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On the Calculation of the Relaxation Effect in Solution of Strong Electrolytes

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DEBYE and Hückel¹ have, as it is known, demonstrated that calculation of the magnitude of the relaxation effect in solutions of strong electrolytes leads, in the most general case of a solution with S types of ions, to the solution of a system of S equations, of the type:

$$\Delta\Delta\psi_i' - \frac{4\pi}{DkT} \sum_j \frac{n_i e_i^2 \omega_i}{\omega_i + \omega_j} \Delta\psi_j' - \frac{4\pi}{DkT} \sum_j \frac{n_j e_j^2 \omega_j}{\omega_i + \omega_j} \Delta\psi_i' = \frac{4\pi}{(DkT)^2} \sum_j \frac{\omega_j k_j - \omega_i k_i}{\omega_i + \omega_j} n_i e_i^2 e_j \frac{\partial}{\partial x} \left(\frac{e^{-\kappa r}}{z} \right), \quad (1)$$

where ψ_i' (or ψ_j') is the additional potential at the location of the i th (j th) ion, appearing as a result of destroying the symmetry of the ion atmosphere.

Here

$n_i (n_j)$ is the number of ions of the i th (j th) type, per unit volume.

$e_i (e_j)$ —charge on the i th (j th) ion.

$\omega_i (\omega_j)$ —reciprocal of coefficient of friction of the i th (j th) ion.

$k_i (k_j)$ —strength of the external field acting on the i th (j th) ion.

D —dielectric constant of the solvent.

k —Boltzmann constant.

T —absolute temperature.

$$\kappa^2 = \frac{4\pi}{DkT} \sum_i n_i e_i^2$$

and Δ signifies the Laplacian operator.

The system of Eqs. (1) can be solved by the usual differential equation methods, only for $S=2$, i.e., when the solution contains a single binary electrolyte.

Onsager and Fuoss² have shown, however, that by use of matrix algebra, this system can be solved, in its most general form. The solution for the additional potential found by them, in the form of a matrix function, comes out to be:

$$\text{grad}_x \psi_i' = (1/3DkT)(\kappa - C^{\frac{1}{2}})_{i\sigma} e_\sigma \mathbf{k}_\sigma, \quad (2)$$

¹ Debye and Hückel, *Physik. Zeits.* **24**, 305 (1923).

² Onsager and Fuoss, *J. Phys. Chem.* **36**, 2689 (1932).

where C is a matrix with the components

$$C_{ji} = \frac{4\pi}{DkT} \left(\frac{n_\sigma e_\sigma^2 \omega_\sigma}{\omega_\sigma + \omega_j} \delta_{ji} + \frac{n_i e_i e_j \omega_i}{\omega_i + \omega_j} \right) \quad (3)$$

and σ indicates summation over all values of i . δ_{ji} is the Kronecker index, which is equal to unity when $i=j$, and to zero when $i \neq j$.

$$\text{That is} \quad \delta_{ji} = \begin{cases} 1, & \text{if } i=j \\ 0, & \text{if } i \neq j. \end{cases}$$

For the case when the concentration of the solution is homogeneous, $\mathbf{k}_i = X \mathbf{e}_i$; and $\text{grad}_x \psi_j' = -\Delta X_j$, where X is the strength of the external electric field. Substituting this expression into (2), and dividing both sides of (2) by X , we obtain the magnitude of the relaxation effect in the form

$$-(\Delta X_i / X) = (1/3DkT)(\kappa - C^{\frac{1}{2}})_{i\sigma} e_\sigma^2 = (\epsilon^2 \kappa / 3DkT) \sum_i (1 - \kappa^{-1} C^{\frac{1}{2}})_{ii} \delta_{ji} z_i^2. \quad (4)$$

Calling $z_i^2 = \delta_{ii} z_i^2$, (4) can be written as follows:

$$-(\Delta X_i / X) = (\epsilon^2 \kappa / 3DkT) z_i \sum_j (1 - \kappa^{-1} C^{\frac{1}{2}})_{ij} \delta_{ji} z_j \quad (5)$$

The next step in calculating the magnitude of the relaxation effect for a mixture of electrolytes consists of transforming the matrix function (5) to simple figures.

