Summary

The dissociation constants of some hydrocarbon derivatives of boric acid have been determined. These constants have been compared and discussed on the basis of the resonances and negativities of the various groups involved.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XI. The Temperature Coefficient of Conductance

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I. Introduction

It has been shown[1] that the conductance of many electrolytes up to concentrations corresponding to the minimum in conductance can be described in terms of the hypothesis that free ions, ion pairs and ion triples are present. The constants describing the equilibria have been calculated as functions of ion size,[2] dielectric constant and temperature. It should therefore be possible to calculate the temperature coefficient of conductance in the above range of concentration. In this paper we shall derive for the case of weakly dissociated electrolytes an explicit expression for the following function

$$\frac{1}{\Lambda}\frac{\mathrm{d}\Lambda}{\mathrm{d}T} = f(a, D, T, c, \eta)$$

where Λ = equivalent conductance, T = temperature, a = ion size, D = dielectric constant, c = concentration and η = solvent viscosity.

II. Calculation of the Temperature Coefficient

For the case of binary electrolytes in solvents of dielectric constant under 10, the conductance over a considerable concentration range is given by the following limiting form of the general conductance equation

$$\Lambda g(c) = \Lambda_0 \sqrt{K}/\sqrt{c} + (\lambda_0 \sqrt{K}/k)\sqrt{c} \qquad (1)$$

Here Λ_0 and λ_0 are limiting conductances for the electrolytes (A^+) (B') and (A_2B^+) (AB_2'), respectively, and K and k are the equilibrium constants[3] for the reactions

$$A^+ + B' \rightleftharpoons AB, \text{ and}$$
$$AB + A^+ \rightleftharpoons A_2B^+, \quad AB + B' \rightleftharpoons AB_2'$$

The function $g(c)$ takes into account the average effects of the free ions on mobility and thermodynamic potential, and reduces to unity in the case of small free ion concentrations. It has a very small temperature coefficient; for tetrabutylammonium nitrate in anisole (D = 4.29 at 25°), for example, at 10^{-3} N, it varied from 0.942 at 95° to 0.951 at −33° or by less than 0.01% per degree. We shall therefore neglect its change with temperature.

Writing (1) in the form

$$\Lambda = \Lambda(\Lambda_0, \lambda_0, K, k, c)$$

we obtain the total differential

$$\frac{\mathrm{d}\ln\Lambda}{\mathrm{d}T} = \frac{1}{\Lambda}\left(\frac{\partial\Lambda}{\partial\Lambda_0}\frac{\mathrm{d}\Lambda_0}{\mathrm{d}T} + \frac{\partial\Lambda}{\partial\lambda_0}\frac{\mathrm{d}\lambda_0}{\mathrm{d}T} + \frac{\partial\Lambda}{\partial K}\frac{\mathrm{d}K}{\mathrm{d}T} + \frac{\partial\Lambda}{\partial k}\frac{\mathrm{d}k}{\mathrm{d}T} + \frac{\partial\Lambda}{\partial c}\frac{\mathrm{d}c}{\mathrm{d}T}\right) \qquad (2)$$

The last term in the parentheses is negligible; it furnishes in the final result a term of the order of the coefficient of cubical expansion of the solvent (about 0.1%), multiplied by (d ln Λ/d ln c) and the latter varies from $(-{}^1/_2)$ through zero to about $(+{}^1/_2)$ in the concentration range considered.

