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The Electrostatic Influence of Substituents on the Dissociation Constants of Organic Acids. II.

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The theory of the influence of substituents on dissociation constants presented in an earlier article of the same title is extended to acids ellipsoidal in shape. Bjerrum's formula is obtained in the limiting case of unit eccentricity of the elliptical section of a prolate ellipsoid of revolution. The influence of dipolar as well as ionic substituents can satisfactorily be treated.

I

IT has been proposed by Bjerrum¹ that the influence of a polar substituent on the dissociation constant of an organic acid is primarily electrostatic in origin. On the basis of this hypothesis, the ratio of the dissociation constants of two similarly constituted acids may be calculated from electrostatic work necessary to transfer a proton from the first acid to the ion of the second. Because of the fruitfulness of Bjerrum's idea, we considered it desirable to introduce certain refinements into the calculation of the work of transfer. In a previous article, we showed² that the electrostatic work is dependent not only upon the charges present and the distance between them, but also upon the shape of the molecule and upon the positions of the charges. We have already presented the equations for a spherical model, and have applied them to several aliphatic acids which approximate a sphere in shape. In the present paper, similar considerations lead to the equations for an ellipsoid of revolution, a model well fitted to treat the longer aliphatic dibasic acids.

We are concerned with four ellipsoids, representing the molecular species HA_1 , A_1^- , HA_2 and A_2^- . For the sake of simplicity, we have assumed that the protons of the carboxyl group and the dipoles in the molecules lie on the line connecting the foci of the ellipsoid, and, in the actual computations, have further assumed that the charges are actually at the foci, although this latter limitation is not inherent in the equations developed. In the present discussion, it is convenient to use confocal elliptical coordinates.

¹ Bjerrum, *Zeits. f. physik. Chemie* **106**, 219 (1923).

² Kirkwood and Westheimer, *J. Chem. Phys.* **6**, 506 (1938).

If r_1 and r_2 are the distances of a point from the two foci, and R the distance between the foci, then $\lambda = (r_1 + r_2)/R$, $\mu = (r_1 - r_2)/R$, and φ is the angle by which the point has been rotated past a fixed plane through the major axis. Since we have chosen an ellipsoid of revolution with all charges on the major axis, the model is axially symmetrical and the angle φ does not enter the formulation.

Following the same reasoning advanced for the spherical model, we approximate the total free energy increment in the reaction $HA_1 + A_2^- \rightleftharpoons HA_2 + A_1^-$ by the sum of the electrostatic contribution, Δw , and the symmetry contribution $RT \log \sigma$, where σ is the statistical factor, equal to four for symmetrical dibasic acids.

$$kT \log K_1 / \sigma K_2 = 2.303 kT \Delta pK = \Delta w$$

$$\Delta W = W(HA_1) + W(A_2^-) - W(HA_2) - W(A_1^-), \quad (1)$$

where $W(HA_1)$, $W(A_2^-)$, $W(HA_2)$ and $W(A_1^-)$ are the electrostatic free energies of the respective molecular species. In order to determine the electrostatic work, Δw , it is first necessary to solve Laplace's equation in confocal elliptical coordinates. Then, from the electrostatic potential of the charges, the electrostatic work

TABLE I. *Effective dielectric constant for varying λ_0 .*

λ_0	D_E (CHARGE)	D_E (DIPOLE)
2.3	7.8	2.7
2.0	11.2	3.3
1.8	15.5	4.0
1.6	25.3	5.7
1.4	51.	11.2
1.3	74.	20.4
1.2	94.	49.
1.1	94.	90.
1.0	78.	78.

can be computed. The actual mathematical treatment is presented in Part III of this paper. In that section it will be shown that, if HA_1 differs from HA_2 by a protonic charge, then

$$\Delta pK = \frac{e^2}{2.303kTR} \times \left\{ \frac{1}{D_i} + \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} \frac{U_n}{1 + (D_i/D)C_n} \right\} \quad (2)$$

$$U_n = (2n+1) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} (-1)^n$$

$$C_n = \frac{\lambda_0 - P_{n-1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n-1}(\lambda_0)/Q_n(\lambda_0)}$$