Onsager and Fuoss² proposed to accomplish this transformation by expanding the matrix function in a Taylor series, and determining the convergence of the series. This method turns out to be very long and complicated. Evaluation of $\Delta X_i / X$ can be accomplished by a much simpler and shorter method, using the Lagrange-Sylvester equation,³ by letting any matrix function appear as a finite matrix polynomial, with a number of terms equal to the order of the matrix, n , and having its highest power equal to $(n-1)$.

³ Lappo-Danilevski, *Theory of Matrix Function and System of Linear Differential Equations* (1932), p. 32.

The Lagrange-Sylvester equation is as follows:

$$f(x) = \sum_{k=1}^{k=n} \frac{(x - \epsilon_1) \cdots (x - \epsilon_{k-1})(x - \epsilon_{k+1}) \cdots (x - \epsilon_n)}{(\epsilon_k - \epsilon_1) \cdots (\epsilon_k - \epsilon_{k-1})(\epsilon_k - \epsilon_{k+1}) \cdots (\epsilon_k - \epsilon_n)} f(\epsilon_k), \quad (6)$$

where $\epsilon_1, \epsilon_2, \epsilon_3 \cdots \epsilon_n$ are characteristic numbers of the matrix x , found by solution of the characteristic equation.

Applying the Lagrange-Sylvester equation to the function $(1 - \kappa^{-1}C^{\frac{1}{2}})$ the latter can be written in polynomial form:

$$(1 - \kappa^{-1}C^{\frac{1}{2}}) = \sum_{k=1}^{k=s} \frac{(C - \epsilon_1) \cdots (C - \epsilon_{k-1})(C - \epsilon_{k+1}) \cdots (C - \epsilon_s)}{(\epsilon_k - \epsilon_1) \cdots (\epsilon_k - \epsilon_{k-1})(\epsilon_k - \epsilon_{k+1}) \cdots (\epsilon_k - \epsilon_s)} (1 - \kappa^{-1}\epsilon_k^{\frac{1}{2}}). \quad (7)$$

And according to (5), for determining $\Delta X_i/X$, with the i, j th element of the polynomial of degree $(S-1)$ and of S terms, it is necessary to operate on the vector z_i .

Thus, the method of evaluating $\Delta X_i/X$ for a mixture of electrolytes, using the Lagrange-Sylvester equation, can be formulated as follows:

1. The matrix C is formed.
2. The characteristic numbers of the matrix C are found by solution of the characteristic equation (the degree of which is equal to the order of the matrix).
3. The function $(1 - \kappa^{-1}C^{\frac{1}{2}})$ is written in the form of the Lagrange-Sylvester polynomial.

4. According to (5), vector z_i is operated on by the j, i th element of this polynomial.

SAMPLE CALCULATIONS

1. For $S=2$, i.e., for the case of a solution containing one binary electrolyte, solution is possible in the general form:

Let n_1 = no. of ions of the first kind, per unit volume.

Let n_2 = no. of ions of the second kind, per unit volume.

According to (3), the matrix C can be expressed for this case as follows:

$$C = \begin{vmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{vmatrix} = \begin{vmatrix} \frac{4\pi}{DkT} \left[\frac{n_1 e_1^2 + \frac{n_2 e_2^2 \omega_2}{\omega_1 + \omega_2}}{\omega_1 + \omega_2} \right] & \frac{4\pi}{DkT} \left[\frac{n_2 e_1 e_2 \omega_2}{\omega_1 + \omega_2} \right] \\ \frac{4\pi}{DkT} \left[\frac{n_1 e_1 e_2 \omega_1}{\omega_1 + \omega_2} \right] & \frac{4\pi}{DkT} \left[\frac{n_2 e_2^2 + \frac{n_1 e_1^2 \omega_1}{\omega_1 + \omega_2}}{\omega_1 + \omega_2} \right] \end{vmatrix}. \quad (8)$$