For the partial derivatives we obtain from (1)

$$\partial\Lambda/\partial\lambda_0 = \sqrt{K}/g\sqrt{c} \qquad \partial\Lambda/\partial\lambda_0 = \sqrt{Kc}/kg$$
$$\partial\Lambda/\partial K = \Lambda/2K \qquad \partial\Lambda/\partial k = -\lambda_0\sqrt{Kc}/k^2g$$

In order to evaluate $\mathrm{d}\Lambda_0/\mathrm{d}T$ and $\mathrm{d}\lambda_0/\mathrm{d}T$, we shall assume that the products $\Lambda_0\eta$ and $\lambda_0\eta$ are independent of temperature,[4] which leads to the result that

$$\frac{\partial\Lambda}{\partial\Lambda_0}\frac{\mathrm{d}\Lambda_0}{\mathrm{d}T} + \frac{\partial\Lambda}{\partial\lambda_0}\frac{\mathrm{d}\lambda_0}{\mathrm{d}T} = -\Lambda\frac{\mathrm{d}\ln\eta}{\mathrm{d}T} = \Lambda\frac{\mathrm{d}\ln\varphi}{\mathrm{d}T} \qquad (3)$$

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(1) Fuoss and Kraus, THIS JOURNAL, **55**, 476, 1019, 2387 (1933).

(2) The "ion size" is an arbitrary constant calculated from experimentally determined dissociation constants. It gives the radius of an imaginary particle whose properties duplicate more or less quantitatively those of the real solute. While the dependence of a on the solvent and solute is gradually becoming clearer as more data are obtained, at present it is only possible to predict the order of magnitude and sometimes the sequence of a-values for different solvents or solutes from independent data. The parameter includes both the size of the lattice ion and the apparent increase of size of the latter due to solvation. (By solvation, we mean either actual compound formation or simply orientation of solvent dipoles in the ionic field, or both.)

(3) For simplicity, we are retaining our earlier assumption that $[A_2B^+] = [AB_2']$.

(4) Walden, *Z. physik. Chem.*, **78**, 257 (1912).

This term accounts for the change of conductance due to the change of fluidity $\varphi = 1/\eta$ of the solvent. The remaining terms of (2) are due to the change produced in the number of conducting particles by the shift of the equilibria with temperature.

In the range of dielectric constant values where (1) applies, we may use the following expression[5] for K

$$K^{-1} = \frac{4\pi Na^3}{1000}\frac{e^b}{b}\left(1 + \frac{4}{b} + \ldots\right) \qquad (4)$$

where N is Avogadro's number and $b = \epsilon^2/aDkT$, with $\epsilon = 4.774 \times 10^{-10}$ e. s. u. and $k = 1.372 \times 10^{-16}$ erg/1°. Differentiating (4) logarithmically, under the assumption that a is *independent of the temperature*, yields

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{1}{T}\left(1 + \frac{D}{T}\frac{\mathrm{d}D}{\mathrm{d}T}\right)\left(b - 1 - \frac{4}{b} + O(b^{-2})\right) \quad (5)$$

In a later section, we shall derive the following asymptotic expansion for k

$$k^{-1} = \frac{64\pi\ Na^3}{3000}\frac{\exp\ (b_3/2)}{b_3{}^2}\left(1 + \frac{8}{3b_3} + \ldots\right),\ b_3 > 10 \qquad (6)$$

where $b_3 = \epsilon^2/a_3DkT$. (The ion size a_3 which determines the triple ion equilibrium is, in general, different from a, the parameter for the simple equilibrium. This is probably due to the fact that the actual positive and negative ions are not equal in size.) On differentiating (6),[6] we obtain[7]

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{T}\left(1 + \frac{T}{D}\frac{\mathrm{d}D}{\mathrm{d}T}\right)\left(\frac{b_3}{2} - 2 - \frac{8}{3b_3} + O(b_3{}^{-2})\right) \qquad (7)$$

Both (5) and (6) contain explicitly the change of dielectric constant with temperature. For solvents whose molecular polarization

$$P = \frac{D-1}{D+2}\frac{M}{\rho}$$

(M = molecular weight, ρ = density) has the following form as a function of temperature

$$P = P_0 + (B/T) \qquad (8)$$

the coefficient $\mathrm{d}D/\mathrm{d}T$ can be calculated from the equation

$$\frac{\mathrm{d}D}{\mathrm{d}T} = \frac{-\rho(D+2)}{M - \rho P}\left(\frac{B}{T^2} + P(\alpha + 2\beta[t - 25])\frac{\rho}{\rho_{25}}\right) \qquad (9)$$

