

# Osmotic Coefficient of Methanol + LiCl, + LiBr, and + LiCH<sub>3</sub>COO at 25 °C

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The osmotic coefficients of methanol + LiCl, + LiBr, and + LiCH<sub>3</sub>COO were determined by the isopiestic method at 25 °C. NaI in methanol solutions up to 4.33 mol·kg<sup>-1</sup> were used as the isopiestic reference with osmotic coefficients calculated from vapor pressure data reported by Barthel and Tomasula. Experimental osmotic coefficient data are reliably represented by the Pitzer model with and without the  $\beta^{(2)}$  term. The parameters for these equations, along with the corresponding standard deviations, are presented for these systems. The set of Pitzer parameters  $b = 3.2$ ,  $\alpha_1 = 2.0$  may be used. Including the  $\beta^{(2)}$  term with  $\alpha_2 = 1.4$  improves the fit for all of the investigated solutes, so that the standard deviations reduce from 0.015 to 0.006 for LiCl, from 0.009 to 0.005 for LiBr, and from 0.005 to 0.004 for LiCH<sub>3</sub>COO in methanol solutions at 25 °C.

## Introduction

The majority of the osmotic and activity coefficient data for aqueous electrolytes has been reported by the isopiestic technique that was performed by Robinson and Stokes (1949). This technique requires nonvolatile solutes, and there is a necessity for very accurate colligative property data for one solute that is used as an isopiestic standard. For aqueous solutions, sodium chloride has normally been used.

Very few osmotic coefficient measurements have been made on nonaqueous electrolyte solutions, in contrast to those of aqueous electrolyte solutions. Barthel et al. (1985) have made accurate vapor pressure lowering measurements on dilute solutions of nine electrolytes. Using these data, Bonner (1987) calculated the osmotic coefficients of solutions of NaI in methanol for 10 concentrations of NaI (0.02 to 0.75 mol·kg<sup>-1</sup>). For higher concentrations of NaI in methanol, direct vapor pressure measurements were reported by Bixon et al. (1979). These data have also been used by Bonner (1987) in order to extend the calculation of osmotic coefficients of NaI in methanol to a concentration of 4.5 mol·kg<sup>-1</sup>, thereby making NaI in methanol an isopiestic reference standard. The data of Bixon et al. (1979), however, are for 24.9 °C, and absolute pressure was measured, which is a much more difficult experiment than the measurement of vapor pressure difference, and large errors are to be expected. Bonner (1987) estimated that his tabulated osmotic coefficient values for NaI were uncertain by about 1%; he has also reported isopiestic data for LiCl, NaNO<sub>3</sub>, tetramethylguanidinium perchlorate, and urea in methanol at 25 °C, using NaI solutions as a primary isopiestic standard.

From an analysis of literature vapor pressure data for NaI in methanol (Bixon et al., 1979; Tomasula et al., 1987; Yamamoto et al., 1995), we found that the vapor pressure difference data of Tomasula et al. (1987) are quite accurate for NaI in methanol solutions to a concentration of 4.33 mol·kg<sup>-1</sup> at 25 °C. These data are also more consistent with the low concentration data of Barthel et al. (1985) than that of Bixon et al. (1979). Hence in this work, for concentrations higher than 0.75 mol·kg<sup>-1</sup>, the osmotic

coefficients of NaI in methanol solutions were calculated from the vapor pressure data of Tomasula et al. (1987). Then, these osmotic coefficients were combined with the dilute solution data of Barthel et al. (1985), and the results were fitted to the Pitzer and Mayorga (1973) model. The precision of both the measurement and the fitting parameters permits the Pitzer model with the  $\beta^{(2)}$  term to be used to calculate osmotic coefficient values at concentrations from 0.02 to 4.33 mol·kg<sup>-1</sup> with an uncertainty of about 0.5%. Therefore, these osmotic coefficients of solutions of NaI in methanol can be used, with more confidence, as reference values for isopiestic measurements of other solutes in methanol at 25 °C.

