

tion? If one makes approximations in  $\psi_v$ , Eq. (A1), instead of directly in Eq. (A3), extra terms will arise (general property of variational methods). Let

$$\psi_v \sim \phi_v^{\text{HF}} = \sum_{i=1}^q a_i \phi_i^{\text{RHF}} \quad (\text{A11})$$

and obtain an approximate  $\tilde{E}_v$  from  $\langle \phi_v^{\text{HF}}, H \phi_v^{\text{HF}} \rangle$ . Taking this expectation value is equivalent to the Van Vleck way of defining a valence-state energy. Then:

$$E_v \cong \tilde{E}_v = \langle \phi_v^{\text{HF}}, H \phi_v^{\text{HF}} \rangle = \sum_{i=1}^q |a_i|^2 E_i^{\text{RHF}} + \sum_{i,j} \bar{a}_i a_j \langle \phi_i^{\text{RHF}}, H \phi_j^{\text{RHF}} \rangle. \quad (\text{A12})$$

The last sum in Eq. (A12) is the off-diagonal terms<sup>8</sup> mentioned in text. Similar off-diagonal terms arise also with the internal correlation part of the wf,<sup>12</sup>  $\chi_v^{\text{int}}$ ,

$$\chi_v^{\text{int}} = \sum_{i=1}^q a_i \chi_i^{\text{int}} \quad (\text{A13})$$

in the form

$$\sum_{i,j} \bar{a}_i a_j \langle \chi_i^{\text{int}}, H \chi_j^{\text{int}} \rangle.$$

Since  $\phi_i^{\text{GRHF}} \cong \phi_i^{\text{RHF}} + \chi_i^{\text{int}}$  (when  $\langle \chi_i^{\text{int}}, \chi_i^{\text{int}} \rangle \ll 1$ ) and  $H$  is diagonal in  $\phi_i^{\text{GRHF}}$  (if the same orbitals used), the RHF and the  $\chi^{\text{int}}$  off-diagonal terms cancel out in the exact  $\psi_v$ .

## Ion-Ion and Ion-Neutral Interactions in Solution and Measurements of Dielectric Constants\*

R. A. MARCUS

*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois*

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Data on dielectric constants of electrolyte solutions are used to evaluate directly the  $r^{-4}$  term in the asymptotic expression for the free energy of interaction of two ions in solution for large separation distance  $r$ . Use is made of the fact that for large separations each ion is in a uniform field due to the other, and that information about ions in uniform fields is obtainable from measurements of dielectric constants. For a  $Z:Z$  electrolyte, for example, the  $r^{-4}$  term is found to be  $Z^2 e^2 \delta / 8 \pi \epsilon_0 r^4$ , assuming the effect of overlapping solvent structures to be of shorter range;  $\epsilon_0$  is the dielectric constant of the solvent and  $\delta$  is the measured decrement in dielectric constant per unit concentration of added electrolyte. A similar result obtained when one of the particles is uncharged,  $\delta$  now referring to the decrement observed when the neutral is added to solution. Typical values of the term are given for various substances using the data on  $\delta$ 's. This determination of the  $r^{-4}$  term permits some evaluation of ion-image force theories.

**T**HE free energy of interaction of two ions in solution as a function of distance of separation  $r$  has sometimes been written in the following asymptotic form for large  $r$ <sup>1</sup>:

$$V(r) = (a/r) + (b/r^4) + (c/r^5) + \dots, \quad (1)$$

where the leading term is the usual Coulombic one, so that  $a$  is the product of the ionic charges divided by the dielectric constant. If one (or both) of the particles has a dipole, then Expression (1) implies a thermal averaging over all orientations of the particle(s). The  $b/r^4$  term arises only from "dielectric image" and thermally averaged ion-dipole forces, if the overlap of the ordered solvent structures of the two ions is of shorter range. We are primarily interested in particles without dipoles (many ions are octahedral, for example) but do not exclude the dipolar case. The higher terms in (1) arise from a variety of short-range effects, such as dispersion interactions, interactions of overlapped solvent structures, dielectric

saturation, corrections to the  $r^{-4}$  term for ion-image and ion-dipole forces at small  $r$ , and so forth. When one of the particles is uncharged Eq. (1) arises as before, but now  $a$  vanishes.