The density as a function of temperature is assumed to be given by the empirical equation

$$\rho = \rho_{25}/(1 + \alpha[t - 25] + \beta[t - 25]^2) \qquad (10)$$

If we substitute (3), (5) and (7) in (2), we obtain

$$\frac{1}{\Lambda}\frac{\mathrm{d}\Lambda}{\mathrm{d}T} = \frac{\mathrm{d}\ln\varphi}{\mathrm{d}T} + \frac{1}{2T}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right)\left(b - 1 - \frac{4}{b}\right) - \frac{A}{2T}\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right)\left(b_3 - 4 - \frac{16}{3b_3}\right) \qquad (11)$$

where

$$A = \lambda_0\sqrt{Kc}/\Lambda kg$$

On substituting (1) in the above expression for $\Lambda g(c)$, we obtain

$$A^{-1} = 1 + (k\Lambda_0/\lambda_0 c)$$

The temperature coefficient (11) is made up of three terms, arising from change with temperature of fluidity and of the equilibrium constants K and k, respectively. The first term may be calculated when the constants a, b, c and d for the fluidity equation

$$\varphi = [(T^2 - aT + b)^{1/2} + T - c]/d \qquad (12)$$

are known. It has been shown[8] that (12) reproduces observed fluidity values with a remarkable degree of accuracy and, furthermore, that it is possible to derive the constants[9] from the structural formula of the solvent by certain addition rules. For highly dissociated salts (small values of b), the fluidity term is, of course, the most important part of the conductance–temperature coefficient. In solvents of low dielectric constant, however, the dissociation terms must also be considered, because they reach the same order of magnitude as the first term. The contribution from K is independent of concentration, but the k term increases numerically with the concentration. Since these last two terms have opposite signs, it is possible to find a concentration such that d ln φ/dT = d ln Λ/dT. At higher concentrations the conductance coefficient is less than the fluidity coefficient.

As a function of temperature, (d ln Λ/dT) varies with T chiefly through the variation of (d ln φ/dT) with T: the dissociation terms may be written as proportional to

$$\frac{\mathrm{d}\ln K}{\mathrm{d}b}\frac{\mathrm{d}b}{\mathrm{d}T} \text{ and } \frac{\mathrm{d}\ln k}{\mathrm{d}b_3}\frac{\mathrm{d}b_3}{\mathrm{d}T}$$

except for terms of higher order which arise from the temperature variation of $(1 + k\Lambda_0/\lambda_0 c)^{-1}$. The coefficients of d$b$/d$T$ and db_3/dT in these

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[5] Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933); Equation (6), together with the asymptotic expansion for $Q(b)$ given on p. 1022.

[6] Ritt, *Bull. Am. Math. Soc.*, **24**, 225 (1918).

[7] Incidentally, (7) also serves indirectly to evaluate the ratio λ_0/Λ_0. From the data, an experimental value of d ln k/dT can be obtained, which, from (7) and $b_3 = \epsilon^2/a_3DkT$ gives a value for a_3. Then λ_0/Λ_0 is evaluated from the relation $\Lambda_0/\lambda_0 = c_{min}/k$.

[8] Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., 1922, p. 137.

[9] Bingham and Spooner, *J. Rheology*, **3**, 221 (1932); *Physics*, **4**, 387 (1933); Bingham and Geddes, *ibid.*, **5**, 42 (1934).

expressions are practically constant, leaving the latter to control the variation. But b (or b_3) contains $(DT)^{-1}$ and D decreases, in general, as T increases, so that the product becomes relatively insensitive to the temperature.

In the following paper of this series, experimental data on the temperature coefficients for several salts in anisole will be presented and compared with the above theoretical discussion. It should be emphasized that the formulas apply only to conductance data in the range of concentration and dielectric constant where (1) reproduces observed values.

