J. Chem. Eng. Data 1986, 31, 54–55

Osmotic Coefficients of Aqueous LiCl and $CaCl_2$ from Their Isopiestic Ratios to NaCl at 50 °C

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Osmotic coefficients for aqueous LiCl and $CaCl_2$ solutions at 50 °C, based on isopiestic ratios to NaCl solutions, are reported for the concentration ranges up to saturation of NaCl. The results are used to assess the internal consistency of the independent data on these two salts and their suitability as isopiestic reference standards at 50 °C.

Introduction

We have recently described (*1*, *2*) an isopiestic system capable of the same high precision (coefficient of variation < 0.1%) up to ~90 °C that characterizes that method at 25 °C. The most valuable application (determination of osmotic and activity coefficients rather than simply isopiestic ratios) demands reference data of comparable quality. Unlike the situation at 25 °C where several solutions have been thoroughly characterized, suitable data are quite scarce at higher temperatures. The recent thorough analysis of the temperature dependence of the thermodynamic properties of aqueous NaCl (*3*) confirms that this is the reference system of choice in the range of water activities down to ~0.75 (at saturation of NaCl). Since our studies have involved a variety of salt types, including quite soluble multivalent transition-metal chlorides and perchlorates, our program requires isopiestic standards for water activities far lower than those compatible with NaCl(aq). For this reason we have begun a program of direct isopiestic comparison of some solutions for which the absolute measurements have been reported in the literature, in order to test the consistency of the reported data.

Since the isopiestic method is relative, it is not possible to prove that a given data set is correct but it can be used to prove conclusively that one or more sets are in error. The method is especially useful for this purpose because of its high precision and because multiple comparisons can be made simultaneously. We recently reported such comparisons among NaCl, KCl, and LiCl at 45 °C (*2*). The consistency between the NaCl and LiCl data, and the fact that LiCl is very soluble, has prompted a more thorough study of this salt as a possible reference standard at low a_w. Since $CaCl_2$ is (along with H_2SO_4) one of the favorite systems for this purpose at 25 °C (*4*, *5*), we have included it in the present study which presents isopiestic ratios among NaCl, LiCl, and $CaCl_2$ at 50 °C from ~0.3 *m* to saturation of the reference salt. Osmotic coefficients are calculated for LiCl and $CaCl_2$ from our experimental isopiestic ratios and Pitzer's NaCl osmotic coefficients.

Experimental Section

Apparatus and Procedures. The system and procedures used were essentially those reported in detail by Moore et al. (*1*) with the slight modifications described by Davis et al. (*2*). One additional change has been the abandonment of glycols as thermostat fluids in favor of water. We have found that evaporation and heat loss can be made tolerable at least up to 75 °C by covering the surface of the water with a thick layer of hollow polyethylene balls (20 mm diameter). They are easily removed for access to the isopiestic units and have caused no complications.

Table I. Experimental Isopiestic Molalities at 50 °C

m_{NaCl}	m_{LiCl}	m_{CaCl_2}	m_{NaCl}	m_{LiCl}	m_{CaCl_2}
0.3395	0.3322	0.2438	2.5117	2.2365	1.4763
0.4533	0.4432	0.3250	2.7332	2.4169	1.5822
0.7224	0.6964	0.5025	3.0225	2.6494	1.7179
1.6164	1.4863	1.0186	3.6157	3.1195	1.9893
1.7762	1.6216	1.1027	3.9772	3.4005	2.1489
1.8960	1.7236	1.1656	4.2384	3.6036	2.2556
2.0540	1.8568	1.2469	4.5829	3.8629	2.4092
2.1904	1.9707	1.3164	4.6946	3.9514	2.4497
2.2339	2.0067	1.3379	4.8265	4.0496	2.5039
2.2415	2.0149	1.3410	5.4655	4.5175	2.7648

Chemicals. The salts were reagent grade materials used without further purification except for preliminary drying when direct weighing was anticipated (only NaCl in this study). For LiCl and $CaCl_2$ gravimetrically (as AgCl) standardized stock solutions were weighed as was the case for NaCl in the lower concentration range. Freshly boiled deionized water was used for all solutions.

