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Least-Squares Analysis of Osmotic Coefficient Data at 25 °C According to Pitzer's Equation. 1. 1:1 Electrolytes

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Pitzer ion-interaction parameters for 93 1:1 electrolytes have been calculated by least-squares analysis of published experimental osmotic coefficient data at 25 °C. The quality of the resulting fit of these data, expressed as the sum of squared residuals, the standard errors in the least-squares estimates, and the variation of the residuals with electrolyte concentration, is shown to be consistently superior to that obtained with the use of parameters taken from previous publications. The discrepancies between the present estimates of the Pitzer parameters and the published values are mainly concentrated in $\beta^{(1)}$. The relative standard error in this parameter depends strongly on the maximum molality represented in the data and is typically at least 1 order of magnitude greater than the relative standard errors in the other parameters. This observation is interpreted by examining the contours of the sum of squared residuals in parameter space. Trends in the quality of fit for different classes of electrolytes are also described.

Introduction

The development of activity coefficient models that are applicable to concentrated solutions has attracted much effort since the inadequacies for such systems of the Debye–Hückel theory and its extensions were first identified in the 1930s. Empirical approaches to the thermodynamic description of concentrated electrolytes have focused on the pronounced increase in the activity coefficients and the osmotic coefficients of most concentrated electrolytes with increasing concentration (above about 1 mol·kg^{-1}) and the dependence of the rate of this increase on the identity of the ions present. Davies (1938) accounted for this phenomenon by addition to the Debye–Hückel expression of terms linear in concentration or ionic strength, with coefficients determined empirically for particular electrolytes. Bromley (1973) and Meissner *et al.* (Meissner and Tester, 1972; Meissner and Kusik, 1973, 1979) proposed more general one-parameter models capable of representing the variation of activity coefficients in very concentrated electrolytes (>10 mol·kg^{-1}), where deviations from linearity are often observed.

The main theoretical limitation of the Debye–Hückel treatment is its assumption that only long-range electrostatic interactions contribute to the potential of mean force acting on a given ion. The earliest successful attempts to avoid this limitation are due to Mayer (1950), who showed that nonideal contributions to the osmotic pressure resulting from interactions between groups of two or more ions can be expressed as the terms in a virial series. While this statistical–mechanical approach allows rigorous inclusion of short-range as well as long-range interaction energies, its basic limitation is the implicit neglect of many-body correlation effects on the structure of the fluid. Thus, the positions of any two particles are correlated both directly (through the intermolecular potential) and indirectly (through the positions of other particles). These correlations are expressed by integral equations resulting from an assumed relation between the pair- and triplet-correlation functions (Lee, 1988; March and Tosi, 1976; Watts and McGee, 1976). Analytical solution of these integral equations is possible only for very simple models of the intermolecular interactions.

Pitzer (1973, 1975, 1990) and his collaborators (Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974) developed a treatment that is intermediate between the extremes represented by these empirical and theoretical approaches. The Gibbs energy of the solution is expanded in terms of the mole numbers of the components, but the coefficients in this expansion are represented as empirical functions of ionic strength. This model postulates empirical expressions for the second and third virial coefficients characterizing all the possible binary interactions between anions and cations, binary interactions between ions of the same sign but different charge numbers, and interactions between various possible groups of three ions. The parameters involved in these empirical functions are obtained from osmotic or activity coefficient data for aqueous solutions of single electrolytes and mixtures of two electrolytes with a common ion.

The Pitzer model has been widely used by chemical engineers (Zemaitis, 1988; Kim and Frederick, 1988a,b; see also Königsberger *et al.*, 1992) and geochemists (Harvie and Weare, 1980; Harvie *et al.*, 1984) concerned with predicting phase and reaction equilibria involving concentrated electrolyte solutions. The usefulness of such predictions is ultimately dependent on the accuracy with which the different possible binary and ternary ionic interactions have been characterized. The characterization of these interactions depends in turn on the availability of good quality experimental data for the relevant electrolytes and electrolyte mixtures over an appropriate concentration range and the reliable estimation of the model-dependent parameters by least-squares analysis of such data. The most comprehensive and recent tabulation of Pitzer parameters was published by Kim and Frederick (1988a,b).

In published tabulations of Pitzer parameters, the quality of the data fit is generally expressed in terms of the sum of squared residuals or the corresponding standard deviation. The standard errors in and the correlations between the least-squares parameter estimates are generally not considered. Since neither the sum of squared residuals nor the corresponding standard deviation reveals the existence of nonrandom trends in the residuals, it is impossible to deduce from the values of these quantities

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whether the Pitzer equation provides an inherently good representation of the data. Zemaitis *et al.* (1986) gave plots of activity coefficient data with Pitzer predictions for several of the more common inorganic electrolytes, but the discussion presented in that monograph was limited in scope and focused primarily on the comparison between the Pitzer model and other empirical correlations. No other systematic examination of the qualitative agreement of the model with experiment for different classes of electrolytes appears to have been made. Such an examination is highly desirable in view of the current popularity of the Pitzer model.

Our current studies of the thermodynamic properties of concentrated electrolytes have shown that for many 1:1 electrolytes the use of Pitzer parameters tabulated by Kim and Frederick (1988a) results in osmotic coefficient predictions that are seriously in error. These errors do not appear to have been recognized in subsequent citations. In this paper, tables of Pitzer parameters generated by our own least-squares analysis of published osmotic coefficient data are presented. The quality of the resulting fits is compared with those obtained by use of tabulated parameters and discussed in relation to the standard errors in and the correlations between the parameter estimates. These considerations lead to the identification of certain inherent difficulties in applying the Pitzer equation to osmotic coefficient data. Finally, the trends in residuals that become evident when the Pitzer equation is applied to various homologous series of electrolytes are described.

Summary of Basic Equations

In this section we summarize briefly the equations that form the basis of the present work. Our discussion here is necessarily brief, and for more detailed information, we refer the reader to the recent review by Pitzer (1990).

The Pitzer model assumes that the excess Gibbs energy of the solution (containing w_w kg of solvent) can be represented in terms of solute molalities m by

$$\frac{\Delta G^{\mathrm{E}}}{RT} = w_{\mathrm{w}}[f(I) + \sum_i\sum_j \lambda_{ij}(I) m_i m_j + \sum_i\sum_j\sum_k \mu_{ijk} m_i m_j m_k] \tag{1}$$

where $f(I)$ is a Debye–Hückel-type function, depending only on ionic strength, $\lambda_{ij}(I)$ is the ionic strength-dependent second virial coefficient between species i and j, and μ_{ijk} is the ionic strength-independent third virial coefficient between species i,j, and k. On carrying out the appropriate differentiations of eq 1 with respect to the molalities, complicated general expressions for the ionic activity coefficients and the osmotic coefficient result. For a solution of a single electrolyte $(\mathrm{M}^{z\mathrm{M}+})_{\nu\mathrm{M}}(\mathrm{X}^{z\mathrm{X}-})_{\nu\mathrm{X}}$ of molality m, appropriate combination of the ionic activity coefficients results in the following much simpler expressions for the mean activity coefficient:

$$\ln \gamma_{\mathrm{MX}} = -|z_{\mathrm{M}} z_{\mathrm{X}}| A_\phi \left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I})\right] + 4m\left(\frac{\nu_{\mathrm{M}}\nu_{\mathrm{X}}}{\nu}\right)\left(B_{\mathrm{MX}} + \frac{I}{2}B'_{\mathrm{MX}}\right) + 6m^2\left(\frac{\nu_{\mathrm{M}}\nu_{\mathrm{X}}}{\nu}\right)\nu_{\mathrm{M}} z_{\mathrm{M}} C_{\mathrm{MX}} \tag{2}$$

and the osmotic coefficient

$$\phi = 1 + \frac{2}{m_{\mathrm{X}} + m_{\mathrm{M}}}\left[-\frac{A_\phi I^{3/2}}{1 + b\sqrt{I}} + m_{\mathrm{M}} m_{\mathrm{X}}(B^\phi_{\mathrm{MX}} + ZC_{\mathrm{MX}})\right] \tag{3}$$

In these equations, A_ϕ is the Debye–Hückel constant for the osmotic coefficient on the natural logarithmic basis which is related the the usual Debye–Hückel constant A by

$$A_\phi = \frac{A \ln 10}{3}$$

The functions B_{MX}, B'_{MX}, and B^ϕ_{MX} are ionic strength-dependent virial coefficients defined by

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha_1^2 I}[1 - (1 + \alpha_1\sqrt{I}) \exp(-\alpha_1\sqrt{I})] + \frac{2\beta^{(2)}_{\mathrm{MX}}}{\alpha_2^2 I}[1 - (1 - \alpha_2\sqrt{I}) \exp(-\alpha_2\sqrt{I})] \tag{4}$$

$$B'_{\mathrm{MX}} = \frac{2\beta^{(1)}_{\mathrm{MX}}}{\alpha_1^2 I^2}\left[-1 + \left(1 + \alpha_1\sqrt{I} + \frac{\alpha_1^2 I}{2}\right)\exp(-\alpha_1\sqrt{I})\right] + \frac{2\beta^{(2)}_{\mathrm{MX}}}{\alpha_2^2 I^2}\left[-1 + \left(1 + \alpha_2\sqrt{I} + \frac{\alpha_2^2 I}{2}\right)\exp(-\alpha_2\sqrt{I})\right] \tag{5}$$

and

$$B^\phi_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}} \exp(-\alpha_1\sqrt{I}) + \beta^{(2)}_{\mathrm{MX}} \exp(-\alpha_2\sqrt{I}) \tag{6}$$

$b = 1.2$, and

$$Z = \sum_i m_i |z_i|$$

For the 1:1 electrolytes considered in the present paper, $\alpha_1 = 2$ and $\alpha_2 = \beta^{(2)}_{\mathrm{MX}} = 0$, so that the second lines of eqs 4 and 5 and the third term of eq 6 vanish identically. Our main concern is the evaluation of the adjustable parameters $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$ and C^ϕ_{MX} from the osmotic coefficient data. C^ϕ_{MX} is related to the constant C_{MX} appearing in eqs 2 and 3 by

$$C_{\mathrm{MX}} = \frac{C^\phi_{\mathrm{MX}}}{2\sqrt{z_{\mathrm{M}} z_{\mathrm{X}}}}$$

The subscript MX is used to emphasize the specificity of the constants to a particular anion–cation pair. With this specificity understood, we henceforth omit this subscript to simplify the notation.

