The calculation of activity coefficients of binary mixed electrolytes

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Abstract

Methods for the calculation of activity coefficients of binary mixed electrolytes are presented. Interrelations between the mixing coefficients are given. Applications of the Gibbs-Duhem equation, cross differential conditions, and higher order limiting laws are shown. Accuracies and the theoretical justifications of the various methods are compared.

I. INTRODUCTION

It is a great honour to be invited to present this R.A. Robinson Memorial Lecture in memory of a great teacher who has made tremendous original contributions to ionic solution chemistry.[1-2] As electrolyte is characterized by its dissociation in a solvent into ions it is therefore only natural to consider the properties and behaviour of ions as individuals. Even though the exact activities of the individual ions are experimentally unattainable and that the concentrations of all the individual ions are not linearly independent due to the electrical neutrality requirement, R.A. Robinson did not share the defeatist view of some thermodynamicists that single ion activities are merely useless mathematical devices, and he was able to split the mean activity coefficient into its separate ionic contributions,[3] and underscored his belief that conventional scales of individual ionic activity consistent with mean activities can, like the pH scale, be enormously useful.[4] In fact, with the use of Debye-Huckel approximation[5] at low concentrations for single ions as well as the cation-cation pairs, he was able to derive the higher order limiting laws (HOLL) in agreement with the cluster expansion derivation of Friedman, and probably was the first to incorporate the HOLL into the semi-empirical calculation of activity coefficients of binary mixed electrolytes.[6] Furthermore, using the chemical model of the association of ionic speices he was able to confirm the prediction of Friedman[7] that the mixing of symmetrical binary electrolytes is independent of the common ion at low concentration.[6] On the other hand, the linear dependence of the ionic concentrations was handled by Friedman[8] who was able to avoid the singularity of the generalized compressibility matrix and thus compute the activity coefficient of the mixed electrolytes in an indirect way. Besides this indirect method which was based on the ab initio statistical mechanical computation of the radial correlation functions, the calculation of activity coeffcieints of binary mixed electrolytes can also be accomplished by determining the mixing coefficients from fitting the experimental activity coefficients semi-empirically. In fitting the experimental data one cannot vary the parameters for the two electrolytes independently because the Gibbs-Duhem cross differential (CD) condition must be satisfied. Therefore, we usually fit the mixing coefficients of one electrolyte and then compute the mixing coefficients of the other electrolyte according to the CD condition, or express the mixing coefficients of the two electrolytes by the same set of parameters which satisfy the CD condition and other conditions such as the HOLL. The first approach was first employed by McKay[9-11], and later generalized by Lim[12,13]. The second approach was adopted by Scatchard[14-16], Pitzer[17-24] and Lim[25-28]. In this article we will present the McKay method in section II. Activity coefficients and the relations between mixing coefficients are shown in section III, other empirical methods in section IV, indirect method of Friedman in section V, and finally the comparison of the various methods in section VI.

II. McKAY METHOD

Although the molarity in the McMillan-Mayer system and the molality in the Lewis-Landall system are the two concentration units usually used by scientists, the electrical concentration of ionic strengths which was proposed by Lewis and Landall[29] is also popular and will be used in this article. In a binary mixture consisting of electrolytes A and B, the ionic strength and the fractional ionic strength due to B are therefore the two independent concentration variables. They may be denoted by I and y respectively. Assuming that A consists of ions 1 and 3 with charges z_1 and z_3 while B consists of ion 2 and a common ion 3 with charges z_2 and z_3, one may define $z_A = |z_1 z_3|/2$, $z_B = |z_2 z_3|/2$ and $u = (1 - y)/z_A + y/z_B$. The stiochiomatric mean activity coefficient of the mixture is then

$$\ln \gamma_{\pm} = \{[(1 - y)/z_A]\ln\gamma_A + (y/z_B)\ln\gamma_B\}/u \tag{1}$$

The interconversions between $\gamma_{\pm}$ and the practical osmotic coefficient ϕ can be given as

$$\phi - 1 = (uI)^{-1} \int_0^{uI} uI \, d \, \ln\gamma_{\pm} \tag{2}$$

and

$$\ln\gamma_{\pm} = (\phi - 1) + \int_0^{uI} (\phi - 1)d \, \ln(uI) \tag{3}$$

The above interconversions are obtained from the well known Gibbs-Duhem equation[30] which is derived from the following Euler theorem

$$\frac{\partial f}{\partial n_w}n_w + \sum_L \frac{\partial f}{\partial n_L}n_L = jf \tag{4}$$

where n_w and n_L are the number of moles of solvent w and solute L respectively, while f is a j-th order homogeneous function:

$$f(kn_w, kn_A, kn_B) = k^j f(n_w, n_A, n_B) \tag{5}$$

k is a multiple constant. For any intensive property $j = 0$, whereas $j = 1$ for any extensive property which is represented by f.