Characteristic equation:

$$\epsilon^2 - (C_{11} + C_{22})\epsilon + (C_{11}C_{22} - C_{12}C_{21}) = 0. \quad (9)$$

Substituting in (9) the expression for C_{11} , C_{22} , C_{12} , C_{21} from (8), and for simplification introducing the factor

$$q = (n_1 e_1^2 \omega_1 + n_2 e_2^2 \omega_2) / [(n_1 e_1^2 + n_2 e_2^2)(\omega_1 + \omega_2)] \quad (10)$$

and solving Eq. (9), we obtain the characteristic numbers: $\epsilon_1 = \kappa^2$; $\epsilon_2 = q\kappa^2$. Knowing the characteristic numbers it is possible, according to (7), to write $(1 - \kappa^{-1}C^{\frac{1}{2}})$ in the form of the following polynomial:

$$(1 - \kappa^{-1}C^{\frac{1}{2}}) = (\kappa^2 - C) / (\kappa^2(1 + \sqrt{q})). \quad (11)$$

Then, according to (5), we must set up

$$\begin{aligned} \sum_i (1 - \kappa^{-1}C^{\frac{1}{2}})_{ji} z_i &= \sum_i \left[\frac{\kappa^2 - C}{\kappa^2(1 + \sqrt{q})} \right]_{ji} z_i \\ &= \sum_i \left(\frac{1}{1 + \sqrt{q}} \delta_{ji} z_i - \frac{1}{\kappa^2(1 + \sqrt{q})} C_{ji} z_i \right) \\ &= \frac{z_j}{1 + \sqrt{q}} - \frac{1}{\kappa^2(1 + \sqrt{q})} (C_{j1} z_1 + C_{j2} z_2). \quad (12) \end{aligned}$$

Inserting in (12), for C_{j1} and C_{j2} , the elements of the j th column of the matrix C (8), we obtain:

$$(1 - \kappa^{-1}C^{\frac{1}{2}})_{j\sigma} z_\sigma = (q/1 + \sqrt{q}) z_j.$$

Consequently,

$$\Delta X_j/X = (\epsilon^2 \kappa / 3DkT)(q/(1+\sqrt{q}))z_j z_i \quad (13)$$

(the result already arrived at in the earlier work of Onsager).

For the case of $S > 2$, the general solution becomes too cumbersome and the final equations become difficult to grasp, so that it is simpler to carry out a complete calculation for a given solution of mixed electrolytes.

Let us take for example* calculation of the magnitude of the relaxation effect for a mixture of 2 electrolytes, HCl and KCl, containing 0.04995 mole of HCl and 0.05016 mole of KCl, in a liter of water solution at 18°C.

We determine the magnitude of $\Delta X_j/X$ for each kind of ions:

Ion	j	Λ_j^0	$\mu_i = \frac{n_i e_i^2}{n_\sigma e_\sigma^2}$	$\omega_{ij} = \frac{\omega_i}{\omega_i + \omega_j} = \frac{\Lambda_i^0}{\Lambda_i^0 + \Lambda_j^0}$
H ⁺	1	315	0.2495	$\omega_{12} = 0.8298$
K ⁺	2	64.6	0.2505	$\omega_{23} = 0.4965$
Cl ⁻	3	65.5	0.5000	$\omega_{13} = 0.8279$

Using the expression $\mu_i = n_i e_i^2 / n_\sigma e_\sigma^2$ and $\omega_{ij} = (\omega_i / (\omega_i + \omega_j)) = (\Lambda_i^0 / (\Lambda_i^0 + \Lambda_j^0))$ the element of the matrix can be rewritten as:

$$C_{j*} = \kappa^2 (\delta_{j*} \sum_i \mu_i \omega_{ij} + \mu_i \omega_{ii}).$$