Description of Least-Squares Calculations

It is difficult to assess the reliability of published values for the Pitzer interaction parameters because details of the least-squares calculations used to produce them are not given. Because the effects that we describe later arise from the mathematical basis of the least-squares calculations as well as the analytical characteristics of Pitzer's equation, we summarize here the most important aspects of the method used in the present work. The general reference used in the construction of computer programs was the monograph by Bates and Watts (1988).

The Pitzer model has the advantage of being linear with respect to the binary (and ternary) interaction parameters. This means that the partial derivative of the function $f(x_i,\mathbf{p})$ (which represents either the activity coefficient given by eq 2 or the osmotic coefficient given by eq 3) with respect to each component of the parameter vector $\mathbf{p}$ (in this case $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ) at each design point x_i (electrolyte molality m) does not depend on any of the parameters. The least-squares estimates of the parameters are therefore defined by the so-called normal equations

$$(\mathbf{X}_0^{\mathrm{T}}\mathbf{X}_0)\hat{\mathbf{p}} = \mathbf{X}_0^{\mathrm{T}}\mathbf{r}_0 \tag{7}$$

which can be solved explicitly:

$$\hat{\mathbf{p}} = (\mathbf{X}_0^{\mathrm{T}}\mathbf{X}_0)^{-1}\mathbf{X}_0^{\mathrm{T}}\mathbf{r}_0 \tag{8}$$

where $\mathbf{X}_0$ is an $N \times P$ matrix in which the i,jth element is the partial derivative of the function with the respect to the jth parameter, evaluated at the ith design point x_i, and $\mathbf{r}_0$ is the N-dimensional vector of residuals. To avoid the numerical difficulties that frequently arise in the inversion of the coefficient matrix, the matrix $\mathbf{X}_0$ is factorized in the form:

$$\mathbf{X}_0 = \mathbf{QR} \tag{9}$$

where $\mathbf{Q}$ is an $N \times N$ orthogonal matrix and $\mathbf{R}$ is an $N \times P$ matrix in which the first P rows form an upper triangular matrix and the remaining elements are zero. The overall quality of the fit can be expressed as the value of the sum of the squared residuals:

$$S(\hat{\mathbf{p}}) \equiv \sum_{i=1}^{N}[y_i - f(x_i,\hat{\mathbf{p}})]^2 \tag{10}$$

or the corresponding standard deviation

$$s = \sqrt{\frac{S(\hat{\mathbf{p}})}{N-P}} \tag{11}$$

The standard errors in each of the parameters may be expressed in terms of s:

$$\sigma(p_i) = s\sqrt{(\mathbf{X}_0^{\mathrm{T}}\mathbf{X}_0)_{ii}^{-1}} \tag{12}$$

where $(\mathbf{X}_0^{\mathrm{T}}\mathbf{X}_0)_{ii}^{-1}$ is the diagonal matrix element of the coefficient matrix. Multiplication of these standard errors by the appropriate critical value of $t(N - P;\ \alpha)$ in turn provides $100(1 - 2\alpha)\%$ confidence intervals. Thus, a value of $\alpha = 0.025$ corresponds to a 95% confidence interval.

Results

We carried out least-squares analysis of osmotic coefficient data for 93 1:1 electrolytes according to the Pitzer equation. These results are shown in Table 1. In addition to estimates of the Pitzer parameters, the output produced included the corresponding standard errors, the confidence intervals, and the parameter correlation matrix. Plots of tabulated (Hamer and Wu, 1972; Staples, 1981) and experimental (Bonner, 1976, 1979, 1982; Macaskill *et al.*, 1977; Platford, 1969) osmotic coefficient data and corresponding values calculated from eqs 3−6 were also constructed for each data set, so as to reveal any systematic trends in the residuals.

It was of particular interest to us to compare the fits of osmotic coefficient data obtained with the Pitzer parameters obtained in the present work with those obtained from the comprehensive tabulation of parameters by Kim and Frederick. This comparison can be achieved by examining the sum of squared residuals obtained with the least-squares estimates and with the published values of the parameters. Assuming that the sum of squared residuals for a data set containing N points obeys the χ^2 distribution with $N - P$ degrees of freedom, where P is the number of optimized parameters, the statistical significance of any difference in the sum of squared residuals can be expressed as the F distribution probability $p(F,N - P,N - P)$, where

$$F = \frac{S(\hat{\mathbf{p}})_{\mathrm{KF}}}{S(\hat{\mathbf{p}})} \tag{13}$$

Very small values of p correspond to very much poorer fits of the data with the published parameters, and when the numerator and denominator in the right-hand member of eq 13 are equal, this probability is equal to 0.5. The use of the F distribution in this way provides a method of comparing the quality of fits obtained from data sets of different sizes.

In considering quantitative tests of this kind, it should be noted that the assumption of a χ^2 distribution for the sum of squared residuals implies that the errors in the experimental data are completely random and distributed with a uniform variance. To assess the validity of this assumption, it is necessary to carry out a detailed error analysis of the procedure by which the osmotic coefficient data were obtained. Most of the data considered here were obtained by isopiestic equilibration. Since it is not clear whether the errors in this technique propagate randomly or nonrandomly, such an error analysis would have to be carried out by Monte Carlo analysis. This is beyond the scope of the present paper.

Errors in the experimental data increase the sum of squared residuals and the standard errors in the parameter estimates. To compensate for these effects, the experimental data are sometimes weighted so as to reduce the effect of less precise experimental data on the fit. In Pitzer's (1990) determination of the parameters, the experimental osmotic coefficient data "were weighted equally up to an ionic strength of 4 mol kg^{-1}, and then as $(4/I)^2$", where I is the molal ionic strength. No theoretical justification for this weighting scheme is given. The selection of an appropriate weighting scheme thus requires knowledge of the error distribution and the details of experimental and data analysis procedures. In this connection it is also worth noting that errors in most of the experimental data used in the present paper were reduced by smoothing and averaging results from various sources (Hamer and Wu, 1972). For this reason, and in view of the above observations about the lack of knowledge of error distributions, the data used in our calculations were weighted equally. It should, of course, be remembered that if appropriately weighted experimental (as distinct from smoothed) data were to be used, the values of the Pitzer parameters would be expected to be different.

The results of our calculations are summarized in Table 1. With the above reservations in mind, these results show that for all electrolytes considered the published Pitzer parameters give a poorer representation of the osmotic coefficient data than those obtained in the present work. An example of this is seen in Figure 1, where osmotic coefficient data for a selection of electrolytes are shown with the Pitzer model predictions using parameters from our work and those tabulated by Kim and Frederick. For each of these examples, the F statistic given by eq 13 is at least 20 and the corresponding probability is vanishingly small.

The nature and extent of the discrepancy between our values of the Pitzer parameters and the tabulated values depend on the molality range of the data. When the maximum molality is large (about 6 mol·kg^{-1} or more), values of $\beta^{(0)}$ and C^{ϕ} compare quite well with tabulated values, but $\beta^{(1)}$ is often very different and has much larger standard errors than the other parameters. On the other hand, for smaller maximum molalities, the standard errors in C^{ϕ} can become large, even though the overall quality of the fit (as expressed by the sum of squared residuals) might

Table 1. Pitzer Ion-Interaction Parameters (*cf.* Eqs 3–5) for 1:1 Electrolytes at 25 °C[a]

