## The Molecular Association of Some Carboxylic Acids in Aqueous Solutions from Conductivity Data.

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From conductivity measurements with hydrochloric acid in aqueous dioxan and aqueous acetone, the product $\Lambda\eta/\eta_0$ (where $\eta$ and $\eta_0$ are the viscosities of solvent and water) is found to be almost constant up to $\eta/\eta_0 = 1\cdot1$. The measured conductivities of formic, acetic, propionic, and $n$-butyric acid solutions, which are assumed to be similarly influenced by the solvent viscosities, after correction, have been used to obtain the dimerisation constants of these acids in aqueous solution at 25°.

THE thermodynamic dissociation constants $(K_a)$ of many carboxylic acids in aqueous solution have been obtained by conductivity measurements. Where a considerable concentration range has been covered, $K_a$ decreases with the concentration, and Katchalsky, Eisenberg, and Lifson (*J. Amer. Chem. Soc.*, 1951, **73**, 5889) considered that this can be attributed to dimerisation. Their value for the dimer dissociation constant $K_d$, where $K_d = [\mathrm{HA}]^2/[\mathrm{H_2A_2}]$, is 6·2 for acetic acid, which is in good agreement with 5·4 derived by MacDougall and Blumer (*ibid.*, 1933, **55**, 2236) from vapour pressures. However, as Davies

and Griffiths (*Z. physikal. Chem.*, Neue Folge, 1954, **2**, 353) have pointed out, MacDougall and Blumer's figure is based upon erroneous data, and a more reasonable estimate gives $K_d = 20 \pm 3$ by this method. Davies and Griffiths themselves (*loc. cit.*), from careful analyses of freezing-point and distribution measurements, obtained $K_d \sim 30$. These last two values therefore suggest that the figure of 6·2 from conductivities is too small, and a reason for this may be the neglect of the viscosities of acetic acid solutions, which increase with the acid concentration.

This point has been considered by Davies (*J. Amer. Chem. Soc.*, 1932, **54**, 3776) with reference to the evaluation of the dissociation constant $K_a$. MacInnes and Shedlovsky's conductivity measurements (*ibid.*, p. 1429) lead to concentration dissociation constants, and when the log values of these are plotted against $c_i$ (where $c_i$ is the ionic concentration), the plot should be linear with a slope value of $2 \times 0\cdot509$, according to Debye and Hückel's theory. Above an acid concentration of 0·01N, however, the plot curves sharply. Davies showed (*loc. cit.*) that if $\Lambda\eta/\eta_0$ is used instead of $\Lambda$, where $\eta$ is the viscosity of the solution and $\eta_0$ is that of water, the plot is linear to much higher concentrations.

It is well known that correction of conductivities by the factor $\eta/\eta_0$ is not exactly substantiated by experiment, and to obtain some information on the error which can result in the present circumstances, the conductivity of hydrochloric acid in dioxan–water and acetone–water has been examined. Although Owen and Waters (*ibid.*, 1938, **60**, 2371) have reported measurements with the first of these solvents, they did not cover the region between water and 20% dioxan. In Table 1 we report measurements in 5% and 10%

TABLE 1. *Conductivity of hydrochloric acid in 5% and 10% dioxan at 25°.*

5% Dioxan, $B = 160\cdot8$, $\Lambda° = 393\cdot7$.

| $10^4c$ | 2·4748 | 3·3398 | 3·5131 | 4·2221 | 4·9860 | 6·0860 |
|---|---|---|---|---|---|---|
| $\Lambda$ | 391·04 | 390·78 | 390·62 | 390·42 | 389·99 | 389·89 |

10% Dioxan, $B = 154\cdot9$, $\Lambda° = 366\cdot3$.

| $10^4c$ | 2·6665 | 3·2453 | 3·3436 | 4·2339 | 4·9112 | 5·0610 | 5·7660 |
|---|---|---|---|---|---|---|---|
| $\Lambda$ | 363·65 | 362·90 | 362·72 | 362·32 | 361·79 | 361·71 | 361·47 |

mixtures. The values of $\Lambda°$ were obtained by plotting $\Lambda + Bc^{\frac{1}{2}}$ against $c$, and extrapolating to $c = 0$; $B$ is the theoretical Onsager slope and $c$ is the concentration in equivs. per l.

Brownson and Cray (*J.*, 1925, **127**, 2923) have measured the conductivity of this acid in aqueous acetone. An obsolete method of deriving the cell constant was used, and a correction has been made by comparing their figures in water with those of Shedlovsky (*J. Amer. Chem. Soc.*, 1932, **54**, 1411) and multiplying the figures in aqueous acetone by the factors derived from the water figures (see Table 2).

