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Osmotic Coefficients of Aqueous LiCl and KCl from Their Isopiestic Ratios to NaCl at 45 °C

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Osmotic coefficients for aqueous LiCl and KCl solutions at 45 °C, based on isopiestic ratios to NaCl solutions, are reported for the concentration ranges up to saturation of NaCl. Significant discrepancies are found between these values and literature data, especially in the case of KCl.

Introduction

In 1965 we reported (*1*) osmotic properties of several aqueous salt solutions, including LiCl and KCl, at 45 °C. That study, carried out by the isopiestic method, suffered several deficiencies: (a) the data covered a limited molality range; (b) since only interpolated reference data were avaliable at 45 °C, only isopiestic ratios relative to NaCl were reported; and (c) the precision of the data, collected by using a prototype apparatus designed for operation above room temperature, was only on the order of 0.5%.

Developments since that initial study have made reinvestigation of these systems worthwhile. (a) We have developed a new apparatus which has proven to yield data up to 80 °C of precision an order of magnitude superior to that of our 1965 study. (b) The three alkali metal chlorides mentioned are among several salts which have been studied as a function of temperature by direct, i.e., absolute, methods since our earlier work (*2*).

The objectives of the present study were therefore: (a) to measure isopiestic ratios of LiCl and KCl to NaCl at 45 °C over a wider concentration range then previously covered and to precision on the order of 0.05% coefficient of variation (relative standard deivation); (b) to test the consistency of the reported absolute data on these three salts by comparing our measured ratios to NaCl with those predicted by the independently reported osmotic coefficients of LiCl, NaCl, and KCl; and (c) to use our measured ratios to calculate the best set of osmotic coefficients consistent with the available reference data.

Experimental Section

Apparatus and Procedures. The apparatus and procedures used were essentially those described by Humphries (*4*) and Moore (*5*). Significant changes were made in three areas, primarily because of the greater demands on precision occasioned by extension to lower concentrations:

(a) For the lowest concentration runs a modified system containing six larger gold-plated silver cups was used in order to provide a larger payload. These cups are the same depth as the smaller ones described earlier but 50 mm in diameter and have a useful capacity of ~8 mL. The data above approximately 1 *m* were collected in the 18-cup assembly described previously (*4*).

(b) In the more dilute region, the weakest link in the measurement is weighing of the salt. We thus adopted the procedure of weighing the salts as previously analyzed stock solutions for all runs in this region. Lithium chloride was weighed as stock solutions for the entire concentration range because of its hygroscopic nature. Both NaCl and KCl were weighed as dry solids for the more concentrated region.

Table I. Summary of Isopiestic Data at 45 °C

NaCl			KCl			LiCl		
av m^a	n^b	cv	av m	n	cv	av m	n	cv
0.5032	3	0.10%	0.5169	3	0.08%			
0.5164	3	0.18				0.5055	2	0.08%
0.7139	3	0.03	0.7380	2	0.03			
0.8539	3	0.03				0.8117	3	0.07
1.0261	3	0.03	1.0707	3	0.15			
1.0781	2	0.04				1.0138	3	0.05
1.3022	3	0.17				1.2112	3	0.05
1.4991	4	0.05	1.5851	4	0.04	1.3842	4	0.08
1.6053	3	0.08				1.4730	3	0.02
2.0716	4	0.04	2.2279	4	0.05			
2.1606	4	0.05	2.3220	4	0.06			
2.3302	4	0.10	2.5206	6	0.10	2.0795	6	0.09
2.5108	4	0.08	2.7329	4	0.06	2.2345	4	0.09
2.5603	3	0.04	2.7885	3	0.01	2.2770	3	0.10
2.6079	4	0.01	2.8445	4	0.01	2.3135	4	0.10
2.7183	5	0.08	2.9722	6	0.09	2.4045	4	0.09
3.0353	3	0.03	3.3415	3	0.07	2.6615	3	0.07
3.2873	4	0.02	3.6510	4	0.03	2.8506	5	0.01
3.5031	6	0.10	3.9104	6	0.10	3.0271	6	0.15
3.7550	6	0.05	4.2195	6	0.06	3.2222	5	0.04
3.9688	4	0.14	4.4879	4	0.05	3.3857	4	0.01
4.0294	5	0.06	4.5609	3	0.04	3.4364	4	0.03
4.5162	6	0.07	5.1776	6	0.05	3.8078	5	0.01
5.0453	6	0.04	sat'd			4.2057	5	0.08

[a] m = molalility. [b] n = number of replicates comprising the reported average.