formula	N	$\beta^{(0)}$	t/s	$\beta^{(1)}$	t/s	C^{ϕ}	t/s	max m	SSR	SSR(KF)	ratio (F)	p	data ref
HBr	34	0.24449	0.01014	−0.00077	0.15254	−0.0011	0.00113	11	2.3126×10^{-2}	3.6960×10^{-2}	1.5982	0.0987	HW
HCl	39	0.20488	0.00295	0.07662	0.06631	−0.00377	0.00023	16	6.7951×10^{-3}	1.1981×10^{-2}	1.7631	0.044633	HW
$HClO_4$	39	0.21879	0.00729	−0.07103	0.16394	0.00184	0.00057	16	4.1539×10^{-2}	5.6223×10^{-2}	1.3535	0.184033	HW
HF	45	−0.02492	0.02143	−2.55098	0.62637	0.00125	0.00134	20	8.1173×10^{-1}	6.4757	7.9777	0	HW
HI	33	0.24076	0.00632	0.35159	0.0861	0.00138	0.00077	10	6.5144×10^{-3}	8.6146×10^{-3}	1.3224	0.224304	HW
HNO_3	51	0.09028	0.00246	0.62777	0.11097	−0.00238	0.00011	28	3.3572×10^{-2}	4.8976×10^{-2}	1.4588	0.097232	HW
LiBr	43	0.24533	0.01356	−0.45398	0.3966	−0.00292	0.00085	20	3.0895×10^{-1}	3.0903×10^{-1}	1.0003	0.499624	HW
$LiBrO_3$	21	0.0888	0.00152	0.24294	0.01068	0.00011	0.00033	5	2.0676×10^{-5}	2.0241×10^{-4}	9.7896	0.000006	B2
LiCl	43	0.21281	0.0008	−0.26973	0.22918	−0.00451	0.00051	19.217	1.0219×10^{-1}	1.0751×10^{-1}	1.052	0.436717	HW
$LiClO_3$	20	0.17037	0.00334	0.23115	0.02085	−0.00521	0.00081	4.2	5.4825×10^{-5}	5.5083×10^{-5}	1.0047	0.4962	B2
$LiClO_4$	26	0.2023	0.00328	0.37299	0.02123	−0.00068	0.00077	4.5	9.0890×10^{-5}	5.8537×10^{-4}	6.4404	0.000016	HW
LiI	23	0.15543	0.00678	0.61801	0.03293	0.01827	0.0022	3	8.8761×10^{-5}	2.4214×10^{-3}	27.2799	0	HW
$LiNO_2$	47	0.12122	0.00177	0.43711	0.05576	−0.00382	0.00011	19.9	5.1705×10^{-3}	5.3498×10^{-3}	1.0347	0.455216	S
$LiNO_3$	43	0.12955	0.00093	0.37829	0.02728	−0.0038	0.00006	20	1.4616×10^{-3}	2.8664×10^{-2}	19.6115	0	HW
LiOH	26	0.0517	0.00631	−0.11226	0.044	−0.00365	0.00138	5	4.6959×10^{-4}	8.3294×10^{-4}	1.7738	0.088441	HW
Li acetate	25	0.11067	0.00268	0.23436	0.01592	−0.00476	0.00069	4	3.9329×10^{-5}	2.0295×10^{-4}	5.1603	0.000147	HW
LiOTs	26	0.01377	0.00494	0.41659	0.03196	0.00585	0.00116	4.5	2.0594×10^{-4}	2.7787×10^{-4}	1.3492	0.23912	HW
$NaBF_4$	14	0.36819	0.20899	−2.03245	0.58949	−0.22149	0.12928	1.2	1.5945×10^{-3}	1.0245×10^{-1}	64.2521	0	P
$NaBO_2$	9	1.31267	0.62345	−4.41694	1.35005	−0.75145	0.56237	0.7	7.9111×10^{-4}	4.2023×10^{-2}	53.119	0.000061	P
NaBr	32	0.11124	0.00225	0.1879	0.02739	−0.00151	0.0003	9	5.6984×10^{-4}	1.6430×10^{-3}	2.8832	0.002845	HW
$NaBrO_3$	23	−0.02348	0.0034	0.20169	0.01528	0.00699	0.00119	2.617	1.4863×10^{-5}	3.4052×10^{-5}	2.2911	0.035472	HW
NaCl	30	0.0771	0.00065	0.26393	0.00556	0.0011	0.00011	6.144	1.3226×10^{-5}	5.4801×10^{-5}	4.1436	0.000214	HW
$NaClO_3$	23	0.01844	0.00112	0.28633	0.00542	0.002	0.00036	3	2.4086×10^{-6}	6.3411×10^{-6}	2.6327	0.01793	HW
$NaClO_4$	29	0.05437	0.00093	0.28042	0.00765	−0.00099	0.00017	6	2.2396×10^{-5}	6.872	306838	0	HW
NaCNS	38	0.12424	0.00481	0.11564	0.12394	−0.00384	0.00033	18	2.7003×10^{-2}	2.7628×10^{-2}	1.0231	0.473261	HW
NaF	17	0.02865	0.00742	0.20206	0.01918	−0.00695	0.00513	1	1.4912×10^{-6}	4.5678×10^{-6}	3.0631	0.022336	HW
NaH_2AsO_4	19	−0.09354	0.00723	0.42289	0.02131	0.02975	0.00423	1.3	4.2224×10^{-6}	9.1989×10^{-5}	21.7861	0	HW
NaH_2PO_4	30	−0.04779	0.00385	0.00173	0.03408	0.00681	0.00066	6.5	5.2871×10^{-4}	2.4986×10^{-3}	4.7258	0.000066	HW
NaI	35	0.13513	0.0028	0.22898	0.0461	−0.00118	0.00029	12	2.3514×10^{-4}	2.9497×10^{-3}	12.5447	0	HW
$NaNO_2$	40	0.0477	0.00226	0.19908	0.03742	−0.00226	0.00021	12.34	1.5667×10^{-3}	1.7603×10^{-3}	1.1236	0.362438	S
$NaNO_3$	34	−0.04876	0.01368	0.57127	0.20369	0.0089	0.00153	10.83	4.0807×10^{-2}	5.3210×10^{-1}	13.0394	0	HW
NaOH	52	0.16407	0.00729	−0.57361	0.34443	−0.00326	0.00032	29	3.3393×10^{-1}	5.2111×10^{-1}	1.5605	0.061378	HW
Na formate	24	0.072	0.00138	0.3185	0.00746	−0.00242	0.0004	3.5	6.4431×10^{-6}	1.6166×10^{-4}	25.0904	0	HW
Na acetate	24	0.13732	0.00213	0.33894	0.0115	−0.00478	0.00061	3.5	1.5298×10^{-5}	1.7324×10^{-5}	1.1324	0.389187	HW
Na propion	23	0.18681	0.00184	0.28358	0.00896	−0.01246	0.0006	3	6.5775×10^{-6}	3.5264×10^{-5}	5.3613	0.000214	HW
Na butyrate	24	0.26024	0.00817	0.17151	0.04415	−0.03341	0.00234	3.5	2.2541×10^{-4}	2.3206×10^{-4}	1.0295	0.473757	HW
Na valerate	24	0.34904	0.01344	−0.07933	0.07258	−0.08285	0.00385	3.5	6.0909×10^{-4}	6.1133×10^{-3}	10.0368	0	HW
Na caproate	26	−0.01392	0.06528	1.52415	0.42206	−0.00487	0.01526	4.5	3.5926×10^{-2}				HW
Na heptylate	27	−0.33716	0.0537	2.18099	0.37708	0.05484	0.01153	5	3.6304×10^{-2}				HW
Na caprylate	14	−0.74671	0.21573	2.50058	1.10712	0.18532	0.06798	3	3.1834×10^{-2}	19.1479	598.3508	0	HW
Na pelargon	14	−0.49686	0.30135	−0.73939	1.33435	0.13821	0.11037	2.5	3.5487×10^{-2}	12.598	355.0032	0	HW
Na caprate	11	−0.26799	0.13452	−2.99979	0.50821	0.09214	0.05958	1.8	8.7960×10^{-4}	1.7586	1999.318	0	HW
Na Hmalon	27	0.02148	0.0071	0.1814	0.005	−0.00085	0.00015	5	6.3912×10^{-6}	4.4589×10^{-5}	6.9766	0.000005	HW
Na Hsucc	27	0.03403	0.00269	0.16406	0.01889	0.00079	0.00058	5	9.1113×10^{-5}	1.0864×10^{-4}	1.1924	0.334946	HW
Na Hadip	13	0.04905	0.01627	0.31675	0.03508	−0.00358	0.01476	0.7	1.1790×10^{-6}	1.5866×10^{-6}	1.3457	0.323808	HW
KBr	28	0.05575	0.00051	0.22877	0.00386	−0.00157	0.0001	5.5	4.7108×10^{-6}	1.8595×10^{-5}	3.9473	0.000521	HW
$KBrO_3$	11	−0.14316	0.02141	0.27926	0.04032	0.02638	0.02451	0.5	4.6041×10^{-7}	1.0315×10^{-5}	22.4039	0.000105	HW
KCl	28	0.04654	0.00046	0.2209	0.00328	−0.00043	0.0001	5	2.9558×10^{-6}	5.7638×10^{-6}	1.95	0.050697	HW
$KClO_3$	13	−0.09779	0.01246	0.25187	0.02687	0.00417	0.0113	0.7	6.9166×10^{-7}	2.0228×10^{-6}	2.9246	0.052764	HW
KCNS	27	0.03911	0.00089	0.24213	0.00622	−0.00199	0.00019	5	9.8671×10^{-6}	4.2953×10^{-5}	4.3532	0.000309	HW
KF	41	0.10038	0.0036	0.02121	0.09137	−0.00161	0.00025	17.5	1.4550×10^{-2}	1.5783×10^{-2}	1.0847	0.401713	HW
KH_2AsO_4	18	−0.13257	0.0053	0.28376	0.01563	0.04336	0.00309	1.3	2.0872×10^{-6}	1.6350×10^{-5}	7.8335	0.000135	HW
KH_2PO_4	20	−0.11253	0.00214	0.05836	0.00753	0.01999	0.001	1.8	1.1933×10^{-6}	6.4923×10^{-6}	5.4406	0.000546	HW
KI	26	0.07265	0.00092	0.27117	0.00598	−0.00386	0.00022	4.5	7.2135×10^{-6}	1.6455×10^{-5}	2.2811	0.026823	HW

