

RELATIONSHIPS BETWEEN IONIC RADII AND PITZER'S PARAMETERS IN 1 : 1 TYPE ELECTROLYTE SOLUTIONS^①

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ABSTRACT

A new expression for the osmotic and activity coefficients in single electrolyte solution is developed by reforming the Pitzer's osmotic equation. As a result, the correlations between the a_{MX} , the sum of the "hard core" radii of ions M^+ and X^- , and the second virial coefficients $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ in Pitzer's equations are obtained. Furthermore, an "ionic overlap" model and its relevant equation are suggested. The relationships between the thermodynamic properties of aqueous electrolytes and the characteristic of their ions (ionic radii and ionic hydration) are discussed quantitatively.

Key words: Pitzer virial parameter osmotic coefficient activity coefficient electrolytic solution ionic radius

1 INTRODUCTION

Pitzer's equations for the osmotic and activity coefficients of electrolytic solutions are successful in application to single or mixed aqueous electrolytes up to the concentration of practical interest. Pitzer's equations contain some virial parameters which represent the short-range interaction forces between ions. One can predict the thermodynamic properties of mixed electrolytes from the parameters of single ones as was highly appreciated by Pythowicz^[1]. This hints that the virial parameters, especially the second virial parameters $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$, have deeper physical meanings. Pitzer himself has already noticed this feature. In this paper, a new expression for the osmotic and activity coefficient in 1:1 type single electrolytes is developed by reforming Pitzer's osmotic equation. Comparing this with Pitzer's equations, correlations between a_{MX} ,

the sum of the "hard core" radii of ions M^+ and X^- , and the second virial parameters, $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$, are obtained. For further investigation of the relationships between a_{MX} and the characteristic of ions involved, an "ionic overlap" model and its relevant equation are suggested, which enable one to discuss quantitatively the thermodynamic properties of aqueous electrolytes in terms of their ionic radii and ionic hydration.

2 EQUATIONS FOR OSMOTIC AND ACTIVITY COEFFICIENTS

The osmotic pressure π of a solution, based on McMillan-Mayer osmotic equilibrium theory, is

$$\pi = CKT -$$

$$\frac{1}{6} \sum_i \sum_j C_i C_j \int_0^\infty \frac{\partial u_{ij}(r)}{\partial r} g_{ij}(r) 4\pi r^3 dr \quad (1)$$

From Equation (1), Pitzer^[3] has derived an equation for osmotic coefficient ϕ in single

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electrolyte solutions

$$\varphi - 1 = -\kappa^3 / [24\pi C(1 + \kappa a_{MX})] + \\ C \{ (2\pi a_{MX}^3 / 3 + 1 / 48\pi - \\ \kappa^4 a_{MX} / C^2 (1 + \kappa a_{MX})^2) \} \quad (2)$$

where a_{MX} is the sum of the "hard core" radii of ions M^+ and X^- and

$$\kappa = [(4\pi e^2 / DkT) \sum_i C_i Z_i^2]^{1/2}$$

However, the final forms of Pitzer's equations contain no a_{MX} , which is replaced with some virial parameters. So, to determine the correlations between a_{MX} and the parameters, the most straight forward way seems to be changing Equation (2) to a form which can be directly compared with the corresponding final equation chosen by Pitzer, while retaining a_{MX} which is independent of any special ions. Equation (2) can be rewritten as

$$-\kappa^3 / [24\pi c(1 + \kappa a_{MX})] = -\kappa^3 / [24\pi c(1 + \kappa a_0)] + \\ \kappa^4 (a_{MX} - a_0) / 24\pi c(1 + \kappa a_{MX})^2 (1 + \kappa a_{MX} / 1 + \kappa a_0) \quad (3)$$

Approximating

$$(1 + \kappa a_{MX}) / (1 + \kappa a_0) = 1 \quad (4)$$

yields

$$-\kappa^3 / 24\pi c(1 + \kappa a_{MX}) = -\kappa^3 / [24\pi c(1 + \kappa a_0)] + \\ \kappa^4 (a_{MX} - a_0) / [24\pi c(1 + \kappa a_{MX})^2] \quad (5)$$

Substituting equation (5) into (2), and taking $l = e^2 / DkT$, $A_\varphi = 1 / 3(2\pi N_A \rho_A / 1,000)^{1/2} \bar{v}^{3/2}$, $B = \kappa / l = (8\pi e^2 / DkT \cdot N_A \rho_A / 1,000)^{1/2}$ and $b = Ba_0$, where N_A is the Avogadro constant, ρ_A is the density of solvent and l is the ionic strength, gives.

