Malaysian Journal of Science **16B**: 27-35 (1995)

Mixing coefficients of ternary mixed electrolytes

Tiong-Koon Lim
Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia

ABSTRACT The cluster expansion theory is used to explain ternary mixed electroytes having a common ion. The mixing coefficients have been studied and their inter relationships are reported. Their possible applications to the calculation of activity coefficients and osmotic coefficients are shown. Higher-order limiting laws are also discussed.

ABSTRAK Teori perkembangan gugusan telah digunakan untuk menjelaskan elektrolit campuran ternari yang mempunyai satu ion biasa. Pekali campuran telah disiasat dan perhubungan antara dilapurkan. Kegunaannya yang mungkin untuk perkiraan pekali aktiviti dan pekali osmotik ditunjukkan. Peraturan tahap tinggi juga dibincangkan.

(mixing coefficients, ternary mixed electroytes)

INTRODUCTION

Ternary mixed electrolytes have been studied using the Harned equations[1-5] and the Pitzer equations [6]. In all these studies, the number of parameters to be optimized is necessarily larger than that used for a binary mixture and this implies that more experimental data are required. Obviously, this will introduce problems, both theoretically and experimentally. It is therefore desirable to study the mixing coefficients of ternary mixtures and thus to find a way to reduce the number of optimizing parameters. This is especially significant when the number of electrolytes in a mixture keeps increasing. Given a fixed order of an equation, one easy way out is, of course, to neglect those parameters which we believe are negligible; this approach is, however, not as acceptable and unambiguous as to reduce the number of parameters from the reformulation of the theory itself. In this article, we will show that the interactions of three electrolytes can be reduced to two binary interaction portions and one ternary interaction part; since the latter consists of the same cluster integrals and possesses similar expressions as the binary interactions, we would expect that the mixing coefficients in a ternary mixture are essentially not much different from those for binary mixtures. Furthermore, similar to the treatment of a binary mixture where the activity coefficients can be separated into a single electrolyte portion and a binary interaction part, for a ternary mixture, the two binary portions can also be evaluated separately and solely from the data of binary mixtures; only the ternary interaction part needs to be determined from the data of ternary mixtures. More importantly, this procedure can be extended to any number of electrolytes in a mixture. The above observations deductions are based on the results of the Cluster expansion theory which was first developed by McMillan and Mayer[7] and later generalized by Friedman[8,9].

It is well known that the applications of the Cluster expansion method to the changes of excess Helmholtz free energy and osmotic coefficients for a binary mixed electrolytes can be done directly[10] whereas only an indirect method is possible for the calculation of the activity coefficients[11]. The thermodynamics of their mixing coefficients are also known[8,12,13]. The calculation of the direct correlation functions can be done from the approximation methods such as the linearized Debye-Huckel approximation, the Percus-Yevick (PY) approximation, the mean spherical approximation, and the hypernetted chain (HNC) approximation[8,9]. However, it is sometimes simpler and more convenient to use semi-empirical methods such as the Scatchard method[14,15], Pitzer's method[16-19], the Higher-order limiting law method[20,21], and recent methods of Lim[22,23]. The thermodynamics of the mixing coefficients in these methods have also been studied[8,12,13,24]. In this paper, the theory for ternary mixed electrolytes with a common ion will be formulated and the thermodynamics of the mixing coefficients are shown.

GENERAL THEORY

Consider a mixture of a solvent w and s electrolytes A, B, C, ..., S. Let 1, 2, ..., s be the positive ions of the electrolytes and s+1 their common negative ions, the corresponding charges being z_1, z_2, ..., z_s for the positive ions and z_{s+1} for negative ion. ν_L^+ and ν_L^- are the numbers of positive and negative ions of electrolyte L with $\nu_L = \nu_L^+ + \nu_L^-$. We may further define $z_A = |z_1 z_{s+1}|/2$, $z_B = |z_2 z_{s+1}|/2$, ..., $z_S = |z_s z_{s+1}|/2$. For a ternary mixture of three electrolytes A, B and C, we have four ions 1, 2, 3 and 4, the change in excess molar Helmholtz free energy upon the mixing at constant ionic strength I, temperature T and volume V of 1 litre can then be written as[8,10]

$$(1)\quad \begin{aligned} \Delta_m A^{ex}/RTV &= -(\Delta_m s_2 + \Delta_m s_3 + \Delta_m s_4 + \ldots) \\ &= y_B(1 - y_B)I^2 \sum_{k=0}^{M-1} g_{Bk} y_B^{\,k} + y_C(1 - y_C)I^2 \sum_{k=0}^{M-1} g_{Ck} y_C^{\,k} \\ &\quad + I^2 \sum_{m,\,n=1}^{M+1} G_{mn}^{BC}\, y_B^m\, y_C^n \end{aligned}$$

where y_B is the fractional ionic strength of B and so forth, and $y_A + y_B + y_C = 1$. The superscript BC of the mixing coefficients $G_{mn}{}^{BC}$ will be omitted throughout this discussion. If the $\Delta_m A^{ex}$ for the mixing of the binary mixture A + B is represented by[8,12,13,21]

$$(2)\quad \Delta_m A^{ex}/RTV = y_B(1 - y_B)I^2 \sum_{k=0}^{M-1} g_k^{AB}\, (1 - 2y_B)^k$$

then the g_{Bk} coefficients are related to $g_k{}^{AB}$:

$$(3)\quad g_{Bk} = \sum_{r=u}^{M-1} \binom{r}{k}(-2)^k g_r^{AB}$$

The g_{Ck} coefficients in the binary mixture A + C are similarly related.