KNO_2	62	0.00358	0.0097	0.13814	0.06855	−0.00026	0.00004	34.12	1.1940×10^{-2}	1.2065×10^{-2}	1.0105	0.484067	S
KNO_3	24	−0.08442	0.00124	0.09174	0.00669	0.0075	0.00035	3.5	5.1762×10^{-6}	3.3059×10^{-5}	6.3867	0.000039	HW
KOH	43	0.17474	0.00383	−0.03152	0.11192	−0.00267	0.00024	20	2.4601×10^{-2}	2.4843×10^{-2}	1.0098	0.487776	HW
K acetate	24	0.15343	0.00204	0.34323	0.01102	−0.00452	0.00058	3.5	1.4036×10^{-5}	3.6497×10^{-5}	2.6002	0.016796	HW
K Hmalon	27	−0.00626	0.00422	0.12427	0.02966	0.00094	0.00091	5	2.2459×10^{-4}	2.5163×10^{-4}	1.1204	0.391461	HW
K Hsucc	26	0.01164	0.00396	0.15241	0.02559	0.00257	0.00093	4.5	1.3210×10^{-4}	1.3524×10^{-4}	1.0238	0.477754	HW
K Hadip	16	−0.01705	0.01892	0.39026	0.04829	0.04098	0.01335	1	8.2415×10^{-6}	5.1584×10^{-5}	6.259	0.001126	HW
KPF_6	11	−0.34306	0.02479	0.06105	0.04668	0.20298	0.02838	0.5	6.1709×10^{-7}	2.6402×10^{-4}	427.8468	0	HW
KOTs	24	−0.09725	0.00463	0.45032	0.02499	0.01145	0.00132	3.5	7.2230×10^{-5}	1.1237×10^{-4}	1.5557	0.159474	HW
RbBr	27	0.03875	0.00065	0.16114	0.00454	−0.00127	0.00014	5	5.2511×10^{-6}	1.6239×10^{-5}	3.0924	0.003798	HW
RbCl	32	0.04661	0.00074	0.13809	0.00805	−0.00162	0.00011	7.8	4.2524×10^{-5}	6.8038×10^{-5}	1.6	0.105831	HW
RbF	24	0.11413	0.00548	0.28568	0.02959	−0.0105	0.00157	3.5	1.0128×10^{-4}	2.1015×10^{-3}	20.7494	0	HW
RbI	27	0.03918	0.00059	0.14254	0.00415	−0.00101	0.00013	5	4.3999×10^{-6}	2.9521×10^{-5}	6.7094	0.000008	HW
$RbNO_2$	90	−0.00232	0.00055	0.17519	0.09382	−0.00002	0.00001	62.3	3.4850×10^{-2}	3.5686	102.3988	0	S
$RbNO_3$	26	−0.0836	0.0031	0.00448	0.02036	0.0068	0.00072	4.6	8.6775×10^{-5}	3.2162×10^{-4}	3.7064	0.001319	HW
Rb acetate	24	0.16295	0.00141	0.32815	0.00761	−0.00561	0.0004	3.5	6.6989×10^{-6}	7.0644×10^{-6}	1.0546	0.452098	HW
$AgNO_3$	38	−0.06701	0.00231	−0.12535	0.04843	0.00286	0.00019	15	3.3720×10^{-3}	6.8919×10^{-3}	2.0439	0.018856	HW
CsBr	27	0.02267	0.00187	0.06223	0.01311	0.00104	0.0004	5	4.3899×10^{-5}	1.0116×10^{-4}	2.3044	0.022982	HW
CsCl	34	0.03679	0.00129	0.01536	0.01944	−0.00097	0.00014	11	$3.7557 \times\times 10^{-4}$	7.1342×10^{-4}	1.8996	0.039444	HW
CsF	24	0.13062	0.00538	0.25737	0.02906	−0.00488	0.00154	3.5	9.7651×10^{-5}	2.1421×10^{-3}	21.9363	0	HW
CsI	23	0.02173	0.00127	0.06481	0.00619	−0.00326	0.00041	3	3.1315×10^{-6}	1.2363×10^{-5}	3.9479	0.001718	HW
$CsNO_2$	63	0.00929	0.00115	0.33195	0.0857	−0.00036	0.00004	36	1.9072×10^{-2}	1.9154×10^{-2}	1.0043	0.493388	S
$CsNO_3$	19	−0.13671	0.00683	0.11632	0.02184	0.03335	0.00358	1.5	6.2073×10^{-6}	3.5265×10^{-5}	5.6812	0.0006	HW
CsOH	17	0.1315	0.00902	0.41789	0.02528	0.00067	0.00565	1.2	4.0519×10^{-6}	8.9493×10^{-5}	22.0867	0	HW
TlCl	4	−2.2752	2.6183	1.3149	3.1451	–	–	0.01	9.4894×10^{-8}	1.1379×10^{-6}	11.9913	0.076974	HW
$TlClO_4$	11	−0.10774	0.00495	0.05739	0.01673	–	–	0.5	1.1379×10^{-6}	3.8362×10^{-6}	3.3713	0.042343	HW
$TlNO_2$	18	−0.65054	0.00325	−0.11092	0.00994	0.37788	0.00182	1.4	1.0009×10^{-6}	1.1836×10^{-6}	1.1825	0.374836	HW
$TlNO_3$	10	−0.13196	0.00783	−0.27007	0.0235	–	–	0.4	1.1300×10^{-6}	6.1155×10^{-6}	5.4119	0.013919	HW
Tl acetate	29	0.00827	0.00254	0.01176	0.02089	−0.00132	0.00047	6	1.6713×10^{-4}	9.8526×10^{-4}	5.8952	0.000012	HW
NH_4Cl	31	0.05192	0.00067	0.19346	0.00675	−0.00298	0.0001	7.405	2.6539×10^{-5}	1.0000×10^{-4}	3.768	0.000385	HW
NH_4ClO_4	22	−0.00536	0.00172	−0.06945	0.00669	−0.00136	0.00071	2.1	1.5804×10^{-6}	1.3945×10^{-5}	8.8237	0	HW
NH_4I	29	0.05677	0.00113	0.28956	0.01234	−0.0031	0.00017	7.5	8.2999×10^{-5}	4.1992×10^{-4}	5.0593	0.000048	B1
NH_4NO_3	49	−0.01555	0.00055	0.84858	0.02257	0.00031	0.00003	25.954	1.2954×10^{-3}	3.5690×10^{-3}	2.7551	0.000405	HW
Me··ClO_4	19	−0.0338	0.00338	0.00634	0.02011	0.00346	0.00087	4	4.2531×10^{-5}	4.2574×10^{-5}	1.001	0.499215	B3
Me_2··ClO_4	26	−0.04358	0.00107	−0.12065	0.01098	0.00244	0.00016	7.5	5.6722×10^{-5}	1.1317×10^{-3}	19.9517	0	B3
Me_3··ClO_4	14	−0.12037	0.01989	−0.128	0.07037	0.016	0.00921	1.8	5.6625×10^{-5}	1.5248×10^{-4}	2.6928	0.057578	B3
Me_4NNO_3	28	0.01273	0.00212	−0.22354	0.02165	0.00106	0.00035	7	2.2288×10^{-4}	5.1262×10^{-3}	22.9998	0	B1
Et_4NNO_3	30	−0.03882	0.00457	−0.72566	0.05296	0.00573	0.00066	8	1.7384×10^{-3}	1.2320×10^{-2}	7.087	0.000001	B1
CN_3H_6Cl	29	−0.0262	0.00242	0.02747	0.03997	0.0017	0.00025	12	1.3989×10^{-3}	1.1496×10^{-2}	8.2179	0	MRB

[a] N, number of data points; t, $t(N-3, 0.025)$ or $t(N-2, 0.025)$; max m, maximum molality in data set; SSR, sum of squared residuals, minimum value; SSR(KF), sum of squared residuals, value obtained using parameters from Kim and Frederick (1988); ratio, SSR(KF)/SSR = F; p, $p(F,N-3,N-3)$ (or $p(F,N-2,N-2)$ if the column for C^ϕ is blank). Abbreviations: formate = $HCOO^-$; acetate = CH_3COO^-; propion = $C_2H_5COO^-$; butyrate = $C_3H_7COO^-$; valerate = $C_4H_9COO^-$; caproate = $C_5H_{11}COO^-$; heptylate = $C_6H_{13}COO^-$; caprylate = $C_7H_{15}COO^-$; pelargon = $C_8H_{17}COO^-$; caprate = $C_9H_{19}COO^-$; Hmalon = $HOOCCH_2COO^-$; Hsucc = $HOOC_2H_4COO^-$; Hadip = $HOOCC_4H_8COO^-$; OTs = p-$CH_3C_6H_4SO_3^-$; Et = C_2H_5; Me = CH_3; Me.. = $CH_3NH_3^+$; Me_2.. = $(CH_3)_2NH_2^+$; Me_3.. = $(CH_3)_3NH^+$; $CN_3H_6^+$ = guanidinium. Literature references for osmotic coefficient data: HW, Hamer and Wu (1972); S, Staples (1981); B1, Bonner (1976); B2, Bonner (1979); B3, Bonner (1982); P, Platford (1969); MRB, Macaskill *et al.* (1977).