On the other hand, the Gibbs-Duhem cross differential condition made it possible to compute the mean activity coefficient of one electrolyte from the mean activity coefficient of another electrolyte. Since the infinitesimal increment in the Gibbs free energy G is an exact differential, the integrability of G results in the cross differential condition and hence the McKay method. The generalized McKay method may be shown as follows. The mean activity coefficients of the two electrolytes can be written as

$$\log \gamma_A(I,y) = \log \gamma^o_A(I) - \sum_{n=1}^{M} \alpha_{An}(I)(I - I_A)^n \tag{6a}$$

$$\log \gamma_B(I,y) = \log \gamma^o_B(I) - \sum_{n=1}^{M} \alpha_{Bn}(I)(I - I_B)^n \tag{6b}$$

where $I_A = (I - y)I$ etc. Assuming that $\gamma_A(I,y)$ can be determined experimentally so that mixing coefficients α_{An} are known at various ionic strengths, then the parameters α_{Bn} can be determined from the cross differential condition[2,12,30]

$$\nu_B{}^+\nu_B{}^-(\frac{\partial \log \gamma_A}{\partial I})_{I_A} = \nu_A{}^+\nu_A{}^-(\frac{\partial \log \gamma_B}{\partial I})_{I_B} \tag{7}$$

Substitute eqs(6) into (7) and integrate from Iy to I we obtain the equality between the right hand sides of (8a) and (8b):

$$f(I,y) = \nu_A{}^+\nu_A{}^- \sum_{n=1}^{M} I^n(1 - y)^n \alpha_{Bn}(I) \tag{8a}$$

$$f(I,y) = \nu_A^{\cdot}\nu_A^{-} \log[\gamma_B^{0}(I)/\gamma_B^{0}(Iy)] - \nu_B^{\cdot}\nu_B^{-} \log[\gamma_A^{0}(I)/\gamma_A^{0}(Iy)] +$$

$$+ \nu_B^{\cdot}\nu_B^{-} \sum_{n=1}^{M} \{n(Iy)^{n-1} \int_{Iy}^{I} \alpha_{An}(x)dx + (Iy)^{n}[\alpha_{An}(I) - \alpha_{An}(Iy)]\} \quad (8b)$$

At a fixed I with variable y we can compute a set of values of $f(I,y)$ from eq(8b), from which we can optimize α_{Bn} at this I according to eq(8a). For a special case where A satisfies the Harned rule[30], namely, all α_{An} are negligible except α_{A1}, and set M = 2 for electrolyte B, then α_{B1} and α_{B2} can be obtained from the plot of $f(I,y)/I_A\nu_A^{\cdot}\nu_A^{-}$ versus I_A. This plot should produce a straight line with α_{B2} as its slope and α_{B1} as intercept[2]. The above procedure may be repeated for all the other ionic strengths. It is obvious that the above method requires the numerical integration. However, we can also do it in an alternative way which requires numerical differentiation[12,13]. In this second method α_{Bn} can be obtained from the experimentally fitted α_{An} according to a general relation as required by the cross differential condition. Thus[12]

$$(j + 1)\alpha_{B,j+1} = (-1)^{j} \frac{z_2}{z_1} \{a_j + \sum_{r=j+1}^{M} [r\binom{r-1}{j} \alpha_{Ar}I^{r-j-1} + \binom{r}{j} \frac{d\alpha_{Ar}}{dI} I^{r-j}]\} - b_j \quad (9)$$

where

$$a_j = -\delta_{jo}(d \log \gamma_A^{0}/dI) + (d\alpha_{Aj}/dI) \quad (10a)$$

$$b_j = -\delta_{jo}(d \log \gamma_B^{0}/dI) + (d\alpha_{Bj}/dI) \quad (10b)$$

the derivatives can be computed using a 3-point Lagrangian formula. Successive evaluation of α_{Bn} results in an explicit equation for these mixing coefficients which are reported elsewhere[13].

III. ACTIVITY COEFFICIENTS AND RELATIONS BETWEEN MIXING COEFFICIENTS

Besides expressing the mean activity coefficients in terms of the Harned coefficients as shown in eq(6), it was pointed out by Friedman[31,32] that despite the fact that activity coefficients have been in much more general use than the excess free energy in application where the behavior of a particular component of a solution is of special interest, the use of a total excess functions[31,33,34] for the representation of the properties of mixed electrolyte solutions offers two advantages over the use of partial molal quantities. Frist, there is no cross differential restrictions on the mixing coefficients of the total excess functions, second, these mixing coefficients can be expressed as combinations of the mixing coefficients of partial molal quantities of different electrolytes. It is therefore more useful to express the activity coefficients of a electrolyte in terms of the mixing coefficients of the excess free energy changes than the Harned coefficients[25]. The changes in excess Gibbs free energy of mixing at fixed temperature and pressure can be given as[31,35]

$$\Delta_m G^{ex} = w_w RTI^2 y(1 - y) \sum_{j=0}^{M-1} g_j(IY)^j \quad (11)$$

where w_w is the mass of solvent in kg, and $Y = 1 - 2y$. Activity coefficients can then be obtained from[35]

