Osmotic Coefficients of Aqueous CaCl₂ Solutions from 3 to 12 m at 50 °C

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Osmotic coefficients for aqueous CaCl₂ solutions at 50 °C, based on isopiestic ratios to aqueous LiCl solutions, are reported for the concentration range from ∼3 to ∼12 m CaCl₂. Significant discrepancies are found between our results and literature data.

Introduction

As a part of our program of isopiestic studies as a function of temperature, we have recently reported (1) an investigation of LiCl and CaCl₂ vs. NaCl at 50 °C. These salts were studied because NaCl is the system which is best characterized at temperatures above 25 °C (2) and LiCl (3) and CaCl₂ (4) have each been studied independently by absolute methods (including direct pressure measurements). Furthermore, we had a special interest in CaCl₂ since it is a salt often chosen at 25 °C as isopiestic reference for the study of systems at concentrations beyond the saturation concentration of NaCl (5–7). Thus the purpose of our earlier experiments was to determine the degree of internal consistency among these independently measured sets of a_w data. Our immediate intent was to identify the data most likely to be useful as isopiestic reference at temperatures greater than 25 °C at water activities lower than those accessible with NaCl(aq). Our conclusion (1), based on the direct simultaneous isopiestic comparison of the three salts, was that the LiCl data of Gibbard and Scatchard (3) were consistent with the NaCl data (2). Our isopiestic ratios of CaCl₂ to NaCl disagree quite significantly from the literature values (4) below approximately 0.8 m, but agreement is remarkably good over the rest of the NaCl range. These results suggest that LiCl has a slight edge over CaCl₂ as an isopiestic reference standard above the saturation point of NaCl at temperatures greater than 25 °C.

Therefore, in spite of a slight drift between our NaCl/LiCl ratios and those of Gibbard and Scatchard at the highest molalities, we take the Gibbard and Scatchard data on LiCl to be the most suitable absolute isopiestic standard for the higher m range.

In the present paper we report the isopiestic ratios of CaCl₂ to LiCl from ∼3.1 m CaCl₂ (5.1 m LiCl) to ∼12.0 m CaCl₂ (18.1 m LiCl) which is just below saturation of CaCl₂. Osmotic coefficients of CaCl₂ are calculated based on these experimental ratios and the literature LiCl data.

Experimental Section

Apparatus and Procedures. The system and procedures used were essentially those reported in detail by Humphries et al. (8) with the slight modifications described by Davis et al. (1).

Chemicals. The salts were reagent grade materials used without further purification. Stock solutions, previously standardized gravimetrically (as AgCl), were weighed from weight burets. 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

Table I. Isopiestic Data at 50 °C

LiCl			CaCl₂		
m^a	n^b	cv,^{c} %	m	n	cv, %
5.0945	4	0.06	3.1040	4	0.05
5.6627	4	0.03	3.4190	5	0.05
6.3624	4	0.03	3.8071	5	0.06
7.2575	3	0.01	4.3090	5	0.08
7.9258	5	0.02	4.6868	5	0.05
8.0817	6	0.05	4.7780	6	0.06
8.6926	6	0.04	5.1300	6	0.05
8.7594	5	0.04	5.1731	6	0.06
9.4200	6	0.06	5.5701	6	0.06
9.7720	6	0.08	5.7881	6	0.04
10.4096	6	0.03	6.1927	6	0.03
10.8983	6	0.08	6.5210	6	0.04
11.3573	6	0.07	6.8370	6	0.03
11.7202	6	0.04	7.0944	6	0.03
12.0877	6	0.05	7.3614	6	0.05
12.6083	6	0.03	7.7452	6	0.05
13.1373	6	0.03	8.1555	6	0.04
13.4901	9	0.04	8.4332	9	0.06
13.6586	6	0.02	8.5626	6	0.05
14.1036	6	0.10	8.9062	7	0.10
14.8878	9	0.02	9.5395	9	0.07
15.4924	6	0.07	10.0160	6	0.07
15.9541	9	0.02	10.3831	9	0.10
16.4011	5	0.09	10.7233	6	0.05
17.4688	9	0.05	11.5493	9	0.10
18.0807	6	0.03	12.0033	6	0.03
18.1034	6	0.06	12.0222	6	0.04

$^a m$ = average isopiestic molalities. $^b n$ = number of replicate samples comprising average. ^{c} cv = coefficient of variation (relative standard deviation) of replicate set.

from reagents obtained from different suppliers.

Results

A total of 27 isopiestic equilibrations were carried out at 50 °C in the concentration range from ∼3 m CaCl₂ to ∼12 m CaCl₂. The results of these measurements are reported in Table I as average isopiestic molalities along with the number of replicate samples comprising the average and the coefficient of variation (relative standard deviation) of each replicate set.