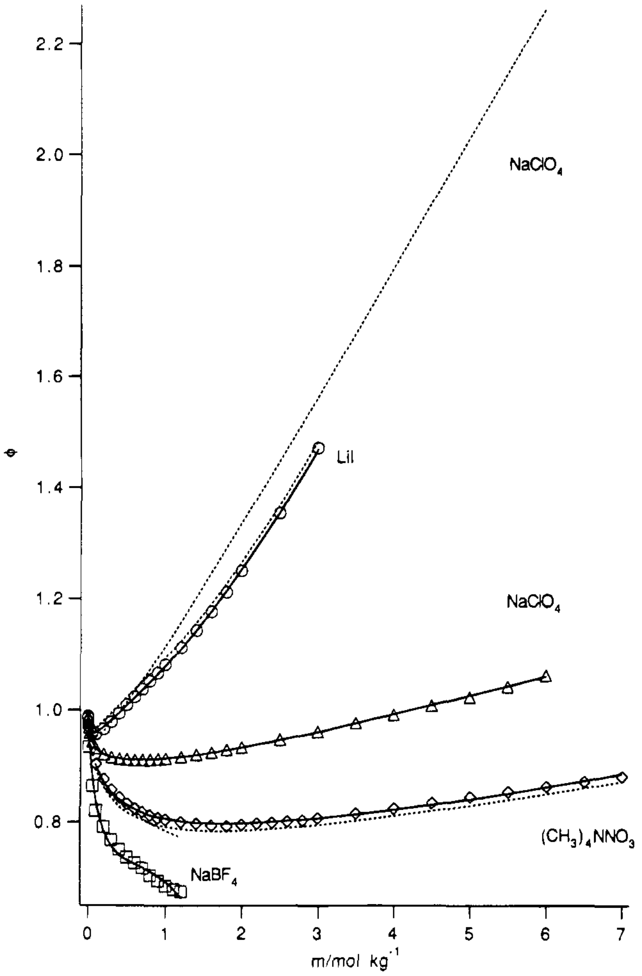

Figure 1. Osmotic coefficient data for a selection of 1:1 electrolytes, with predictions of the Pitzer equation. Solid curves: parameters determined in the present work. Dashed curves: parameters taken from Kim and Frederick (1988a). Data for NaClO$_4$ and LiI from Hamer and Wu (1972), for (CH$_3$)$_4$NNO$_3$ from Bonner (1976), and for NaBF$_4$ from Platford (1969).

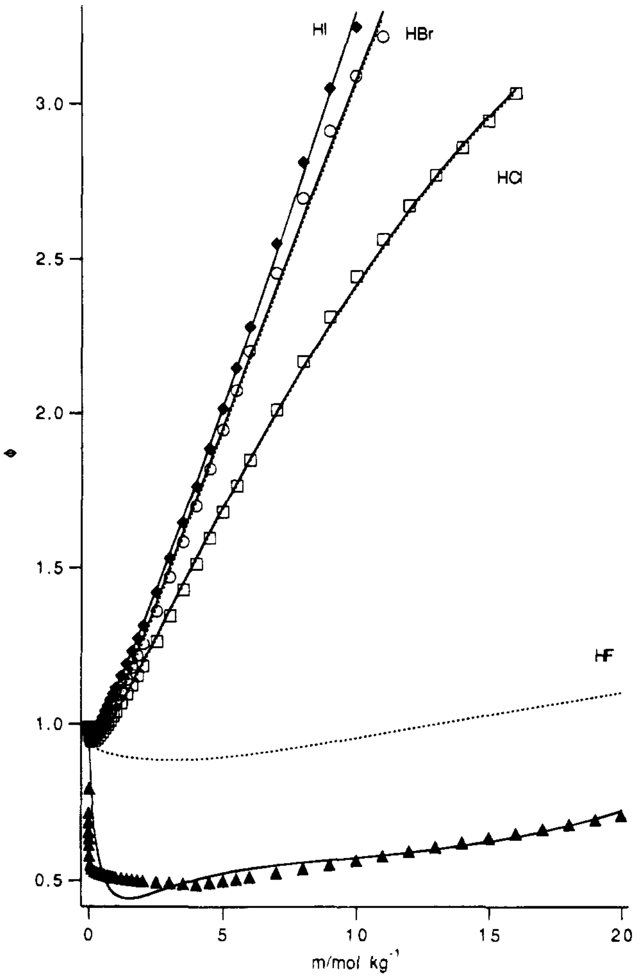

Figure 2. Osmotic coefficient data for hydrohalic acids, with predictions of the Pitzer equation. Solid curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

be very good. These effects can be understood by noting that the partial derivative of the Pitzer expression for ϕ with respect to $\beta^{(1)}$ is proportional to $\exp(-\alpha\sqrt{I})$, which becomes negligible at high m. Only data for $m < 1$ mol/kg are useful for determining this parameter, but in this region, the osmotic coefficient is fairly close to 1. Conversely, in the low-molality region, the exponential term is dominant and accounts for most of the variation in the data (from a physical standpoint, the effect of the third virial coefficient is expected to be small for low concentrations), so that it is difficult to estimate C^{ϕ}.

This behavior is exemplified by HBr osmotic coefficient data, for which we estimated the Pitzer parameters and 95% confidence limits to be $\beta^{(0)} = 0.24449 \pm 0.01014$, $\beta^{(1)} = -0.00077 \pm 0.15254$, and $C^{\phi} = -0.00110 \pm 0.00113$, and Kim and Frederick obtained $\beta^{(0)} = 0.24153$, $\beta^{(1)} = -0.16119$, and $C^{\phi} = -0.00101$ (no standard errors were provided by these authors). The difference between the two predictions is, in this case, relatively small and approximately constant, despite the quite large discrepancy in $\beta^{(1)}$. This difference results in a sum of squares ratio of 1.5982. The two predictions for HBr and the other hydrohalic acids are shown in Figure 2. The difference in the Pitzer predictions of osmotic coefficient is also seen to be approximately constant for the other hydrohalic acids (with the exception of HF) and nitric and perchloric acids (Figure 3).

The dependence of the quality of fit on the values of the parameters can also be investigated by examining the variation of the sum of squared residuals in the vicinity of the minimum in parameter space. In Figure 4, the sum of squared residuals is shown for HBr as a function of $\beta^{(0)}$ and $\beta^{(1)}$, with C^{ϕ} set equal to its least-squares value. The minimum in the function is seen to be defined much less sharply with respect to $\beta^{(1)}$ than with respect to $\beta^{(0)}$. This is consistent with the very much larger standard errors in $\beta^{(1)}$.

In least-squares analysis of data with functions where terms involving one optimized parameter become negligible over a certain region of the data, it is sometimes possible to determine parameters separately by consideration of limiting regions of the data. The extent to which this is possible depends on the correlation between the different parameter estimates. In the specific case of the Pitzer equation, this could involve determination of the third virial coefficient C^{ϕ} from the concentrated solution region, where the exponential term multiplying $\beta^{(1)}$ is negligible, and use of the dilute solution data to obtain $\beta^{(0)}$ and $\beta^{(1)}$. For the specific case of HBr, the parameter intercorrelation matrix is as follows:

	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}
$\beta^{(0)}$	1.000000	−0.689273	−0.968942
$\beta^{(1)}$	−0.689273	1.000000	0.632652
C^{ϕ}	−0.968942	0.632652	1.000000

The parameter estimates for this electrolyte are seen to be quite strongly correlated, especially those of $\beta^{(1)}$ and C^{ϕ}.

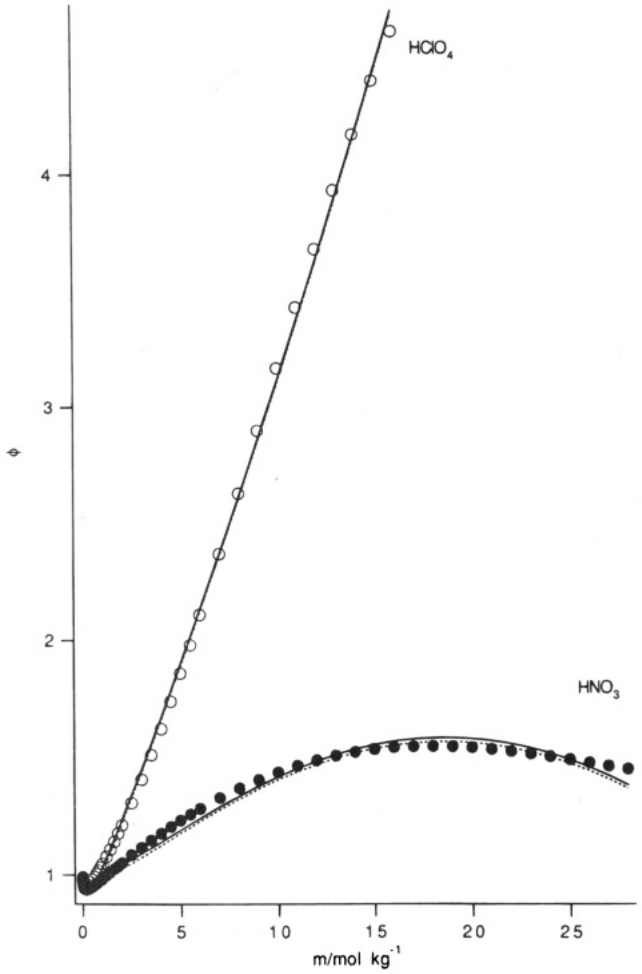

Figure 3. Osmotic coefficient data for 1:1 oxyacids, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Data taken from Hamer and Wu (1972).

This means that it is not possible to change the value of one of these parameters (for example, with the intention of better reproducing the concentrated solution data) without changing the other parameter.

Discussion

The molality range represented in the data was observed to be an important factor in two respects. First, the quality of fit (as expressed by both the sum of squared residuals and the standard errors in the parameters) is best in cases where the experimental data are over a relatively narrow range (up to a maximum molality of 4−6 mol·kg^{-1}). Second, the use of Pitzer parameters derived from fits of osmotic or activity coefficient data for a given electrolyte over a small molality range does not necessarily result in good predictions at higher molality. Thus, the model does not appear to have good extrapolative capacity.

These observations can be interpreted in terms of both the particular analytical form of the Pitzer equation and the underlying physical assumptions. As remarked earlier, the difficulties encountered in obtaining accurate estimates of the $\beta^{(1)}$ parameter result from the exponential variation of the corresponding partial derivative of the function. A further consequence of this is that the variation of the osmotic coefficient with molality is predicted to be asymptotically quadratic. (Since the third virial coefficient is usually small (about 0.001), the contribution of the quadratic term is for some electrolytes insignificant, and the variation of ϕ with molality is effectively linear.) This condition was satisfied for relatively few of the electrolytes examined. From a physical standpoint, this is a direct consequence of the assumption that the ionic third virial coefficient is independent of ionic strength. This assumption is intuitively less reasonable in very concentrated solutions.