In this paper, osmotic coefficients of binary solutions of LiCl, LiBr, and LiCH<sub>3</sub>COO were determined by an improved isopiestic technique at 25 °C. While there is limited information for the osmotic coefficient of LiCl and LiBr in methanol in the literature, information for the solution of LiCH<sub>3</sub>COO in methanol has not been reported. Osmotic coefficients from vapor pressure measurements can be found in the literature for methanol solutions of LiCl and LiBr at 25 °C (Skabichevskii, 1969; Tomasula et al., 1987).

## Experimental Section

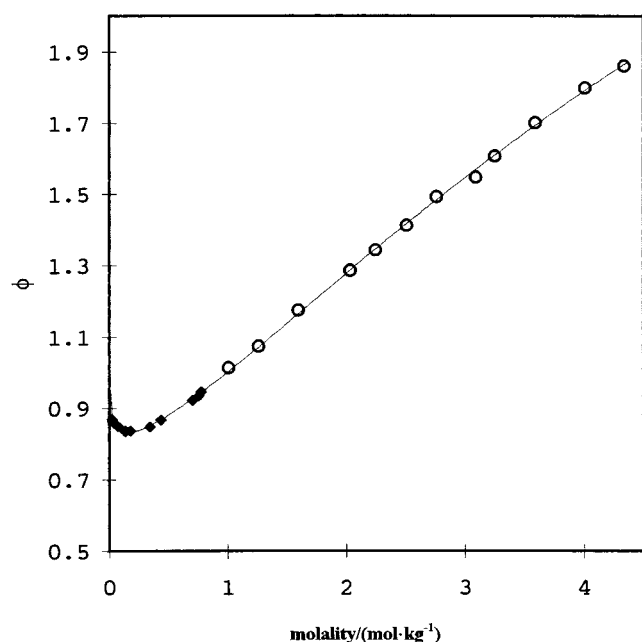
**Materials.** The salts and methanol were obtained from Merck except for lithium acetate, which was obtained from Fluka. They were all suprapur reagents (NaI, GR, min 99.5%; LiCl, GR, min 99.5%; LiBr, GR, min 99.5%; LiCH<sub>3</sub>COO·2H<sub>2</sub>O, GR, min 99.5%; methanol, GR, min 99.8%). NaI, LiCl, and LiBr were dried in an oven at about 120 °C for 24 h. Anhydrous lithium acetate was prepared by heating LiCH<sub>3</sub>COO·2H<sub>2</sub>O to 150 °C as described by Vogel (1989). Methanol with an initial water content of about 0.1% was dried with magnesium as described by Vogel (1989). The purity of methanol was checked by Shimadzu gas chromatography, and purity of about 99.99% was found for the methanol used.

**Apparatus and Procedure.** The isopiestic apparatus employed is essentially similar to the one used previously (Oches et al. 1990; Kabiri-Badr and Zafarani-Moattar, 1995). This apparatus consisted of a five-leg manifold

**Table 1. Osmotic Coefficients of NaI in Methanol Solutions from Vapor Pressure Data of Barthel et al. (1985) and Tomasula et al. (1987)**

$m/(\text{mol}\cdot\text{kg}^{-1})$	$\phi^a$	$m/(\text{mol}\cdot\text{kg}^{-1})$	$\phi^b$
0.024 53	0.869	0.7782	0.948
0.027 42	0.864	1.0098	1.014
0.070 71	0.851	1.2617	1.074
0.135 07	0.835	1.5965	1.175
0.135 46	0.837	2.0350	1.285
0.180 10	0.838	2.2485	1.342
0.347 04	0.848	2.5108	1.411
0.439 13	0.868	2.7632	1.492
0.703 14	0.923	3.0928	1.547 <sup>c</sup>
0.754 94	0.936	3.2513	1.607
		3.5932	1.701
		4.0088	1.799
		4.3383	1.861

<sup>a</sup> From Bonner (1987). <sup>b</sup> Osmotic coefficients calculated from vapor pressure depression data of Tomasula et al. (1987). <sup>c</sup> Value discarded in fitting to Pitzer model.