$$\ln\gamma_A/\gamma_A^{0} = -z_A yI\Phi + (z_A/RTw_w)(\frac{\partial \Delta_m G^{ex}}{\partial I} - \frac{y}{I} \frac{\partial \Delta_m G^{ex}}{\partial y}) \quad (12a)$$

$$\ln\gamma_B/\gamma_B^{0} = z_B(1 - y)I\Phi + (z_B/RTw_w)(\frac{\partial \Delta_m G^{ex}}{\partial I} + \frac{1 - y}{I} \frac{\partial \Delta_m G^{ex}}{\partial y}) \quad (12b)$$

where

$$\Phi = [(1 - \phi_B^{0})z_B^{-1} - (1 - \phi_A^{0})z_A^{-1}]/I \quad (13)$$

with ϕ_J^{0} being the osmotic coefficient of pure electrolyte J.

Friedman[41] has also shown that the Harned mixing coefficients are divergent and can be reformulated into the convergent mixing coefficients of A_n and B_n. In terms of these modified Harned coefficients activity coefficients are defined as

$$\ln\gamma_A/\gamma_A{}^0 \;=\; z_A I y \sum_{n=0}^{M-1} A_n(-IY)^n \tag{14a}$$

$$\ln\gamma_B/\gamma_B{}^0 \;=\; z_B I(1-y) \sum_{n=0}^{M-1} B_n(IY)^n \tag{14b}$$

Substitute eq(11) into eq(12) we arrive at

$$(\ln\gamma_A/\gamma_A{}^0)/[z_A y I] \;=\; -\,\Phi + \sum_{n=0}^{M-1} [g_n D_n(+) + g_n' E_n(+)] \tag{15a}$$

$$(\ln\gamma_B/\gamma_B{}^0)/[z_B(1-y)I] \;=\; \Phi + \sum_{n=0}^{M-1} [g_n D_n(-) + g_n' E_n(-)] \tag{15b}$$

where

$$D_n(\pm) \;=\; [(n+2)(YI)^n \pm nI(YI)^{n-1}]/2 \tag{16a}$$

$$E_n(\pm) \;=\; [I(YI)^n \pm (YI)^{n+1}]/2 \tag{16b}$$

In terms of modified Harned coefficients the equations become

$$(\ln\gamma_A/\gamma_A{}^0)/[z_A y I] \;=\; -\,\Phi + \sum_{n=0}^{M-1} I^n\{A_n[(-Y)^n - f_{1n}/2] + B_n f_{1n}/2\} \tag{17a}$$

$$(\ln\gamma_B/\gamma_B{}^0)/[z_B(1-y)I] \;=\; \Phi + \sum_{n=0}^{M-1} I^n\{A_n f_{1n}/2 + B_n[Y^n - f_{1n}/2]\} \tag{17b}$$

where

$$\begin{aligned} f_{kn} \;&=\; (n+2)^{-1} \quad &\text{if } n-k \text{ is even,} \\ &=\; (n+1)^{-1} \quad &\text{if } n-k \text{ is odd,} \end{aligned} \tag{18}$$

From eq(12) various different interrelations between activity coefficients of A and B can be obtained. Similar expression for the osmotic coefficients can also be derived as follows[35]:

$$uI(1-\phi) = (1-y)I(1-\phi_A{}^0)/z_A + yI(1-\phi_B{}^0)/z_B + [\Delta_m G^{ex} - I(\partial\,\Delta_m G^{ex}/\partial I)]/(W_W RT) \tag{19}$$

The osmotic function Φ can also be expressed in terms of the Harned coefficients:

$$\begin{aligned} \Phi \;&=\; [Ig_1 + (B_0 - A_0)]/2 \;=\; \sum_{n=0}^{M-1} (B_n - A_n)I^n f_{1n}/2 \\ &=\; \sum_{n=1}^{M-1} [I^{n-1}\ln10/(n+1)](\alpha_{An}/z_A - \alpha_{Bn}/z_B) \end{aligned} \tag{20}$$

Finally, the interrelations between the mixing coefficients are obtainable as shown below:

$$\ln10\,\alpha_{Ln} \;=\; -z_L \sum_{m=n}^{M} t_{mn}I^{m-n}L_{m-1} \tag{21a}$$

$$\ln10\,\alpha_{Ln} \;=\; z_L(2\delta_{LA}-1)\{\delta_{n1}\Phi + \sum_{k=n-1}^{M} (-2)^{n-2}I^{k-n+1}(2\delta_{LA}-1)^{k+1}[\epsilon_{nk}g_k \tag{21b}$$
$$+\; (2\delta_{LA}-1)\epsilon_{n,k-1}g'_{k-1}/(k-n+1)]\}$$

$$L_n \;=\; -\ln10 \sum_{k=n}^{M} \alpha_{L,k+1}I^{k-n}\,2^{-k}\binom{k}{n}/z_L \tag{22a}$$

$$2(2\delta_{LB}-1)^n L_n \;=\; (2\delta_{LB}-1)[2\delta_{no}\Phi - (n+1)Ig_{n+1} - g'_{n-1}] + (n+2)g_n + Ig'_n \tag{22b}$$