$$\varphi - 1 = -[Z_M Z_X |A_\varphi I^{1/2} / (1 + bI^{1/2}) + \\ m \{ 3vA_\varphi^2 \cdot [2a_{MX}^3 / l^3 + \\ |Z_M Z_X|^2 (3a_{MX} - 2a_0) / l \cdot \\ (1 + Ba_{MX} I^{1/2})^{-2} \} / 2] \quad (6)$$

Then making another approximation

$$(1 + Ba_{MX} I^{1/2})^{-2} \approx Q e^{-aI^{1/2}} \quad (7)$$

Where Q and a are constant parameters,

substituting equation (7) into (6), one finally obtains

$$\varphi - 1 = -|Z_M Z_X |A_\varphi I^{1/2} / (1 + bI^{1/2}) + \\ m \{ 3vA_\varphi^2 [2a_{MX}^3 / l^3 + |Z_M Z_X|^2 \times \\ Q(3a_{MX} - 2a_0) e^{-aI^{1/2}} / l / 2] \} \quad (8)$$

The equation for the mean activity coefficient γ_{MX} , corresponding to equation (8), is

$$\ln \gamma_{MX} = -|Z_M Z_X |A_\varphi [I^{1/2} / (1 + bI^{1/2}) + \\ 2\ln(1 + bI^{1/2}) / b + 3mvA_\varphi^2 \{ 2a_{MX}^3 / l^3 + \\ |Z_M Z_X|^2 (3a_{MX} - 2a_0) / l \cdot Q / a^2 [1 - (1 + aI^{1/2} - \\ a^2 I / 2) e^{-aI^{1/2}}] \} \} \quad (9)$$

For parameters b , a , Q and a_0 , Pitzer has determined that $b = 1.20$ and $a = 2.0$ which is accepted here but a_0 is treated as independent with b .

3 THE CORRELATIONS OF a_{MX} WITH $\beta_{MX}^{(0)}$ AND $\beta_{MX}^{(1)}$

For 1 : 1 type aqueous electrolytes, equations (8) and (9) can be simplified to

$$\varphi - 1 = -A_\varphi I^{1/2} / (1 + bI^{1/2}) + \\ m(6A_\varphi^2 a_{MX}^3 / l^3 + 3A_\varphi^2 Q \cdot (3a_{MX} - \\ 2a_0) \cdot l^{-1} e^{-aI^{1/2}}) \quad (10)$$

$$\ln \gamma_{MX} = -A_\varphi [I^{1/2} / (1 + bI^{1/2}) + \\ 2\ln(1 + bI^{1/2}) / b] + \\ mA_\varphi^2 \{ 2a_{MX}^3 / l^3 + \\ (3a_{MX} - 2a_0) Q / (la^2 I) [1 - \\ (1 + aI^{1/2} - a^2 I / 2) e^{-aI^{1/2}}] \} \quad (11)$$

where $b = 1.20$, $a = 2.0$; $Q = 0.62$ and $a_0 = 1.92$ nm, and at 25 °C, $A_\varphi = 0.391$ and $l = 0.715$ nm. Adjusting a_{MX} to fit the experimental data^[4] of osmotic and activity coefficients of the 26 electrolytes listed in Table 1, the standard derivations σ of φ and $\log \gamma_{MX}$ are respectively less than 0.008 and 0.006 up to a concentration of

Table 1 Values of a_{MX} of 1 : 1 type electrolytes (25 °C)

electrolyte	a_{MX} / nm	C_{MX}^0	$\sigma(\log)$	$C_{max} / \text{mol} \cdot \text{kg}^{-1}$
HCl	0.406	0.00305	0.002	4.0
HBr	0.425	0.00905	0.0005	3.0
HI	0.457	-0.00063	0.002	3.0
HClO ₄	0.406	0.00986	0.002	3.0
LiCl	0.389	0.00369	0.0015	6.0
LiBr	0.398	0.01068	0.001	2.5
LiI	0.442	-0.00502	0.0045	2.5
LiClO ₄	0.434	-0.00186	0.003	3.0
NaCl	0.319	0.00029	0.002	6.0
NaBr	0.343	0.0000	0.0005	4.0
NaI	0.371	-0.00081	0.001	3.5
NaClO ₄	0.300	-0.00431	0.0025	4.0
KCl	0.278	-0.00217	0.0015	4.8
KBr	0.289	-0.00254	0.002	5.5
KI	0.315	-0.00504	0.0025	4.5
RbCl	0.258	-0.00093	0.0002	5.0
RbBr	0.252	-0.00161	0.0005	5.0
RbI	0.248	-0.00087	0.0005	5.0
CsCl	0.203	0.00284	0.001	4.0
CsBr	0.192	0.00257	0.001	4.0
CsI	0.187	-0.00138	0.001	3.0
LiAc	0.349	-0.00397	0.001	4.0
NaAc	0.386	-0.00709	0.0005	3.5
KAc	0.398	-0.00672	0.0005	3.5
RbAc	0.401	-0.00558	0.0002	3.5
CsAc	0.406	-0.00728	0.0005	3.5