Further, if HA_1 differs from HA_2 by a point dipole of moment M inclined at an angle ζ to the major axis of the ellipsoid, then

$$\Delta pK = \frac{eM \cos \zeta}{2.303kTR^2} \times \left\{ \frac{1}{D_i} + \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} \frac{Y_n}{1 + (D_i/D)C_n} \right\} \quad (3)$$

$$Y_n = n(n+1)(2n+1) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} (-1)^n.$$

In these formulas, P_n represents a Legendre function of the first kind, D is the dielectric

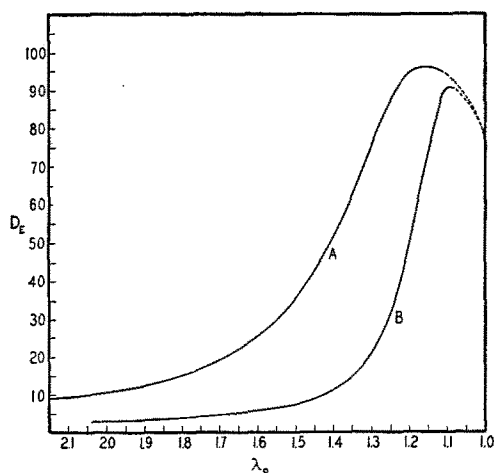


FIG. 1. Curve A is the plot of D_E for a charged substituent against λ_0 , curve B is the plot for a dipolar substituent. The slope of the curves at $\lambda_0=1$ has not been determined.

constant of the solvent, D_i the internal molecular dielectric constant² and $\lambda=\lambda_0$ is the equation of the ellipsoidal cavity in the solvent created by the molecule.

Q_n represents a Legendre function of the second kind; Q_0 and Q_1 are given by the equations

$$Q_0(\lambda) = \frac{1}{2} \log_e \frac{\lambda+1}{\lambda-1}$$

$$Q_1(\lambda) = \frac{\lambda}{2} \log_e \frac{\lambda+1}{\lambda-1} - 1$$

and the rest can be obtained from the first two by means of the recursion formula,

$$(n+1)Q_{n+1}(\lambda) = (2n+1)Q_n(\lambda) - nQ_{n-1}(\lambda).$$

As in the previous article, an effective dielectric constant, D_E , is defined in terms of the Bjerrum equation.^{1, 3} For the case in which HA_1 has a charge in excess of HA_2 ,

$$\Delta pK = e^2/2.303D_ERkT \quad (4)$$

and in the case in which HA_1 contains a dipole in excess of HA_2

$$\Delta pK = eM \cos \zeta / 2.303D_ER^2kT. \quad (5)$$

In Table I the values of D_E accurate to 1 percent for molecules in water at 25° computed from Eqs. (2), (3), (4) and (5) for both dipolar and charged substituents are recorded for typical values of λ_0 . D_i , as previously, has been set equal to 2.00.

In Fig. 1, D_E has been plotted against λ_0 . At large values of λ_0 the charges are brought close together in the medium of low dielectric constant, and D_E approaches the internal molecular dielectric constant D_i . On the other hand, as λ_0 decreases toward 1, the ellipsoid thins out into a rod, and at λ_0 equal to 1 disappears altogether, leaving the charges immersed only in the solvent. As in the spherical case, the values of the effective dielectric constant depends primarily upon the existence of a low internal dielectric constant, only secondarily upon its exact value.

With the ellipsoid as with the sphere, values of D_E greater than the dielectric constant of the solvent are obtained. With the ellipsoid, how-

³ Eucken, Zeits. f. angew. Chemie 45, 203 (1932).

ever, since the effective dielectric constant must approach D as the ellipsoid vanishes, the values of D_E go through a maximum.

Here again our theoretical treatment is in agreement with the experimental fact that, for the same value of λ_0 the effective dielectric constant is much greater in the case in which the substituent is charged than in the case in which the substituent contains a dipole.