$$g_n = -\ln 10 \sum_{k=n+1}^{M} [\alpha_{Bk}/z_B + (-1)^n \alpha_{Ak}/z_A] I^{k-n-1} h_{nk} \tag{23a}$$

$$g_n = \sum_{k=n}^{M} [(-1)^n A_k + B_k] I^{k-n} f_{nk} \tag{23b}$$

$$g'_n = \ln 10 \sum_{k=n+1}^{M} I^{k-n-1} [(-1)^n \alpha_{A,k+1}/z_A + \alpha_{B,k+1}/z_B] \bar{h}_{nk} \tag{23c}$$

$$g'_n = -(n+2) \sum_{k=n+1}^{M-1} I^{k-n-1} f_{nk} [(-1)^n A_k + B_k] \tag{23d}$$

$$g'_n = [(-1)^n A_n + B_n - (n+2)g_n]/I \tag{23e}$$

where

$$t_{mn} = 2^{n-1} \binom{m-1}{n-1} \tag{24}$$

$$\varepsilon_{nk} = k!(2k - n + 3)/[(n-1)!(k-n+1)!] \tag{25}$$

$$h_{nk} = \sum_{m=n}^{k} \binom{m}{n}/[(k+1)2^m] \tag{26}$$

$$\bar{h}_{nk} = \sum_{m=n+1}^{k} f_{nm} \binom{k}{m}(n+2)/2^k \tag{27}$$

and note that L = A or B in the above equations.

If we express the change in the excess Gibbs function of the solvent by

$$\Delta_m G_w^{ex}/w_w RT = \Delta_m u I(1 - \phi) = -I^2 y(1 - y) \sum_{n=0}^{M-1} w_n(I) Y^n \tag{28}$$

then from the relation that $\Delta_m G_w^{ex} = \Delta_m G^{ex} - I \partial \Delta_m G^{ex}/\partial I$, we have

$$w_n = \partial(I^{n+1} g_n)/\partial I \tag{29}$$

We have already known that the Harned coefficients must satisfy the cross differential condition from which the McKay method was developed, it can further be shown that a necessary condition for the cross differential condition to be satisfied is as follows

$$\alpha_{BM}/z_B + (-1)^{M-1} \alpha_{AM}/z_A = \text{constant} \tag{30}$$

where the constant was identified[12] to be $-2^{M-1}(M+1)g_{M-1}/\ln 10$. The above equation is equivalent to the consistency condition[12,25,35]

$$g'_{M-1} = \partial g_{M-1}/\partial I = 0 \tag{31}$$

which requires that g_{M-1} to be a constant independent of I. We note that the cross differential restriction does not apply to the mixing coefficients of g_n, except the last one g_{M-1}. They must also satisfy the higher order limiting laws (HOLL). The HOLL for g_0 are known to be[6,8,31,32,36]:

$$d \ln g_0/dI^{1/2} = 6z_1^2 A_\phi = \lambda_0 \qquad \text{for symmetrical mixtures} \tag{32a}$$

$$\lim_{I \to 0} g_0 = 3(z_1 - z_2)^2 A_\phi^2 \ln I \qquad \text{for unsymmetrical mixtures} \tag{32b}$$

whereas for unsymmetrical mixtures the HOLL for g_1 is[8,36]

$$\lim_{I \to 0} g_1 = (12\pi A_\phi)^3 (z_2 - z_1)^3 (z_1 + z_2 + z_3) i_3 I^{-1/2} \tag{33}$$

where A_ϕ is the Debye Huckel limiting slope[24,37,38]. However, the HOLL of g_1 for symmetrical mixtures is yet to be found. The Kappa graph integral i_3 has been evaluated[32,39,40]. From eq(32) we immediately reach an important conclusion that at

very low concentrations g_0 and g'_0 should have the same sign for symmetrical mixtures whereas they must be of different signs for unsymmetrical mixtures. Furthermore, the mixing for symmetrical mixtures are indepedent on the common ion at low concentrations[6,31,32].

IV. SEMI-EMPIRICAL METHODS

Besides the empirical methods of Harned and McKay, other semi-empirical methods all express the activity coefficients of the two electrolytes by a same set of parameters so that the activity coefficeints of an electrolyte can be predicted once the parameters are determined from the other electrolyte. Different methods were devised according to their different approximations to the g_n coefficients. Usually the degree M of the activity coefficient equation is chosen to be two which is adequate for msot cases. The followings are some best known methods.

(A) Method S (Scatchard)[14-16]

$$g_0 = b_{01} + b_{02}I/2 + b_{03}I^2/3 \tag{34a}$$

$$g_1 = b_{12}/2 + b_{13}I/3 \tag{34b}$$

$$g'_0 = b_{02}I/2 + 2b_{03}I/3 \tag{34c}$$

$$g'_1 = b_{13}/3 \tag{34d}$$

where b_{ij} are parameters to be optimized. For a second degree equation we can set $b_{12} = b_{13} = 0$.