The cluster expansion terms in eq (1) can be expressed as

$$\begin{aligned} \Delta_m s_2 &= -y_B(1 - y_B)I^2 S_{B0}{}^{(2)} - y_C(1 - y_C)I^2 s_{C0}{}^{(2)} \\ &\quad - I^2(s_{11}{}^{(2)} y_B y_C) \\ (4)\quad \Delta_m s_3 &= -y_B(1 - y_B)I^2(s_{B0}{}^{(3)} + y_B s_{B1}{}^{(3)}) - y_C(1 - y_C)I^2 \\ &\quad (s_{C0}{}^{(3)} + y_C s_{C1}{}^{(3)}) - y_B y_C I^2 (s_{11}{}^{(3)} + y_B s_{21}{}^{(3)} \\ &\quad + y_C s_{12}{}^{(3)}) \\ \Delta_m s_4 &= -y_B(1 - y_B)I^2\,[s_{B0}{}^{(4)} + y_B s_{B1}{}^{(4)} + y_B{}^2 s_{B2}{}^{(4)}] \\ &\quad - y_C(1 - y_C)I^2[s_{C0}{}^{(4)} + y_C s_{C1}{}^{(4)} + y_C{}^2 s_{C2}{}^{(4)}] \\ &\quad - y_B y_C I^2\,[s_{11}{}^{(4)} + y_B s_{21}{}^{(4)} + y_B{}^2 s_{31}{}^{(4)} + y_C s_{12}{}^{(4)} \\ &\quad + y_C{}^2 s_{13}{}^{(4)} + y_B y_C s_{22}{}^{(4)}] \end{aligned}$$

etc., so that

$$(5)\quad \begin{aligned} g_{Bn} &= \sum_{k=n+2} s_{Bn}^{(k)} \quad , (n \geq 0) \\ g_{Cn} &= \sum_{k=n+2} s_{Cn}^{(k)} \quad , (n \geq 0) \\ G_{mn} &= \sum_{k=m+n} s_{mn}^{(k)} \quad , (m,n \geq 1) \end{aligned}$$

The summation limit in eq (5) equals to the highest order of s_k used; e.g., this number is 4 in our present expansion. The corresponding cluster integrals are

$$(6)\quad \begin{aligned} s_{B0}{}^{(2)} &= (z_1 - z_2)^2 X_2 \\ s_{C0}{}^{(2)} &= (z_1 - z_3)^2 X_2 \\ s_{11}{}^{(2)} &= -2(z_1 - z_2)(z_1 - z_3)X_2 \\ s_{B0}{}^{(3)} &= -(z_1 - z_2)^2[(z_1{}^2 + z_1 z_4 + z_4{}^2) \\ &\quad + (z_1 + z_2 + z_4)(z_1 + z_2 + 2z_4)]X_3 \\ s_{B1}{}^{(3)} &= (z_1 - z_2)^3(z_1 + z_2 + z_4)X_3 \\ s_{C0}{}^{(3)} &= -(z_1 - z_3)^2[(z_1{}^2 + z_1 z_4 + z_4{}^2) \\ &\quad + (z_1 + z_3 + z_4)(z_1 + z_3 + 2z_4)]X_3 \\ s_{C1}{}^{(3)} &= (z_1 - z_3)^3(z_1 + z_3 + z_4)X_3 \\ s_{11}{}^{(3)} &= \{(z_1{}^2 + z_1 z_4 + z_4{}^2)[2z_1 z_4 + 2z_2 z_3 \\ &\quad - 2z_1(z_1 - z_2) - 2z_1(z_1 - z_3)] \\ &\quad + 2(z_1 - z_2)(z_1 - z_3)(z_1 + z_4)(2z_1 + z_2 \\ &\quad + z_3 + 2z_4)\}X_3 \\ s_{21}{}^{(3)} &= -(z_1 - z_2)^2(z_1 - z_3)(3z_1 + 2z_2 + z_3 + 3z_4)X_3 \\ s_{12}{}^{(3)} &= -(z_1 - z_3)^2(z_1 - z_2)(3z_1 + z_2 + 2z_3 + 3z_4)X_3 \\ s_{B0}{}^{(4)} &= \{+(z_1 - z_2)^2[(z_1 + z_2 + 2z_4)^2 + 4(z_1 + z_4)^2 \\ &\quad + 2(z_1 + z_4)(z_2 + z_4)]\}X_4 \\ s_{B1}{}^{(4)} &= \{-(z_1 - z_2)^3[(z_1 + z_2 + 2z_4) + 2(z_1 + z_4)]\}X_4 \\ s_{B2}{}^{(4)} &= (z_1 - z_2)^4 X_4 \\ s_{C0}{}^{(4)} &= \{+(z_1 - z_3)^2[(z_1 + z_3 + 2z_4)^2 + 4(z_1 + z_4)^2 \\ &\quad + 2(z_1 + z_4)(z_3 + z_4)]\}X_4 \\ s_{C1}{}^{(4)} &= \{-(z_1 - z_3)^3[(z_1 + z_3 + 2z_4) + 2(z_1 + z_4)]\}X_4 \\ s_{C2}{}^{(4)} &= (z_1 - z_3)^4 X_4 \\ s_{11}{}^{(4)} &= -12(z_1 + z_4)^2(z_1 - z_2)(z_1 - z_3)X_4 \\ s_{21}{}^{(4)} &= 12(z_1 - z_2)^2(z_1 - z_3)(z_1 + z_4)X_4 \\ s_{12}{}^{(4)} &= 12(z_1 - z_3)^2(z_1 - z_2)(z_1 + z_4)X_4 \\ s_{22}{}^{(4)} &= -6(z_1 - z_2)^2(z_1 - z_3)^2 X_4 \\ s_{31}{}^{(4)} &= -4(z_1 - z_2)(z_1 - z_3)[(z_1 - z_2)^2 - 3z_4(z_1 + z_2 \\ &\quad + z_4)]X_4 \\ s_{13}{}^{(4)} &= -4(z_1 - z_3)(z_1 - z_2)[(z_1 - z_3)^2 - 3z_4(z_1 + z_3 \\ &\quad + z_4)]X_4 \end{aligned}$$

