

Higher-order Limiting Laws and the Pitzer Methods for Symmetrical Mixed Electrolytes

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The Pitzer method with higher-order limiting laws is examined and discussed. The reason for its inability to produce convincing results is identified. Improvements in terms of theory and accuracy are proposed. The experimental activity coefficients for the mixture HCl–KCl in water at 25 °C were used for testing. The results are analysed and discussed.

Since it was reported in 1973, the Pitzer method^{1–4} has become one of the most popular methods for the calculation of activity coefficients. The equations for mixed electrolytes generally consist of two types of mixing parameters, ψ_{ij} and θ_{ij} . The derivatives $\theta' = \partial\theta_{ij}/\partial I$ are also needed. Several different approximations of the mixing parameter θ_{ij} have been used. Besides taking θ to be a constant, which violates higher-order limiting laws (HOLL), Pitzer also suggested using the same mathematical form for both the mixing parameters θ_{ij} and the pure-electrolyte parameter B_{MX} .^{5,6} This method is meant for symmetrical mixtures only, and requires the determination of two concentration-independent constants $\theta^{(0)}$ and $\theta^{(1)}$. However, Pitzer has shown that in order to satisfy the HOLL, $\theta^{(0)}$ and $\theta^{(1)}$ must be interdependent.⁵ This method with the HOLL constraint has been applied to the data for enthalpy of mixing⁶ and activity and osmotic coefficients.⁷ The results calculated using the HOLL were found to be less accurate than those obtained without or violating HOLL. This is unexpected because, for symmetrical mixtures, HOLL considers mainly insignificant differences in short-range interactions which should result in only very small improvement in accuracy. It is therefore important to identify the cause of this negative effect in order to improve the method and to provide a minimum basis which is more exact and theoretically sound. The method should produce results at least as good as those calculated without HOLL, in order to gain confidence in our method and to extend it to the systems where HOLL effects are significant, *e.g.* the enthalpy of mixing.⁸ In fact, Pitzer and Phutela⁶ did apply their method with HOLL to enthalpy of mixing data, and similar negative effects were observed. This clearly illustrates that further improvements are needed.

Method

We consider a binary mixture of electrolytes A and B with a common ion X with charge z_3 , the other two ions are M and N with charges z_1 and z_2 , respectively. The change in excess free energy of mixing can then be given by:^{9,10}

$$\Delta_m G^{\text{ex}} = RTV I_A I_B \sum_{j=0}^{\infty} g_j (I - 2I_B)^j \quad (1)$$

In this paper we will deal only with symmetrical mixtures. In this case the HOLL concerning the first mixing coefficient g_0 is well known:^{5,9,11–15}

$$d \ln g_0 / dI^{1/2} = \lambda_0 = 6z_1^2 A_\phi \quad (2)$$

where A_ϕ is the Debye–Hückel limiting slope.^{5,14} A special equation which expresses the mixing coefficients g_n in terms of the Pitzer parameters has been reported previously,¹⁶ here

we will reproduce the general relation as follows:

$$g_0 = K_3 \theta_{MN} + K_6 I \psi_{MNX} \quad (3)$$

$$K_3 = 8/v_A v_A^- v_B v_B^-; K_6 = K_3/v_A v_A^+ \quad (4)$$

where v_A , v_A^+ *etc.* are the number of ions, with their usual meaning, and $g_1 = 0$. Pitzer has suggested taking ψ as a constant and expressed θ_{MN} in resemblance to the pure electrolyte parameter B_{MX} as⁵

$$\theta_{MN} = \theta_{MN}^{(0)} + h \theta_{MN}^{(1)} \quad (5)$$

where $\theta_{MN}^{(0)}$ and $\theta_{MN}^{(1)}$ are adjustable constants and h is a function of I :

$$h = [1 - (1 + 2v)c]/2v^2 \quad (6)$$

$$c = \exp(-2v) \quad (7)$$

$$v = \alpha I^{1/2}/2 \quad (8)$$

If we take the proportionality variable between the $\theta^{(0)}$ and $\theta^{(1)}$ as k , that is

$$\theta_{MN}^{(1)} = k \theta_{MN}^{(0)} \quad (9)$$

then it is easy to show that the HOLL eqn. 2 becomes

$$d \ln g_0 / dI^{1/2} = r \lambda_0 \quad (10)$$

with $r = -2k/3(1+k)\lambda_0$. Pitzer has shown that eqn. 2 will be satisfied exactly if $k = s$, where