(B) Method P (Pitzer)[17-22]

$$g_0 = K_1B_{MX} + K_2B_{NX} + K_3\theta_{MN} + I(K_4C^*_{MX} + K_5C^*_{NX} + K_6\Psi_{MNX}) \tag{35a}$$

$$g_1 = K_7C^*_{MX} + K_8C^*_{NX} + K_9\Psi_{MNX} \tag{35b}$$

where B and C^* are I-dependent parameters for pure electrolytes and can be predetermined, while θ and Ψ are I-dependent parameters for the mixing of electrolytes and are to be optimized. According to the consistency condition, which is a necessary condition for the cross differential condition to be satisfied, g_1 must be a I-independent constant[12], and in fact Pitzer had suggested that C^* and Ψ be taken as I-independent constants so that this consistency condition is satisfied. g'_0 and g'_1 can be obtained from differentiating g_0 and g_1 respectively with respect to I. K_n are constants depending only on the charge type and for symmetrical mixtures all K_n vanish except K_3 and K_6.[13,23,24] While Ψ is assuming to be a constant, the general form of θ can be written either by[23,24]

$$\theta_{MN} = {}^E\theta.\delta + {}^S\theta(1 + kh) \tag{36a}$$

or

$$\theta_{MN} = \theta_0f_1 + \mu f_2 \tag{36b}$$

μ and k are adjustable parameters and h and θ_0 are functions of I[17,24]:

$$h = [1 - (1 + 2v)c]/2v^2 \tag{37}$$

$$c = \exp(-2v) \tag{38}$$

$$v = \alpha I^{1/2}/2 \tag{39}$$

α is chosen to be 2 for most cases. ${}^E\theta$ is the electrostatic contribution to θ which

is I-dependent whereas $^S\theta$ is the short range contribution which is assumed to be a constant.

(i) For symmetrical mixtures, we have $^E\theta = 0$,

$$\theta_0 = \lim_{I->0} \theta = g_0(0) \exp(\lambda_0 I)/K_3 \tag{40}$$

Also $-1 < k < 0$. If HOLL is to be satisfied exactly, then[18]

$$k = -9z_1^2 A_\phi/(\alpha + 9z_1^2 A_\phi) = s \tag{41}$$

but we should point out that the above k value does not correspond to the optimum value.[24]

(ii) For unsymmetrical mixtures, we usually take δ to be 0 or 1 although the theoretical δ is[23]

$$\delta = \nu_A \nu_A^- \nu_B \nu_B^-/z_1 z_2 (z_1 + z_2)^2 \tag{42}$$

and

$$\theta_0 = [3(z_1 - z_2)^2 A_\phi^2 \ln I - L_0]/K_3 \tag{43}$$

with

$$L_0 = K_1(\beta_{MX}^{(0)} + \beta_{MX}^{(1)}) + K_2(\beta_{NX}^{(0)} + \beta_{NX}^{(1)}) \tag{44}$$

$\beta^{(n)}$ etc have their usual meanings[17,18]. f_1 and f_2 are functions of I which satisfied the following conditions[23,24,28]

$$\lim_{I->0} f_1 = 1 \quad , \quad \lim_{I->0} f_2 = 0 \tag{45}$$

Typical examples of the Pitzer methods are

P-I	θ, θ', ψ are independent cosntants
P-II	$\theta = {}^E\theta + {}^S\theta$
P-III	$\theta = {}^S\theta (1 + kh)$
P-4	$\theta = \theta_0 h + \mu I^{3/2}$
P-4f	$\theta = \theta_0 p + \mu P$

where

$$p = (1 - c)/2\nu \quad , \quad P = [(1 - \nu) - (1 + \nu)c]/2\nu^2 \tag{46}$$

When the value of k is given by eq(41) P-III becomes P-6 for symmetrical mixtures.

(C) Method RWR (Robinson-Wood-Reilly)[6]

$$g_0 = \mu \exp[6z_1^2 A_\phi I^{1/2}/(1 + a_0 I^{1/2})] + \nu I \tag{47a}$$

$$g_1 = 0 \tag{47b}$$

This is probably the first semi-empirical calculation which has incorporated the HOLL. Although the method is for symmetrical mixtures only, it can readily be extended to unsymmetrical mixtures by choosing the appropriate g_0.

(D) Method H (Higher Order Limiting Law)[25,35,42,43]

$$g_0 = \lambda \omega(I) + \mu I + \nu I^{3/2} \tag{48a}$$

$$g_1 = \text{constant} \tag{48b}$$

where for symmetrical mixtures[28]

$$\lambda = g_0(0) , \qquad \omega(I) = \exp(\lambda_0 I^{1/2}) \tag{49a}$$

While for unsymmetrical mxitures[28]

$$\lambda = 3(z_1 - z_2)^2 A_*^2 , \qquad \omega(I) = \ln I \tag{49b}$$

This method H is a refinement of the RWR method by including the $I^{3/2}$ factor as observed by Scatchard and Prentiss[44], and by introducing the consistency condition of eq(48b). For unsymemtrical mixtures λ can also be taken as a variable without violating the HOLL because $\omega \rightarrow -\infty$ when $I \rightarrow 0$.

