

# Comments on The Pitzer Equations Formulated on the Assumption of Complete Dissociation of Strong Electrolytes

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Received July 9, 1999; final manuscript received April 24, 2000

[S0047-2689(00)00104-5]

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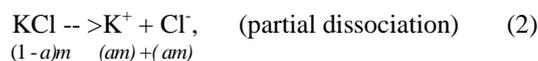
## 1. Introduction

In the past decade at least three articles<sup>1-3</sup> have been published in this journal which are based on the Pitzer equations formulated on the assumption of complete dissociation of strong electrolytes at all concentrations: KCl(aq),<sup>1</sup> NaBr(aq),<sup>2</sup> and NaCl(aq).<sup>3</sup> The author of these articles should be complimented for his very painstaking and precise calculations of the various parameters in the Pitzer equations. However, in this current author's opinion,<sup>4</sup> these equations are so complex that they suggest that there is some conceptual error. To quote some articles in Chemistry in Britain, Franks<sup>5</sup> points out that "tinkering with the Debye-Hückel equation may produce better fits to experimental data over increasingly wider ranges of concentration, but it is only a curve fitting exercise." He writes this in support of the article by Darvell and Leung<sup>6</sup> which states, "Given a sufficient number of terms, and arbitrary constants, a fit to experimental data of any underlying functionality can always be found—and there can be no suggestion that the fitted functions have any basis in physical fact. Thus one can fit linear polynomials to logarithmic functions, but gain no insight into the underlying phenomena or data structure...activity itself, as a problem, is believed by many to have been solved and that any attempt to query it is taken as heresy." Also, they write<sup>7</sup> "A plethora of fitted constants with no physical meaning, as adduced by Franks, is of no use for teaching or research." Continuing,<sup>8</sup> "Many theories and equations are used to interpret the behavior of ions in solution, however, there is continuing debate on whether they have outlined their usefulness..."

According to this current author,<sup>4</sup> the above complex state of the mathematical description of the solution properties is due to the conventional assumption<sup>9</sup> that strong electrolytes are completely dissociated in aqueous solutions. In recent years, it has been shown by this current author<sup>10-15</sup> that strong electrolytes are indeed only partially dissociated in aqueous solutions, and this has been confirmed experimentally<sup>16</sup> and supported by molecular dynamic simulations<sup>17</sup> for saturated solutions. By using the degrees of dissociation and hydration numbers derived from vapor pressure, solvent activity or osmotic coefficient data, it was shown that many solution properties can be explained quantitatively using simple mathematical equations. The work on NaCl(aq) from 'zero to saturation' at 25 °C was published by Heyrovská,<sup>11</sup> and extended to all alkali halides,<sup>12</sup> many more 1:1 electrolytes in a review article,<sup>13</sup> and for 1:2 electrolytes.<sup>14</sup> Compared below are (1) the Pitzer equations based on complete dissociation



where  $m$  moles of KCl dissociate completely into  $2m$  moles of ions, which is also the total number ( $2m$ ) of moles of solute in the solution, and (2) those by the present author based on partial dissociation<sup>10-15</sup>



where  $m$  moles of KCl dissociate into  $2am$  moles of ions and the total number of moles of solute is  $im = (1+a)m$ , where  $i$  is the van't Hoff factor.

## 2. Concentration Dependence of the Osmotic Coefficient, $\phi$

Based on a complete dissociation description in a recent paper,<sup>1</sup> the concentration dependence of  $\phi$  [ $= (55.5/vm)\ln(a_A)$ , where  $vm$  is the number of moles of ions,  $a_A$  (the vapor pressure ratio) is the solvent (A) activity] is described by the equation [refer to Eq. (6)]:

$$\phi = 1 - z_M z_X A_\phi I^{1/2} / (1 + bI^{1/2})$$

$$+ m(2v_M v_X / v)(\beta_{MX}^{(0)} + \beta_{MX}^{(1)} c_{xp}(-aI^{1/2}))$$

$$+ m^2(4v_M^2 v_X z_M / v_M^2) C_{MX} \quad (\text{complete dissociation}) \quad (3)$$

