

111. *The Strengths of Six Monocarboxylic Acids in 25% Aqueous Acetone and 20% Aqueous Sucrose.*

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The dissociation constants of propionic, benzoic, phenylacetic, diphenylacetic, β -phenylpropionic, and cinnamic acids in 25% aqueous acetone and 20% aqueous sucrose at 25° have been measured by the conductivity method, and in both mixed solvents preserve the sequence observed in water (except K for diphenylacetic acid in aqueous acetone). It is significant, however, that the strengths in aqueous sucrose are consistently higher than those exhibited in water (diphenylacetic acid again excluded), despite the fact that the latter solvent has the greater dielectric constant. The behaviour of diphenylacetic acid in both solvents is distinctly anomalous.

THE vast majority of dissociation constants of organic acids on record refer to aqueous solutions, and complete agreement has not been reached as to whether they will remain substantially in the same order if the solvent is changed. In a previous communication (Dippy, J., 1941, 550) the conclusion was reached, however, that the general sequence is interrupted in another solvent only by the incursion of special factors, and reference was made to the recent measurements of Elliott and Kilpatrick (*J. Physical Chem.*, 1941, **45**, 454, 466, 472) which showed that among several series of monosubstituted benzoic acids, examined in four different solvents, the truly anomalous members were salicylic, *o*-toluic, and *m*-hydroxybenzoic acids. In the first two of these

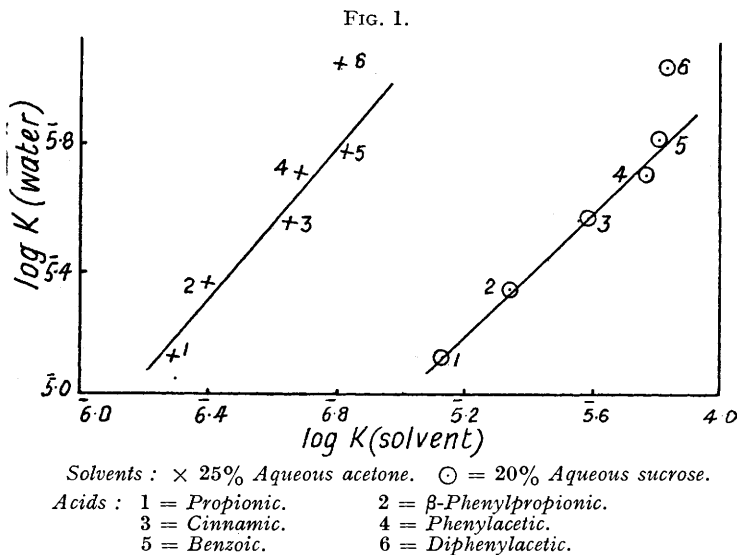
there is undoubtedly a "special factor" which is likely to be influenced by change of solvent (cf. Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., 1940, p. 207). The sequence of strengths obtained in our measurements upon six monocarboxylic acids in 25% aqueous acetone and 20% aqueous sucrose have already been mentioned (Dippy, *loc. cit.*); it was our intention to extend the investigation, but as this is unavoidably postponed, we record the data thus far obtained. The actual values of 10^5K are included in Table I, together with the dissociation constants in water at the same temperature (*Chem. Reviews*, 1939, 25, 151) for comparison.

The values of dielectric constant (D) are due to Akerlöf (*J. Amer. Chem. Soc.*, 1932, 54, 4125), and these are comparable with the figures quoted in International Critical Tables.

TABLE I.

Acid.	Dissociation constants (10^5K) at 25°.		
	25% Aqueous acetone ($D = 64.0$).	20% Aqueous sucrose ($D = 73.6$).	Water ($D = 78.5$).
Diphenylacetic	0.653	7.43	11.5
Benzoic	0.681	6.55	6.27
Phenylacetic	0.499	5.53	4.88
Cinnamic (<i>trans</i>)	0.461	3.74	3.65
β -Phenylpropionic	0.240	2.23	2.19
Propionic	0.183	1.40	1.34