**Figure 1.** Osmotic coefficients of NaI in methanol at 25 °C:  $\blacklozenge$ , calculated by Bonner (1987) from vapor pressure data of Barthel et al. (1985);  $\circ$ , calculated from vapor pressure lowering data of Tomasula et al. (1987).

attached to round-bottom flasks. The five flasks were typically used as follows. Two flasks contained the standard NaI solutions, two flasks contained either LiCl, LiBr, or LiCH<sub>3</sub>COO solutions, and the central flask was used as a methanol reservoir. The apparatus was held in a constant temperature bath for at least 96 h for equilibration at (25.0 ± 0.005) °C. On the basis of the activity measurements, the maximum error has been previously verified as ±0.0002 for the isopiestic technique used.

## Results and Discussion

Osmotic coefficients  $\phi$  for the solution of NaI in methanol as a function of molality  $m$  were calculated from vapor pressure lowering,  $\Delta p = p^* - p$ , data of Tomasula et al. (1987), using the following relations

$$\phi = -\ln(a_s)/\nu m M_s \quad (1)$$

$$\ln(a_s) = \ln(p/p^*) + (B - V_s^*)(p - p^*)/RT \quad (2)$$

**Table 2. Experimental Isopiestic Molalities of LiCl with NaI Reference Standard in Methanol and Osmotic Coefficients of LiCl in Methanol at 25 °C**

$m_{\text{NaI}}/(\text{mol}\cdot\text{kg}^{-1})$	$m_{\text{LiCl}}/(\text{mol}\cdot\text{kg}^{-1})$	$\phi_{\text{LiCl}}$	$m_{\text{NaI}}/(\text{mol}\cdot\text{kg}^{-1})$	$m_{\text{LiCl}}/(\text{mol}\cdot\text{kg}^{-1})$	$\phi_{\text{LiCl}}$
0.2109	0.2244	0.785	2.1981	2.3313	1.257
0.2705	0.2891	0.788	2.3449	2.4820	1.297
0.2708	0.2881	0.791	2.4467	2.6005	1.318
0.5742	0.5982	0.863	2.4530	2.6097	1.318
0.5698	0.5989	0.854	2.5106	2.6508	1.343
0.6334	0.6640	0.870	2.5376	2.7076	1.336
0.7864	0.8145	0.916	2.9043	3.0584	1.446
0.9583	1.0006	0.951	2.9553	3.1091	1.460
1.2177	1.2775	1.012	3.0027	3.1504	1.476
1.2885	1.3613	1.023	3.1841	3.3149	1.532
1.4462	1.5233	1.067	3.2001	3.3258	1.539
1.5883	1.6780	1.101	3.2928	3.4138	1.565
1.6869	1.7748	1.132	3.3780	3.4872	1.592
1.8474	1.9469	1.173	3.6040	3.6838	1.662
1.8430	1.9515	1.166	3.8388	3.8793	1.736
1.8999	2.0136	1.180	4.1752	4.1803	1.828

Here,  $a_s$  is the activity of the solvent,  $\nu_+$  and  $\nu_-$  are number of cations and anions,  $\nu = \nu_+ + \nu_-$  is the stoichiometric number of the salt,  $M_s$  is the molecular weight of the solvent,  $T$  is the absolute temperature,  $p$  is the vapor pressure of the solution, and  $p^*$  is that of pure solvent. The second term on the right-hand side of eq 2 is the correction for nonideality of the solvent vapor,  $B$  is the second virial coefficient, and  $V_s^*$  is the molar volume of pure solvent. For methanol, the values of  $V_s^* = 4.073 \times 10^{-5} \text{ m}^3\cdot\text{mol}^{-1}$ ,  $B = -2.075 \times 10^{-3} \text{ m}^3\cdot\text{mol}^{-1}$  (taken from Kudchadker and Eubank (1970)), and  $p^* = 16957.7 \text{ Pa}$  (taken from Barthel et al. (1985)) were used at 25 °C.