with[25,8]

$$(7)\quad \begin{aligned} X_2 &= 3A_\phi{}^2 \ln I \\ X_3 &= 2(12\pi A_\phi)^3\, I^{1/2} \int \triangle\, d\{ij\} \\ X_4 &= (12\pi A_\phi)^3\, I^{1/2} \int (\boxminus + \tfrac{2}{3} \boxtimes)\, d\{ijk\} \end{aligned}$$

A_ϕ is the well known Debye-Huckel limiting slope[17].

It was shown by Friedman[10] that the difference in thermodynamic coefficients in the Lewis-Randall and McMillan-Mayer systems are negligible at low concentrations and modest at moderate concentrations. In the semi-empirical fitting these differences may not be significant as they can be absorbed in the procedure of the optimization of parameters. Therefore, for convenience, we will neglect this conversion factor between the Lewis-Randall and the McMillan-Mayer system[26], and use the Gibbs free energy changes $\Delta_m G^{ex}$ and the Helmholtz free energy changes $\Delta_m A^{ex}$ interchangeably. If we define γ_L to be the mean activity coefficient of electrolyte L in the mixture, and

$$(8)\quad g_L^{ex}(y_B, y_C, ..., y_S, I) = (RT/z_L)\ln\gamma_L$$

then the excess free energy G^{ex} can be written as

$$(9)\quad G^{ex}(y_B, y_C, ..., y_S, I) = \Delta_m G^{ex}(y_B, y_C, ..., I) + \sum_{L=A}^{S} y_L G^{ex}(\delta_{BL}, \delta_{CL}, ..., \delta_{SL}, I)$$

where δ_{KL} has a value of 1 if K = L, and zero otherwise, and

$$(10)\quad G^{ex}(y_B, y_C, ..., y_S, I) = G_w^{ex}(y_B, y_C, ..., I) + I\sum_{L=A}^{S} y_L g_L^{ex}(y_B, y_C, ..., y_S, I)$$

where G_w^{ex} is the excess Gibbs free energy for the solvent w. For a ternary mixture, $\Delta_m G^{ex}$ may be given by eq (1) while g_L^{ex} may be defined by

$$(11a)\quad g_A^{ex}(y_B,y_C,I) = g_A^{ex}(0,0,I) - \frac{\ln 10RT}{z_A}\left\{\sum_{k=1}^{M+1}(y_B^k A_{Bk} + y_C^k A_{Ck}) + \sum_{m,\,n=1}^{M+1} A_{mn} y_B^m y_C^n\right\}$$

$$(11b)\quad g_B^{ex}(y_B,y_C,I) = g_B^{ex}(1,0,I) - \frac{\ln 10RT}{z_B}\left\{\sum_{k=1}^{M+1}(y_C^k B_{Ck} + y_A^k B_{Ak}) + \sum_{m,\,n=1}^{M+1} B_{mn} y_A^m y_C^n\right\}$$

$$(11c)\quad g_C^{ex}(y_B,y_C,I) = g_C^{ex}(0,1,I) - \frac{\ln 10RT}{z_C}\left\{\sum_{k=1}^{M+1}(y_B^k C_{Bk} + y_A^k C_{Ak}) + \sum_{m,\,n=1}^{M+1} C_{mn} y_A^m y_B^n\right\}$$

From equating the relations (9) and (10), we may generalize the procedure used by Friedman[12] to obtain the general relationship between g_L^{ex} and $\Delta_m G^{ex}$ as follows:

$$(12)\quad g_L^{ex}(y_B,y_C,...,y_S,I) = g_L^{ex}(\delta_{BL}, \delta_{CL}, ..., \delta_{SL}, I) + \frac{\partial \Delta_m G^{ex}}{\partial I} + \sum_{K=B}^{s} \frac{\delta_{KL} - y_K}{I}\frac{\partial \Delta_m G^{ex}}{\partial y_K} - RTI\sum_{\substack{K=A \\ (K\neq L)}}^{s} y_K \Phi_{KL}$$

where $\Phi_{KL} = \Phi_K - \Phi_L$, and

$$(13)\quad \Phi_L = G_w^{ex}(\delta_{BL}, \delta_{CL}, ..., \delta_{SL}, I)/RTI^2 = (1 - \phi_L^o)/Iz_L$$

with ϕ_L^o being the osmotic coefficient for the pure electrolyte L.

Substituting eq (1) into eq (12), we have

$$(14a)\quad g_A^{ex}(y_B,y_C,I) = g_A^{ex}(0,0,I) + RTI\left\{-(y_B\Phi_{BA} + y_C\Phi_{CA}) + \sum_{k=1}^{M+1}[f_1^B(k)y_B^k + f_1^C(k)y_C^k] + \sum_{m,\,n=1}^{M+1}[f_1(m,n)y_B^m y_C^n]\right\}$$

$$(14b)\quad g_B^{ex}(y_B,y_C,I) = g_B^{ex}(1,0,I) + RTI\left\{-(y_A\Phi_{AB} + y_C\Phi_{CB}) + \sum_{k=0}^{M+1}[f_2^B(k)y_B^k + (G_{1k} + f_1^C(k))y_C^k] + \sum_{m,\,n=1}^{M+1}[f_1(m,n) + (m+1)G_{m+1,n}]y_B^m y_C^n\right\}$$