(c) In the past we have depended on thorough initial pumping to remove all air which impedes equilibration. Since residual air is more detrimental at the lower concentrations, we adopted the policy of an additional pumping after the system had equilibrated in the thermostat for about 12 h. The system, while still immersed in the thermostat bath, was repeatedly opened momentarily to the evaluated ballast. This process was continued for some 10–20 exposures spaced at 15-s intervals by the simple device of rotating a stopcock slowly past the open position. Additional direct pumping on the system after it is at run temperature would risk boiling of the solutions.

Materials. The salts were reagent grade materials used without further purification except for drying of the NaCl and KCl when they were weighed directly. Indistinguishable results were obtained with duplicate reagents from three different suppliers. All stock solutions were analyzed gravimetrically for chloride, weighed as AgCl. Deionized distilled water was used and was boiled just prior to use to expel dissolved gases.

Results

Twenty-four isopiestic equilibrations were carried out at 45.00 ± 0.01 °C. Seven of these runs involved triplicates of a NaCl solution and either a LiCl or a KCl solution in the concentration range between 0.5 and 1.5 *m*. Runs in the higher concentration range involved simultaneous equilibration of 3–6 replicate samples of a solution of each of the three salts. Table I displays the average experimental isopiestic molalities for each run. The second column under each salt's heading gives the number of replicates comprising the average molality, and the

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Table II. Parameters for Best Empirical Fit[a] of R and ϕ Data for LiCl and KCl at 45 °C

	LiCl, m = 0.81–4.20		KCl, m = 0.52–5.18	
Y	R	ϕ	R	ϕ
X	$m^{1/4}$	$m^{1/4}$	$m^{1/4}$	$m^{1/4}$
A	0.25000	0.25000	−0.25000	−0.25000
B	1.50000	1.50000	1.50000	1.50000
a_0	0.25609	−1.85150	0	−0.19786
a_1	−0.85641	5.07124	0.00055	0.49983
a_2	0.68729	−5.23221	0.25650	−0.52410
a_3	−0.12424	1.91927	−0.24963	0.22677
a_4	0	0	0.052817	0
% variation	99.78	99.98	99.89	99.97
std dev	0.00176	0.00213	0.00074	0.00089

[a] The equation fit to each set of data is

$$Y = 1 + \frac{Am^{1/2}}{1 + Bm^{1/2}} + \sum_i a_i X^i \qquad (3)$$

where Y is either R to NaCl or ϕ for one of the salts and X is found to be $m^{1/4}$ for best fit in each case.

third column indicates the precision as the coefficient of variation (cv).

The pooled cv (i.e., weighted average) for all salts over all runs was 0.06%. This result is approximately an order of magnitude superior to our initial study (*1*). The present work also extends the concentration ranges studied to both higher and lower molalities. In spite of the poorer precision of our earlier data, the smoothed values at rounded molalities agree, within the reported errors of the earlier work, with our current measurements. The larger previous errors were, therefore, apparently random.

Experimental isopiestic ratios for LiCl and KCl relative to NaCl were calculated from the isopiestic molalities

$$R_{\text{exptl}} \equiv \nu_1 m_1 / \nu_2 m_2 \qquad (1)$$

where 1 = NaCl and 2 = LiCl or KCl. This isopiestic ratio, calculated from the measured equilibrium molalities, is a purely experimental number. Since literature osmotic coefficients of LiCl, NaCl, and KCl at 45 °C are now available which are based on independent measurements on the three salts, an R value can also be calculated from the relationship

$$R_{\text{calcd}} \equiv \frac{\phi_2 \text{ at } m_2}{\phi_1 \text{ at } m_1} \qquad (2)$$

Thus, while R_{exptl} is a purely experimental ratio of molalities, R_{calcd} is the ratio predicted by the respective literature ϕ's at these same molalities.

The ϕ's needed for eq 2 were generated from van Hook's computer fit of the available data using the fitting coefficients in ref 2. Our program exactly duplicates his output at selected molalities so that the ϕ's we used to generate R_{calcd} are identically those predicted at our m's by van Hook's equations.

Figure 1 shows plots of R vs. m for LiCl and KCl. Although the experimental points show some erratic tendencies consistent with a wavy line, the experimental points tend to define smoother and more monotonic curves while those calculated from literature osmotic data (eq 2), especially for KCl, trace out oscillating functions. The uncertainties of the experimental molalities are much smaller than the diameters of the data points in Figure 1, while the literature values deviate considerably farther from our experimental line than is consistent with our experimental error but are still as close to our line as required by the acknowledged uncertainty of the literature data on which Van Hook's equation is based.