In Table 1 we present osmotic coefficients of NaI calculated from the vapor pressure data of Tomasula et al. (1987), together with the results of Bonner (1987) for low molalities. These osmotic coefficient data are presented in Figure 1 along with a line that was generated using Pitzer model.

Several models are available in the literature for the correlation of osmotic coefficients as a function of molalities. The Pitzer and Mayorga(1973) model has been successfully used for aqueous electrolyte solutions and has the following form

$$\phi - 1 = |Z_+ Z_-| f^\phi + m[(2\nu_+ \nu_-)/\nu] B^\phi + m^2 [2(\nu_+ \nu_-)^{3/2}/\nu] C^\phi \quad (3)$$

where

$$f^\phi = -A_\phi I^{1/2}/(1 + bI^{1/2}) \quad (4)$$

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) \quad (5)$$

and

$$A_\phi = (1/3)(2\pi N d_0)^{1/2} (e^2/4\pi\epsilon_0 DkT)^{3/2} \quad (6)$$

Here  $\beta^{(0)}$ ,  $\beta^{(1)}$ , and  $C^\phi$  are Pitzer's ion-interaction parameters,  $\alpha_1$  and  $b$  are adjustable parameters, and  $A_\phi$  is the Debye-Hückel constant for the osmotic coefficient.  $Z_+$  and  $Z_-$  are positive and negative ionic charges. In eq 6,  $N$  is Avogadro's number,  $e$  is the proton charge,  $\epsilon_0$  is the permittivity of vacuum, and  $k$  is the Boltzmann constant. The ionic strength  $I$  is on the molal scale. For aqueous electrolyte solutions,  $b = 1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$  is used and the quantity  $\alpha_1$  is usually assigned a value of  $2.0 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$  except for 2-2 electrolytes. Pitzer (1991) found that good agreement with observed properties was obtained for the

**Table 3. Experimental Isopiestic Molalities of LiBr with NaI Reference Standard in Methanol and Osmotic Coefficients of LiBr in Methanol at 25 °C**

$m_{\text{NaI}}/$ (mol·kg <sup>-1</sup> )	$m_{\text{LiBr}}/$ (mol·kg <sup>-1</sup> )	$\phi_{\text{LiBr}}$	$m_{\text{NaI}}/$ (mol·kg <sup>-1</sup> )	$m_{\text{LiBr}}/$ (mol·kg <sup>-1</sup> )	$\phi_{\text{LiBr}}$
0.1864	0.1929	0.806	1.8361	1.8729	1.208
0.2708	0.2791	0.817	1.8943	1.9345	1.223
0.2891	0.2993	0.815	2.0398	2.0815	1.263
0.4159	0.4314	0.834	2.0642	2.1113	1.267
0.5190	0.5378	0.855	2.3149	2.3632	1.337
0.6011	0.6241	0.871	2.4667	2.5118	1.381
0.6391	0.6578	0.887	3.1333	3.1252	1.586
0.7746	0.7889	0.929	3.2160	3.1931	1.615
0.9823	1.0025	0.979	3.3894	3.3421	1.670
1.1190	1.1497	1.007	3.6247	3.5401	1.744
1.2647	1.2931	1.051	3.7357	3.6453	1.773
1.5883	1.6250	1.137	3.8879	3.7555	1.828
1.6837	1.7183	1.166	4.0889	3.9015	1.898
1.7730	1.8105	1.190			

**Table 4. Experimental Isopiestic Molalities of LiCH<sub>3</sub>COO with NaI Reference Standard in Methanol and Osmotic Coefficients of LiCH<sub>3</sub>COO in Methanol at 25 °C**