$$(14c)\quad g_C^{ex}(y_B,y_C,I) = g_C^{ex}(0,1,I) + RTI\{-(y_A\Phi_{AC} + y_B\Phi_{BC}) + \sum_{k=0}^{M+1} [f_2^C(k)y_C^k + (G_{k1} + f_1^B(k))y_B^k] + \sum_{m,\,n=1}^{M+1} [f_1(m,n) + (n+1)G_{m,n+1}] y_B^m y_C^n\}$$

where

$$f_1^L(k) = I(g'_{L,k-1} - g'_{L,k-2}) + (2-k)(g_{L,k-1} - g_{L,k-2})$$

$$(15)\quad f_1(m,n) = IG'_{mn} + (2-m-n)G_{mn}$$

$$f_2^L(k) = I(g'_{L,k-1} - g'_{L,k-2}) + (k+1)g_{L,k} + (1-2k)g_{L,k-1} + (k-2)g_{L,k-2}$$

After some manipulation of eq (14), we obtain the relationship between those mixing coefficients which are defined in eqs (1) and (11):

$$(16a)\quad -\frac{\ln 10}{z_A} A_{Lk} = I[f_1^L(k) - \delta_{k1}\Phi_{LA}]$$

$$(16b)\quad -\frac{\ln 10}{z_A} A_{mn} = If_1(m,n)$$

$$(16c)\quad -\frac{\ln 10}{z_B} B_{Ak} = F_1^B(k) - I\Phi_{AB}\delta_{k1}$$

$$(16d)\quad -\frac{\ln 10}{z_B} B_{Ck} = F_2^B(k) - I\Phi_{CB}\delta_{k1}$$

$$(16e)\quad -\frac{\ln 10}{z_A} B_{mn} = F^B(m,n)$$

where

$$(17a)\quad F_1^B(k) = (-1)^k\{-Ik(g_{B,k-1} - g_{B,k-2}) + \sum_{i=k}^{M+1} [f_5^B(k)\binom{i}{k} - I(g_{Bi} - g_{B,i-1})(i+1)\binom{i}{k-1}]\}$$

$$(17b)\quad F_2^B(k) = F_1^B(k) + F_1(k) + F_2(k) + f_4^C(k)$$

$$(17c)\quad F^B(m,n) = IG_{2-m,n} + F_1^B(m,n) + F_2(m,n) + F_3(m,n) + F_4(m,n)$$

with

$$(18a)\quad F_1(k) = IG_{1,k-1} + (-1)^{k+1} \sum_{i=\max(1,k-1)}^{M+1} (I^2G'_{i1} + IG_{i1})\binom{i}{k-1}$$

$$(18b)\quad F_2(k) = (-1)^k \sum_{i=0}^{k-2} \sum_{j=\max(1,i)}^{M+1} (-1)^{k-i}\binom{j}{i} \{f_6(j,k-i) + I[(j+1)G_{j+1,k-i-1} - (k-i)G_{j,k-i}]\}$$

$$(18c)\quad f_4^C(k) = f_5^C(k) - Ik(g_{C,k-1} - g_{C,k-2})$$

$$(18d)\quad f_5^B(k) = I^2(g'_{B,k-1} - g'_{B,k-2}) + 2I(g_{B,k-1} - g_{B,k-2})$$

$$(18e)\quad f_6(m,n) = I^2G'_{mn} + 2IG_{mn}$$

and

$$(19a)\quad F_1^B(m,n) = I(-1)^{m+n} \sum_{k=m+n-1}^{M+1} [\frac{f_5^B(k)}{I} C_{kmn}\delta_{+,M+1-m-n} - (k+1)(g_{Bk} - g_{B,k-1})(C_{k,n-1,m} + C_{k,n,m-1}) + G_{k1}C_{k,n-1,m}\delta_{+,M+2-m-n}]$$

$$(19b)\quad F_2(m,n) = \sum_{i=0}^{\min(M+1-m;n-1)} \sum_{j=i+m}^{M+1} f_6(j,n-i)C_{jim}(-1)^{m-i}$$

$$(19c)\quad F_3(m,n) = I \sum_{i=0}^{\min(M+2-m,n-1)} \sum_{j=\max(1,i+m-1)}^{M+1} (-1)^{m+i-1} (j+1)G_{j+1,n-i}C_{j,i,m-1}$$

$$(19d)\quad F_4(m,n) = I \sum_{i=0}^{\min(M+1-m,n-2)} \sum_{j=i+m}^{M+1} (-1)^{i+m}C_{jim} [(j+1)G_{j+1,n-i-1} - (n-i)G_{j,n-i}]$$

Note that $G_{om} = G_{mo} = G'_{om} = G'_{mo} = 0$ while

$$(20)\quad C_{ijk} = i!/j!k!(i-j-k)!$$

in which $C_{ijk} = 0$ if any member of the set $\{i, j, k, i - j - k\}$ is negative. Also,

(21) $$\delta_{+,j} = \begin{cases} 0 \text{ if j is negative} \\ 1 \text{ if j is zero or positive.} \end{cases}$$

Similar equations for C_{Ak}, C_{Bk} and C_{mn} coefficients can be obtained from eqs (16c-16e) by interchanging all the B and C, together with the changing of all G_{ij} and G'_{ij} into G_{ji} and G'_{ji}.