Confidence in the nominal compositions of these reagents was enhanced by the fact that the data reported on each salt are based on two or three separate stock solutions prepared from reagents obtained from different suppliers.

Results

Twenty successful equilibrations were carried out involving two or three samples of each of the three salts. If the coefficient of variation (CV ≡ relative standard deviation) of replicates of any one of the three sample sets exceeded 0.1% that entire set was discarded on the assumption that true isopiestic equilibrium had not been reached. If further equilibration did not eliminate the discrepancy, the discordant samples were discarded and a new set weighed out.

The precision of the measurements reported in Table I is indicated by the run average CV's for replicates tabulated in the fourth column of the table. The weighted average CV's for each salt over all runs were 0.04_8%, 0.03_7%, and 0.04_0% for NaCl, LiCl, and $CaCl_2$, respectively. The overall weighted average CV for all salts and all runs was 0.04_2%.

The experimental isopiestic ratios were fitted to a modified Debye–Hückel-like term (with empirically adjusted *A* and *B*) with the residual least-squared to a power series in $m^{1/4}$ as recommended by Rard (*6*). Coefficients for generation of *R* at any *m* are given in Table III along with coefficients for fits of the osmotic coefficients to an equation of the same form.

The osmotic coefficients in Table II were generated from Pitzer's (*3*) NaCl ϕ's and our experimental isopiestic ratios. The reference osmotic coefficients were also fitted for greater ease in all of the calculations, and the coefficients for $\phi(m)$ of NaCl are included in Table III for the reader's convenience. The smoothing to rounded molalities was done by two procedures, one involving $\phi(m)$ and the other $R(m)$, to assess the uncertainties introduced by the curve-fitting. The two smoothing procedures gave a maximum discrepancy of 0.06% for LiCl and 0.08% for $CaCl_2$, well within the cumulative uncertainties of the results. The smoothed values are the averages of those obtained by the two procedures. Given the better than 0.1% precision of our isopiestic ratios and the presumed accuracy of the NaCl reference data, we believe that the osmotic

0021-9568/86/1731-0054$01.50/0

Table II. Smoothed Osmotic Coefficients at 50 °C

m	ϕ_{LiCl}	Δ_1, %	ϕ_{CaCl_2}	Δ_2, %
0.3	(0.942_6)	$+0.3_0$	(0.856_1)	(-0.8_9)
0.4	0.942_0	-0.5_3	0.869_9	-1.3
0.5	0.947_4	-0.8_0	0.891_1	-1.1
0.6	0.955_7	-0.8_4	0.915_5	-0.8_3
0.7	0.965_7	-0.7_6	0.941_7	-0.5_0
0.8	0.976_5	-0.6_5	0.968_8	-0.2_3
0.9	0.987_8	-0.5_2	0.996_6	-0.0_2
1.0	0.999_5	-0.4_0	1.024_8	$+0.0_8$
1.2	1.023_5	-0.1_9	1.082_7	$+0.2_5$
1.4	1.047_9	-0.0_4	1.142_4	$+0.3_0$
1.5	1.060_2	0.0_0	1.173_0	$+0.2_6$
1.6	1.072_7	$+0.0_5$	1.204_1	$+0.2_6$
1.8	1.097_6	$+0.0_9$	1.268_1	$+0.1_7$
2.0	1.122_9	$+0.1_1$	1.334_9	$+0.1_4$
2.5	1.187_7	$+0.0_7$	(1.514_1)	$(+0.4_7)$
3.0	1.255_3	$+0.0_3$		
3.5	1.326_2	-0.0_8		
4.0	1.401_0	$+0.2_1$		
4.5	1.480_0	$+0.4_0$		

[a] Values are averages of two smoothing procedures, one using empirical fit of $\phi(m)$ and the other $R(m)$ for interpolation. Both procedures use the empirical $\phi(m)$ of the Pitzer NaCl reference data. $\Delta_1 \equiv (\phi_{LiCl\,ex} - \phi_{Gibbard})$; $\Delta_2 \equiv (\phi_{CaCl_2\,ex} - \phi_{Atkinson})$.