$m_{\text{NaI}}/$ (mol·kg <sup>-1</sup> )	$m_{\text{LiAc}}/$ (mol·kg <sup>-1</sup> )	$\phi_{\text{LiAc}}^a$	$m_{\text{NaI}}/$ (mol·kg <sup>-1</sup> )	$m_{\text{LiAc}}/$ (mol·kg <sup>-1</sup> )	$\phi_{\text{LiAc}}^a$
0.2304	0.2452	0.787	1.5184	2.0426	0.851
0.3340	0.3736	0.761	1.5581	2.1016	0.856
0.3956	0.4522	0.754	1.6005	2.1706	0.860
0.5251	0.6124	0.761	1.6293	2.2090	0.867
0.5968	0.7121	0.757	1.6499	2.2401	0.870
0.8107	1.0175	0.761	1.6696	2.2696	0.873
0.8465	1.0581	0.771	1.7545	2.3843	0.890
0.9542	1.2086	0.783	1.8401	2.5362	0.895
0.9932	1.2705	0.783	2.0607	2.8453	0.938
1.3866	1.8429	0.833	2.1748	3.0102	0.958

<sup>a</sup> LiCH<sub>3</sub>COO.2–2 salts if one simply added another term to  $B^\phi$  as follows:

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha_1 I^{1/2}) + \beta^{(2)} \exp(-\alpha_2 I^{1/2}) \quad (7)$$

From data analysis on the osmotic coefficient data of NaI in methanol solutions we found that at concentrations in the range of (0.02 to 4.33) mol·kg<sup>-1</sup>, the values of  $b = 3.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> and  $\alpha_1 = 2.0$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> were satisfactory at 25 °C. The value of  $b = 3.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> was also recommended by Barthel and Lauer mann (1986) for NaI in methanol solutions. For methanol solutions,  $A_\phi = 1.294$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> was calculated using eq 6. The values of density  $d_0 = 786.36$  kg·m<sup>-3</sup> and relative permittivity of  $D$

= 32.63 were taken from Barthel et al. (1985) for methanol. Three ion-interaction parameters,  $\beta^{(0)} = 0.322$  04,  $\beta^{(1)} = 0.030$  40, and  $C^\phi = -0.009$  31 were obtained for NaI in methanol solutions at 25 °C. Using this set of Pitzer parameters, the osmotic coefficient may be reproduced with an average absolute error of 0.6% (standard deviation of  $\sigma(\phi) = 0.007$ ) for NaI in methanol solutions in the range (0.02 to 4.33) mol·kg<sup>-1</sup> at 25 °C. We found that better agreement with osmotic coefficient data was obtained by adding the  $\beta^{(2)}$  exp(- $\alpha_2 I^{1/2}$ ) term with  $\alpha_2 = 1.4$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> to  $B^\phi$ . In this case,  $\beta^{(0)} = 0.408$  30,  $\beta^{(1)} = 1.044$  30,  $\beta^{(2)} = -0.875$ , and  $C^\phi = -0.022$  24 were obtained, so that using this set of parameters, the osmotic coefficients are reproducible with an average absolute error of 0.5% (standard deviation  $\sigma(\phi) = 0.006$ ) for NaI in methanol solutions in the range (0.02 to 4.33) mol·kg<sup>-1</sup> at 25 °C.

After the establishment of sodium iodide in methanol solution as a reference standard, the isopiestic equilibrium of solutions as reported in Tables 2–4 enabled the calculation of the osmotic coefficient,  $\phi$ , of methanol solutions of LiCl, LiBr, and LiCH<sub>3</sub>COO from

$$\phi = (\nu^* m^* \phi^*) / (\nu m) \quad (8)$$

where  $m$  is the molality of LiCl, LiBr, or LiCH<sub>3</sub>COO,  $m^*$  is the molality of the reference standard in isopiestic equilibrium with these solutions,  $\phi^*$  is the osmotic coefficient of the isopiestic reference standard, and  $\nu$  and  $\nu^*$  are the stoichiometric ionization numbers of the investigated solutes and reference standard, respectively ( $\nu^* = 2$  for NaI;  $\nu = 2$  for LiCl, LiBr, and LiCH<sub>3</sub>COO).