II

The equations presented in Part I will now be applied to some actual molecules which approximate an ellipsoid of revolution. We have compared the first and second dissociation constants of three dicarboxylic acids, succinic, glutaric and suberic, and have compared the dissociation constants of chloracetic acid and of β -chlorpropionic acid with the dissociation constants of the corresponding unsubstituted acids. Chloracetic acid, intermediate in shape between a sphere and an ellipsoid, has been treated by both methods. In order to fix the boundaries of the molecules, we have again estimated the partial molar volume in aqueous solution from Traube's rule,⁴ and have made use of the following equation relating λ_0 , R , and the molecular volume, V , of an ellipsoid of revolution:

$$\lambda_0^3 - \lambda_0 = (6/\pi)(V/R^3). \quad (6)$$

This equation must be solved simultaneously with Eqs. (4) and (5) and with Fig. 1 to obtain the value of R in particular cases. We note that

$$\frac{D_E \text{ (charge)}}{(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}} = \frac{e^2}{2.303kT\Delta pK} \left(\frac{\pi}{6V} \right)^{\frac{1}{3}}$$

and

$$\frac{D_E \text{ (dipole)}}{(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}} = \frac{eM \cos \zeta}{2.303kT\Delta pK} \left(\frac{\pi}{6V} \right)^{\frac{1}{3}}.$$

We have prepared a table of D_E (charge)/ $(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}$ and D_E (dipole)/ $(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}$ for various values of λ_0 and can, then, estimate the value of λ_0 for any particular case by linear interpolation. From this value of λ_0 and Eq. (6), R is easily obtained. These values are presented in Table II. The values of R , computed for the acids selected,

⁴ Traube, Saml. chem. chem-tech., Vortr. 4, 255 (1899).

TABLE II.

λ_0	$D_E \text{ (CHARGE)}/(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}$	$D_E \text{ (DIPOLE)}/(\lambda_0^3 - \lambda_0)^{\frac{1}{3}}$
2.3	3.6	0.60
2.0	6.1	0.99
1.8	9.7	1.58
1.6	18.7	3.1
1.4	46.	9.2
1.3	77.	22.0
1.2	117.	74.
1.1	154.	239.
1.0	∞	∞

TABLE III. R in A.

ACID	ΔpK	MAXI-MUM	FREE ROTA-TION	THIS PAPER*	BJERRUM
Succinic acid	0.77	6.66	4.66	5.85	3.99
Glutaric acid	0.47	7.39	5.15	7.00	6.53
Suberic acid	0.28	11.46	6.38	9.30	10.9
Chloracetic acid	1.90	3.39	2.99	2.90	0.55
β -Chlorpropionic acid	0.85	4.61	3.69	4.20	1.06

* The values of R in this column are given to the nearest 0.05A. For the chloracids, ζ was computed as the angle between the carbon-chlorine bond and the line joining the midpoint of this bond with the point of location of the proton on the extension of the terminal carbon-carbon bond into the carboxyl group. The values of $\cos \zeta$ are 0.59 and 0.94 for chloracetic and β -chlorpropionic, respectively. The carbon-chlorine bond moment was taken as 1.56 Debye units.

with the aid of Table II, are presented in Table III.

Since the computed values of R in Table III refer to a single configuration of the molecule, they are not strictly suitable for comparison with the mean distances calculated on the basis of free or inhibited rotations. Here, as in the previous paper,² we have stated the maximum and the free rotation distances in order to exhibit a possible range of variation of the interprotonic distance. The values of ΔpK were taken from Landholt-Börnstein.⁵

It is at once seen that both the Bjerrum formula and the present treatment give reasonable values for the long aliphatic dibasic acids. The advantage of the present treatment over the simple Bjerrum approximation is most clearly exemplified in the cases of the chloro-acids.