Reverse relations can also be obtained from the following relationships:

(22) $$\Delta_m G^{ex}(y_B,y_C,I) = \frac{I}{2}\{\int_0^{y_C} [g_C^{ex}(y_B,y,I) - g_A^{ex}(y_B,y,I)]dy + \int_0^{y_B} [g_B^{ex}(y,0,I) - g_A^{ex}(y,0,I)]dy + \int_0^{y_B} [g_B^{ex}(y,y_C,I) - g_A^{ex}(y,y_C,I)]dy + \int_0^{y_C} [g_C^{ex}(0,y,I) - g_A^{ex}(0,y,I)]dy\} - Iy_B \int_0^1 [g_B^{ex}(y,0,I) - g_A^{ex}(y,0,I)]dy - Iy_C \int_0^1 [g_C^{ex}(0,y,I) - g_A^{ex}(0,y,I)]dy$$

which gives

(23a) $$Ig_{Ln} = \sum_{k=n+1}^{M+1} \frac{\ln 10}{k+1}\left(\frac{f^L_{Mk}}{z_L} - \frac{A_{Lk}}{z_A}\right), (L = B,C; n = 0,1,..,M)$$

(23b) $$2IG_{mn} = \ln 10 \left[\frac{A_{m,n-1}}{nz_A} - \frac{\bar{f}^C_{M,m,n-1}}{nz_C} + \frac{A_{m-1,n}}{mz_A} - \frac{\bar{f}^B_{M,n,m-1}}{mz_B}\right], (m,n=1,2,..,M+1)$$

Here, we have replaced A_{Bm} and A_{Cm} by A_{m0} and A_{0m}, and defined

(24a) $$\bar{f}^L_{Mmn} = f^L(M,m,n) + f^L_{Mmn}\delta_{+,M+1-m-n}$$

with

(24b) $$f^L(M,m,n) = \sum_{i=0}^{\min(M+1-m,n-1)} \sum_{j=i+m}^{M+1} L_{j,n-i}C_{jin}(-1)^{i+m}$$

(24c) $$f^L_{Mmn} = \sum_{k=m+n}^{M+1} L_{Ak}C_{kmn}(-1)^{m+n}$$

except when n = 0, in which case we define $\bar{f}^L$ as follows

(25a) $$\bar{f}^B_{MmO} = B_{Cm} + f^B_{Mm} + f^B(M,m)$$

(25b) $$\bar{f}^C_{Mmo} = C_{Bm} + f^C_{Mm} + f^C(M,m)$$

with

(25c) $$f^L(M,k) = \sum_{i=\max(0,k-M-1)}^{\min(M+1,k-1)} \sum_{j=\max(1,i)}^{M+1} L_{j,k-i}\binom{j}{i}(-1)^i$$

(25d) $$f^L_{Mk} = \sum_{j=k}^{M+1} L_{Aj}\binom{j}{k}(-1)^k$$

Note that L = B or C.

Now we can turn to the equations for the osmotic coefficient ϕ. Similar to the treatment for the activity coefficients, we can equate the right hand sides of eqs (9) and (10), and take note of eq (12) and the following relationship:

(26) $$G^{ex}(\delta_{BL}, \delta_{CL}, ..., \delta_{SL}, I) - Ig_L^{ex}(\delta_{BL}, \delta_{CL}, ..., \delta_{SL}, I) = RTI^2\,\Phi_L$$

then we can obtain

(27) $$G_w^{ex} = \Delta_m G^{ex} - I\frac{\partial \Delta_m G^{ex}}{\partial I} + \sum_{L=A}^{S} RTI^2 y_L \Phi_L$$

or equivalently the following equation:

(28) $$-\frac{\Delta_m G_w^{ex}}{RTI}\sum_L (\phi - \phi_L^o)\frac{y_L}{z_L} = -\frac{\Delta_m G^{ex}}{RTI} + \frac{\partial \Delta_m G^{ex}}{RT\partial I}$$

Substituting eq (1) into eq.(28) we find, for a ternary mixture,

(29) $$\sum_{L=A}^{C} (\phi - \phi_L^o)\frac{y_L}{z_L} = y_B(1 - y_B)I \sum_{k=0}^{M-1} (Ig'_{Bk} + g_{Bk})y_B^k + y_C(1 - y_C)I \sum_{k=0}^{M-1} (Ig'_{Ck} + g_{Ck})y_C^k + I \sum_{m,n=1}^{M+1} (IG'_{mn} + G_{mn})y_B^m y_C^n$$

If we define

(30) $$\Delta_m G_w^{ex} = -RTI^2\{y_B(1 - y_B)\sum_{k=0}^{M-1} w_{Bk}y_B^k + y_C(1 - y_C)\sum_{k=1}^{M-1} w_{Ck}y_C^k + \sum_{m,n=1}^{M+1} w_{mn}y_B^m y_C^n\}$$

then one can readily see from eq (28) or eq (29) that

$$(31)\quad w_{Bk} = \frac{\partial I g_{Bk}}{\partial I},\quad w_{Ck} = \frac{\partial I g_{Ck}}{\partial I},\quad w_{mn} = \frac{\partial I G_{mn}}{\partial I}$$