TABLE 2. *Conductivity of hydrochloric acid in aqueous acetone at 20°.*

| $10^4c$ | 4·00 | 10·0 | 20·0 | 40·0 | 100·0 | 200·0 | $\Lambda°$ | $B$ |
|---|---|---|---|---|---|---|---|---|
| 8% Acetone | 350·8 | 349·3 | 347·7 | 345·4 | 341·9 | 336·9 | 353·5 | 140 |
| 16·4% Acetone | 298·9 | 297·5 | 295·9 | 294·3 | 291·0 | 287·6 | 301·5 | 132 |

The products $\Lambda°\eta/\eta_0$ given by the above data are shown in Table 3. They increase by about 4% for a 25% increase in viscosity with dioxan–water and decrease by the same amount for a similar increase in the viscosity of the acetone–water solvent. The nature of the organic constituent evidently has some influence.

TABLE 3. *Limiting conductivities, viscosities, and $\Lambda°\eta/\eta_0$ values.*

| Solvent | $\Lambda°$ | $10^2\eta$ | $\Lambda°\eta/\eta_0$ | Solvent | $\Lambda°$ | $10^2\eta$ | $\Lambda°\eta/\eta_0$ |
|---|---|---|---|---|---|---|---|
| Water | 426·2 | 8·949 | 426·2 | 8% Acetone | 353·5 | 10·6 | 418·7 |
| 5% Dioxan | 393·7 | 9·76 | 429·4 | 16·4% Acetone | 301·5 | 12·15 | 409·3 |
| 10% ,, | 366·3 | 10·52 | 430·6 | | | | |

The viscosities of dioxan–water were interpolated from Geddes's data (*ibid.*, 1933, **55**, 4832) and those of acetone–water from the International Critical Tables, **5**, 22, and from Olson and Konecny (*J. Amer. Chem. Soc.*, 1953, **75**, 5801).

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In general, the figures given in Table 3 reasonably justify correcting the conductivities of carboxylic acids for the viscosities of the solutions. Following the procedure of MacInnes and Shedlovsky (*ibid.*, 1932, **54**, 1429) we can write

$$\Lambda_{\epsilon} = \Lambda_{(HCl)} - \Lambda_{(NaCl)} + \Lambda_{(NaA)}$$

where $\Lambda_{\epsilon}$ is the conductivity at an ionic concentration $c_i$ and A is the carboxylate anion. Allowing for the viscosity factor, we then have

$$\Lambda^* = \Lambda\eta/\eta_0, \quad \Lambda^*c/\Lambda_{\epsilon} = \alpha$$

Taking $K'_a$ as the thermodynamic dissociation constant where dimerisation is not considered, and $\alpha$ as the degree of dissociation, we have

$$K'_a = \alpha^2 c f_H f_A/(1 - \alpha)$$

The activity coefficients can be calculated from the limiting form of the Debye–Hückel expression, $-\log f_i = 0.509(\alpha c)^{\frac{1}{2}}$. Extrapolation of $K'_a$ against $c$ gives $K_a$, the true thermodynamic dissociation constant. At any concentration $c$, if $x$ is the true concentration of HA, then

$$x = (\alpha c)^2 f_H f_A/K_a$$

and since $[H_2A_2] = (c - \alpha c - x)/2$, the dimerisation constant $K_d$ is given by

$$K_d = 2x^2/(c - \alpha c - x)$$

The resulting calculations are given in Table 4, the conductivity data of Saxton and Darken (*ibid.*, 1940, **62**, 846) being used for formic and *n*-butyric acids, of MacInnes and Shedlovsky for acetic acid (*loc. cit.*), and of Belcher (*ibid.*, 1938, **60**, 2744) for propionic acid. The viscosities of formic and acetic acid solutions were interpolated from data in the International Critical Tables (Vol. 5), those of propionic acid were derived from Landolt–Börnstein's " Tabellen " (Hauptband, p. 157), and those of *n*-butyric acid from the figures of Bury and Grindley (*J.*, 1936, 1003).

