

DIELECTRIC SATURATION AND ASSOCIATION IN AQUEOUS THALLOUS ION SOLUTIONS*

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It has been suggested at various times (Bell and George 1953 ; Davies 1957) that dielectric saturation of the solvent may be in part responsible for the failure of the Bjerrum (1926) theory to account for association of simple thallos salts in aqueous solution. While it has recently been pointed out (Panckhurst 1962) that dielectric saturation cannot account for the major anomalies of such solutions it is of interest to estimate the effects of such saturation. Ritson and Hasted (1948) have shown that the decrease with concentration of the bulk dielectric constant of electrolyte solutions can be attributed to appreciable dielectric saturation in the immediate vicinity of the positive ions. Assuming a dielectric continuum their calculations, and those of Grahame (1950) indicate that at a distance $r_s = r_+ + 2r_w$ from the centre of a positive univalent ion (where r_+ and r_w are the radii of positive ion and water molecule respectively) the microscopic dielectric constant has almost reached that of the bulk solvent. This microscopic variation can be incorporated in the Bjerrum theory to give a rough estimate of saturation effects.

* Manuscript received September 22, 1961.

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The Bjerrum theory gives the association constant as

$$K = \frac{4\pi N}{1000} \int_a^q r^2 \exp\left(-\frac{U}{kT}\right) dr, \quad (1)$$

where a is the distance of closest approach of ion-pairs, q is the distance of closest approach of free ions, and U is the potential energy of the ion-pair at distance r . q is defined as the distance at which the probability function $r^2 \exp(-U/kT)$ is a minimum. The simple Debye-Hückel model gives

$$U_{D-H} = -e^2/D_0 r, \quad (2)$$

for a 1:1 electrolyte, where D_0 is the bulk solvent dielectric constant, and hence $q_{D-H} = e^2/2D_0 kT$. Using equation (2), equation (1) can be integrated using tabulated functions if a value for a is assumed. It will be assumed here for comparative purposes that a is equal to the sum of the Pauling radii since for Tl^+ ion-pairs the ions are probably in contact. With this assumption the calculated association constants (K_{D-H}) for some 1:1 thallous salts are given in Table 1, together with the experimental values. The well-known disagreement is apparent.

TABLE 1
EXPERIMENTAL AND CALCULATED THERMODYNAMIC ASSOCIATION CONSTANTS IN AQUEOUS SOLUTION
AT 25 °C

Ion-Pair	a (Å)	$K_{\text{expt.}}$	K_{D-H}	K_1	K_2	K_4
		(l. mole ⁻¹)				
Tl ⁺ F ⁻	2.80	1.2*	0.57	0.87	1.05	1.6
Tl ⁺ OH ⁻	2.84	5.0†	0.53	0.83	1.00	1.4
Tl ⁺ Cl ⁻	3.25	4.8*	0.23	0.48	0.58	0.72
Tl ⁺ Br ⁻	3.39	7.6‡	0.12	0.37	0.47	0.57

* Bell and George (1953).

† Bell and Panckhurst (1957).

‡ Nair and Nancollas (1957).

Other K values in Table 1 allow for saturation effects as follows. It is assumed that the microscopic dielectric constant (D) is continuous, and is given from $r=0$ to $r=r_s$ by $D=(r/r_s)^n D_0 = m^n D_0$, and n values of 1, 2, and 4 will be considered. For the thallous ion $r_s = 4.24$ Å using Pauling's radius for r_+ . The potential energy of ions of charges Z_i, Z_j a distance r apart is given by

$$U = - \int_{\infty}^r \frac{Z_i Z_j e^2}{D r^2} dr.$$

For oppositely charged univalent ions, allowing for microscopic dielectric variation, this becomes, for $m \geq 1$,

$$U_n = - \frac{e^2}{D_0 r} = U_{D-H},$$

and for $m \leq 1$

$$U_n = -\frac{n}{n+1} \cdot \frac{e^2}{D_0 r_s} \left(1 + \frac{1}{nm^{n+1}} \right). \quad (3)$$

The minimum in the probability expression $r^2 \exp(-U_n/kT)$ can be shown to be $q_n = r_s \beta^{1/n+1}$, where $\beta = e^2/2D_0 r_s kT$. For the thallous ion in aqueous solution at 25°C, $\beta = 0.8414$. Hence $q_n < r_s$, and U_n given by equation (3) is appropriate at all distances involved in the calculation of K_n from equation (1). Ions approaching closer than q_n are regarded as associated. K_n values can now be obtained for the various U_n by graphical integration of equation (1) and are given in Table 1.

It is clear that on the present model dielectric saturation has an effect on the calculated association constants. However, the relative order of the K_n 's is in the inverse order of the assumed a distances, which is not the order of the $K_{\text{expt.}}$ values. This will always be the case with a model in which saturation effects are a function of charge and size alone as long as the assumed a values are in the same relative order as distances of closest approach of paired ions. In the present case K_4 is greater than $K_{\text{expt.}}$ for TlF, suggesting that the saturation effect has been overestimated for $n=4$, while at the same time for TlBr, K_4 is very much smaller than $K_{\text{expt.}}$. Electrostrictive pressure might also reduce saturation effects (Schellman 1957). It is concluded that while dielectric saturation may have some effect on the association constants, it is not a major one and cannot account for anomalous association effects for thallous salts. In cases where ions retain a primary hydration shell in ion-pair formation saturation effects would be even smaller.

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