Using a primitive model with zero core diameter, we can compute the approximate g_{BO}, g_{CO} and G_{11} coefficients as follows:

$$g_{B0} = \eta_1{}^2 B_{11} + \eta_2{}^2 B_{22} + \eta_4{}^2 h^2 B_{44} - 2\eta_1\eta_2 B_{12} + 2\eta_1\eta_4 h B_{14} - 2\eta_2\eta_5 B_{24}$$

$$(32)\quad g_{C0} = \eta_1{}^2 B_{11} + \eta_3{}^2 B_{33} + \eta_4{}^2 h'^2 B_{44} - 2\eta_1\eta_3 B_{13} + 2\eta_1\eta_4 h' B_{14} - 2\eta_3\eta_5 B_{34}$$

$$G_{11} = -2\eta_1{}^2 B_{11} - 2\eta_4{}^2 hh' B_{44} + 2\eta_1\eta_2 B_{12} + 2\eta_1\eta_3 B_{13} - 2\eta_1\eta_4 (h+h') B_{14} - 2\eta_2\eta_3 B_{23} + 2\eta_2\eta_4 h' B_{24} - 2\eta_3\eta_4 h B_{34}$$

with[8,16]

$$(33)\quad B_{ij} = -(z_i z_j/4I) J_{ij} = 1/2 \int_o^\infty [(1+k_{ij})\exp(q_{ij}) - (1 + q_{ij} + q^2_{ij}/2)] 4\pi r^2 dr$$

where $k_{ij} = 0$ for the above mentioned model, and

$$(34)\quad \eta_i = 2/z_i(z_i - z_4) \qquad (i = 1, 2, 3)$$

$$\eta_4 = \frac{2(2z_4 - z_2 - z_3)}{z_4(z_2 - z_4)(z_3 - z_4)},\ \eta_5 = \frac{2}{z_4(z_4 - z_1)}$$

$$h = \frac{(z_3 - z_4)(z_2 - z_1)}{(z_4 - z_1)(2z_4 - z_2 - z_3)},\ h' = \frac{(z_2 - z_4)(z_3 - z_1)}{(z_4 - z_1)(2z_4 - z_2 - z_3)}$$

For $x < 1$, we have

$$(35)\quad J(x) = -\sum_{p=3}^{11} \frac{x^{p-1} p^{p-3}}{p!(p-3)!} (\ln|x| + K_p)$$

the constants K_p have been reported by Pitzer[16,17] up to $p = 6$. However, by considering additional terms in the expansions of the integrand, more accurate values of K_p can be obtained. Our K_p values are calculated from

$$(36)\quad K_m = 2C + \ln m - B_m$$

where C is the Euler constant, $B_3 = 11/6$, $B_4 = 17/6$, $B_5 = 203/60$, $B_6 = 681/180$, $B_7 = 21119/5145$, $B_8 = 1064697/245760$, $B_9 = 76256503/16533720$, $B_{10} = 4.8022233968$, $B_{11} = 4.9273543920$. For $x \geq 1$, J(x) can be evaluated numerically. Numerical calculation of J(x) by Chebyshev approximations has also been devised by Harvie[17,27].

When k_{ij} is not zero, the method of evaluation of J_{ij} has been described by Friedman[8]. We apparently take excess care over the K_p values because this can help to remove the unnecessary additional uncertainty in deciding the negligibility of the higher-order virial coefficients.

INDIRECT METHOD OF FRIEDMAN

The equations derived in the preceeding section are useful for direct computation or for fitting experimental data. However, since the derivatives of ionic concentrations with respect to ionic chemical potentials are obtainable from the radial distribution functions, the inverse of these derivatives results in the derivatives of molecular chemical potentials with respect to ionic strength and fractional ionic strengths, Friedman has proposed an indirect method to determine the mixing coefficients[9,11] of the activity coefficients, and other mixing coefficients for the derivative quantities. In this method, we have

$$(37)\quad I = \sum_{i=1}^{3} C_i/\eta_i$$

$$(38)\quad C_1 = \eta_1 I_A,\ C_2 = \eta_2 I_B,\ C_3 = \eta_3 I_C,\ C_4 = -\sum_{i=1}^{3} z_i C_i/z_4$$

$$(39)\quad \rho = \sum_{i=1}^{4} C_i = \sum_{L=A}^{C} I_L/z_L$$

and[9]

$$(40)\quad M_{ij} = \left(\frac{\partial C_i}{\partial \mu_j}\right)_{T,\mu_w} = (C_i\delta_{ij} + C_i G_{ij} C_j)/kT$$

where

$$(41)\quad G_{ij} = \int I[g_{ij}(r) - 1] 4\pi r^2 dr$$

and $g_{ij}(r)$ is the radial distribution function.

Noticing that

$$g_L^{ex} = (\mu_L - \mu_L^{id})/\nu_L z_L \tag{42}$$

where the superscript id signifies ideal state, and defining $g_{Ly}^{ex} = \partial g_L^{ex}/\partial y$ and $g_{LI}^{ex} = \partial g_L^{ex}/\partial I$, we compute all the mixing coefficients from the following derivatives with the use of the M_{ij} values:

$$\mu_{AI} = \frac{\nu_A^+}{ID}\,[C_1\Delta_{23} - C_2\Delta_{321} - C_3\Delta_{213}]$$

$$\mu_{AY_B} = \frac{-I\nu_A^+\eta_1\eta_2}{D}\,[\frac{\Delta_{321}}{\eta_1} + \frac{\Delta_{23}}{\eta_2}]$$

$$\mu_{AY_C} = \frac{-I\nu_A^+\eta_1\eta_3}{D}\,[\frac{\Delta_{213}}{\eta_1} + \frac{\Delta_{23}}{\eta_3}]$$

$$\mu_{BI} = \frac{\nu_B^+}{ID}\,[-C_1\Delta_{321} + C_2\Delta_{13} - C_3\Delta_{123}] \tag{43}$$

$$\mu_{BY_B} = \frac{I\nu_B^+\eta_1\eta_2}{D}\,[\frac{\Delta_{13}}{\eta_1} + \frac{\Delta_{321}}{\eta_2}]$$

$$\mu_{BY_C} = \frac{I\nu_B^+\eta_1\eta_3}{D}\,[\frac{-\Delta_{123}}{\eta_1} + \frac{\Delta_{321}}{\eta_3}]$$