It will be seen that, if the result for diphenylacetic acid in aqueous acetone is omitted, the sequence of strengths of these acids in the two partly aqueous solutions is the same as for solutions in water. The most



striking feature, however, is the fact that (diphenylacetic acid excluded) the strengths of the acids in 20% aqueous sucrose are distinctly *greater* than those for aqueous solution, despite the fact that the dielectric constant of the former is appreciably smaller than that of the latter solvent. This enhancement of strength recalls that observed by Bartlett and Dauber (*J. Amer. Chem. Soc.*, 1940, 62, 1339) on addition of alcohols to a solution of hydrochloric acid in dioxan. A change of solvent means a change, not only in dielectric constant of the medium but also in chemical environment for the solute, and this alteration might make a marked contribution to the displacement of acid strengths; compared with acetone the molecule of sucrose must clearly exert a more influential chemical rôle. It is also noteworthy that Elliott and Kilpatrick (*loc. cit.*) have shown that certain organic acids exhibit different strengths in solvents of the same dielectric constant, and that Moore and Johns (*J. Amer. Chem. Soc.*, 1941, 63, 3336) find that the K 's of picric acid in certain ketones and nitriles are governed not so much by the dielectric constant of the medium as by the electron-sharing capacity of the radicals constituting it.

The strength of diphenylacetic acid is not so strikingly anomalous in aqueous acetone, but this is discerned by plotting $\log K_{\text{water}}$ against $\log K$ for the partly aqueous solvents in turn (a method of comparison used by La Mer, Kilpatrick, and others). Fig. 1 shows that, whereas a straight line connects the points representing five of the acids, that for diphenylacetic acid lies apart. If some spatial interaction of groups in the phenylacetic system has an effect upon acid strength, it can be expected (cf. Hammett, *op. cit.*) that the displacement of K with change of solvent will not follow the same trend as in acids in which the normal, recognised polar influences alone operate. This has been well illustrated by the data for the anomalous salicylic and *o*-toluic acids, and in view

of the similarity between *o*-toluic and phenylacetic acids, on spatial grounds, it seems reasonable to connect the abnormalities noted in both acids. The tendency in the phenylacetic system is favoured by the progressive substitution of phenyl groups, and does not become appreciable until diphenylacetic acid is reached. There is some evidence of slight abnormality in phenylacetic acid, however, if the data are examined along the lines employed by Wooten and Hammett (*J. Amer. Chem. Soc.*, 1935, 57, 2289); both phenyl- and diphenyl-acetic acids show a diminution in relative strength when the acid is transferred from water to either partly aqueous solvent, and this is similar to the effect of transferring *o*-toluic acid, for example, from water to *n*-butyl alcohol as noted by these investigators. Although some form of spatial interaction has been implied as the cause of the anomalous behaviour of the phenylacetic acids, the present discussion is not concerned with the nature of the special effect operating; it needs only to be an effect which is modified differently by different solvents.

EXPERIMENTAL.

The conductivity measurements were made by means of the equipment and procedure described by Dippy and Williams (J., 1934, 161), but included in the bridge circuit was a variable condenser (max. capacity 0.002 μ F.). The cells were of bottle type with blacked electrodes; two cells were used on each run. The "AnalaR" acetone was purified by the method of Dippy, Jenkins and Page (J., 1939, 1386). The aqueous acetone, containing 25% of acetone (w/v at 25°), was made from freshly distilled components for each individual run ($\kappa = 0.65$ —1.2 gemmho). The 20% aqueous sucrose (w/v at 25°) was made from dried "AnalaR" sucrose ($\kappa = 5.6$ —6.4 gemmho—this is a large increase upon the conductivity water, $\kappa = ca.$ 1 gemmho).

The organic acids were specimens prepared for earlier investigations, and the sodium salts were made as required (see Dippy and Williams, *loc. cit.*). The sodium chloride, of "AnalaR" quality, was recrystallised; the hydrochloric acid was also pure and redistilled (constant-boiling fraction).

Values of Λ_0 (acid) were obtained from series of measurements on solutions of the sodium salts, and the results were interpreted graphically with the use of the Debye Hückel-Onsager equation as described in our earlier papers. To convert Λ_0 (salt) into Λ_0 (acid) the difference Λ_0 (HCl) - Λ_0 (NaCl) ("normal" solvent corrected) had to be evaluated; for aqueous acetone this was 284.7 - 83.7 = 201.0. Whereas in the plot of $\Lambda - \sqrt{C}$ for hydrochloric acid all the points could be extrapolated, yet the solvent-corrected curve for sodium chloride was sensibly linear only between concentrations of 0.014 and 0.004 g.-mol./l. Both straight lines were inclined at approximately the angles of the theoretical Onsager slopes, *i.e.*, 53° and 35°, respectively (see Fig. 2). Unsatisfactory results were obtained with aqueous sucrose solutions of hydrogen chloride and sodium chloride. Hence, Λ_0 (HCl) - Λ_0 (NaCl) for this medium was derived by application of Walden's rule. When the rule is applied to sodium chloride in water and in 25% aqueous acetone the following agreement is noted:

	Λ_0 .	η .	Product.
Water	126	0.008937	1.127
25% Aqueous acetone	84	0.01327	1.115

The value of 1.115 being used for the constant and that of 0.0171 for the viscosity of 20% aqueous sucrose, a figure of 156.3 is derived for Λ_0 (HCl) - Λ_0 (NaCl); the values of Λ_0 (acid) obtained by means of this are included in Tables IV and V. A regular fall in mobility occurs as the size of the anion increases, the sequence in both solvents being the same.

In calculating the dissociation constants of the acids, the normal solvent correction was applied to the measured conductivities; this is an arbitrary procedure. In simple aqueous solutions no solvent correction is applied in the case of weak acids, but with partly aqueous solutions the circumstances are quite different. In 25% aqueous acetone the acid possesses a strength one-tenth of that exhibited by it in water, and so Λ_0 is relatively small, yet the conductivity of the solvent has changed very slightly. Again, in the case of 20% aqueous sucrose the acid strengths compare with those in water but the conductivity of the solvent is considerably greater. Examination of the computations of K for a selected acid in each partially aqueous solvent (Table II) gives reasonable justification for the use of the "normal" solvent correction. Actually, it seems likely from our calculations that if the "true" solvent correction were known it would be rather less than the "normal" correction, and so in the case of aqueous sucrose solutions the enhancement of strength (compared with data for water) would be still further accentuated.

FIG. 2.

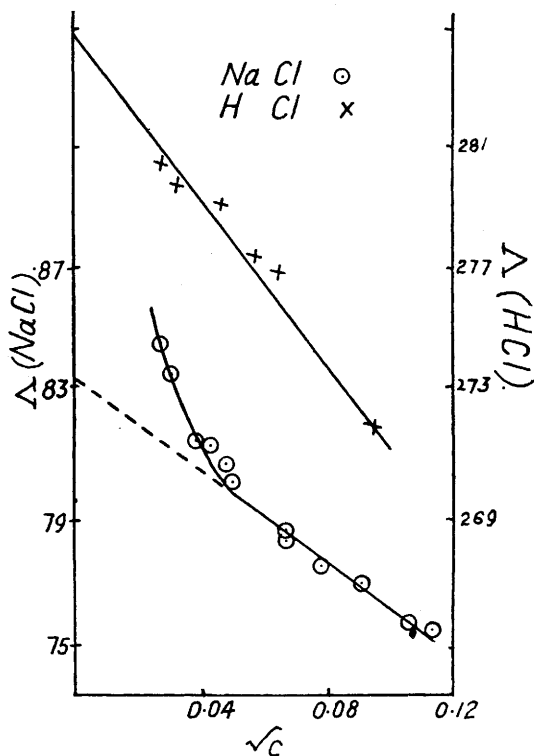


TABLE II.

25% Aqueous acetone.				20% Aqueous sucrose.			
β -Phenylpropionic acid.				Benzoic acid.			
10 ³ C.	10 ⁸ K _{class.} (uncorr.).	10 ⁸ K _{class.} (corr.).	10 ⁸ K _{therm.} (corr.).	10 ³ C.	10 ⁸ K _{class.} (uncorr.).	10 ⁸ K _{class.} (corr.).	10 ⁸ K _{therm.} (corr.).
9.786	2.62	2.48	2.41	5.023	7.71	6.93	6.61
4.466	2.67	2.47	2.41	2.051	7.93	6.63	6.39
2.587	2.64	(2.40)	(2.35)	1.811	8.35	6.91	6.67
1.518	2.75	2.45	2.41	1.163	8.76	6.84	6.63
1.225	2.76	2.42	2.38	0.674	9.14	6.41	6.25

The uncorrected classical dissociation constants rise steadily with increasing dilution and this trend is overcome by making the full solvent correction. Actually, the slight opposite trend noticeable in the corrected classical constants is to be anticipated, and this is more or less rectified when the thermodynamic constants are derived. The latter data were calculated along the orthodox lines (see Dippy and Williams, *loc. cit.*). The constants of the Onsager equation had to be deduced for these two media, as well as the values of A in the Debye-Hückel equation. $-\log f = A\sqrt{c}$. The following figures (based on bulk properties) were derived :

	a.	b.	A.
25% Aqueous acetone	0.3103	44.64	0.63
20% Aqueous sucrose	0.2516	32.58	0.54

TABLE III.