(E) Method LA (All Mixing Coefficients)[27]

$$g_0 = (A_0 + B_0)/2 + A_1 I \tag{50a}$$

$$g'_0 = -2A_1 \tag{50b}$$

$$g_1 = 0 \tag{50c}$$

(F) Method LC (Consistency Test)[27]

$$g_0 = (A_0 + B_0)/2 + A_1 I \tag{51a}$$

$$g'_0 = -2A_1 \tag{51b}$$

$$g_1(I_m,Y_i) = g_1(I_n,Y_j) = 0 \tag{51c}$$

where I_m and I_n are any two total ionic strength and Y_i is a fractional ionic strength at fixed I_m whereas Y_j is at fixed I_n. All the mixing coefficients are to be optimized based on eq(51c), from one ionic strength to another.

(G) Method HA (HOLL All Mixing Coefficients)[28]

$$g_0 = [A_0 + B_0 + I(A_1 + B_0)]/2 \tag{52a}$$

$$g'_0 = -(A_1 + B_1) \tag{52b}$$

$$g_1 = (B_1 - A_1)/3 \tag{52c}$$

$$g'_1 = 0 \tag{52d}$$

$$B_0 = 2[\lambda\omega(I) + \nu I^{3/2}] - A_0 , \quad B_1 = 3g_1 + A_1 \tag{52e}$$

where $\lambda,\omega(I)$ are the same as in eq(49). We also note that g_0' is a function of I while g_1 is a constant although both A_1 and B_1 are functions of I.

V. INDIRECT METHOD OF FRIEDMAN

All the above mentioned methods require the knowledge of the experimental data of one of the electrolytes, this need not be the case in the *ab initio* method which needs only the computation of the radial correlation functions. Here we will present an indirect method which was developed by Friedman and his coworker.[8] In this method we have to compute the generalized compressibility function[45,46]

$$M_{ij} = \left(\frac{\partial c_i}{\partial \mu_j}\right)_{T,\mu_w} = (c_i\delta_{ij} + c_iG_{ij}c_j)/RT \tag{53}$$

where

$$G_{ij} = \int [g_{ij}(r) - 1]4\pi r^2 dr \tag{54}$$

and $g_{ij}(r)$ is the radial correlation function. Athough M_{ij} is a singular matrix for ionic electrolytes, Friedman was able to handle this singularity and compute the activity coefficients of a mixed electrolyte in an indirect way. Let us define

$$l_A = z_1(z_1 - z_3)/2 \quad , \quad l_B = z_2(z_2 - z_3)/2 \tag{55a}$$

$$h = (z_2 - z_1)/(2z_3 - z_1 - z_2) \quad , \quad D = M_{11}M_{22} - M_{12}M_{21} \tag{55b}$$

then

$$\partial \ln\gamma_A/\partial I = [v_A^+(c_2 M_{12} - c_1 M_{22})/(v_A D) - 1]/I \tag{56a}$$

$$\partial \ln\gamma_B/\partial I = [v_B^+(c_1 M_{21} - c_2 M_{11})/(v_B D) - 1]/I \tag{56b}$$

$$\partial \ln\gamma_A/\partial y = \frac{z_A}{l_A}\left\{\frac{I}{RTD}\left(\frac{M_{12}}{l_B} + \frac{M_{22}}{l_A}\right) + \left[\frac{1}{1-y} + \frac{2hz_1}{z_3(1-hY)}\right]\right\} \tag{56c}$$

$$\partial \ln\gamma_B/\partial y = \frac{z_B}{l_B}\left\{\left[\frac{1}{y} - \frac{2hz_2}{z_3(1-hY)}\right] - \frac{I}{RTD}\left(\frac{M_{12}}{l_A} - \frac{M_{11}}{l_B}\right)\right\} \tag{56d}$$

At a fixed I we can compute various values of $\partial \ln\gamma_A/\partial y$ at different y according to eq(56c), then these data may be used to optimize A_n from The following eq:

$$\partial \ln\gamma_A/\partial y = z_A I \sum_{n=0}^{M-1} [A_n(-I)^n(Y^n - 2nyY^{n-1})] \tag{57}$$

Similarly we can optimize B_n coefficients. Finally, from these A_n and B_n we can compute $\ln\gamma_A$ and $\ln\gamma_B$ respectively from eqs(14a) and (14b). Furthermore, g_n and g'_n can also be obtained from eqs(23b) and (23d).