2 mol / kg. At higher concentration, the terms $m^2 C_{MX}^0$ and $(3/2)m^2 C_{MX}^0$ are respectively added to the right sides of equations (10) and (11) to ensure that a_{MX} only relates to the interaction of ion-pairs. They then give

$$\varphi - 1 = (\varphi - 1)_1 + m^2 C_{MX}^0 \quad (12)$$

$$\ln \gamma_{MX} = (\ln \gamma_{MX})_1 + (3/2)m^2 C_{MX}^0 \quad (13)$$

Where $(\varphi - 1)_1$ and $(\ln \gamma_{MX})_1$ are respectively the terms on the right sides of equations (10) and (11). Equations (12) and (13) can better represent the experimental data of the 26 electrolytes: the σ of $\lg \gamma_{MX}$ is less than 0.003 for most electrolytes up to a concentration, noted as C_{max} , of 3 mol / kg, as shown in Table 1.

Pitzer's equation^[2] for the osmotic coef-

ficients of single electrolytes is

$$\varphi - 1 = -|Z_M Z_X| A_\varphi I^{1/2} / (1 + bI^{1/2}) + m^2 2(v_M v_X)^{-1/2} v^{-1} C_{MX}^0 e^{-aI^{1/2}} + m^2 2(v_M v_X)^{1/2} v^{-1} C_{MX}^0 \quad (14)$$

By comparing the terms on the right side of equation (8) with those of equation (14), one obtained

$$\beta_{MX}^{(0)} = 6v^2 / 4v_M v_X \cdot A_\varphi^2 \cdot a_{MX}^3 / I^3 \quad (15)$$

$$\beta_{MX}^{(1)} = 3|Z_M Z_X| I^{1/2} / 4v_M v_X \cdot A_\varphi^2 \cdot Q(3a_{MX} - 2a_0) / I \quad (16)$$

For 1 : 1 type electrolytes, equations (15) and (16) can be simplified to

$$\beta_{MX}^{(0)} = 6A_\varphi^2 a_{MX}^3 / I^3 = 2.52 \times 10^{-3} a_{MX}^3 \quad (17)$$

$$\beta_{MX}^{(1)} = 3A_\varphi^2 Q(3a_{MX} - 2a_0) / I = 0.04(3a_{MX} - 2a_0) \quad (18)$$

Using the values of a_{MX} in Table 1, the values of $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ are calculated, and they are quite close to those determined by Pitzer. In Table 2, some comparisons are listed.

Table 2 Comparisons of the second

electrolyte	virial parameters $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$			
	Pitzer's $\beta_{MX}^{(0)}$	Pitzer's $\beta_{MX}^{(1)}$	this work $\beta_{MX}^{(0)}$	this work $\beta_{MX}^{(1)}$
HCl	0.1775	0.2945	0.1686	0.3336
HBr	0.1960	0.3564	0.1934	0.3564
LiCl	0.1494	0.3074	0.1483	0.3132
NaClO ₄	0.0554	0.2755	0.0680	0.2064
CsI	0.0244	0.0262	0.0165	0.0708
KAc	0.1426	0.3237	0.1449	0.3096

4 "IONIC OVERLAP" MODEL

We further consider whether the a_{MX} can be represented by the ionic radii or, in another word, whether the thermodynamic properties of aqueous electrolytes can be estimated from the characters of their ions. The value of a_{MX} is larger than the sum of Pauling crystal radii of ions M^+ and X^- but less than the sum of their hydration radii. Conway^[5] considered that it is due to the penetration of the anion and cation hydration shells. Rasaiah and Friedman found that^[6] when the distance between a pair of an

anion-cation pair is less than the sum of their Pauling radii and a water molecule diameter, the short range interaction force should be taken into account. Marcus^[7] has compiled the average distances, noted as d , between ions and the nearest water molecules and obtained

$$d = (0.137, 6 \pm 0.003, 1) + (1.016, 7 \pm 0.026, 6)r_p \text{ (nm)} \quad (19)$$

where r_p is the ionic Pauling radius. The first term on the right side of equation (19) is just equal to the water molecule radius r_w , so d is approximately equal to $r_p + r_w$.