Gibbard and Scatchard's (3) LiCl osmotic coefficients were used as isopiestic reference data in order to calculate osmotic coefficients for CaCl₂ from our experimental isopiestic ratios based on the molalities in Table I. The resulting ϕ's at experimental molalities were then fit to a power series in $m^{1/4}$ with no model-dependent terms and, from this fit, ϕ's at rounded m's were calculated. (The model-dependent terms were omitted because we found the power series was able to account for the curvature just as well without them.) In order to expose any excessive polynomial ripple errors in the $\phi(m)$ function, we also smoothed the data by first fitting the experimental R's and then calculating $R(m)$ at rounded molalities. These $R(m)$ values at rounded molalities were then used to calculate ϕ's at rounded m. The discrepancies introduced by the two smoothing procedures averaged ∼0.09% over the 3–12 m range and, without the 3 m point, ∼0.05%. The largest errors occur, as expected, near the ends of the data range where the empirical equation begins to tail due to its not

Table II. Parameters for Best Empirical Fit[a] of R and ϕ Data for $CaCl_2$ at 50 °C

	molality range 3.1–12.0	
Y	R	ϕ
X	$m^{1/4}$	$m^{1/4}$
a_0	38.7390	298.3297
a_1	−102.8376	−768.4563
a_2	103.8116	734.4480
a_3	−45.87261	−307.0891
a_4	7.484550	47.53778
% variation	99.96	99.99
av % dev	0.06	0.11

[a] The equation fit to each set of 27 data points is $Y = \sum_i a_i X^i$ where Y equals R or ϕ and $X = m^{1/4}$. Inclusion of a Debye-Hückel-like term to accommodate some of the curvature does not improve the fit of these high-concentration data.

Table III. $CaCl_2$ Osmotic Coefficients at 50 °C

m^a	$\phi_{exptl}{}^b$	$\phi_{lit.}{}^c$	$\Delta,^d$ %
0.5	0.891	0.901	−1.1
1.0	1.024_8	1.024	0.0_8
1.5	1.173_0	1.170	0.2_6
2.0	1.334_9	1.333	0.1_4
2.5	(1.514_1)	1.507	(0.4_7)
3.0	1.680_8	1.690	$−0.5_5$
3.5	1.853_2	1.875	−1.2
4.0	2.037_7	2.057	$−0.9_5$
4.5	2.213_0	2.232	$−0.8_6$
5.0	2.368_5	2.391	$−0.9_5$
5.5	2.499_7	2.531	$−1.2_5$
6.0	2.605_2	2.646	$−1.5_7$
6.5	2.686_0	2.732	$−1.7_1$
7.0	2.745_2	2.787	$−1.5_2$
7.5	2.786_0	2.813	$−0.9_7$
8.0	2.810_5	2.813	$−0.0_9$
8.5	2.823_0	2.794	1.0_3
9.0	2.826_4	2.768	2.0_7
9.5	2.823_4		
10.0	2.816_5		
10.5	2.808_4		
11.0	2.800_8		
11.5	2.795_7		
12.0	(2.795_9)		

[a] m = $CaCl_2$ molality. [b] ϕ_{exptl} = experimental $CaCl_2$ osmotic coefficients (0.5–2.5 m based on NaCl reference; 3.0–12.0 m based on LiCl reference). [c] $\phi_{lit.}$ = Ananthaswamy and Atkinson $CaCl_2$ osmotic coefficients (4). [d] $\Delta \equiv (\phi_{exptl} - \phi_{lit.})$.

being constrained by experimental data.

The coefficients for the fits of both $R(m)$ and $\phi(m)$ are compiled in Table II. We have not reported here a new set of osmotic coefficients for $CaCl_2$ in the lower m range, based on LiCl reference, since we have previously reported (1) a set based on NaCl, and the NaCl osmotic coefficients are assumed to be superior as reference data. We did calculate the $CaCl_2$ osmotic coefficients based on LiCl for this range and compared the results with those based on NaCl. We found the agreement

to be comparable to that between our experimental ϕ_{LiCl} based on NaCl and the original Gibbard and Scatchard data. While the numbers are comparable, they do clearly demonstrate the effects of accumulated fitting errors especially near the ends of the fitting ranges. Thus we have indicated, by parentheses, the tenuous nature of our smoothed values near the ends of the ranges.

The smoothed ϕ's for the whole concentration range are given in Table III along with a comparison to the literature data on $CaCl_2$ which have recently been reviewed and evaluated by Ananthaswamy and Atkinson (4). The agreement in the range between 3 and ~8.5 m is not quite as good as what we had found at lower concentrations (1). The discrepancies, which were small and positive in the low concentration range, are all negative and, up to ~7.5 m, tend to hover between −1% and −1.5%. At ~8 m our values begin to trend higher than those of ref 4, a divergence that continues to grow up to ~9 m as is evidenced by a direct comparison with the extrapolations of Jakli and van Hook's measurements (9). Thus our curve does not flatten out as indicated in Table III and Figure 5 of ref 9. However, our ϕ vs. m curve does have negative curvature, beyond an inflection point below 1 m and, after reaching a maximum at ~9 m, eventually begins a slow decrease, probably because of the increasing importance of ion-pairing as concentration increases (10).

One final qualification should be borne in mind. Although the uncertainty in the experimental data is on the order of 0.05% and smoothing errors are also on the order of 0.05% (except at the extreme ends of the ranges), the reliability of our ϕ_{CaCl_2} values above 3 m is limited by the accuracy of the Gibbard and Scatchard LiCl data. At this point we have no independent check on the validity of their data at concentrations beyond the saturation point of NaCl.

We are presently extending these studies to 75 °C and will shortly be in a position to examine trends with increasing temperature.

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