VI. COMPARISON OF THE VARIOUS METHODS

Figure 1 shows the accuracies of the various methods for the overall results of nine symemtrical mixtures[43]. Whether the HOLL is satisfied or not is indicated by Y (yes) or N (no). The number of points whose absolute differences $|\log\gamma_A(cal) - \log\gamma_A(obs)|$ have exceeded the experimental tolerance of 0.002 as estimated by Bates and Robinson[47] are shown inside the parentheses. Similarly, Figure 2 shows the accuracies of the methods for the overall results of eight unsymemtrical mixtures.[42]
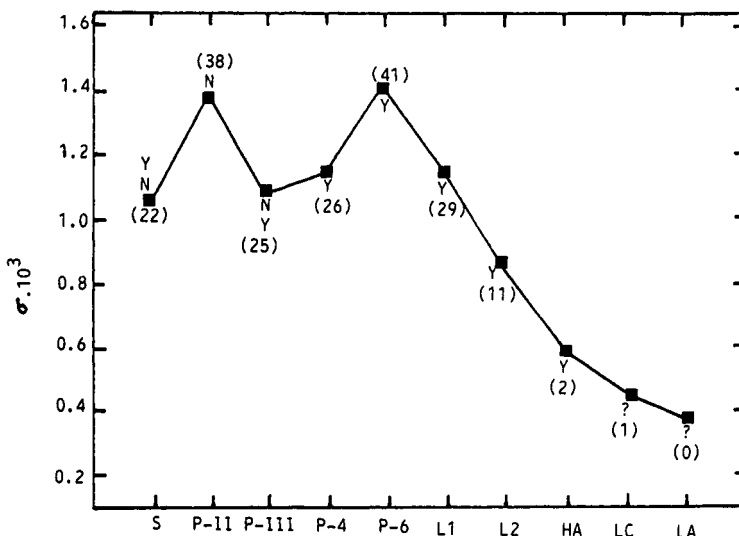

Fig. 1.   Overall results of nine symmetrical binary mixtures
NaCl+NaX, X = acetate, propionate, hydrogen malonate,
                    hydrogen succinate & trichloroacetate
NaBr+NaX, X = formate, acetate and propionate
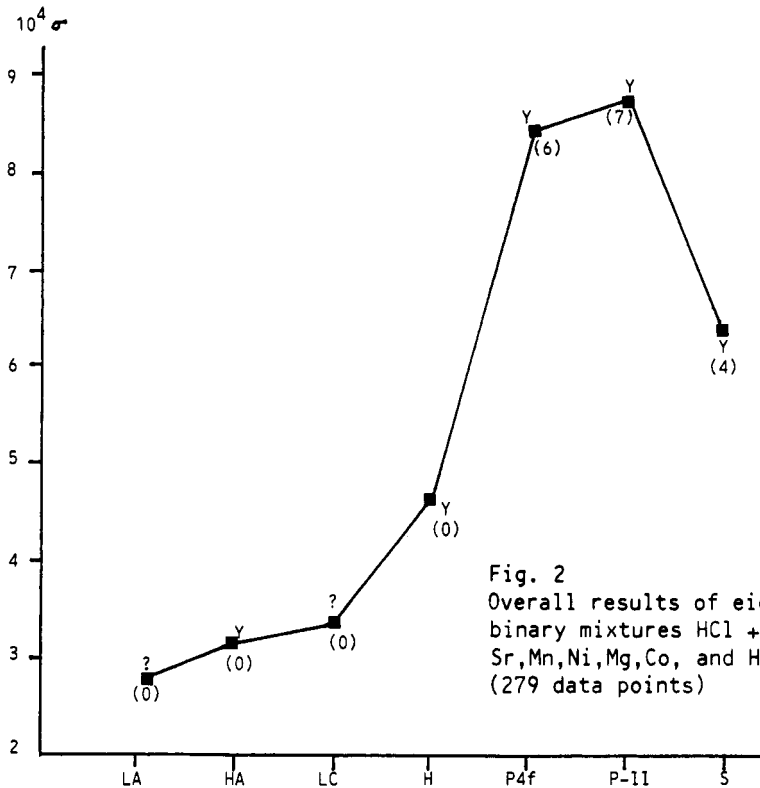
HCl+KCl (374 data points)

Fig. 2
Overall results of eight unsymmetrical binary mixtures HCl + MCl_2, M = Ca,Ba, Sr,Mn,Ni,Mg,Co, and HBr + $SrBr_2$ (279 data points)

The accuracies of the various methods may be explained by their g_0 expressions, which can generally be written as

$$g_0(I) = f_1(I) + f_2(I)I + f_3(I)I^2 \tag{58}$$

We see that the method S is the only method in which all f_i are constants. But since it is also the only method with non zero f_3, its results can be better than the Pitzer methods. On the other hand, method H for unsymmetrical mxitures, methods L1 and L2 for symmetrical mixtures, and method P all have used I-dependent f_1 but constant f_2. The reason that P-IV are more accurate than P-II is self obvious especially for symemtrical mixtures. The method H is more accurate than method P probably because of the $I^{3/2}$ factor and the non zero g_1, whereas L1 and P4 have same accuracy because their g_0 expressions are nearly the same. By right L2 should be more accurate than L1 as it is the case. All the other methods LA, LC and HA have employed I-dependent f_1 and f_2 and therefore produced the best results. The method A is probably the best because all its mixing coefficients were optimized at different ionic strengths independently, whereas the other two methods have to make use of the results at other ionic strengths.