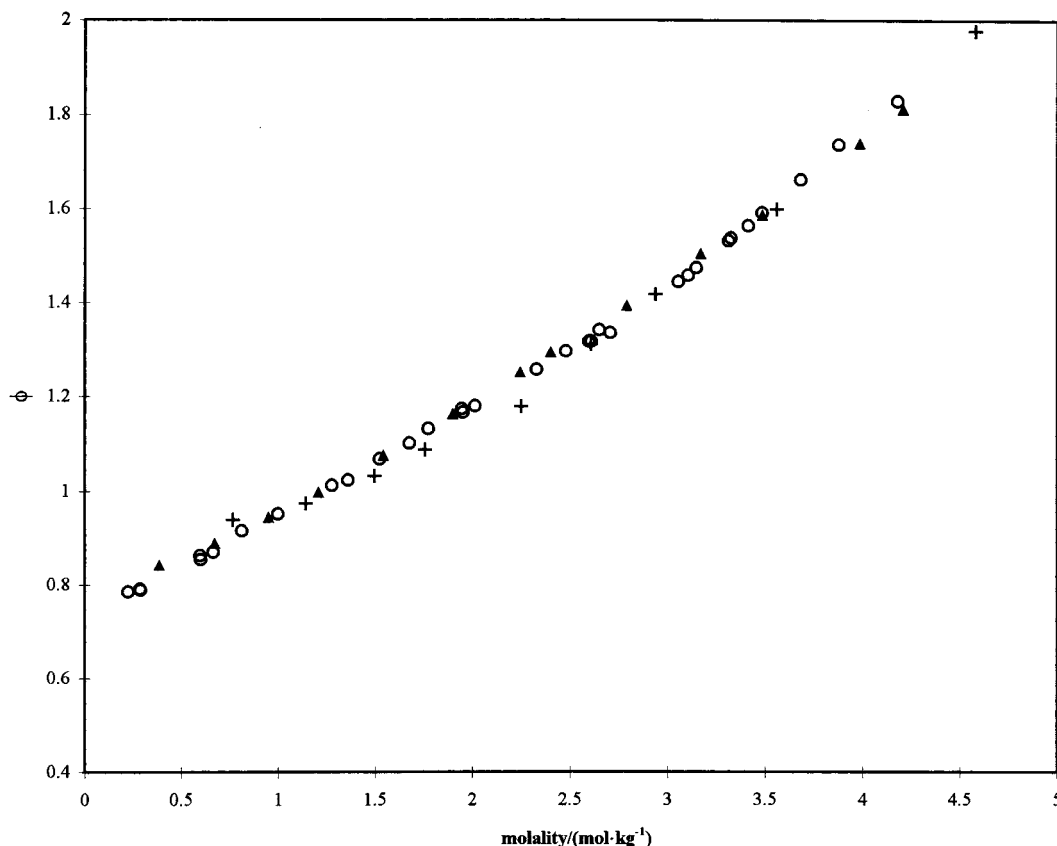
Pitzer ion-interaction parameters were calculated using the osmotic coefficient data of Tables 2–4 and are collected in Table 5. Both forms of the Pitzer model (with and without the  $\beta^{(2)}$  term) were considered. On the basis of the standard deviations, we note that, for all the investigated systems, better agreement is obtained with the Pitzer model with the  $\beta^{(2)}$  term and  $b = 3.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup>,  $\alpha_1 = 2.0$  kg<sup>1/2</sup>·mol<sup>-1/2</sup>, and  $\alpha_2 = 1.4$  kg<sup>1/2</sup>·mol<sup>-1/2</sup>.