The approximations and possible sources of error involved in this formulation have been discussed in the previous paper.² They include neglect of electrical saturation and electrostriction, the use of an internal molecular dielectric constant, the use of Traube's rule, and

⁵ Landholt-Börnstein, *Physikalische-Chemische Tabellen*, Erg. IIIc.

the difficulty in obtaining a structural value of R with which to compare our value, due to present ignorance concerning rotation in polyatomic molecules in aqueous solution. We are further limited by the fact that we have placed the charges or dipoles at the foci of the ellipsoid.

III

In the third part of this paper, we wish to derive the equations presented in Part I. Laplace's equation, in confocal elliptical coordinates for an axially symmetric potential ψ , is

$$(\lambda^2 - 1) \frac{\partial^2 \psi}{\partial \lambda^2} + 2\lambda \frac{\partial \psi}{\partial \lambda} + (1 - \mu^2) \frac{\partial^2 \psi}{\partial \mu^2} - 2\mu \frac{\partial \psi}{\partial \mu} = 0. \quad (7)$$

This equation must be satisfied both inside and outside the ellipsoid, λ_0 , forming the boundary between the molecule of dielectric constant D_i and the solvent of dielectric constant D . The potential ψ_i in the interior of the molecule, satisfying Eq. (7) may be written as follows

$$\psi_i = \frac{1}{D_i} \sum_{k=1}^v \frac{e_k}{|r - r_k|} + \sum_{n=0}^{\infty} B_n P_n(\mu) P_n(\lambda), \quad (8)$$

where the B_n are constants, ψ_i having no singularities except at the positions of the point charges $e_1 \cdots e_2$, characterizing the average charge distribution of the molecule. Since the potential must vanish at an infinite distance from the molecule, the solution, ψ_e , of Eq. (7) outside the boundary ellipsoid may be expressed in the form

$$\psi_e = \sum_{n=0}^{\infty} A_n P_n(\mu) Q_n(\lambda), \quad (9)$$

where the P_n and Q_n are the Legendre functions of the first and second kinds, respectively. The boundary conditions namely, continuity of the potential and of the normal component of the dielectric displacement everywhere on the boundary ellipsoid, λ_0 , require the following relations to be satisfied.

$$\begin{aligned} \psi_i(\lambda_0, \mu) &= \psi_e(\lambda_0, \mu) \\ -1 &\leq \mu \leq +1 \end{aligned} \quad (10)$$

$$D_i \left(\frac{\partial \psi_i}{\partial \lambda} \right)_{\lambda=\lambda_0} = D \left(\frac{\partial \psi_e}{\partial \lambda} \right)_{\lambda=\lambda_0}.$$

Before applying the boundary condition we introduce into Eq. (8) the Neumann expansion for each of the terms $1/|r - r_k|$

$$\begin{aligned} \sum_{k=1}^v \frac{e_k}{|r - r_k|} &= \frac{2}{R} \sum_{n=0}^{\infty} (2n+1) \beta_n P_n(\mu) Q_n(\lambda) \\ \beta_n &= \sum_{k=1}^v e_k P_n(\mu_k) \end{aligned} \quad (11)$$

valid when each charge e_k is situated at a point μ_k on the ellipse, $\lambda=1$, which is the line joining the foci. R is the distance between the foci. Substitution of (8) and (9) into Eq. (10) and use of the property of orthogonality of the $P_n(\mu)$ in the interval, $-1 \leq \mu \leq +1$, yields the following set of linear equations for the determination of the A_n and B_n

$$\begin{aligned} (2/R)(2n+1)(\beta_n/D_i)Q_n(\lambda_0) \\ + B_n P_n(\lambda_0) &= A_n Q_n(\lambda_0) \\ D_i B_n P_n'(\lambda_0) \\ + (2/R)(2n+1)\beta_n Q_n'(\lambda_0) &= D A_n Q_n'(\lambda_0). \end{aligned} \quad (12)$$