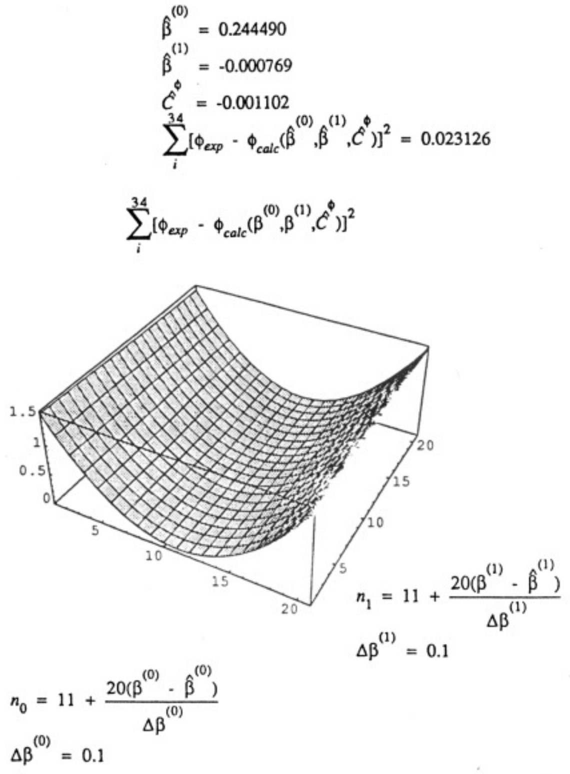

Figure 4. Variation of the sum of squared residuals for a fit of HBr osmotic coefficient data to the Pitzer equation, as a function of Pitzer parameters $\beta^{(0)}$ and $\beta^{(1)}$ (with C^{ϕ} fixed at its least-squares estimate). Data taken from Hamer and Wu (1972).

In view of the importance of the molality range represented in the data, it is difficult to make a general statement regarding the applicability of the Pitzer equation to a particular class of compounds since the maximum molality is generally determined by solubility. Rigorous comparisons of the trends in agreement with the model in homologous series of electrolytes are therefore difficult. Some general remarks can nevertheless be made.

Inorganic Strong Acids (and HF). For perchloric acid and the hydrogen halides (with the exception of HF), the agreement is very good up to maximum molalities of at least 10 mol·kg^{-1} (Figures 2 and 3). There is, however, a slight curvature in the osmotic coefficient data which is imperfectly reproduced by the Pitzer equation. The case of HF is distinguished by the very large discrepancy between the two Pitzer predictions and also by the considerably poorer representation of the data as compared with the strong acids. The Pitzer parameters for this electrolyte cannot be regarded as reflecting the specific interactions between hydrogen and fluoride ions, since no account is taken of the presence of HF molecules and their aggregates. In this respect, the model can be regarded as essentially inapplicable. The agreement for nitric acid is noticeably worse than that of perchloric acid (Figure 3), but the molality range for this electrolyte (up to 28 mol·kg^{-1}) is considerably larger. The least-squares calculation has the effect of transmitting the pronounced deviation occurring in the vicinity of this maximum molality to lower molalities.

Lithium Halides. For lithium bromide and lithium chloride up to about 20 mol·kg^{-1}, the osmotic coefficient (Figure 5) shows a curvature that passes below and above the fitted curve, resulting in fits that are relatively poor

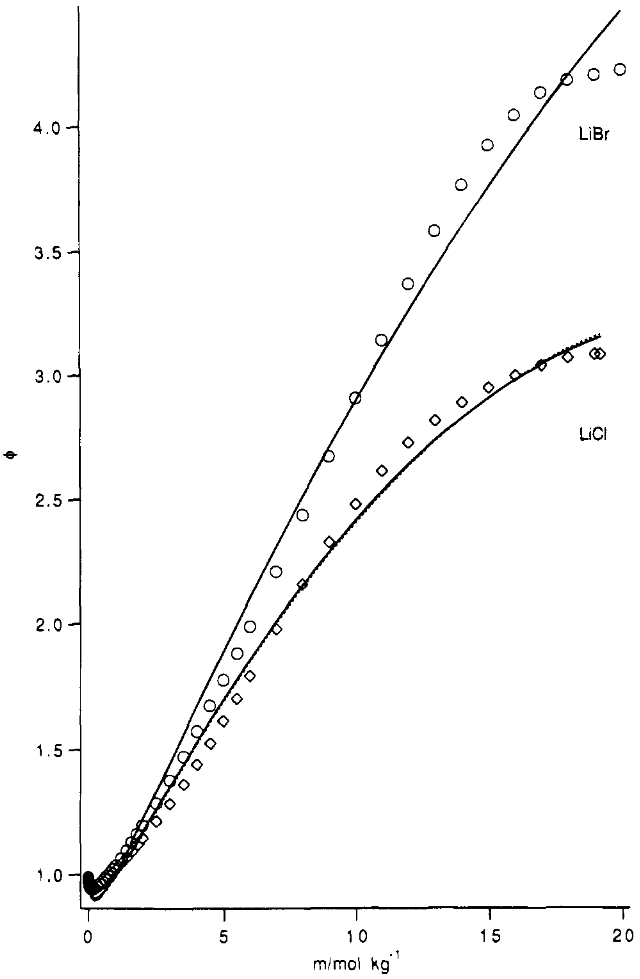

Figure 5. Osmotic coefficient data for lithium halides, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

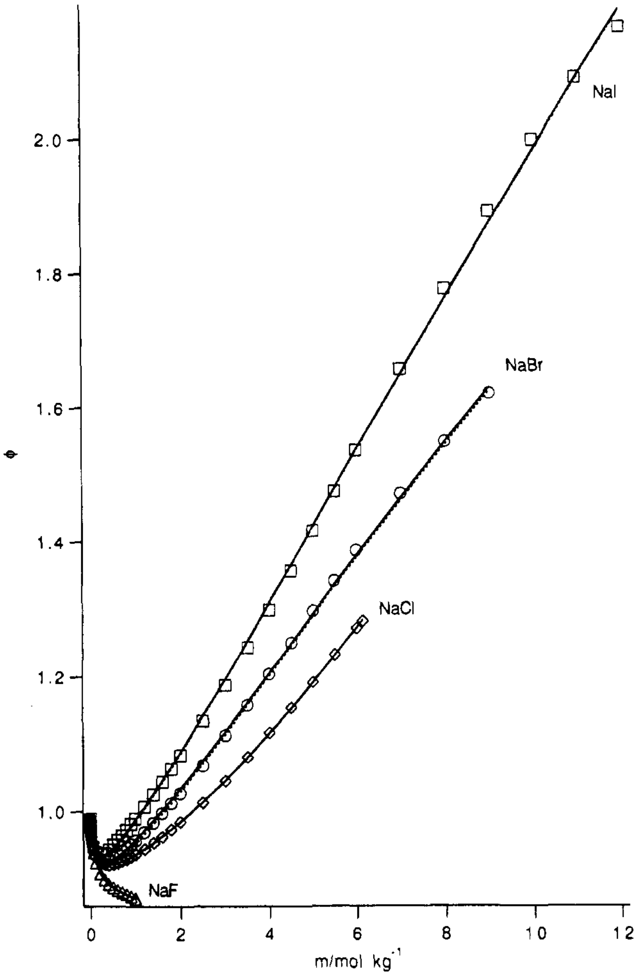

Figure 6. Osmotic coefficient data for sodium halides, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

(the sums of squared residuals are about 0.3 and 0.1, respectively). This curvature is qualitatively similar to that referred to for the hydrogen halides but more pronounced. Lithium bromide was the only electrolyte for which our estimates of the Pitzer parameters were essentially the same as those of Kim and Frederick. For lithium iodide (Figure 1), the use of tabulated parameters gives predicted osmotic coefficient values that are consistently too high by about 0.015.

Other Alkali-Metal Halides. The maximum molalities obtainable for the sodium halides are considerably lower than for the lithium halides (for example, 8 mol·kg^{-1} for NaBr). The fits are generally excellent (sums of squares <0.0001), as seen for the sodium halides (Figure 6). Similar remarks apply to the other alkali-metal salts of strong acids (including *p*-toluenesulfonates) and quaternary ammonium compounds.

Nitrates and Nitrites. The osmotic coefficient data for the alkali-metal nitrates (Figure 7) follow quite different qualitative trends from those observed for the alkali-metal halides. The behavior of lithium nitrate is similar to that of nitric acid in showing a downward trend for very concentrated solutions, but it is noteworthy that the data are fitted much better than those for the lithium halides (Figures 1 and 5) or nitric acid (Figure 3). The behavior of sodium nitrate is exceptional and quite poorly represented by the Pitzer equation with the present and published parameters. The comparison between the two fits of this case is particularly interesting. The fit with the tabulated parameters is very good up to about 6 mol·kg^{-1}, but the deviations become progressively worse as the molality increases. The pattern of residuals is more like what would be expected if only the data up to 6 mol·kg^{-1} had been included in the least-squares calculation, or if the data at higher molalities were given very low weightings. No mention of such weighting is made by Kim and Frederick; they merely quote a maximum molality of 10.83 mol·kg^{-1}. Although our fit appears to be on average poorer, this is outweighed by the very much larger deviations obtained with the tabulated parameters at high concentrations. Observations of this type are characteristic of least-squares analyses in systems for which weighting of the data is important. Data for potassium, rubidium, cesium, and silver nitrates show a very similar pattern of variation and almost lie on the same graph. Indeed, data for cesium nitrate have been omitted from the figure for clarity, being essentially identical to those for rubidium nitrate. Both Pitzer fits are reasonably good for all these electrolytes, but use of the tabulated parameters for $AgNO_3$ gives noticeably poorer agreement.