$$s = -9z_1^2 A_\phi / (\alpha + 9z_1^2 A_\phi) \quad (11)$$

However assuming this arbitrary mathematical expression of θ_{MN} and making it satisfy HOLL condition may produce results which cast doubt on the validity of HOLL. It is therefore more appropriate to solve eqn. 2 directly to obtain the exact solution of θ_{MN} at very dilute concentrations θ_0 :

$$\theta_0(I) = g_0(0)/(K_3 a) \quad (12)$$

where

$$a(I) = \exp(-\lambda_0 I^{1/2}) \quad (13)$$

and $g_0(0)$ is a limiting constant of $g_0(I)$ at $I = 0$. After the exact θ_0 is obtained, a general form of θ_{MN} may be defined as

$$\theta_{MN} = \theta_0 f_1 + \mu f_2 \quad (14)$$

where μ is an adjustable constant, and f_1 and f_2 are functions of I which satisfied the following conditions

$$\lim_{I \rightarrow 0} f_1 = 1; \lim_{I \rightarrow 0} f_2 = 0 \quad (15)$$

We can then assign different versions of the Pitzer method according to different assumptions on θ_{MN} as follows:

Pitzer	I	II	III	4a	4b	4c	4d	4e	4f	4g	6
f_1	a	a	ha	c	q	q	1	q	p	qa	qa
f_2	0	0	$1-h$	C	I	0	0	Q	P	QA	0

Note that in the Pitzer I method we take θ , θ' and ψ as three independent constants; in Pitzer II, $\theta = E_\theta + s_\theta$ with $E_\theta = E_{\theta'} = 0$ for symmetrical mixtures; and in Pitzer III we used eqn. 5 while $\theta = \theta^{(0)}(1 + sh)$ is used in Pitzer 6. Method 6 is the Pitzer method with the HOLL constraint.^{5,7} Functions c , h and a have already been defined in eqn. 6, 7 and 13, we also define $C = I^{1/2}c$, $A = I^{1/2}a$, and other functions are

$$H = [(3 - 2v) - (3 + 4v + 2v^2)c]/4v^3 \tag{16}$$

$$q = (1 + sh)/(1 + s) \tag{17}$$

$$Q = H + (h - 1)/(1 + s) \tag{18}$$

$$p = (1 - c)/2v \tag{19}$$

$$P = [(1 - v) - (1 + v)c]/2v^2 \tag{20}$$

The activity coefficients can be computed from these mixing parameters according to the equation

$$\log \gamma_A/\gamma_A^* = r_1 I y \theta_{MN} + r_1 I^2 (y - y^2) \theta'_{MN} + (r_2 I^2 y + r_3 I^2 y^2) \psi_{MNX} S \tag{21}$$

where y = ionic strength fraction due to B. γ_A^* is the trace activity coefficient of A in the mixture when θ_{MN} and ψ_{MNX} vanished. And

$$\begin{aligned} r_1 &= 4v_A^+ / v_A v_B v_B^- \\ r_2 &= 8/v_A^2 v_B v_B^- \\ r_3 &= (4v_A v_A^+ - 8v_B v_B^+) / v_A^2 v_B^2 v_B^+ v_B^- \end{aligned} \tag{22}$$

Results and Discussion

A simple method for the unsymmetrical mixtures which incorporated HOLL has been reported by Lim *et al.*^{10,17,18} For symmetrical mixtures the following modifications may be used to satisfy the corresponding limiting laws:^{9,13,16}

$$\begin{aligned} g_0 &= a_1 \exp(\lambda_0 I^{1/2}) + a_2 I + a_3 I^{3/2} \\ g_1 &= \text{const.} \end{aligned} \tag{23}$$

where

$$a_1 = g_0(0) \tag{24}$$

and λ_0 is the same constant as defined in eqn. 2. The method has also been tested and the results are satisfactory.^{19,20} It is interesting to observe, eqn. 10, that (a) when $k = 0$, $\theta = \theta^{(0)}$ and $r = 0$ then the Pitzer III method reduces to Pitzer II and HOLL will not be satisfied, the same is obviously also applied to Pitzer I; (b) when $k = s$, then $r = 1$ and it reduces to method 6 so that HOLL will be satisfied exactly. The important difference between Pitzer III and Pitzer 6 is thus very clear. We have used the optimum k for the former whereas a special k ($= s$) was used for the latter in order to make r equal unity. It is for this reason that the results of Pitzer 6 should necessarily be worse than those of Pitzer III. It is also for the same reason that the results of Pitzer III should be better than those of Pitzer II. However, no comparison can be made with Pitzer I because in this method the two parameters θ and θ' were assumed to be independent, which is mathematically incorrect. On the other hand, one cannot be certain why $k = 0$ should be worse than $k = s$, and,