Cell constants : $a = 0.1380$; $b = 0.0734$.

25% Aqueous acetone solution.				25% Aqueous acetone solution.			
10°C (equiv./l.).	Λ .	$10^6 K_{\text{class.}}$	$10^6 K_{\text{therm.}}$	10°C (equiv./l.).	Λ .	$10^6 K_{\text{class.}}$	$10^6 K_{\text{therm.}}$
Propionic acid.				Benzoic acid.			
<i>a</i> 13.54	3.10	1.93	1.87	<i>a</i> 14.09	5.73	7.01	6.71
<i>a</i> 7.586	4.09	1.90	1.85	<i>a</i> 6.877	8.30	7.28	7.02
<i>a</i> 5.014	5.00	1.87	1.83	<i>a</i> 4.819	10.0	(7.38)	(7.15)
<i>b</i> 4.087	5.54	1.88	1.84	<i>b</i> 3.662	11.2	7.08	6.87
<i>b</i> 2.471	7.09	1.88	1.84	<i>b</i> 2.355	13.8	7.06	6.87
<i>b</i> 1.746	8.85	1.84	1.81	<i>b</i> 1.496	17.4	7.17	7.01
$\kappa = 0.80$ gemmho.	12 Determinations : Λ_0 (acid) = 261.0.			$\kappa = 0.63$ gemmho.	11 Determinations : Λ_0 (acid) = 259.5.		
Phenylacetic acid.				Diphenylacetic acid.			
<i>a</i> 10.75	5.62	5.18	4.99	<i>a</i> 2.476	13.0	6.83	6.67
<i>a</i> 6.017	7.52	5.23	5.07	<i>a</i> 1.369	17.1	6.61	6.48
<i>a</i> 4.056	9.14	5.24	5.10	<i>a</i> 1.181	18.2	6.52	6.40
<i>b</i> 3.445	9.86	5.20	5.06	<i>b</i> 1.000	19.8	6.57	6.46
<i>b</i> 2.345	11.8	5.11	4.98	<i>b</i> 0.838	21.8	6.73	6.62
<i>b</i> 1.580	14.2	5.06	4.95	<i>b</i> 0.616	24.9	6.56	6.47
$\kappa = 0.82$ gemmho.	16 Determinations : Λ_0 (acid) = 258.7.			$\kappa = 0.80$ gemmho.	15 Determinations : Λ_0 (acid) = 254.5.		
β -Phenylpropionic acid.				Cinnamic acid.			
<i>a</i> 9.786	4.02	2.48	2.41	<i>a</i> 12.60	5.00	4.89	4.74
<i>a</i> 4.466	5.92	2.47	2.41	<i>a</i> 6.448	6.90	4.80	4.67
<i>b</i> 2.587	7.65	(2.40)	(2.35)	<i>a</i> 4.229	8.25	4.53	4.45
<i>b</i> 1.518	10.0	2.45	2.41	<i>b</i> 3.097	10.1	4.94	(4.85)
<i>b</i> 1.225	11.1	2.42	2.38	<i>b</i> 1.926	12.5	4.85	4.77
$\kappa = 0.75$ gemmho.	10 Determinations : Λ_0 (acid) = 255.0.			$\kappa = 0.91$ gemmho.	13 Determinations : Λ_0 (acid) = 255.6.		

TABLE IV.

Cell constants : $c = 0.1411$; $d = 0.0743$.