Concerning the problem of the HOLL requirement, we know that b_{o1} and b_{o2} in method S must be of the same sign for symmetrical mixtures and opposite signs for unsymemtrical mixtures. Although the results of all the eight unsymemtrical mixtures have satisfied the HOLL, most of the symmetrical mixtures we have tested do not. This has cast some doubt on this method, because it is very difficult to dictate the outcome of the signs of b_{ij} parameters. As for Pitzer's methods, P-II does not satisfy HOLL for symmetrical mixtures although it does satisfy HOLL for unsymmetrical mixtures but with worse accuracy as compared to other methods. P-III does not satisfy HOLL for unsymmetrical mixtures and for most of the symmetrical mixtures. However, the chocie of optimum k value will significantly improve the accuracies at the expense of HOLL. Both P4 and P4f satisfied HOLL. For the other remaining methods they all have satisfied the HOLL except LA and LC where the test of HOLL is not feasible until we can substantially improve our experimental techniques.

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APPENDIX 1.   SUMMARY OF THE METHOD FOR SYMMETRICAL BINARY MIXTURES

	HOLL	f_1	f_2	f_3	g_1	g'_o
P		$K_3\theta$	$K_6\psi$	0	0	$f'_1 + f_2$
P-II	N	$\theta = {}^S\theta$	$K_6\psi$	0	0	f_2
P-III	N/Y	$\theta = {}^S\theta(1+kh)$	$K_6\psi$	0	0	$f'_1 + f_2$
P4	Y	$\theta = \theta oh + \mu I^{3/2}$	$K_6\psi$	0	0	$f'_1 + f_2$
P6	Y	$\theta = {}^S\theta(1+sh)$	$K_6\psi$	0	0	$f'_1 + f_2$
S	N/Y	b_{o1}	$b_{o2}/2$	$b_{o3}/3$	0	$b_{o2}/2 + 2b_{o3}I/3$
RWR	Y	$\lambda \exp[Q/(1+a_oI^{1/2})]$	μ	0	0	$f'_1 + f_2$
L1	Y	$\lambda\exp(Q) + vI^{3/2}$	μ	0	const	$f'_1 + f_2$
L2	Y	$\lambda\exp(\beta I^{1/2}) + vI^{3/2}$	μ	0	const	$f'_1 + f_2$
LA	?	$(A_O + B_O)/2$	A_1	0	$(B_1 - A_1)/3 = 0$	$-2A_1$
LC	?	$(A_O + B_O)/2$	A_1	0	$g_1(I_1) = g_1(I_2) = 0$	$-2A_1$
HA	Y	$\lambda\exp(Q) + vI^{3/2}$ $(B_O = 2f_1 - A_O)$	$A_1 + 1.5\ g_1$ $(B_1 = 2f_2 - A_1)$	0	const	$-2f_2$

$$g_o = f_1 + f_2 I + f_3 I^2, \quad Q = 6z_1^2 A_\star I^{1/2}, \quad \theta_o = g_o(0)\exp(Q)/K_3$$
At low I, sign (g_o) = sign (g'_o)

APPENDIX 2.   SUMMARY OF THE METHODS FOR UNSYMMETRICAL BINARY MIXTURES

	HOLL	f_1	f_2	f_3	g_1	g'_o
P		$K_1 B_{MX} + K_2 B_{NX} + K_3\theta$	$K_4 C^\phi_{MX} + K_5 C^\phi_{NX} + K_6\psi$	0	$K_7 C^\phi_{MX} + K_8 C^\phi_{NX} + K_9\psi$	$f_1' + f_2$
P-I	N	$\theta = $ const	...	...	...	f_2
P-II	Y	$\theta = {}^E\theta + {}^S\theta$	...	...	...	$f_1' + f_2$
P-III	N	$\theta = {}^S\theta(1+kh)$	...	...	...	$f_1' + f_2$
P4f	Y	$\theta = \theta_0 p + \mu P$	...	...	...	$f_1' + f_2$
S	Y	b_{01}	$b_{02}/2$	$b_{03}/3$	0	$f_2 + 2f_3 I$
H	Y	$\lambda \ln I + vI^{3/2}$	μ	0	const	$f_1' + f_2$
LA	?	$(A_0 + B_0)/2$	A_1	0	$(B_1 - A_1)/3 = 0$	$-2A_1$
LC	?	$(A_0 + B_0)/2$	A_1	0	$g_1(I_1) = g_1(I_2) = 0$	$-2A_1$
HA	Y	$\lambda \ln I + vI^{3/2}$ $(B_0 = 2f_1 - A_0)$	$A_1 + 1.5\ g_1$ $(B_1 = 2f_2 - A_1)$	0	const	$-2f_2$

$$g_o = f_1 + f_2 I + f_3 I^2, \quad \lambda = 3(z_1 - z_2)^2 A_\star^2, \quad \theta_o = (\lambda \ln I - L_o)/K_3$$
At low I, sign (g_o) = - sign (g'_o).