Different sets of Pitzer parameters have been given for LiCl in methanol at 25 °C. Tomasula et al. (1987) used their own vapor pressure lowering data and the direct vapor pressure data given in Janz and Tomkins (1972) and reported two set of Pitzer parameters for LiCl in methanol with average absolute error of 0.9 and 1% in reproducing  $\phi$  values, respectively. Standard deviations of their fit with  $b = 1.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> are  $\sigma(\phi) = 0.011$  and 0.013, respec-

**Table 5. Pitzer Parameters for Methanol Solutions of LiCl, LiBr, and LiCH<sub>3</sub>COO Calculated from Osmotic Coefficients<sup>a</sup> at 25 °C**

no. of data	molality range/(mol·kg <sup>-1</sup> )	$\sigma(\phi)$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\phi$	source <sup>b</sup>
LiCl + Methanol							
32	0.22–4.18	0.006	-0.114 58	-3.953 03	3.421	0.064 78	1
		0.015	0.021 67	0.095 48	0.0	0.014 31	1
9	0.77–4.56	0.010	0.420 78	5.556 46	-3.651	-0.005 46	2
		0.015	0.126 75	0.759 09	0.0	0.033 82	2
13	0.38–4.21	0.002	0.232 58	0.276 34	-0.066	0.010 10	3
		0.003	0.339 43	1.506 25	0.0	0.002 49	3
LiBr + Methanol							
27	0.19–3.90	0.005	0.002 75	-2.66 65	2.238	0.055 42	1
		0.009	0.248 42	0.060 83	0.0	0.016 49	1
11	0.22–4.34	0.013	-0.041 33	-3.001 58	2.552	0.064 75	2
		0.017	0.193 99	0.089 61	0.0	0.030 80	2
LiCH <sub>3</sub> COO + Methanol							
20	0.24–3.01	0.004	0.192 24	1.394 40	-1.202	-0.010 17	1
		0.005	0.055 42	0.061 13	0.0	0.143 65	1

<sup>a</sup>  $b = 3.2$  kg<sup>1/2</sup>·mol<sup>-1/2</sup>;  $\alpha_1 = 2.0$  kg<sup>1/2</sup>·mol<sup>-1/2</sup>;  $\alpha_2 = 1.4$  kg<sup>1/2</sup>·mol<sup>-1/2</sup> were used throughout. <sup>b</sup> (1) this work; (2) Tomasula et al. (1987); (3) Bonner (1987).

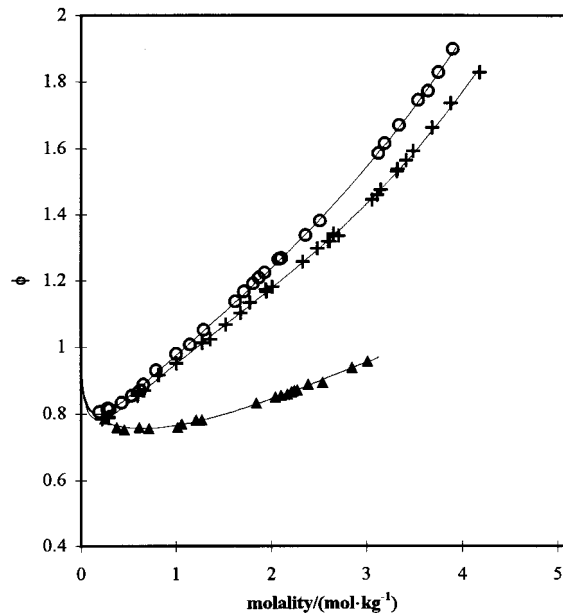


**Figure 2.** Comparison of osmotic coefficients of LiCl in methanol at 25 °C. ○, this work; ▲, Bonner (1987); +, calculated from vapor pressure lowering data of Tomasula et al. (1987).

tively. Examination of Tomasula et al. (1987) vapor pressure lowering data reveals that for molalities less than  $1 \text{ mol}\cdot\text{kg}^{-1}$ , only a single measurement has been carried out; therefore, their calculated Pitzer parameters may not successfully be applied to the dilute region. In the calculation of our Pitzer parameters, however, both the dilute and higher concentration regions were considered and more experimental data points were used.

