \leq 4.0 \quad (7)$$
$$\sigma = 0.00160$$

Na₂SO₄
$$\phi = -0.007326 \; m^3 + 0.057192 \; m^2 -$$
$$0.137197 \; m + 0.75746 \qquad 0.70 \leq m \leq 3.0 \quad (8)$$
$$\sigma = 0.00022$$

The computer with an IBM 1627 plotter was used to generate plots of experimental R and calculated ϕ vs. m for the four salts at 80°C. Figure 1 shows a tracing of the best fit lines through the experimental R data (Table I and Equations 1-4). Figure 2 is a similar display of the ϕ vs. m results embodied in Equations 5-8.

DISCUSSION

As indicated previously (2), the immediate goal of our work is to accumulate sufficient high-quality data to allow resolution of some apparent inconsistencies in the available temperature-dependence data for some salts. The earlier work had indicated that if the apparent inflections in ϕ vs. T curves were real, such anomalies must come above 60°C. We can now conclude that their existence must be presumed to be above 80°C if at all.

In all but two cases, BaCl₂ at 45°C (1) and LiCl at 100°C (3), smooth curves can be drawn through our 80°C data and all existing data points up to 100°C within the reported experimental uncertainties. The 100°C LiCl data appear, by extension of our lower T measurements, to be some 3% low as has already been suggested by their authors (6). The literature values of R for the lower concentrations of BaCl₂ at 45°C are low by as much as 1.5%. We are currently working to clarify this temperature region for all the salts studied in this work using the more sophisticated system now available. In the course of that study, we also expect to collect the information needed to fill gaps in the 60°C data, thereby making possible a comprehensive analysis of the osmotic behavior of a representative group of salts over the entire range from 0-100°C.

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