Table III. Parameters for Best Empirical Fit[a] of *R* and ϕ Data at 50 °C

	R^b to NaCl		ϕ^c		
	LiCl	$CaCl_2$	NaCl	LiCl	$CaCl_2$
m	0.4–4.5	0.3–2.5	0.1–6.0	0.4–4.5	0.3–2.5
A	0.25000	−0.25000	0.25000	0.25000	0.25000
B	1.50000	1.50000	1.00000	1.00000	1.50000
a_0	1.84263	3.04511	0.085443	2.27942	4.33833
a_1	−6.77479	−12.21148	−0.50779	−8.84803	−18.74804
a_2	8.76563	17.40738	0.26949	11.99269	28.70535
a_3	−4.92984	−10.55641	−0.14637	−7.40889	−19.87498
a_4	1.05413	2.46997	0.11622	1.85953	5.50436
std dev	0.00059	0.00133	0.00070	0.00080	0.00178

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

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

where Y is either R or ϕ and X is $m^{1/4}$. [b] R's are always our experimental isopiestic ratios to NaCl as reference salt, i.e., $R_{salt} \equiv (\nu m)_{NaCl}/(\nu m)_{salt}$. [c] The ϕ's are Pitzer's smoothed data at 50 °C for NaCl, and for LiCl and $CaCl_2$ are calculated from $\phi_{salt} \equiv R\phi_{NaCl}$, where R is our experimental isopiestic ratios to NaCl, and ϕ_{NaCl} are Pitzer's values generated at experimental molalities by using the NaCl coefficients in the table.

coefficients in Table II are the best available at this time for both salts. We believe the uncertainty in the smoothed values, in the molality ranges of validity indicated, should be on the order of 0.2% for LiCl and 0.3% for $CaCl_2$.

All of the literature data on $CaCl_2$ have recently been reviewed (*7*) and best-fit osmotic coefficients proposed for the range from 0 to 100 °C. Our results disagree quite significantly from their recommended values below about 0.8 *m* (see the right-hand column of Table II), but agreement is remarkably good over the rest of the common range. Our values appear to fit quite smoothly between the lower temperature data and those at higher temperatures (*8*) but, until our measurements are extended to higher temperatures, it seems idle to pursue that point further.

Agreement of our LiCl values with the absolute measurements of Gibbard and Scatchard (*9*), as indicated by the % differences tabulated in column 3 of Table II, is excellent in the range 1–4 *m*. There seems to be a distinct trend to slightly lower values than Gibbard and Scatchard at the lower *m*'s but this is just where our vapor pressure data are the weakest. Our data also show a tendency to higher values at the highest molalities, a trend which is troubling since we anticipate use of the Gibbard and Scatchard LiCl data as primary standards at concentrations above those accessible to NaCl(aq). The average deviation from Campbell and Bhatnagar (*10*) is much larger (>2.6%).

We have made one other attempt to test the internal consistency of our LiCl results, that by comparing the current 50 °C results to those we recently reported at 45 °C. As expected (*11*), the 50 °C osmotic coefficients are slightly lower than the 45 °C values at the higher molalities, but the difference is really within experimental uncertainty from 1.2 to 3.0 *m*. At a few points in this range the $\phi_{50°C}$ is actually higher than $\phi_{45°C}$ indicating that the ϕ vs. *T* curves might be passing through a maximum at these *m*'s as they do for all *m*'s for NaCl. The limited data we have at both *T*'s below 1.0 *m* indicate reversion to the more normal order. The isopiestic ratios do not cross although the *R* vs. *m* curves do come closer together in the middle *m* range than at both higher and lower *m*'s.

Clearly, the 5-deg temperature difference is too small to allow a definitive *T*-dependence statement. We are therefore already extending these measurements on both LiCl and $CaCl_2$ vs. NaCl to 75 °C and the relative LiCl/$CaCl_2$ behavior to higher concentrations at both temperatures. At this point LiCl(aq) appears to be the best candidate for an isopiestic standard for lower water activities at temperatures above 25 °C.

Registry No. LiCl, 7447-41-8; $CaCl_2$, 10043-52-4.

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Received for review May 31, 1985. Accepted August 15, 1985. This research was supported by a grant from Research Corporation.