For LiCl in methanol solutions, a few accurate isopiestic equilibrium molalities of LiCl with NaI as a reference standard have been given by Bonner (1987) at 25 °C. To compare the isopiestic data reported by Bonner (1987) and our isopiestic data, the osmotic coefficients of LiCl in methanol were also calculated for the data of Bonner (1987) and were fitted to Pitzer model. The Pitzer parameters resulting from the fit are also included in Table 5. Comparisons of our osmotic coefficient data to that of Bonner (1987) and Tomasula et al. (1987) are shown in Figure 2 for LiCl in methanol solution at 25 °C. Figure 2 shows that our data agree well with the data given by Bonner (1987).

Isopiestic studies have not been reported on LiBr in methanol. There are, however, vapor pressure results from which osmotic coefficients can be calculated. Tomasula et al. (1987) have determined vapor pressure lowering data for LiBr in methanol. Then, they have calculated the osmotic coefficient data with the help of eqs 1 and 2, and these data have been correlated with a three-parameter Pitzer model ( $b = 1.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ ) with an average absolute error of 1.1% (corresponding to the standard deviation of  $\sigma(\phi) = 0.015$ ). However, osmotic coefficients and Pitzer's ion-interaction parameters have not been reported. Moreover, as in the case of LiCl in methanol solutions, at molalities less than  $1 \text{ mol}\cdot\text{kg}^{-1}$ , there is only a single measurement at  $0.2174 \text{ mol}\cdot\text{kg}^{-1}$  as reported by Tomasula et al. (1987).



**Figure 3.** Osmotic coefficients of LiBr, LiCl, and LiCH<sub>3</sub>COO in methanol at 25 °C. ○, LiBr; +, LiCl; ▲, LiCH<sub>3</sub>COO. Lines were generated using the Pitzer model (with the  $\beta^{(2)}$  term) with the appropriate parameters from Table 5.

Correlation of our osmotic coefficient–molality data of LiBr in methanol solutions were carried out with the three-parameter Pitzer model with an average absolute error of 0.8% (standard deviation of  $\sigma(\phi) = 0.009$ ). Here again, the Pitzer model with a  $\beta^{(2)}$  term was found to represent the osmotic coefficients of LiBr in methanol satisfactorily using the parameters  $b = 3.2 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ ,  $\alpha_1 = 2.0 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ , and  $\alpha_2 = 1.4 \text{ kg}^{1/2}\cdot\text{mol}^{-1/2}$ . Thus, the average absolute error

was reduced to 0.4% corresponding to the standard deviation of  $\sigma(\phi) = 0.005$ .

Similarly, the osmotic coefficient data of Table 4 for lithium acetate in methanol was correlated with both forms of the Pitzer model using the same parameters as were used for LiCl and LiBr in methanol. The average absolute error of fit with the three-parameter Pitzer model is 0.3% (standard deviation of  $\sigma(\phi) = 0.005$ ). Again, including the  $\beta^{(2)}$  term improved the fit, and an average absolute error of less than 0.3% (standard deviation of  $\sigma(\phi) = 0.004$ ) was obtained for lithium acetate in methanol solutions.

For all of the investigated solutions, the osmotic coefficients are represented in Figure 3 along with the lines that were generated using the Pitzer model (with  $\beta^{(2)}$  term).

### Acknowledgment

The authors thank Mr. J. Jahanbin for his assistance in preparing graphs.

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Received for review August 11, 1997. Accepted November 14, 1997.

JE970193E