Osmotic coefficient data for the alkali-metal nitrites (Staples, 1981) are shown in Figure 8. These electrolytes are of interest in that very high molalities are possible (for example, 62.3 mol·kg^{-1} for $RbNO_2$). Since the solubility of other compounds limits the availability of osmotic coefficient data to much lower molalities, the nitrites provide an exacting test of the correlative ability of the Pitzer equation. As observed for the nitrates, three general patterns of variation are evident, but the similarities in

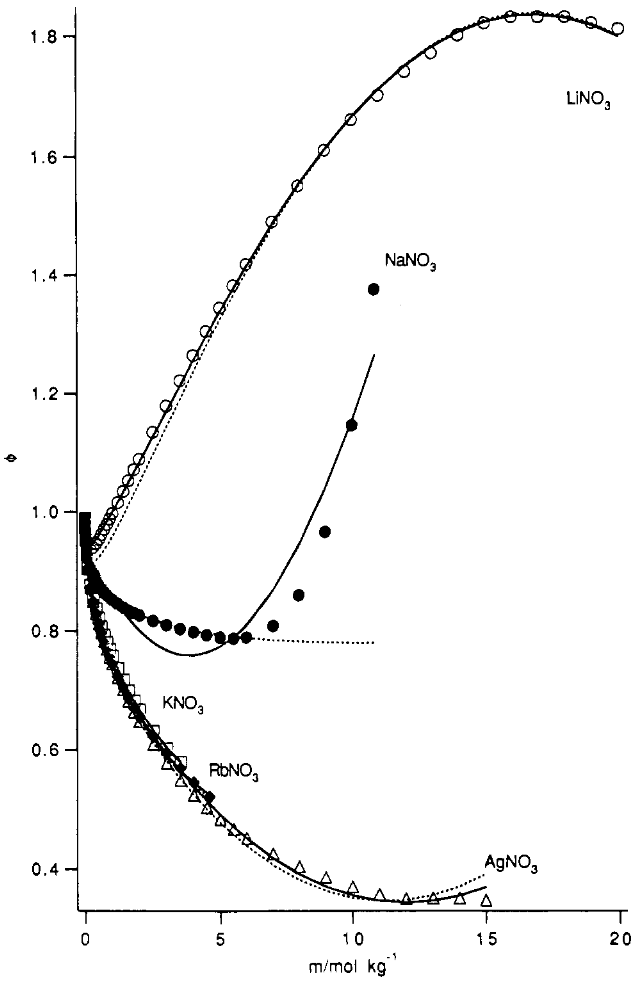

Figure 7. Osmotic coefficient data for alkali-metal and silver nitrates, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

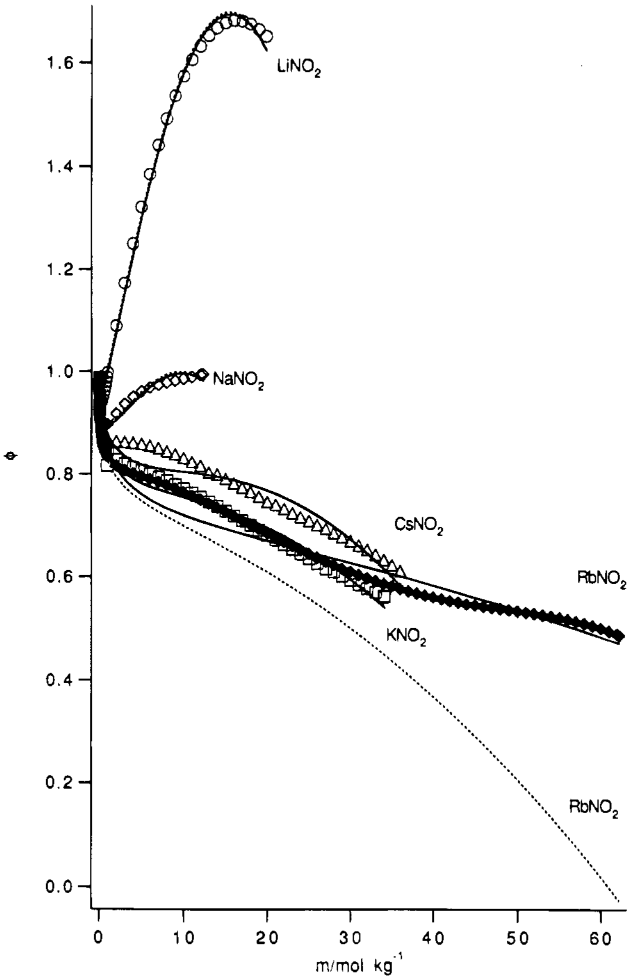

Figure 8. Osmotic coefficient data for alkali-metal nitrites, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Staples (1981).

the variation of the osmotic coefficient for KNO_2, $RbNO_2$, and $CsNO_2$ are less pronounced. Use of the tabulated parameters for $RbNO_2$ gives noticeably inaccurate predictions over the whole composition range, and these deviations become progressively more pronounced with increasing molality. The Pitzer equation is obviously less successful in correlating the osmotic coefficient behavior of KNO_2, $RbNO_2$, and $CsNO_2$ than it was for the corresponding nitrates. The data show quite subtle changes of slope that are probably not capable of being represented by any simple three-parameter equation. Noting that in the Pitzer equation one term is proportional to $\exp(-\alpha\sqrt{I})$ and therefore diminishes with increasing concentration (thus reducing by one the effective number of adjustable parameters), we can expect the Pitzer equation to have a rather limited usefulness for electrolytes for which most of the data correspond to high concentrations.

Salts of Carboxylic Acids. The Pitzer model in the form applied in the present paper and by Kim and Frederick assumes the solutions to consist only of solvent, anions, and cations. No account is taken of incomplete dissociation or reactions involving the formation of other ionic species or neutral molecules (hydrolysis or complexation). The salts of carboxylic acids constitute a major class of hydrolyzing electrolytes to which the Pitzer model has been applied, with excellent results for sodium formate, acetate, propionate, and butyrate (Figure 9). Fits of osmotic coefficient data published by Hamer and Wu (1972) for the higher carboxylate salts are considerably less successful, as shown in Figure 10. Since these substances have a well-known tendency to form micellar aggregates at higher concentrations, it is hardly surprising that they are not described well by the model. The deviations between our own fits and predictions using the tabulated parameters are extremely large (greater than 1). These errors appear to result from very large values given for $\beta^{(1)}$ (−7.73638 for sodium caprylate (octanoate), −10.3798 for sodium pelargonate (nonanoate), and −7.40138 for sodium caproate (decanoate)).

Pitzer (1990) has described an elaboration of his model that includes the contributions of neutral molecules to the osmotic coefficient and the ionic activity coefficients and the corresponding ionic contributions to the molecular activity coefficients. These terms are linear in the appropriate molalities and can therefore be regarded as generalized Setschenow (salting-out) coefficients. In principle, application of Pitzer's theory to solutions of hydrolyzing electrolytes such as sodium carboxylates (NaOOCR) would therefore require constants characterizing the interactions between the Na^-, OH^-, and $RCOO^-$ ions and the RCOOH molecule, in addition to the $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for the $Na^-{-}RCOO^-$ and $Na^+{-}OH^-$ ion pairs. Noting that the $Na^+{-}OH^-$ parameters can be determined independently, a total of six adjustable parameters is required.

The simultaneous determination of all these parameters from a single data set is difficult from a statistical point of view, since as the number of parameters increases, the relative decrease in the sum of squared residuals eventually becomes statistically insignificant. In such cases, these extra parameters cannot be regarded as meaningfully

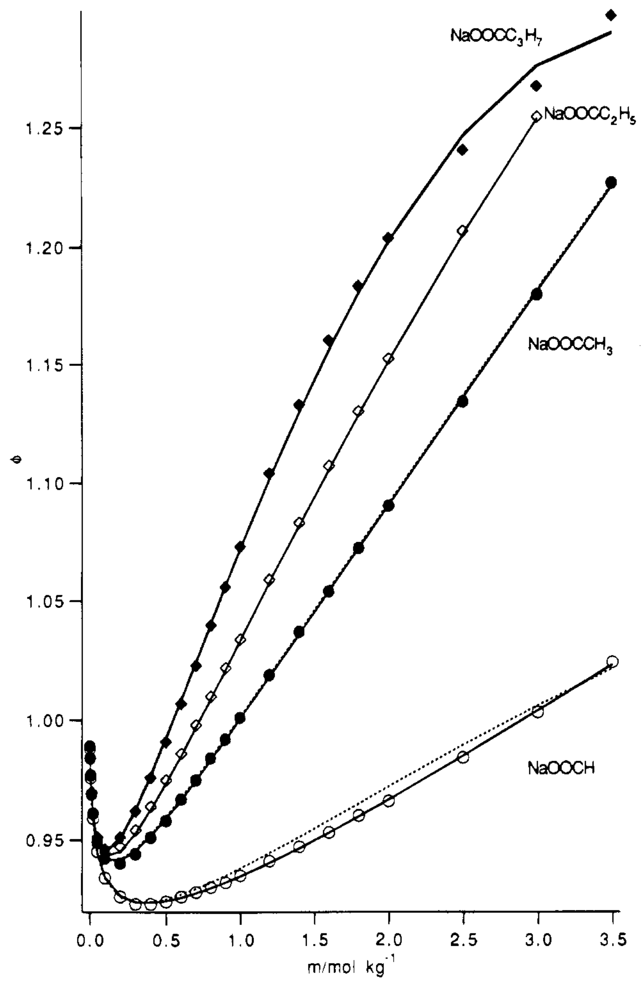

Figure 9. Osmotic coefficient data for sodium carboxylates, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

