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ON BRÖNSTED'S PRINCIPLE OF SPECIFIC INTERACTION

BY

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The principle of specific interaction of ions was formulated by BRÖNSTED[1] in 1921 two years before the publication of the theory of DEBYE and HÜCKEL[2] in 1923. These two theories were later combined into a single formulation by GUGGENHEIM[3]. The mathematical aspect of this formulation has recently been analysed and criticized by SCATCHARD[4]. The present article is inspired by SCATCHARD's analysis. Starting from different premises I reach conclusions the most important of which confirm SCATCHARD's. It is more difficult to say whether we are in complete agreement because SCATCHARD's article is unfortunately so condensed that clarity has been sacrificed to brevity. In particular some of the symbols used by SCATCHARD are inadequately defined and I have been unable to interpret them. I shall return later to a discussion of SCATCHARD's analysis.

Consider a solution containing n_w moles of the solvent water and n_i moles of the ionic species i. The Gibbs function G can be expressed in the form

$$G = n_w\mu_w^0 + \Sigma_i n_i\mu_i^{\ominus} - RT\Sigma_i\left(n_i - n_i ln\frac{n_i}{n_w}\right) + G^{corr} + G^{el} + G^s \qquad (1)$$

where μ_w^0 denotes the chemical potential of pure water and $\mu_i^{\ominus}$ is at the given temperature a constant characteristic of the ionic species i at infinite dilution in water. The terms $RT\Sigma_i$ are an approximate form for an ideal dilute solution and G^{corr} denotes terms, unimportant at high dilution, to correct for the previous terms being only approximate. G^{el} denotes the contribution due to electrostatic interactions between the ions regarded as rigid charged spheres with a common diameter. The form of G^{el} is given by the theory of DEBYE and HÜCKEL[2], modified if neces-

sary according to the treatment of GRONWALL[5]. The term G^s represents the remaining contribution due to short range interactions. This article is concerned with G^s, but not with G^{corr} nor with G^{el}.

The osmotic coefficient φ is defined by

$$\mu_w^0 - \mu_w = \varphi RT \frac{\Sigma_i n_i}{n_w} \tag{2}$$

where μ_w denotes the chemical potential of water in the solution and μ_w^0 the chemical potential of pure water. The activity coefficient γ_i of the ionic species i is defined by

$$\mu_i - \mu_i^{\ominus} = RT \ln \frac{n_i \gamma_i}{n_w} \tag{3}$$

where μ_i denotes the chemical potential of the ionic species i. It is scarcely necessary to mention that quantities such as μ_i and γ_i are physically significant only when combined to relate to salts or other combinations with zero net charge[6]. For the sake of tidiness we have used mole ratios n_i/n_w instead of the more usual molalities m_i. If we were to replace n_i/n_w by m_i in formula (3) the value of $\mu_i^{\ominus}$ would be changed by a constant term, but the value of the activity coefficient γ_i would be unaffected.

From comparison of (1) with (2) and (3) it is evident that when G^{corr}, G^{el} and G^s vanish, φ and all γ_i's become unity. It is further clear that $1-\varphi$ and $\ln \gamma_i$ can be decomposed linearly in the same manner as G, namely

$$1 - \varphi = 1 - \varphi^{el} - \varphi^{corr} - \varphi^s \tag{4}$$

$$\ln \gamma_i = \ln \gamma_i^{corr} + \ln \gamma_i^{el} + \ln \gamma_i^s. \tag{5}$$

In formula (4) it is implied that φ^{el} is given by the theory of Debye and Hückel and that φ^{el} is comparable with unity, while φ^{corr} and φ^s are much smaller quantities. This article is concerned only with the terms φ^s and $\ln \gamma_i^s$. Incidentally the superscript ^{s} corresponds to the superscript $'''$ used by SCATCHARD.