$$\mu_{CI} = \frac{\nu_C^+}{ID}\,[-C_1\Delta_{213} - C_2\Delta_{123} + C_3\Delta_{12}]$$

$$\mu_{CY_B} = \frac{I\nu_C^+\eta_1\eta_2}{D}\,[\frac{-\Delta_{123}}{\eta_1} + \frac{\Delta_{213}}{\eta_2}]$$

$$\mu_{CY_C} = \frac{I\nu_C^+\eta_1\eta_3}{D}\,[\frac{\Delta_{12}}{\eta_1} + \frac{\Delta_{213}}{\eta_3}]$$

$$\mu_{AI}^{id} = RT\nu_A/I$$

$$\mu_{AY_B}^{id} = -RT\,[\frac{\nu_A^+}{y_A} + \frac{\nu_A^-\eta_4 h}{y_o}]$$

$$\mu_{Ay_C}^{id} = -RT\,[\frac{\nu_A^+}{y_A} + \frac{\nu_A^-\eta_4 h'}{y_o}]$$

$$\mu_{BI}^{id} = RT\nu_B/I$$

$$\mu_{By_B}^{id} = RT\,[\frac{\nu_B^+}{y_B} - \frac{\nu_B^-\eta_4 h}{y_o}]$$

$$\mu_{By_C}^{id} = -RT\,[\frac{\nu_B^-\eta_4 h'}{y_o}]$$

$$\mu_{CI}^{id} = RT\nu_C/I$$

$$\mu_{Cy_B}^{id} = -RT\,[\frac{\nu_C^-\eta_4 h}{y_o}]$$

$$\mu_{Cy_C}^{id} = -RT\,[\frac{\nu_C^+}{y_C} - \frac{\nu_C^-\eta_4 h'}{y_o}]$$

where $y_o = \eta_5 - \eta_4 h y_B - \eta_4 h' y_C$, and

$$D = M_{11}M_{22}M_{33} + M_{21}M_{32}M_{13} + M_{12}M_{23}M_{31} - M_{13}M_{22}M_{31} - M_{11}M_{23}M_{32} - M_{12}M_{21}M_{33} \tag{44}$$

$$\Delta_{12} = M_{11}M_{22} - M_{12}^2$$

$$\Delta_{13} = M_{11}M_{33} - M_{13}^2$$

$$\Delta_{23} = M_{22}M_{33} - M_{23}^2$$

$$\Delta_{123} = M_{11}M_{23} - M_{21}M_{13}$$

$$\Delta_{213} = M_{22}M_{13} - M_{12}M_{23}$$

$$\Delta_{321} = M_{33}M_{12} - M_{13}M_{23}$$

For example, the mixing coefficients A_{Bk}, A_{Ck} and A_{mn} can be obtained from the following equation

$$g_{AY_B}^{ex} = (\mu_{AY_B}^{id} - \mu_{AY_B}^{id})/\nu_A z_A \tag{46}$$

$$= -\frac{\ln 10RT}{z_A}\,\{\sum_{k=1}^{M+1} k y_B^{k-1} A_{Bk} + \sum_{m,n=1}^{M+1} m A_{mn} y_B^{m-1} y_C^{n}\}$$

We can first calculate g_{Ay}^{ex} values at different y_B and y_C with the aid of eq (43), the A_{mn} mixing coefficients can then be optimized using eq (46). Coefficients B_{Ak}, B_{Ck}, B_{mn}, C_{Ak}, C_{Bk}, C_{mn} may be obtained in a similar way. g_{Bk}, g_{Ck} and G_{mn} can then be computed from eqs (23a) and (23b).

Although this method appears to be simple, the actual calculation is, in fact, tedious and time consuming. Furthermore, the accuracy to a large extent depends on the choice of the ionic pair potentials. However, with rapid advances in computing technology, we believe this method has great potential.

DISCUSSION

One important advantage of our above formulation is that in the calculation of the activity coefficients of electrolyte A in the ternary mixture, we need to compute or optimize only the mixing coefficients G_{mn} which characterize the interactions of A, B and C, while the contributions from the part of binary mixtures A + B and A + C can be predetermined. This is because the mixing coefficients g_{Bk} and g_{Ck} are known from the two binary mixtures. This advantage is especially significant in semi-empirical fitting methods because they will be less practical if too many parameters are to be optimized. The above remarks are, of course, equally valid in the computation of osmotic coefficients and other thermodynamic functions.

In addition to the Debye-Huckel limiting law that characterizes the limiting behaviour of a single electrolyte at infinite dilution, there are higher-order limiting laws[8,10,11,13,28,30] that characterize electrolyte mixtures. From equations 5-7, we see that

$$\text{(47a)} \quad \lim_{I\to 0} g_{B0} = s_{B0}^{(2)} , \qquad \lim g_{C0} = s_{C0}^{(2)}$$

$$\text{(47b)} \quad \lim_{I\to 0} g_{B1} = s_{B1}^{(3)} + s_{B1}^{(4)} , \quad \lim_{I\to 0} g_{C1} = s_{C1}^{(3)} + s_{C1}^{(4)}$$

$$\text{(47c)} \quad \lim_{I\to 0} G_{11} = s_{11}^{(2)}$$

$$\text{(47d)} \quad \lim_{I\to 0} G_{21} = s_{21}^{(3)} + s_{21}^{(4)} , \quad \lim_{I\to 0} G_{12} = s_{12}^{(3)} + s_{12}^{(4)}$$

where eqs.(47a) and (47b) are well-known limiting laws for the binary mixtures[10,11,13,28] whereas eqs (47c) and (47d) are additional ones for ternary mixtures. However, they are valid for unsymmetrical mixtures only, for symmetrical mixtures, they all vanish. According to Friedman[8,13] we have

$$\text{(48)} \quad g_{BO}(I) = g_{BO}(O)\exp(6z_1^2A_\phi I^{1/2})$$

for binary mixing coefficients. A similar relationship for ternary mixing coefficients G_{11} can also be proposed:

$$\text{(49)} \quad G_{11}(I) = G_{11}(O)\exp(6z_2z_3A_\phi I^{1/2})$$

We note that the ternary mixing coefficient G_{11} has a similar I-dependence as the binary mixing coefficient g_{B0} or g_{C0}, but with opposite sign. Similarly, G_{21} and G_{12} are equivalent to g_{B1} and g_{C1}. In common with the Debye-Huckel limiting law, the higher-order limiting laws are also independent to the details of the short range ionic interactions but cannot be deduced from the laws of thermodynamics alone.