Therefore, since the cycling of the calculated R appears to be an artifact of the curve-fitting procedure, we conclude that the literature equations for $\Phi = f(m)$ should not be relied upon if accuracy of better than 1% is required. Precise values of the R's may be calculated from the isopiestic molalities in Table 1 or read from a plot like that in Figure 1.

For convenience in recovering data at any m in the experimental range, we have computer fit our experimental R values (relative to NaCl) and ϕ values (see later) as functions of m for both LiCl and KCl using a polynomial regression with no model-dependent term. We did use a Deybe–Hückel-like leading term because a term of the form $Am^{1/2}/(1 + Bm^{1/2})$, with arbitrary empirical A and B, does accomodate most of the curvature leaving only the small residual to be fit by the polynomial regression program. The equation and best fit coefficients for both R and ϕ are given in Table II. We found that polynomials in m (to integral powers, i.e., $x = m$) fit the KCl data satisfactorily but that a series in $m^{1/4}$ (i.e., $x = m^{1/4}$), as recommended by Rard (*6*), worked best for both salts. Analysis of the results shows that the equation may be used to generate reliable R values for any m within the experimental molality ranges and that the resulting R's may be combined with any absolute osmotic data on any one of the three salts to generate ϕ values for the other two with an uncertainty of ~0.2% or

Table III. Osmotic Coefficients[a] at 45 °C of LiCl and KCl at Experimental Molalities

LiCl				KCl			
m	ϕ_{exptl}	ϕ_{lit}	$\Delta\phi \times 10^4$	m	ϕ_{exptl}	ϕ_{lit}	$\Delta\phi \times 10^4$
0.8117	0.9861	0.9835	+26	0.5169	0.9011	0.8995	+16
1.0138	1.0070	1.0049	+21	0.7380	0.9017	0.8975	+42
1.2112	1.0286	1.0270	+16	1.0707	0.9053	0.8998	+55
1.3842	1.0474	1.0742	+2	1.5851	0.9147	0.9105	+42
1.4730	1.0600	1.0577	+23	2.2279	0.9280	0.9303	−23
2.0795	1.1350	1.1339	+11	2.3220	0.9333	0.9334	−1
2.2345	1.1503	1.1543	−40	2.5206	0.9364	0.9401	−37
2.2770	1.1544	1.1600	−56	2.7329	0.9405	0.9470	−65
2.3135	1.1606	1.1649	−43	2.7885	0.9427	0.9488	−61
2.4045	1.1717	1.1771	−54	2.8445	0.9440	0.9506	−66
2.6615	1.2050	1.2123	−73	2.9722	0.9479	0.9545	−66
2.8506	1.2376	1.2387	−11	3.3415	0.9598	0.9646	−48
3.0271	1.2589	1.2638	−49	3.6510	0.9663	0.9711	−48
3.2222	1.2880	1.2919	−39	3.9104	0.9746	0.9747	−1
3.3857	1.3128	1.3157	−29	4.2195	0.9838	0.9763	+75
3.4364	1.3194	1.3231	−37	4.4879	0.9912	0.9750	+162
3.8078	1.3779	1.3784	−5	4.5609	0.9941	0.9741	+200
4.2057	1.4440	1.4388	+52	5.1776	1.0134	0.9569	+565

[a] ϕ_{exptl} calculated from our experimental isopiestic ratios using van Hook's ϕ_{NaCl} as reference data. $\Delta\phi \equiv (\phi_{\text{exptl}} - \phi_{\text{lit}})$.

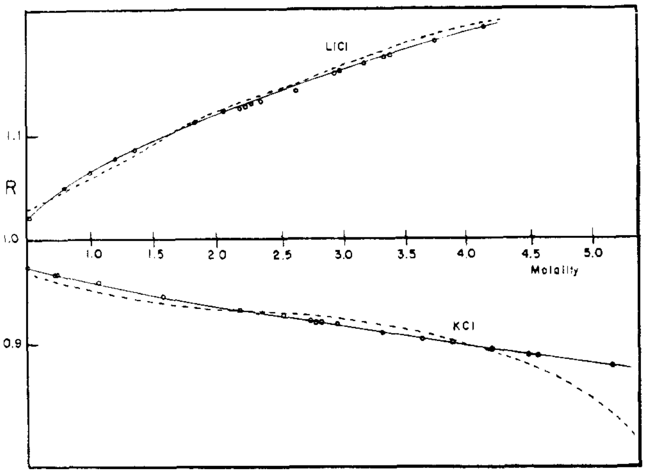

Figure 1. Isopiestic ratios to NaCl for LiCl and KCl at 45 °C. Data points are experimental. The dashed lines are calculated from literature equations (ref 2).

with the uncertainty of the chosen reference data, whichever is larger.