The essential approximation underlying GUGGENHEIM's treatment is that G^s should have a form analogous to that for a regular

mixture of non-electrolytes. For such a mixture of molecular species α, β, ... we have the useful and simple approximation

$$G^s = \frac{1}{2}\frac{\Sigma_\alpha \Sigma_\beta n_\alpha n_\beta l_{\alpha\beta}}{\Sigma_\alpha n_\alpha} \quad (l_{\alpha\beta} = l_{\beta\alpha}) \tag{6}$$

where n_α denotes the number of moles of the species α and $l_{\alpha\beta}$ is a constant characteristic of the pair $\alpha\beta$. For the solution of ionic species i, k, ... in water w we write correspondingly

$$G^s = \frac{1}{2}\frac{n_w^2 l_{ww}}{n_w + \Sigma_i n_i} + \frac{n_w \Sigma_i n_i l_{wi}}{n_w + \Sigma_i n_i} + \frac{1}{2}\frac{\Sigma_i \Sigma_k n_i n_k l_{ik}}{n_w + \Sigma_i n_i}. \tag{7}$$

We now expand in powers of n_i/n_w and neglect terms of second and higher order, obtaining

$$\left.\begin{aligned} G^s = \frac{1}{2} n_w l_{ww} - \frac{1}{2}\Sigma_i n_i l_{ww} + \frac{1}{2}\frac{(\Sigma_i n_i)^2}{n_w} l_{ww} - \ldots \\ + \Sigma_i n_i l_{wi} - \frac{\Sigma_i n_i \Sigma_k n_k l_{wk}}{n_w} + \ldots \\ + \frac{1}{2}\frac{\Sigma_i \Sigma_k n_i n_k l_{ik}}{n_w} - \ldots \end{aligned}\right\} \tag{8}$$

Differentiating with respect to n_w and denoting the mole ratio n_i/n_w by r_i, we obtain for the corresponding term μ_w^s of μ_w

$$\mu_w^s = -\frac{1}{2}(\Sigma_i r_i)^2 l_{ww} + \Sigma_i r_i \Sigma_k r_k l_{wk} - \frac{1}{2}\Sigma_i \Sigma_k r_i r_k l_{ik} \tag{9}$$

and consequently

$$\frac{\varphi^s RT}{\Sigma_i r_i} = \frac{1}{2} l_{ww} - \Sigma_i y_i l_{wi} + \frac{1}{2}\Sigma_i \Sigma_k y_i y_k l_{ik} \tag{10}$$

where

$$y_i = \frac{r_i}{\Sigma_k r_k} = \frac{n_i}{\Sigma_k n_k} \text{ so that } \Sigma_i y_i = 1. \tag{11}$$

We can now rewrite (10) in the form

$$\frac{\varphi^s RT}{\Sigma_i r_i} = \frac{1}{2}\Sigma_i \Sigma_k y_i y_k L_{ik} \tag{12}$$

where L_{ik} is defined by

$$L_{ik} \equiv l_{ik} - l_{wi} - l_{wk} + l_{ww}. \tag{13}$$

Alternatively we can write

$$\frac{\varphi^s RT}{\Sigma_i r_i} = \frac{1}{2} \Sigma_i \Sigma_k y_i y_k M_{ik} + \frac{1}{2} \Sigma_i y_i L_{ii} \tag{14}$$

where M_{ik} is defined by

$$M_{ik} \equiv L_{ik} - \frac{1}{2} L_{ii} - \frac{1}{2} L_{kk} \equiv l_{ik} - \frac{1}{2} l_{ii} - \frac{1}{2} l_{kk} \tag{15}$$

so that

$$M_{ii} \equiv 0. \tag{16}$$

It is important to distinguish sharply M_{ik} occurring in (14) and satisfying the identity (16) from L_{ik} occurring in the formally simpler (12) but not satisfying any identity analogous to (16). This distinction between M_{ik} and L_{ik} was overlooked by GUGGENHEIM, nor is the distinction clearly defined by SCATCHARD.