The value of  $b$  has been computed theoretically (together with other coefficients) for particular models of the ions.<sup>1</sup> It is the purpose of the present publication to point out that  $b$  can be obtained instead directly from experimental measurements of dielectric constants of electrolyte or other solutions, under the above presumption that the solvent structure interaction is of shorter range. The fact that the  $b/r^4$  term is a leading term in the asymptotic expression (1) is not intended to imply that is necessarily an important term for the values of  $r$  which contribute appreciably to integrals appearing in statistical mechanical expressions for thermodynamic properties of mixtures. The term has been assumed, however, to be a contributor to salting out effects.<sup>2</sup>

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<sup>1</sup> See, for example, S. Levine and H. E. Wrigley, *Discussions Faraday Soc.* **24**, 43 (1957).

<sup>2</sup> (a) See, for example, J. 'O' M. Bockris, *Modern Aspects of Electrochemistry* (Butterworths Scientific Publications, London, 1954), Vol. I, p. 97. (b) Compare J. G. Kirkwood, *Proteins, Amino Acids and Peptides*, edited by E. J. Cohn and J. T. Edsall (Reinhold Publishing Corporation, New York, 1943), pp. 279-280.

We consider first the free energy of a system in which an electrical condenser is immersed in a solution. The free energy depends on the dielectric constant  $\epsilon$  through the term (2), in the case of weak fields, i.e., in the case of no dielectric saturation,<sup>3</sup>

$$(\mathbf{D}_0^2/8\pi\epsilon)V, \quad (2)$$

where  $\mathbf{D}_0$  is the dielectric displacement and  $V$  is the volume of solution between the electrodes.

When a *dilute* solution contains added ions or neutral molecules of Type  $i$ ,  $N_i/V$  per unit volume, the dielectric constant of the system differs from that for zero concentration  $\epsilon_0$  by an amount which is a linear function of  $N_i/V$ :<sup>4</sup>

$$\epsilon_0 - \epsilon = \sum_i \delta_i N_i / V, \quad (3)$$

where  $\delta_i$  is characteristic of the solute. The free energy of interaction of this system with the external field minus that of interaction of the solvent with the field of the same  $\mathbf{D}_0$  is obtained from (2) and (3):

$$\Delta F = (\mathbf{D}_0^2/8\pi) \{ \epsilon_0^{-1} - \epsilon^{-1} \} V \cong \mathbf{D}_0^2 \sum_i \delta_i N_i / 8\pi\epsilon_0^2, \quad (4)$$

when  $\epsilon - \epsilon_0$  is small.

The contribution per added  $i$  particle,  $\Delta F_i$ , is seen from (3) to be

$$\Delta F_i = \mathbf{D}_0^2 \delta_i / 8\pi\epsilon_0^2 = \delta_i \mathbf{E}_0^2 / 8\pi, \quad (5)$$

where  $\mathbf{E}_0$  is the field in the absence of electrolyte.

We consider now the long-range contributions to (1). At sufficiently large separation distances, the field of one ion, 1,  $\mathbf{E}_1$  is essentially uniform over the region occupied by another, 2, and the presence of this second ion in a uniform field gives rise to a term due to replacing the solvent at this  $r$  by an ion. We have seen, however, that this term is given by (5), with  $\mathbf{E}_0$  now replaced by  $\mathbf{E}_1$ . Similarly, an analogous effect occurs because of the presence of the first ion in the field of the second. The total contribution to the term is therefore

$$\Delta F_{12} = (\delta_1 \mathbf{E}_2^2 + \delta_2 \mathbf{E}_1^2) / 8\pi. \quad (6)$$