We assume that for an aqueous ion, it is regarded as a particle together with its primitive shell. The particle's radius R , called as the effective radius, is taken as $r_p + r_w$, but not as the generally accepted value $r_p + 2r_w$. When two oppositely charged aqueous ions M^+ and X^- approach and the distance between them is less than the sum of their effective radii, their primitive hydration shells will overlap till the distance is equal to a_{MX} . The extent of overlap depends on the hydration strengths of the two ions. This process is represented as

$$a_{MX} = R_M + R_X - \delta_i \delta_x \quad (20)$$

here δ_i is defined as the overlap coefficient of ion i and, as R_i , only depends on the characteristics of ion i . The values of a_{MX} obtained are fitted to determine R_i and δ_i , with δ_{H^+} being taken as 0.27 nm in advance. The results together with the values of d and $r_p + r_w$, for comparison, are listed in Table 3 and r_w is taken as 0.14 nm. It can be seen that there quite good agreement between the calculated values of R and the reported values of d or $r_p + r_w$ for most ions. According to Conway^[8], the proton H^+ in aqueous solutions exists as H_3O^+ , as shown in Fig. 1. This can be understood as a proton and a water molecule forming H_3O^+ , while the other three water molecules constitute its primitive hydration shells. So the value of d is 0.28 nm which is exactly equal to the calculated value of R .

Table 3 Values of R and δ

ion	R / nm	δ / nm ^{1/2}	d / nm	$r_p + r_w$ / nm
H ⁺	0.280	0.27		
Li ⁺	0.174	0.1516	0.207+0.005	0.200
Na ⁺	0.239	0.3286	0.237+0.002	0.235
K ⁺	0.270	0.4432	0.273+0.003	0.273
Rb ⁺	0.288	0.5300	0.288+0.004	0.288
Cs ⁺	0.312	0.6428	0.308+0.004	0.309
Cl ⁻	0.312	0.6783	0.312+0.002	0.321
Br ⁻	0.331	0.6938	0.333+0.002	0.335
I ⁻	0.386	0.7800	0.361+0.001	0.356
ClO ₄ ⁻	0.431	1.1272	0.434+0.004	0.432
Ac ⁻	0.201	0.1646		

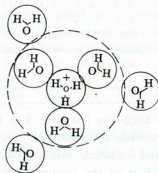


Fig. 1 Aqueous proton [ref. 8]

A plot of δ of the cations Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ and the anions Cl^- , Br^- , I^- and ClO_4^- versus their r_p is shown in Fig. 2, where there exist a good linear relations between δ and r_p .

So, it is obtained

$$\delta = A(r_p - r_0) \quad (21)$$

where $A = 3.95 \text{ nm}^{-1/2}$ and $r_0 = 0.016 \text{ nm}$. Then equation (20) can be rewritten as

$$a_{MX} = (r_M + r_w) + (r_X + r_w) - A^2(r_M - r_0)(r_X - r_0) \quad (22)$$

where r_M and r_X are the Pauling of ions M^+ and X^- respectively. Using equations (22) and (11), the mean activity coefficients of 17 electrolytes are calculated, noted as γ_{cal} , from their ionic radii. The comparisons of γ_{cal} with the observed values γ_{obs} are listed in Table 4.

Table 4 Comparisons of γ_{cal} with γ_{obs}
at various ionic strengths

electrolyte	$\ln \gamma_{cal} - \ln \gamma_{obs}$				
	$I / \text{mol} \cdot \text{kg}^{-1}$				
	0.5	1	2	3	4
LiCl	0.03	0.05	0.08	0.10	
LiBr	0.03	0.03	0.02		
LiI	-0.03	-0.06			
LiClO ₄	0.01	0.03	0.06	0.10	
NaCl	0.03	0.07	0.13	0.18	
NaBr	0.005	0.01	0.03	0.04	0.04
NaI	-0.05	-0.07	-0.12	-0.17	
NaClO ₄	0.02	0.05	0.12	0.19	
KCl	0.01	0.02	0.05	0.08	
KBr	-0.01	-0.02	-0.01	-0.005	0.02
KI	-0.05	-0.09	-0.14	-0.17	
RbCl	0.01	0.02	0.04	0.05	0.08
RbBr	0.005	0.01	0.02	0.03	0.05
RbI	-0.005	-0.01	-0.02	-0.03	-0.04
CsCl	0.03	0.04	0.05	0.05	0.06
CsBr	0.03	0.04	0.06	0.06	0.07
CsI	0.01	0.01	0.01	0.02	0.05

The $|\Delta \ln \gamma|$ are less than 0.05 for most electrolytes while ionic strength I is up to 1 mol/kg and for some, even up to 4 mol/kg. The revelation of the relationships between ionic crystal radii and the osmotic and activity coefficients will be helpful understanding Pitzer's theory of electrolytes, taking the hydration ions as the elementary units for the particle interactions in the McMillan-Mayer statistical model, and hence understanding the thermodynamic behaviors of electrolyte solutions.

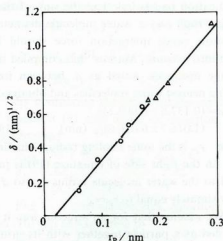


Fig. 2 The linear relations between δ and r_p

○—cations; △—anions

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