Up to this point no distinction has been made between cations and anions. We now denote cations by R and anions by X. Formula (14) becomes

$$\left.\begin{aligned} \frac{\varphi^s RT}{\Sigma_i r_i} &= \Sigma^{+-} y_R y_X \left(M_{RX} + \frac{L_{RR}}{2\, y_-} + \frac{L_{XX}}{2\, y_+} \right) \\ &+ \frac{1}{2} \Sigma_R \Sigma_{R'} y_R y_{R'} M_{RR'} + \frac{1}{2} \Sigma_X \Sigma_{X'} y_X y_{X'} M_{XX'} \end{aligned}\right\} \tag{17}$$

where Σ^{+-} denotes summation over pairs of ions of opposite sign, and y_+, y_- are defined by

$$y_+ \equiv \Sigma^+ y_R \qquad y_- \equiv \Sigma^- y_X \quad \text{so that} \quad y_+ + y_- = 1. \tag{18}$$

We now introduce BRÖNSTED's principle of specific interaction: "In a dilute salt solution of constant total concentration ions will be uniformly influenced by ions of their own sign." This implies

$$M_{RR'} = M_{RR} \equiv 0 \quad \text{and} \quad M_{XX'} = M_{XX} \equiv 0 \tag{19}$$

so that (17) reduces to

$$\frac{\varphi^s RT}{\Sigma_i r_i} = \Sigma^{+-} y_R y_X \left(M_{RX} + \frac{L_{RR}}{2 y_-} + \frac{L_{XX}}{2 y_+} \right). \tag{20}$$

We can rewrite (20) formally as

$$\frac{\varphi^s RT}{\Sigma_i r_i} = \Sigma^{+-} y_R y_X N_{RX} \tag{21}$$

where N_{RX} is defined by

$$N_{RX} = M_{RX} + \frac{L_{RR}}{2 y_-} + \frac{L_{XX}}{2 y_+} \tag{22}$$

but N_{RX} is not independent of the composition of the solution.

If all the cations have the same charge and all the anions have the same charge, so that every electrolyte present consists of the same number ν_+ of cations and the same number ν_- of anions, then

$$y_+ = \frac{\nu_+}{\nu_+ + \nu_-} \qquad y_- = \frac{\nu_-}{\nu_+ + \nu_-} \tag{23}$$

and N_{RX} becomes a constant characteristic of the electrolyte composed of the ions R and X. When electrolytes of more than one electrical type are present, N_{RX} varies with the relative proportions of electrolytes of the several types. N_{RX} is then not a constant. This is the important conclusion reached by SCATCHARD, but expressed rather differently.

So much for the osmotic coefficient. We shall now derive analogous relations for the activity coefficients. By differentiation of (8) with respect to n_i we obtain, using the definitions (11), (13) and (15),

$$\left.\begin{aligned} \ln \gamma_i^s &= \frac{\Sigma_k n_k (l_{ww} - l_{wk} - l_{wi} + l_{ik})}{n_w} = \Sigma_k y_k L_{ik} \\ &= \Sigma_k y_k \left(M_{ik} + \frac{1}{2} L_{kk} + \frac{1}{2} L_{ii} \right). \end{aligned}\right\} \tag{24}$$

When we introduce the notation R, R' for cations and X, X' for anions formula (24) becomes

$$\left.\begin{aligned} ln\,\gamma_k^s &= \Sigma_{X'}\, y_{X'}\left(M_{RX'} + \frac{1}{2}L_{X'X'} + \frac{1}{2}L_{RR}\right) \\ &\quad + \Sigma_{R'}\, y_{R'}\left(\frac{1}{2}L_{R'R'} + \frac{1}{2}L_{RR}\right) \\ &= \Sigma_{X'} y_{X'}\left(M_{RX'} + \frac{1}{2}L_{X'X'}\right) + \Sigma_{R'} y_{R'}\frac{1}{2}L_{R'R'} + \frac{1}{2}L_{RR} \end{aligned}\right\} \tag{25}$$

where we have used the principle of specific interaction in the form

$$M_{RR'} = M_{R'R'} = 0. \tag{26}$$

We now consider an electrolyte composed of ν_R ions R and ν_X ions X and we define

$$q_R = \frac{\nu_R}{\nu_R + \nu_X} \qquad q_X = \frac{\nu_X}{\nu_R + \nu_X}. \tag{27}$$

From (26) and the analogous formula for γ_X^s we deduce for the mean activity coefficient of the electrolyte

$$\left.\begin{aligned} ln\,\gamma_{R,X}^s &= \Sigma_{X'} y_{X'}\left(q_R\, M_{RX'} + \frac{1}{2}L_{X'X'} + \frac{1}{2}\frac{q_R L_{RR}}{y_-}\right) \\ &\quad + \Sigma_{R'}\, y_{R'}\left(q_X\, M_{R'X} + \frac{1}{2}L_{R'R'} + \frac{1}{2}\frac{q_X L_{XX}}{y_+}\right). \end{aligned}\right\} \tag{28}$$