in fact, Pitzer *et al.*^{6,7} reported cases where $k = 0$ is better than $k = s$. However, since r may not equal 1 for Pitzer III, HOLL may not be satisfied exactly in this method, and we may expect to obtain the correct shape for its θ curves and g_0 curves but perhaps with certain disproportions or dislocations. Nevertheless, from eqn. 10 we know that k must be in the range $-1 < k < 0$, or HOLL will not be satisfied at all.

One must be very careful in the selection of f_1 and f_2 . First, one must be sure that $\theta_0 f_1$ exhibits the correct behaviour of a limiting function and cannot become a constant; secondly, condition 15 must be satisfied and finally, $g_0 \rightarrow 0$ when $I \rightarrow 0$ as predicted by Scatchard and Prentiss.²¹ Note that we have already shown that the acceptable expressions for the limiting function of θ include $\theta^{(0)}(1 + s)q$ and θ_0 , although θ_0 is probably preferable.

It has already been shown that methods I and II do not satisfy HOLL. Now we will show also that method 4a does not satisfy HOLL for our test case. This is because in our test case $\alpha \approx \lambda_0$ so that $c/a \approx 1$ and thus $\theta_0 f_1$ becomes very close to a constant $g_0(0)/K_3$, which implies that HOLL are violated.

All the methods mentioned in this paper can therefore be classified into three categories: (A) those which do not satisfy HOLL, *e.g.* methods I, II and 4a; (B) those with HOLL leading term but without the correction term f_2 , *e.g.* methods 6, 4c and 4d; (C) those with both HOLL leading terms and the correction terms, namely methods III, 4b, 4e, 4f and 4g where both the f_1 and f_2 are non-zero.

Next we will make a comparison of all the methods with respect to their accuracies and their g_0 values. For this we need accurate experimental data.

Experimental activity coefficients of the binary mixture HCl-KCl in water at 25°C were chosen²² to test the various versions either with or without HOLL. First, the Debye-Hückel parameter A_ϕ was determined using experimental densities of water²³ in the range 253.15–383.15 K, and static relative permittivities²⁰ in the range 273.15–373.15 K. The temperature-dependent equation was then found to be

$$\begin{aligned} A_\phi &= 0.390291 + 0.66696 \times 10^{-3} \Delta T + 0.20898 \times 10^{-5} \Delta T^2 \\ &+ 0.46493 \times 10^{-8} \Delta T^3 + 0.39490 \times 10^{-11} \Delta T^4 \\ &+ 0.42877 \times 10^{-12} \Delta T^5 \end{aligned} \tag{25}$$

where

$$\Delta T = T - 298.15 \text{ K} \tag{26}$$

Numerical values of A_ϕ at different temperatures and pressures have been tabulated by Bradley and Pitzer and Beyer and Staples,²⁴ however, an analytical expression may be more useful especially for calculations at different temperatures. Similarly, the Pitzer parameters for pure electrolytes²⁵ are readjusted by including the non-linear term α_{MX} as an optimizing parameter. Those values which are needed in our present calculation are listed in Table 1. With these predetermined parameters the mixing parameters for the mixture can then be optimized using various different methods, these mixing parameters are reported in Table 2. Finally, the mixing coefficients, θ_{MN} , θ'_{MN} and g_0 are calcu-

Table 1 Input parameters for pure electrolytes^a

J	b	α_J	$\beta_J^{(0)}$	$\beta_J^{(1)}$	C_J^\dagger
HCl	1.2	2.383 641	0.187 888	0.309 702	−0.001 126
KCl	1.2	2.323 995	0.052 976	0.235 939	−0.001 670

^a $\alpha = (\alpha_{HCl} + \alpha_{KCl})/2$.