20% Aqueous sucrose solution.				20% Aqueous sucrose solution.			
10°C (equiv./l.).	Λ .	$10^5 K_{\text{class.}}$	$10^5 K_{\text{therm.}}$	10°C (equiv./l.).	Λ .	$10^5 K_{\text{class.}}$	$10^5 K_{\text{therm.}}$
Propionic acid.				Benzoic acid.			
<i>c</i> 21.68	5.41	1.47	1.40	<i>c</i> 5.023	23.0	6.93	6.61
<i>c</i> 10.30	7.63	1.41	1.36	<i>c</i> 2.051	34.1	6.63	5.39
<i>c</i> 9.128	8.23	1.46	1.40	<i>d</i> 1.181	36.7	6.91	6.67
<i>d</i> 7.508	8.86	1.40	1.35	<i>d</i> 1.163	44.5	6.84	6.63
<i>d</i> 6.267	9.64	1.38	1.34	<i>d</i> 0.6740	54.8	6.41	6.25
$\kappa = 6.54$ gemmho.	21 Determinations : Λ_0 (acid) = 210.0.			$\kappa = 5.89$ gemmho.	21 Determinations : Λ_0 (acid) = 207.2.		
Phenylacetic acid.				Diphenylacetic acid.*			
<i>c</i> 7.968	17.0	5.99	5.68	<i>c</i> 0.151	106.3	(8.92)	(8.74)
<i>c</i> 3.827	23.8	5.83	5.58	<i>c</i> 0.127	107.7	7.85	7.76
<i>c</i> 3.181	25.9	5.82	5.59	<i>d</i> 0.118	106.3	8.96	6.86
<i>d</i> 2.484	28.8	5.71	5.50	<i>d</i> 0.0947	115.5	7.33	7.24
<i>d</i> 1.097	42.4	5.91	5.73	<i>d</i> 0.0831	117.7	6.33	6.26
$\kappa = 6.39$ gemmho.	15 Determinations : Λ_0 (acid) = 205.0.			$\kappa = 6.29$ gemmho.	12 Determinations : Λ_0 (acid) = 201.2.		
β -Phenylpropionic acid.				Cinnamic acid.			
<i>c</i> 4.437	14.8	2.52	(2.43)	<i>c</i> 2.681	23.5	4.02	3.88
<i>c</i> 2.243	20.0	2.41	2.34	<i>c</i> 1.608	30.0	4.06	3.93
<i>c</i> 1.745	22.6	2.42	2.36	<i>c</i> 1.399	31.7	4.00	3.88
<i>d</i> 1.570	22.7	2.20	2.15	<i>d</i> 0.9980	35.8	3.71	3.61
<i>d</i> 1.246	25.5	2.24	2.18	<i>d</i> 0.8061	39.9	3.81	3.72
<i>d</i> 0.8140	31.4	2.29	2.23	<i>d</i> 0.6730	44.1	3.99	3.90
$\kappa = 5.93$ gemmho.	16 Determinations : Λ_0 (acid) = 203.5.			$\kappa = 6.10$ gemmho.	16 Determinations : Λ_0 (acid) = 204.3.		

* The small solubility of this acid in aqueous sucrose and the high conductivity of the solvent account for the less regular constants.

The results obtained with the six organic acids are contained in Tables III and IV (in each case the total number of determinations is indicated and one "run" is given in detail). The data for sodium chloride and hydrochloric acid in aqueous acetone are listed in Table V.

TABLE V.

Cell constants: $e = 0.1380$; $f = 0.0734$.

25% Aqueous acetone.

Hydrochloric acid.			Sodium chloride.					
10^3C (equiv./l.).	\sqrt{C} .	$\Lambda_{\text{corr.}}$.	10^3C (equiv./l.).	\sqrt{C} .	$\Lambda_{\text{corr.}}$.	10^3C (equiv./l.).	\sqrt{C} .	$\Lambda_{\text{corr.}}$.
<i>e</i> 9.486	0.097	271.6	<i>e</i> 11.36	0.107	75.77	<i>e</i> 13.36	0.116	75.36
<i>e</i> 4.055	0.064	276.9	<i>e</i> 6.395	0.080	77.50	<i>e</i> 8.519	0.092	76.91
<i>f</i> 3.022	0.055	277.2	<i>e</i> 4.541	0.068	78.56	<i>e</i> 4.471	0.067	78.48
<i>f</i> 1.995	0.045	278.8	<i>f</i> 2.531	0.050	80.61	<i>f</i> 2.738	0.052	79.86
<i>f</i> 1.112	0.033	279.5	<i>f</i> 1.585	0.040	81.35	<i>f</i> 1.873	0.043	81.10
<i>f</i> 0.7351	0.027	280.2	<i>f</i> 0.726	0.027	84.63	<i>f</i> 0.925	0.030	83.49
$\kappa = 1.0$ gemmho.	Λ_0 (acid) = 284.7		$\kappa = 0.70$ gemmho.	Λ_0 (acid) = 83.7		$\kappa = 0.70$ gemmho.	Λ_0 (acid) = 83.7	

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