If, but only if, all the electrolytes present are of the same electrical type so that

$$y_+ = q_R \qquad y_- = q_X \tag{29}$$

formula (28) reduces to

$$ln\,\gamma_{R,X}^s = q_R\,\Sigma_{X'} y_{X'} N_{RX'} + q_X\,\Sigma_{R'} y_{R'} N_{R'X} \tag{30}$$

where each N_{RX} is independent of the composition and is given by

$$N_{RX} = M_{RX} + \frac{L_{XX}}{2\,q_R} + \frac{L_{RR}}{2\,q_X}. \tag{31}$$

This conclusion is also in agreement with SCATCHARD's.

If we want to obtain formulae of comparable simplicity in mixtures of electrolytes of several types, we have to supplement the principle of specific interaction

$$M_{RR'} = M_{RR} = 0 \qquad M_{XX'} = M_{XX} = 0 \tag{32}$$

by the additional assumptions

$$L_{RR} = L_{R'R'} = L_{XX} = L_{X'X'} = L. \tag{33}$$

Formula (20) then reduces to

$$ln\ \gamma^s_{R,X} = q_R \Sigma_{X'} y_{X'} M_{RX'} + q_X \Sigma_{R'} y_{R'} M_{R'X} + L. \tag{34}$$

This may be rewritten in the form

$$ln\ \gamma^s_{R,X} = q_R \Sigma_{X'} y_{X'} N_{RX'} + q_X \Sigma_{R'} y_{R'} N_{R'X} \tag{35}$$

where $N_{RX'}$, $N_{R'X}$ defined by

$$N_{RX'} = M_{RX'} + \frac{L}{q_R} \tag{36}$$

$$N_{R'X} = M_{R'X} + \frac{L}{q_X} \tag{37}$$

respectively depend on the electrical type of the electrolyte whose activity coefficient is being considered, but not on the electrical type of the other electrolytes present. It seems that GUGGENHEIM's previous treatment of mixtures of electrolytes of different electrical types involved the tacit assumption expressed by (33). I can see no convincing physical basis for this assumption except as an approximation on the grounds that L_{RR} and L_{XX} are likely to be much less specific than M_{RX}.

I now return to an examination of SCATCHARD's analysis. SCATCHARD begins his discussion with his formula (10)

$$B = \frac{\Sigma_i c_i b_i}{c} + \frac{1}{2} \frac{\Sigma_{ij} c_i c_j b_{ij}}{c^2} \tag{S 10}$$

where c_i denotes the equivalent concentration of species i and c the total equivalent concentration. I am not at all clear why this formula contains equivalent concentrations rather than ionic

concentrations; nor am I sure whether SCATCHARD attaches importance to the distinction. The situation is complicated by his quoting as the relation between equivalent concentrations c_i and molalities m_i

$$\nu c = \Sigma_i c_i \nu_i = \Sigma_i m_i$$

Since neither ν nor ν_i is defined, I cannot say with certainty that this formula is wrong, but it does look strange. However, I shall assume that these matters are trivial and return to the discussion of formula (S10). SCATCHARD attaches special importance to the presence of the terms in b_i and states that "GUGGENHEIM avoids the thermodynamic error by the usually improbable assumption that every b_i is zero". Now we can always define quantities b'_{ij} by

$$b'_{ij} = b_{ij} + \frac{1}{2} b_i + \frac{1}{2} b_j$$

and then, since $\Sigma_i c_i = 2c$ rewrite (S10) as

$$B = \frac{1}{2} \frac{\Sigma_{ij} c_i c_j b'_{ij}}{c^2}$$

The question whether the b_i are zero or not is consequently meaningless until the b_{ij} have been unambiguously defined and SCATCHARD has omitted to do this. Presumably SCATCHARD's b_{ij} correspond closely to my M_{ij} and not to my L_{ij}. To sum up, SCATCHARD's premises are ambiguous but my premises lead to conclusions in considerable, if not complete, agreement with his.

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