Table 2 Pitzer's parameters for the mixture HCl–KCl–H₂O at 25 °C

method	$-\psi_{\text{MNX}}$	$\theta^{(0)}$	$^*\theta$	θ_{MN}	$\theta^{(1)}$	θ'_{MN}	$g_0(0)$	μ
I	0.012 109			0.010 219		0.001 097	0.020 438 ^a	
II	0.011 375		0.009 518				0.019 036 ^a	
III	0.011 890	0.011 272			−0.007 965		0.006 614 ^a	
4a	0.011 446						0.019 986	−0.004 671
4b	9097.37						−0.000 060	4548.68
4c	0.002 705						−0.000 060	
4d	0.002 576						−0.000 147	
4e	0.016 601						0.000 035	−0.006 614
4f	0.013 779						0.000 374	−0.079 496
4g	0.010 940						0.006 808	−0.013 320
6	0.011 802	0.010 971			−0.006 569		0.008 804 ^a	

a Calculated from $g_0(0) = \lim_{I \rightarrow 0} (K_3 \theta_{\text{MN}} + IK_6 \psi_{\text{MNX}})$; for methods 4a–4g, $\theta_{\text{MN}} = \theta_0 f_1 + \mu f_2$.

lated. The estimated errors of the various methods are then given in Table 3. Note that the probable uncertainty value is 0.002 as estimated by Bates and Robinson.²⁶ In addition, the graphs of θ vs. $I^{1/2}$ were plotted in Fig. 1 while g_0 vs. $I^{1/2}$ were shown in Fig. 2.

From Table 3 we find that all the three methods in the category B produced the worst results, *ca.* 10% of data points are beyond experimental uncertainty for methods 4c and 4d. Since all these three methods have the same characteristic of consisting only of the HOLL leading term $\theta_0 f_1$, it clearly indicated that the HOLL leading term alone is not adequate and that the second correction term f_2 is needed. Indeed, when the correction terms are added, those methods in category C produce the best results, except method 4b. The failure of method 4b merely suggests that this correction term cannot be represented by a simple linear form. The reason for this is not difficult to visualize because this correction term is only a duplication of the $K_6 I \psi$ which is another term in g_0 besides θK_3 . However, if we replace I by $I^{3/2}$ in f_2 , then the result of this 4b method can be greatly improved. g_0 and g'_0 have the same sign at $I \rightarrow 0$ in all the methods in these two categories, thus fulfilling the basic requirement of the HOLL. We see that all the g_0 and g'_0 are positive at $I \rightarrow 0$ except using methods 4c and 4d, where all their g_0 and g'_0 are negative. Needless to say, g_0 and g'_0 have opposite signs at $I \rightarrow 0$ in all the three methods in category A, a sure sign that the HOLL is not satisfied.

Perhaps method III needs special mention, it has positive g_0 and g'_0 at $I \rightarrow 0$ which indicates that the HOLL is qualitatively satisfied, but its value of r in eqn. 10 equals 1.61 which shows that the HOLL is not satisfied exactly. Its g_0 curve therefore exhibits only approximately the correct shape

which distinguishes it from other methods in category A where the HOLL is not satisfied. Considering accuracy, the inclusion of f_2 has made it more accurate than those other methods without the correction term, and its optimum k makes it slightly better than Pitzer II, but it is slightly worse than the methods 4e, 4f and 4g in which the HOLL is satisfied exactly and the correction terms are non-vanishing.

From Fig. 2 we see that all the four methods 4c, 4d, 4e and 4f which used θ_0 as their limiting functions all have vanishing g_0 values at $I = 0$, whereas the other two methods 4g and 6 which make use of q as their limiting function have slightly larger values of g_0 at $I = 0$. Since we would expect to get vanishing g_0 at $I = 0$, as predicted by Scatchard and Prentiss,²¹ we may conclude that θ_0 is probably a better representation for the limiting function than q . This of course is also supported by the fact that θ_0 is an exact solution of eqn. 2 while q is only an arbitrary function which was made to satisfy eqn. 2. Moreover, methods 4e and 4f also produced more accurate results than 4g, as expected. The result of method 6 is better than 4d, probably because its q is multiplied by a variable $\theta^{(0)}$. Compared to the *ab initio* calculation we see that the small values of g_0 at $I \rightarrow 0$ in methods 4c and 4d are negative, in agreement with the *ab initio* results of Friedman using a primitive model.^{10,11} This probably sug-

Table 3 Estimated errors in the various Pitzer methods for the mixture HCl–KCl–H₂O at 25 °C

method	Δ_{max}^a	$10^3 \sigma^b$	n^c	no. of parameters
I	0.0019	0.92	none	3
II	0.0021	0.96	1	2
III	0.0022	0.95	1	3
4a	0.0021	0.95	1	3
4b	0.0094	3.29	9	3
4c	0.0029	1.29	4	2
4d	0.0029	1.29	4	2
4e	0.0019	0.90	none	3
4f	0.0019	0.92	none	3
4g	0.0020	0.94	1	3
6	0.0022	0.95	1	2

^a $\Delta = |\log \gamma_{\text{A}}(\text{obs}) - \log \gamma_{\text{A}}(\text{cal})|$. ^b σ = standard deviation in $\log \gamma_{\text{A}}$. ^c n is out of a total of 42 points, the number of points whose Δ values exceeded 0.002.