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(Note:  $a$  in the above equation is a constant and is not the degree of dissociation.) On the other hand, based on partial dissociation arguments,<sup>10-15</sup> the concentration dependence of  $a_A$  (solvent activity) is given by

$$a_A = \exp(-vm\phi/55.51) = N_{A,s} = n_{Af_s}/(n_{Af_s} + im) \quad (\text{partial dissociation}). \quad (4)$$

where  $n_{Af_s} = (55.51 - mn_s)$  is the number of moles of free water,  $n_s$  being the hydration number. Thus,  $a_A$  represents the mole fraction of free solvent,  $N_{A,s}$ , and the osmotic coefficient,  $\phi$  is simply

$$\phi = (-55.51/vm) \ln(N_{A,s}) \quad (\text{partial dissociation}). \quad (5)$$

### 3. Concentration Dependence of Mean Ionic Activity, $a_{\pm} = my_{\pm}$

$a_{\pm}$ , another nonideal quantity, is evaluated<sup>9</sup> most directly from the measured emf,  $\Delta E$ , of concentration cells as follows (say for a 1:1 electrolyte):

$$\Delta E = -(RT/F) \ln(a_B) = -(2RT/F) \ln(a_{\pm}), \quad (6)$$

where  $\gamma_{\pm} = (a_{\pm}/m)$  is the molal mean ionic activity coefficient, a nonideality correction factor, assuming the 'ionic molality'  $m_{+} = m_{-} = m$ , as per complete dissociation.

The recent best-fitting equation [refer to Eq. (7)<sup>1</sup>] for  $\ln \gamma_{\pm}$  based on the assumption of complete dissociation is:

$$\begin{aligned} \ln \gamma_{\pm} = & -z_M z_X A_{\phi} [I^{1/2}/(1+bI^{1/2}) + (2/b) \ln(1+bI^{1/2})] \\ & + m(2v_{MX}/v) \{2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)}/a^2 I) \\ & x [1 - (1 + \alpha_A^{1/2} - \alpha^2 I/2) \exp(-\alpha I^{1/2})]\} \\ & + m^2 (2v_M^2 v_{XM} I v) (3C_{MX}) \end{aligned} \quad (\text{complete dissociation}). \quad (7)$$

On the other hand, based on the idea of partial dissociation.  $\ln a_{\pm}$  [see Eq. (6)] is directly proportional to the logarithm of the mole ratio,  $r_s = (am/n_{Af_s})$ , where the "ionic molal ity" is  $am$  [and not  $m$  as in Eq. (7)].

$$\begin{aligned} \ln a_{\pm} = & \ln(my_{\pm}) \\ = & -\delta_A \ln[am/(55.51 - mn_s)r_s^0] \end{aligned} \quad (\text{partial dissociation}). \quad (8)$$

The values of the constants,  $S_A$  and  $r_s^0 = (am/n_{Af_s})^0$ , were obtained from the slope and intercept (at  $\Delta E = 0$ ), respectively, of the  $\Delta E$  vs  $\ln(r_s)$  linear dependence.  $\Delta E$  (cal) was then calculated for the entire concentration range by using the  $\delta_A$  and  $r_s^0$  values in Eq. (8). These were found to reproduce the  $\Delta E$  values to within  $\pm 0.002$  V (maximum for the saturated solution) in all cases.<sup>10-15</sup>

Similarly, the elaborate equations of Pitzer for the molal volumes have also been replaced<sup>11,13,18</sup> by much simpler < equations based on the volumes of ions and ion pairs.

### 4. Acknowledgments

The author is grateful to the Academy of Sciences of the Czech Republic for the award of a research grant (Grant No. GA AV CR 440401) and to Dr. L. Novotny for moral support.

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