Solution gives the following expression for the B_n

$$\begin{aligned} B_n &= \frac{2(2n+1)\beta_n}{R} \left(\frac{1}{D} - \frac{1}{D_i} \right) \\ &\times \frac{Q_n(\lambda_0)Q_n'(\lambda_0)}{P_n(\lambda_0)Q_n'(\lambda_0) - (D_i/D)P_n'(\lambda_0)Q_n(\lambda_0)}, \end{aligned} \quad (13)$$

where $P_n'(\lambda_0)$ and $Q_n'(\lambda_0)$ are the first derivatives of the Legendre functions. The derivatives may be eliminated with the aid of the recursion formula,

$$\begin{aligned} (\lambda^2 - 1)P_n'(\lambda) &= n[\lambda P_n(\lambda) - P_{n-1}(\lambda)] \\ B_n &= \frac{2(2n+1)\beta_n}{R} \left(\frac{1}{D} - \frac{1}{D_i} \right) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} \\ &\times \left[1 + \left(\frac{D_i}{D} \right) \frac{\lambda_0 - P_{n-1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n-1}(\lambda_0)/Q_n(\lambda_0)} \right]^{-1}. \end{aligned} \quad (14)$$

The electrostatic work of charging the molecule is obtained by substitution of Eqs. (8) and (14) into the general formula

$$W = \frac{1}{2} \sum_{k=1}^v e_k \psi_i(1, \mu_k), \quad (15)$$

all charges being located on the line $\lambda=1$. We are interested in calculating ΔW for a set of molecules HA_1 , HA_2 , A_1^- and A_2^- .

$$\Delta W = W(HA_1) + W(A_2^-) - W(HA_2) - W(A_1^-). \quad (16)$$

Use of Eqs. (8), (14) and (15) under the assumption that all species have the same size and shape yields

$$\begin{aligned} \Delta W = & \frac{e}{D_i} \sum_{k=1}^s \frac{e_k}{r_k} \\ & + \frac{1}{R} \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} (2n+1) \alpha_n \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} \\ & \times \left[1 + \left(\frac{D_i}{D} \right) \frac{\lambda_0 - P_{n-1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n-1}(\lambda_0)/Q_n(\lambda_0)} \right]^{-1} \end{aligned} \quad (17)$$

$$\alpha_n = 2e \sum_{k=1}^s e_k P_n(\mu_k),$$

where the sums extend over the set of charges $e_1 \cdots e_s$ which the acid HA_2 contains in excess of those of HA_1 and r_k is the distance of charge e_k in HA_2 from the proton, e , located at the focus $(1, 1)$ of the ellipsoid. In the symmetrical dibasic

acid, the set of charges $e_1 \cdots e_s$ consists of a single proton, e , located at the other focus, $(1, -1)$ and Eq. (17) becomes, since $P_n(-1) = (-1)^n$,

$$\begin{aligned} \Delta W = & \frac{e^2}{R} \left\{ \frac{1}{D_i} + \left(\frac{1}{D} - \frac{1}{D_i} \right) \sum_{n=0}^{\infty} 2(2n+1)(-1)^n \right. \\ & \times \left. \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} \left[1 + \left(\frac{D_i}{D} \right) \frac{\lambda_0 - P_{n-1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n-1}(\lambda_0)/Q_n(\lambda_0)} \right]^{-1} \right\}. \end{aligned} \quad (18)$$

Eqs. (1) and (18) lead to Eq. (2). When HA_2 contains a dipole moment located at the focus $(1, -1)$, in addition to the charges constituting HA_1 , we find

$$\alpha_n = 2eM \cos \zeta$$

$$\lim_{x \rightarrow 0} \left\{ \frac{1}{x!} \left[P_n \left(\frac{2x}{R} - 1 \right) - P_n(-1) \right] \right\} \quad (19)$$

$$= -2(-1)_n n(n+1) \frac{eM \cos \zeta}{R},$$

where $M \cos \zeta$ is the component of the dipole moment along the axis of the ellipsoid. By symmetry it is readily seen that its component perpendicular to the axis contributes nothing. Eqs. (1), (17) and (19) lead to Eq. (3).