TABLE 4. *Dimerisation constants at 25°.*

| $10^3c$ | $\Lambda_{\epsilon}$ | $\Lambda^*$ | $10^5K'_a$ | $K_d$ | $10^3c$ | $\Lambda_{\epsilon}$ | $\Lambda^*$ | $10^5K'_a$ | $K_d$ |
|---|---|---|---|---|---|---|---|---|---|
| Formic acid, $10^5K_a = 18.24$. | | | | | Acetic acid, $10^5K_a = 1.751$. | | | | |
| 98.86 | 395.04 | 17.917 | 18.21 | 110 | 50.00 | 386.15 | 7.397 | 1.740 | 15.0 |
| 185.30 | 393.47 | 13.298 | 18.20 | 152 | 52.30 | 386.10 | 7.242 | 1.743 | 21.1 |
| 200.14 | 393.24 | 12.817 | 18.19 | 129 | 100.00 | 385.32 | 5.257 | 1.731 | 16.5 |
| 207.15 | 393.17 | 12.608 | 18.18 | 121 | 119.45 | 385.09 | 4.822 | 1.732 | 21.7 |
| 361.80 | 391.55 | 9.6740 | 18.14 | 133 | 200.00 | 384.37 | 3.731 | 1.716 | 19.2 |
| 396.76 | 391.26 | 9.2611 | 18.10 | 97 | 230.79 | 384.14 | 3.478 | 1.715 | 21.5 |
| 463.43 | 390.76 | 8.5968 | 18.10 | 117 | | | | | |
| 546.81 | 390.22 | 7.9491 | 18.09 | 127 | *n*-Butyric acid, $10^5K_a = 1.5195$ | | | | |
| 655.63 | 389.60 | 7.2882 | 18.04 | 113 | 14.412 | 378.59 | 12.385 | 1.5154 | 10.5 |
| 734.04 | 389.20 | 6.9082 | 18.02 | 116 | 20.740 | 378.30 | 10.365 | 1.5138 | 10.6 |
| 975.35 | 388.18 | 6.0295 | 17.91 | 103 | 30.612 | 377.95 | 8.5641 | 1.5120 | 11.9 |
| | | | | | 60.446 | 377.27 | 6.1242 | 1.5045 | 11.8 |
| Propionic acid, $10^5K_a = 1.347$. | | | | | 78.623 | 376.98 | 5.3762 | 1.4998 | 11.6 |
| 75.352 | 381.06 | 5.2369 | 1.338 | 22 | 93.044 | 376.79 | 4.9427 | 1.4935 | 10.4 |
| 101.64 | 380.70 | 4.5175 | 1.335 | 22.5 | 123.53 | 376.44 | 4.2926 | 1.4880 | 11.3 |
| 192.95 | 379.70 | 3.2783 | 1.317 | 15 | 160.79 | 376.10 | 3.7588 | 1.4768 | 10.7 |
| | | | | | 200.32 | 375.81 | 3.3622 | 1.4650 | 10.4 |
| | | | | | 253.84 | 375.47 | 2.9805 | 1.4514 | 10.3 |

*Discussion.*—The average dimerisation constants, together with those obtained by other methods, are :

| | Formic | Acetic | Propionic | *n*-Butyric |
|---|---|---|---|---|
| Conductivity (25°) | $120 \pm 12$ | $19 \pm 2$ | $20 \pm 3$ | $11 \pm 0.6$ |
| Distribution (25°) | — | 28 [a] | — | 10 [b] |
| F. p. (0°) | — | 28 [a] | — | 11 [b] |
| V. p. (25°) | — | $20 \pm 3$ [a] | — | — |

[a] Davies and Griffiths, *loc. cit.*    [b] Griffiths, Thesis, University of Wales, 1952.

Considering their magnitude, the agreement by different methods is reasonable. Certainly, the present value for acetic acid is in better accord with the independent values than is that of Katchalsky *et al.* (*loc. cit.*).

It cannot be claimed that the viscosity corrections are exact, and a 5% error in these means an error of 15% in $K_d$. Furthermore, with formic and *n*-butyric acids, where the measurements extend to 3N and 1·2N, respectively, the higher concentrations give $K_d$ values which decrease steadily from those given in Table 4. This may be because errors in the viscosity factor become more important in these regions, or it may be that $K_a$, the thermodynamic dissociation constant, is different from what it is in dilute solutions. Since the dielectric constants of these solutions have not yet been measured, an estimate of possible changes in $K_a$ cannot be made.

Apart from propionic acid, our $K_a$ values are slightly different from those given by the original authors. The reason for this is that their method was to plot the logarithm of the concentration dissociation constants against $\sqrt{c_i}$ and extrapolate. In the present analysis, $K_a'$ is practically constant in very dilute solutions and a more exact extrapolation is possible. A final adjustment was made by trying slight variation in the extrapolated value of $K_a$ until $K_d$ showed no sudden trends with the acid concentration.

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