For this case, matrix C will be expressed as follows:

$$\begin{vmatrix} 0.3782\kappa^2 & 0.2070\kappa^2 & 0.2066\kappa^2 \\ 0.0426\kappa^2 & 0.7094\kappa^2 & 0.1244\kappa^2 \\ 0.0860\kappa^2 & 0.2518\kappa^2 & 0.8310\kappa^2 \end{vmatrix}. \quad (14)$$

Characteristic equation:

$$(\epsilon/\kappa^2)^3 - 1.9186(\epsilon/\kappa^2)^2 + 1.1142(\epsilon/\kappa^2) - 0.1956 = 0.$$

* Example from the work of Fuoss and Onsager.

Characteristic numbers:

$$\epsilon_1 = \kappa^2, \quad \epsilon_2 = 0.5832\kappa^2, \quad \epsilon_3 = 0.3354\kappa^2, \quad (15)$$

$$(1 - \kappa^{-1}C^{\frac{1}{2}})_{j\sigma} z_\sigma = \left[\frac{(C - \epsilon_2)(C - \epsilon_3)}{(\epsilon_1 - \epsilon_2)(\epsilon_1 - \epsilon_3)} (1 - \kappa^{-1}\epsilon_1^{\frac{1}{2}}) + \frac{(C - \epsilon_1)(C - \epsilon_3)}{(\epsilon_2 - \epsilon_1)(\epsilon_2 - \epsilon_3)} (1 - \kappa^{-1}\epsilon_2^{\frac{1}{2}}) + \frac{(C - \epsilon_1)(C - \epsilon_2)}{(\epsilon_3 - \epsilon_1)(\epsilon_3 - \epsilon_2)} (1 - \kappa^{-1}\epsilon_3^{\frac{1}{2}}) \right] z_\sigma$$

or, substituting for ϵ_1 , ϵ_2 and ϵ_3 their values from (15)

$$(1 - \kappa^{-1}C^{\frac{1}{2}})_{j\sigma} z_\sigma = (1/\kappa^4)(0.2679C^2 - 0.99106C\kappa^2 + 0.72316\kappa^4) = (0.2679/\kappa^4)C_{j\sigma} z_\sigma - (0.99106/\kappa^2)C_{j\sigma} z_\sigma + 0.72316z_i. \quad (16)$$

Expressing this polynomial for each j , and bearing in mind that for the given example $z_1 = z_2 = 1$, and $z_3 = -1$, the value of $(1 - \kappa^{-1}C^{\frac{1}{2}})_{j\sigma} z_\sigma$ can be found.

The calculations have shown the following results:

Ion	j	$z_j(1 - \kappa^{-1}C^{\frac{1}{2}})_{j\sigma} z_\sigma$	$z_j \sum C_{j\sigma} z_\sigma^{(n)}$
		(Our calculation)	(Values from Onsager and Fuoss)
H ⁺	1	0.4213	0.4212
K ⁺	2	0.1757	0.1758
Cl ⁻	3	0.2982	0.2982

The results thus agree perfectly with those of Onsager and Fuoss, but the method of calculation is considerably simpler than that proposed by them.

The author would like to express her appreciation to M. N. Olevski and V. A. Pleskov for valuable assistance in carrying out this work.

Errata: Exchange of Energy Between Organic Molecules and Solid Surfaces

Part I. Accommodation Coefficients and Specific Heats of Hydrocarbon Molecules

OTTO BEECK, *Shell Development Company, Emeryville, California*
(J. Chem. Phys. 4, 680 (1936))

IN line 11 of the abstract read "constant volume" instead of "constant pressure."

The last term in brackets of the first part of Eq. (2) should read $\frac{3}{4}\left(Cv - \frac{3R}{2}\right)$ instead of $\frac{3}{4}\left(Cv - \frac{R}{2}\right)$.

Eq. (10) is arrived at from Eq. (8), not (5), and the double parenthesis should enclose the whole expression before the last term.