Since we need to optimize only the mixing coefficients G_{mn}, the present equations are useful enough to be incorporated into our Higher Order Limiting Law All Mixing Coefficient method[23].

Finally, it is necessary to point out the advantage of the use of our unsymmetrical equations of g_L^{ex}. Although one can express all the three g_L^{ex} by a single symmetrical equation together wiht the rotation of the symbols A, B and C, our unsymmetrical equations are prefered because all the three g_L^{ex} are now represented by the same set of parameters so that g_B^{ex} and g_C^{ex} can be computed once the parameters in the g_A^{ex} equation are determined. We note that this problem does not arise in a binary mixture and has never been studied before.

REFERENCES

1 Lietzke M.H. and Herdklotz R.J. (1971) *J. Inorg. Nucl. Chem.* **33**: 1649.

2 Lietzke M.H., Hupf H.B. and Stoughton R.W. (1969) *J. Inorg. Nucl. Chem.* **31**: 3481.

3 Lietzke M.H. and Daugharty C. (1972) *J. Inorg. Nucl. Chem.* **34**: 2233.

4 Lietzke M.H. and Danford M.D. (1972) *J. Inorg. Nucl. Chem.* **34**: 3789.

5 Christenson P.G. (1973) *J. Chem. Eng. Data* **18**: 286.

6 Chan C.Y., Khoo K.H. and Lim T.K. (1979) *J. Solution Chem.* **8**: 41 (1979).

7 McMillan W.G. Jr. and Mayer J.E. (1945) *J. Chem. Phys.* **13**: 276; Mayer J.E. (1950) *J. Chem. Phys.* **18**: 1426.

8 Friedman H.L. (1962) *Ionic Solution Theory*, Wiley, New York; (1960) *J. Chem. Phys.* **32**: 1134, 1351; Reilly P.J. and Wood R.H. (1969) *J. Phys. Chem.* **73**: 4292.

9 Friedman H.L. (1985) *A Course in Statistical Mechanics*, Prentice-Hall, New Jersey.

10 Friedman H.L. and Krishnan C.V. (1974) *J. Phys. Chem.* **78**: 1927.

11 Friedman H.L. and Ramanathan P.S. (1970) *J. Phys. Chem.* **74**: 3756.

12 Friedman H.L. (1980) *J. Solution Chem.* **9**: 525.

13 Lim T.K., Zhong E.C. and Friedman H.L. (1986) *J. Phys. Chem.* **90**: 144.

14 Scatchard G. (1961), *J. Am. Chem. Soc.* **83**: 2636; Scatchard G. (1968) *J. Am. Chem. Soc.* **90**: 3124.

15 Scatchard G., Rush R.M. and Johnson J.S. (1970) *J. Phys. Chem.* **74**: 3786

16 Pitzer K.S. (1973) *J. Phys. Chem.* **77**: 268 (1973); Pitzer K.S. (1975) *J. Solution Chem.* **4**: 249.

17 Pitzer K.S. (1991) *Activity Coefficients in Electrolyte Solutions*, Pitzer K.S. ed., CRC Press, Boca Raton, Florida.

18 Pitzer K.S. (1984) *J. Chem. Soc. Faraday Trans.* I, **80**: 3451.

19 Harvie C.E. and Weare J.H. (1980) *Goechim. Cosmochim. Acta* **44**: 981; Lim T.K. (1990) *J. Chem. Soc. Faraday Trans.* **86**: 3897.

20 Lim T.K., Chan C.Y. and Khoo K.H. (1980) *J. Solution Chem.* **9**: 507.

21 Lim T.K. (1982) *Int. J. Quantum Chem.* **S16**: 247.

22 Lim T.K. (1987) *J. Solution Chem.* **16**: 917.

23 Lim T.K. (1992) *J. Solution Chem.* **21**: 121.

24 Lim T.K. (1985) *J. Chem. Soc. Faraday Trans.* I, **81**: 1195.

25 Dixon M. and Hutchinson P. (1975) *J. Phys. Chem.* **79**: 1820; Haga E. (1953) *J. Phys. Soc., Japan* **8**: 714.

26 Friedman H.L. (1972) *J. Solution Chem.* **1**: 387, 413, 419.

27 Harvie C.E. (1981) *Theoretical Investigations in Geochemistry and Atom Surface Scattering*; Ph.D. dissertation, U.C. San Diego, # AAD82-03026, University Microfilm International, Ann Arbor, MI.

28 Robinson R.A., Wood R.H. and Reilly P.J. (1971) *J. Chem. Thermodyn.* **3**: 461.

29 K.S. Pitzer (1983) *J. Phys. Chem.* **87**: 2360 (1983).

30 Vanhees J., Francois J.P., Mullens J., Yperman Y. and L.C. Van Poucke L.C. (1985) *J. Phys. Chem.* **89**: 2661.