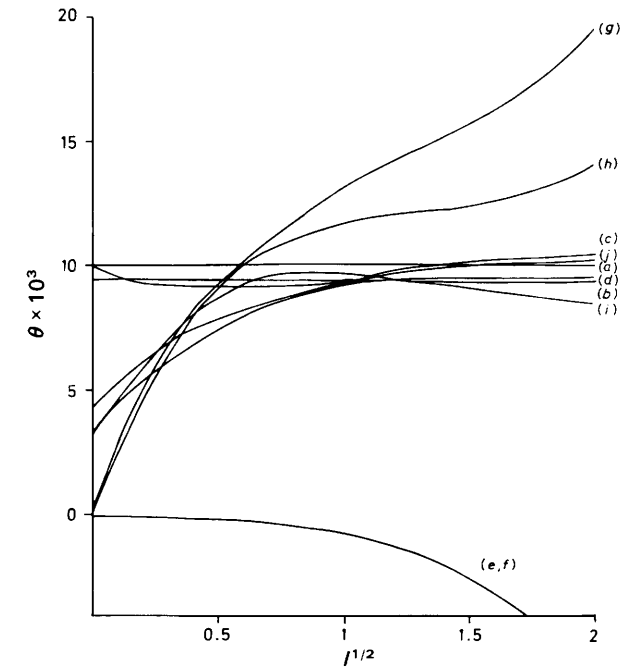


Fig. 1 θ_{MN} curves for various Pitzer methods: (a) I, (b) II, (c) III, (d) 4a, (e) 4c, (f) 4d, (g) 4e, (h) 4f, (i) 4g, (j) 6

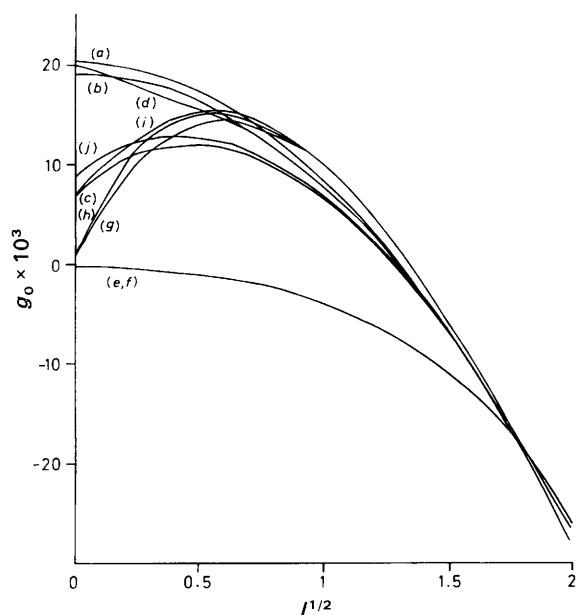


Fig. 2 g_0 curves for various Pitzer methods: (a)–(j) as Fig. 1

gests that the HOLL leading term may be equivalent to the primitive model while the addition of the correction term may have gone beyond the primitive model and be equivalent to other more realistic models.

Finally, for those methods in category A we see that the methods II and 4a are of the same accuracy as the method 4g, whereas method I is as accurate as methods 4e and 4f. Unfortunately, none of the methods in this category satisfy the HOLL and their accurate results could be just fortuitous. They probably were obtained at the expense of accuracy at $I < 0.1$. Indeed, the θ and g_0 values at $I = 0$ were made unreasonably high in these three methods, in order to assure the reasonably good results at $I > 0.1$.

In conclusion, although we know that the simpler methods I and II can produce accurate results, there is no doubt that HOLL must be included in order to provide an accurate and theoretically sound method. Since method 6 is still unable to accomplish this goal beyond doubt, further improvements are

required. Based on the criteria of the theoretical grounds, accuracies and g_0 values, we may arrive at the conclusion that methods 4e and 4f are the two best methods.

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