III. Asymptotic Expansion for k_3

We shall now derive the expansion (6) for the triple ion constant which was used above. The final formula reproduces the previous values of log k, which were obtained by planimeter integration, to within a few hundredths of a logarithm unit for values of $b_3 \geqslant 10$.[10]

The general formula for k in our fourth paper[11] contains an error which, fortunately, does not affect the results: the upper limit of integration for θ should not extend to π for all values of the distance r. The limits are 0 and π for $r \geqslant 2a$ and 0 and $2\pi/3$ for $r = a$. For $2a > r \geqslant a$, the upper limit is arc $\cos(r/2a)$. Integrating from $(2\pi/3)$ to π contributes a very small amount to the integral, because the integrand becomes unity for $r = a$, $\theta = 2\pi/3$ and approaches zero exponentially for larger values. Practically the entire value of the integral for large (*i. e.*, $\geqslant 10$) values of b comes from values of the integrand in the neighborhood of $r = a$, $\theta = 0$.

If distances are measured in multiples of a, we have then

$$k^{-1} = \frac{2\pi Na^3}{1000}\int_1^X x^2 dx \int_0^{2\pi/3} \exp\left(\frac{b}{x} - \frac{b}{(1 + x^2 + 2x\cos\theta)^{1/2}}\right)\sin\theta\, d\theta \qquad (13)$$
$$= 2\pi Na^3 I(b)/1000$$

In (13), k^{-1} is represented as the volume under a surface in the x-θ plane. As pointed out in the previous paragraph, this volume has an exponential peak near the point (1,0): we therefore look for the asymptotic expansion[12] of k^{-1} by integrating approximately near this point.

Introducing new variables δ and ϵ by the equations

$$\delta = x - 1$$
$$\epsilon = \theta - 0$$

we find for the integration near $\theta = 0$ the expression

$$e^{b/2}\int_{(0)} \epsilon\left(1 - \frac{\epsilon^2}{6}\right)e^{-b\epsilon^2/16}\, d\epsilon$$

which is practically equal to

$$\frac{8e^{b/2}}{b}\left(1 - \frac{128}{3b^2} + \ldots\right) \qquad (14)$$

For the integration near $\delta = 0$, we have

$$\int_{(0)} (1 + 2\delta + \delta^2)e^{-3b\delta/4}\, d\delta$$

which gives

$$\frac{4}{3b}\left(1 + \frac{8}{3b} + \frac{8}{3b^2} + \ldots\right) \qquad (15)$$

Combining the above results, we obtain

$$I(b) \sim \frac{32}{3b^2}e^{b/2}\left(1 + \frac{8}{3b} + O(b^{-2})\right) \qquad (16)$$

and

$$-\ln k \sim \ln\frac{64\pi Na^3}{3000} + \frac{b}{2} - 2\ln b + \ln\left(1 + \frac{8}{3b} + O(b^{-2})\right) \qquad (17)$$

which is the result used above in deriving (7). The relative error in using (17) instead of the planimeter method to evaluate the logarithm of k is of the order of b^{-3}, because the leading term of (17) is $b/2$ and the error is in terms containing b^2 in the denominator.

Summary

1. A theoretical derivation of the temperature coefficient of the conductance of electrolytes in solvents of low dielectric constant is presented.

2. This coefficient is shown to contain three terms: a viscosity term and two terms arising from the shift of the simpler ionic equilibria with temperature.

3. The dependence of the coefficient on temperature and concentration is discussed.

4. An asymptotic expansion for the calculation of the triple ion constant, valid for solvents of dielectric constant under 10, is obtained.

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[10] For simplicity, we shall drop the subscript on b_3 throughout this section.

[11] Fuoss and Kraus, THIS JOURNAL, **55**, 2387 (1933).

[12] Fuoss, *ibid.*, **56**, 1030 (1934).