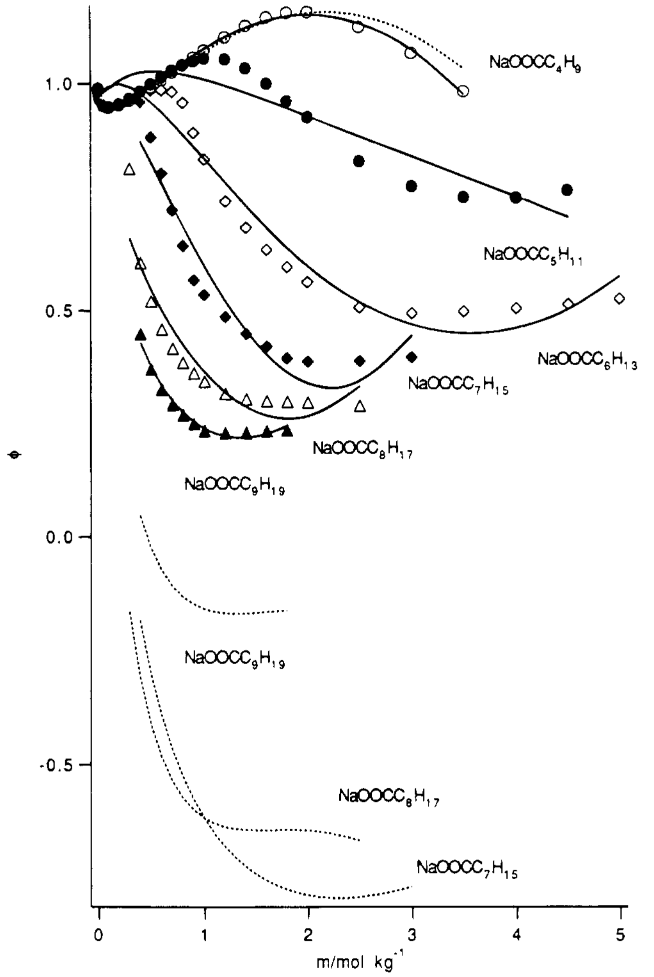

Figure 10. Osmotic coefficient data for sodium carboxylates, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

determined, since their inclusion does not result in a significantly improved representation of the data. Major simplifications are, however, possible under some limiting conditions. For example, in a 4 M aqueous solution of sodium acetate (pK_a = 4.78), a rough calculation shows that the OH^- and CH_3COOH species are present only in millimolar amounts and can be regarded as making an insignificant contribution to the activity of water and the osmotic coefficient. In this case, the hydrolysis of the electrolyte can be neglected to a good approximation, and we can regard the Pitzer parameters as being entirely determined by the interaction between Na^- and CH_3COO^- ions. This probably explains why the Pitzer model fits the osmotic coefficient data for the lower carboxylates so well. Since the dissociation constants of the organic acids are of similar magnitude to that of acetic acid, similar remarks can be applied to the other carboxylates. With the Na^+-RCOO^- thus determined, the other Pitzer parameters required for a complete thermodynamic description of such systems could be determined from accurate pH measurements in buffers of various compositions.

Hydroxides. Osmotic coefficient data for solutions of lithium, sodium, and potassium hydroxides are shown in Figure 11. The fits of Pitzer's equation for these strong bases are seen to be quite poor compared with those for the strong acids and the other alkali-metal salts but improve in the sequence LiOH, NaOH, KOH. It is of interest to consider the poor agreement in the case of NaOH in relation to the possibility of incomplete dissociation. Barnes *et al.* (1966) have estimated that the dissociation constant for the NaOH molecule varies from about $10^{0.5}$ to $10^{-0.1}$ as temperature increases from 0 to 225 °C, so that at 25 °C, an association constant of about 0.3 is expected. This is of the same order as the equilibrium constants postulated by Johnson and Pytkowicz (1979) in their ion-association approach to the nonideal properties of concentrated electrolytes. For 2:1 and 1:2 electrolytes, Harvie *et al.* (1984) have determined that ion association should be taken into account for cases where the association constant is greater than 20. Therefore, an association constant of about 0.3 for NaOH(aq) is probably much less than the value necessary to cause an appreciable deviation from the Pitzer activity coefficient model. In other words, the empirical three-parameter function in Pitzer's theory is quite capable of correlating experimental osmotic coefficient data for systems characterized by this degree of association without the explicit consideration of the association equilibrium. For electrolytes with a strong tendency toward ion association (such as the divalent metal sulfates), Pitzer (1990) recommends the use of a nonzero value of $\beta^{(2)}$, which results in the inclusion of the extra terms in eqs 4–6. The value of $\beta^{(2)}$ can in turn be related to the ion-association constant.

Although from the above remarks it appears that incomplete dissociation does not in itself provide a satisfactory explanation of the relatively poor behavior of the model for NaOH, it is of interest to note that a rough calculation gives a degree of association of about 38%, assuming that the product of the equilibrium constant and the total

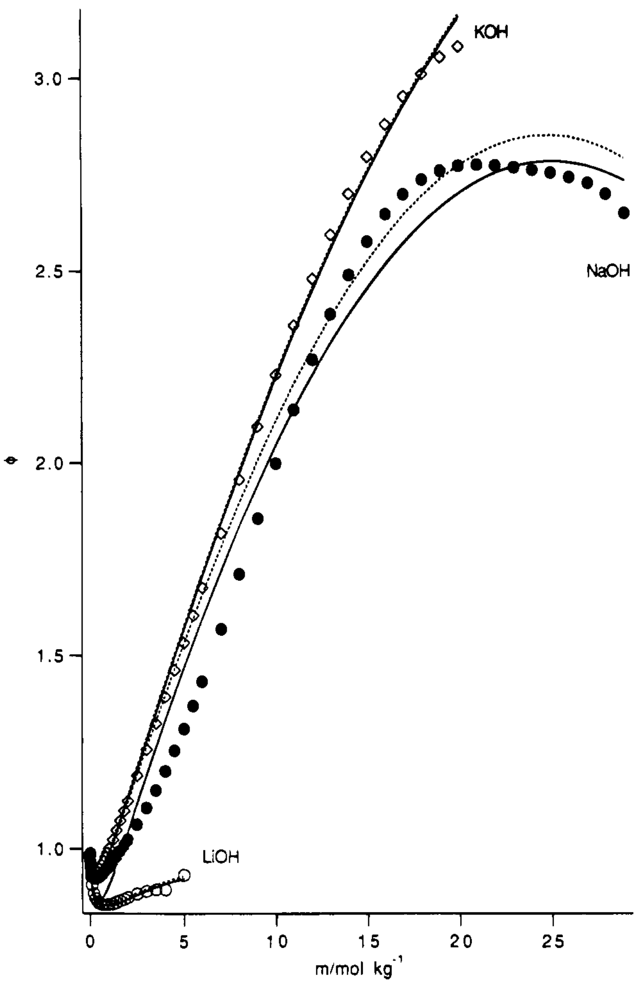

Figure 11. Osmotic coefficient data for alkali-metal hydroxides, with predictions of the Pitzer equation. Dashed curves: parameters taken from Kim and Frederick (1988a). Solid curves: parameters determined in the present work. Data taken from Hamer and Wu (1972).

molality of NaOH is about 1. While the neglect of activity coefficient effects in this estimate means that the true figure might be considerably different, it seems that the presence of the neutral molecule cannot be neglected, even for fairly low concentrations. Application of the Pitzer model to this system would in principle require constants describing interactions between the Na^+ and OH^- ions with the NaOH molecule, in addition to the Na^+-OH^- binary interaction constants. In contrast to NaOH, the data for KOH are represented quite well. (Data for CsOH lie on the same curve as for KOH but are available over a much smaller concentration range and have been omitted from Figure 11 for clarity.)

Conclusions

The discussion presented in this paper shows that the least-squares analysis of osmotic coefficient data according to Pitzer's equation is intrinsically difficult and very far from being a trivial exercise in curve fitting. We have presented a table of Pitzer parameters and their standard errors, calculated from published data. The resulting fits of these data are consistently better than those obtained by use of published tabulations of ion-interaction parameters, but the quality of the fit, as reflected by the trends in the residuals, the sum of squared residuals, and the standard errors of the parameter estimates, is strongly dependent on the maximum molality represented in the data. In particular, it is difficult to obtain accurate estimates of both $\beta^{(1)}$ and C^{ϕ} from the same data set, and the estimates of these parameters are in general highly correlated. A further important observation is that Pitzer parameters determined from data in the low-molality region do not always permit accurate extrapolation to higher molalities. Consequently, the use of Pitzer parameters in contexts other than those in which they were determined must be practiced with caution.

When the maximum molality in the data is high, the standard errors in $\beta^{(1)}$ tend to be very large because the partial derivative of the Pitzer equation with respect to this parameter diminishes exponentially with increasing concentration. This means that in the limit of high concentrations, the osmotic coefficient is described by a two-parameter quadratic function, which is rather limited in its correlative power. On the other hand, when the maximum molality is low, most of the variation in the data is accounted for by this exponential term, so that the standard errors in C^{ϕ} tend to be high.

The above observations on the molality range dependence of the parameters and the correlation between parameter estimates lead to the conclusion that the choice of data-weighting scheme and/or objective function is important (May and Murray, 1988). This choice cannot be made reliably without consideration of the error distribution in the 'real' experimental data and cannot be made at all for the data published in tabulations such as those by Hamer and Wu (1972) and Staples (1981).

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