If the charges on the ions are  $Z_1 e$  and  $Z_2 e$ ,  $\mathbf{E}_1$  and  $\mathbf{E}_2$  become  $-Z_1 e / \epsilon r^2$  and  $-Z_2 e / \epsilon r^2$  at large distances, and  $b$  in Eq. (1) becomes

$$b = (\delta_1 Z_2^2 + \delta_2 Z_1^2) e^2 / 8\pi\epsilon_0^2, \quad (7)$$

since  $\epsilon$  is close to  $\epsilon_0$ . Equation (7) also applies when one of the particles is neutral. For a  $Z:Z$  electrolyte or for an ion of charge  $Z$  interacting with a neutral molecule (7) becomes

$$b = \delta Z^2 e^2 / 8\pi\epsilon_0^2, \quad (8)$$

where  $\delta$  is the decrement of dielectric concentration per unit added electrolyte in the first instance or per unit added neutral solute in the second. Measurements of  $\delta$  can be made directly in either case.<sup>4</sup> When the electrolyte is not symmetrical (e.g., 2:1) some division of the decrement into contributions  $\delta_1$  and  $\delta_2$  is needed in order to use Eq. (7). We note further that in the case of a polar neutral solute in a less polar solvent, the "decrement"  $\delta$  will be negative.

Typical values of  $\delta$  have been found to be of the order of 8 for small neutral molecules in water, about 15 to 20 for a pair of small univalent ions in water, and about 25 to 40 for an analogous pair in methanol.<sup>4</sup> The ratio of the  $r^{-4}$  term to the Coulombic term in (1) is seen to be  $\delta / 8\pi\epsilon_0 r^3$ . For a value of  $r$  of 8 Å and a  $\delta$  of 25 this ratio equals 0.096 in methanol as solvent and equals 0.041 in water as solvent at room temperature. At 6 Å these figures are about 2.5 times as large. The contribution of the  $e^2/\epsilon_0 r$  term to the free energy of interaction at 8 Å is 0.53 and 1.23 kcal mole<sup>-1</sup> in water and methanol, respectively, from which the magnitude of the second term in (1) can be deduced for various conditions.

The dielectric constant depression caused by addition of ions has been discussed in terms of restricted rotation of the water molecules in the innermost solvation layer. In this way Hasted and co-workers were able to account for their results in water.<sup>4</sup> The effect in methanol was too large to be explained in solely this way. (It was assumed that an added structure-breaking effect occurred in which linear hydrogen-bonded methanol chains were ruptured.<sup>4</sup>) Similar arguments would apply, therefore, to any similar theoretical calculation of the  $r^{-4}$  term in (1).

Wrigley and Levine<sup>1</sup> have estimated the  $r^{-4}$  term theoretically by an electrostatic calculation in which the innermost layer of water molecules was considered bound to the ion. Their coefficient is of the same order of magnitude as that determined from the experimental data in the present paper. This agreement thus parallels that of Hasted and co-workers for theoretically calculated dielectric constant depressions. For methanol as solvent, however, such a model would not be adequate since it is also inadequate to explain the large decrement of dielectric constant. A similar objection would apply to a theoretical calculation of the  $r^{-4}$  term in methanol by the usual electrostatic ion-dielectric image force theory.<sup>5</sup> The direct evaluation of the  $r^{-4}$  term from the dielectric constant data circumvents this difficulty, although it does not offer a way of calculating the shorter-range terms in (1).

<sup>3</sup> For example, E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1959), pp. 411-414.

<sup>4</sup> J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.* **16**, 1 (1948); G. H. Haggis, J. B. Hasted, and T. S. Buchanan, *ibid.* **20**, 1452 (1952); J. B. Hasted and G. Roderick, *ibid.* **29**, 17 (1958); J. A. Lane and J. A. Saxton, *Proc. Roy. Soc. (London)* **A214**, 531 (1952).

<sup>5</sup> In the usual electrostatic dielectric image calculation, the ions are treated as low dielectric constant cavities embedded in a continuous dielectric solvent and ordinary electrostatics is used. See, for example, Ref. 2(b). The  $r^{-4}$  term in Eq. (11) there ( $n=0$ ) is the electrostatically calculated value of the  $r^{-4}$  term in the present Eq. (1).