Sodium chloride solutions are among the primary isopiestic reference standards at 25 °C (*7*) and this salt has been more extensively studied than any other at higher temperatures. We have previously tested the internal consistently of Smith's boiling point data (*8*) by making direct comparison of NaCl and KBr solutions at 60 and 80 °C. van Hook's equation was fit to these and more recent data and, for NaCl, generates a smooth, monotonic curve at the temperatures of interest to us without the obvious ripples and divergences characteristic of the KCl data (Figure 1).

Given this superiority of the available NaCl data, we have used van Hook's ϕ (m, T) for NaCl as reference values and have calculated, and compiled in Table III, the osmotic coefficients for LiCl and KCl at our experimental molalities.

We have used two different procedures to obtain ϕ's at rounded m's. (The two approaches were compared in order to determine the amount of uncertainty being introduced into calculations, e.g., of ϕ from R, by the use of our least-squared fits. In the first method the data were first smoothed by using the computer fit of $R(m)$ from Table II. These equations were then used to calculate the NaCl m's isopiestic with rounded m's of the test salt from which the ϕ's at these rounded m's were then calculated by using van Hook's ϕ's for NaCl (Table IV). In the alternative procedure we first calculated ϕ's for the test salts at experimental m's (the values in Table III) using van Hook's reference data. These experimental ϕ's were then fit to eq 3 and the resulting best-fit parameters (which are included in Table II) were then used to calculate ϕ's at rounded m's.) In no case did the discrepancy between the two smoothing procedures exceed 0.1%. Although the smoothing error is minimal it must be borne in mind that even the experimental ϕ values in Table III already contain the uncertainty of the reference ϕ data. Since we believe the data for NaCl to be superior to the other absolute values available we include in Table III a comparison of van Hook's computer generated ϕ's for LiCl and KCl with those based on our experimental R's and the literature ϕ_{NaCl} data. The discrepancies, which are much larger than the experimental uncertainty in the R's, vary cyclically as expected given the comparison in Figure 1.

Table IV. Osmotic Coefficients[a] of LiCl and KCl at Rounded Molalities at 45 °C

m	ϕ_{LiCl}	ϕ_{KCl}	m	ϕ_{LiCl}	ϕ_{KCl}	m	ϕ_{LiCl}	ϕ_{KCl}
0.5		0.900_9	1.2	1.028_8	0.907_6	3.0	1.255_5	0.948_8
0.6		0.901_1	1.4	1.050_8	0.911_0	3.5	1.330_4	0.962_7
0.7		0.901_6	1.5	1.061_9	0.912_9	4.0	1.409_1	0.977_2
0.8	0.983_8	0.902_4	1.6	1.073_3	0.914_8	4.5	(1.492_1)	0.992_2
0.9	0.995_5	0.903_4	1.8	1.096_7	0.919_0	5.0		1.007_5
1.0	1.006_8	0.904_6	2.0	1.120_9	0.923_5	5.2		(1.013_7)
			2.5	1.185_5	0.935_6			

[a] Generated from eq 3 with the coefficients in columns 3 and 5 of Table II. The NaCl reference ϕ's (ref 2 and 3) used to generate these ϕ's have been compared with those recently recommended by Pitzer et al. (ref 10). Up to 4 m the largest discrepancy is 0.2% at ~1 m with most values closer than 0.1%. The equation we used begins to diverge at 5 m NaCl which affects only the LiCl value at 4.0 m and the projected value at 4.5 m which may be too high by 0.5–1.0%.

On the basis of the analysis presented above, we believe that the ϕ's labeled "experimental" in Table III are the best available at 45 °C for LiCl and KCl and that values generated by using the empirical fit from Table II will be within 0.1% of the measured value at any m within the experimental range. Equation 3 must not be used outside the indicated ranges even as a rough guide since the polynomials characteristically diverge wildly when not constrained by the data. Furthermore, since we have placed no theoretical constraints on the fit, the equation may not be integrated to yield activity coefficients.

Registry No. LiCl, 7447-41-8; KCl, 7447-40-7.

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