

**250. Chemical Constitution and the Dissociation Constants of Mono-carboxylic Acids. Part XIX.\* Some Substituted Benzoic and Phenylacetic Acids in 10 and 25% (w/w) Acetone–Water Solutions.**

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The dissociation constants of thirty-one aromatic monocarboxylic acids in 10% and 25% (w/w) acetone–water mixtures have been determined at 25° by a conductimetric method. The acids are composed mainly of mono-substituted benzoic and phenylacetic systems, and the measurements consequently offer information on the relative change of substituent effect with change of solvent. The dissociation constants are discussed in terms of the dielectric constants of the solvents, and also the application of the Hammett equation is examined. The anomalous behaviour of *ortho*-substituted benzoic acids is understood in terms of steric inhibition of mesomerism.

PAST determinations of organic acid strengths in non-aqueous and partially aqueous solvents have been aimed generally at the derivation of relative acidities rather than individual acid-dissociation constants. In the present work, the conductimetric determination of the thermodynamic dissociation constants of a series of monosubstituted aromatic carboxylic acids in 10 and 25% acetone–water mixtures was carried out with a view to providing information accurate enough to shed further light on the quantitative variation of substituent group effects with change in solvent. These data, together with those from the literature for aqueous solution, are shown in Table I, in the form of  $pK_a$  values.

The Brønsted equation predicts that  $pK_a$  for a given acid should vary linearly with the reciprocal of the dielectric constant ( $D$ ) in constitutionally similar solvents. This linearity is tested in Table I by comparing the values of  $\delta pK/\delta(1/D)$ , obtained for each acid, between the pairs of data for water and 10% aqueous acetone (slope -1) and those for 10 and 25% aqueous acetone (slope -2). Although all slopes are steep, inspection shows that, with the exceptions of salicylic and *o*-acetylbenzoic acid, *ortho*-substituted acids have steeper slopes (*ca.* 400) than *meta*- and *para*-substituted acids (*ca.* 250). Pronounced non-linearity is found for *o*-fluoro-, *m*-hydroxy-, and *p*-hydroxy-, and *p*-methoxy-benzoic acids and for *p*-tolyl- and *p*-nitrophenyl-acetic acids.

Steep slopes for sterically hindered substituted acetic acids<sup>1</sup> have been explained in terms of the primary steric effect but in *ortho*-substituted benzoic acids an alternative explanation must be sought. *ortho*-Substituents generally enhance the strength of benzoic acid, irrespective of their polarity, an effect attributed to steric interaction which twists the carboxyl group out of the plane of the ring, thereby reducing  $-M$ , the acid-weakening conjugation.<sup>2</sup> Hetzer and Davis<sup>3</sup> found an exception to this general rule with benzoic and *o*-toluic acids in benzene as solvent, in that the unsubstituted acid is the stronger. These authors stress the importance of carboxyl-group solvation in the *ortho*-interaction in aqueous solution and suggest that in benzene, where this solvation is absent, the polar characteristics of the *ortho*-substituent will have the dominating effect on the acid strength; for this reason also the strength should exhibit a marked dependence on the dielectric constant of the solvent. If in the present work we suppose carboxyl-group solvation to diminish with increasing acetone content of the solvent, smaller relative enhancement (*i.e.*, greater increase in  $pK$ ) of acid strength in these media should result from the reduced steric interaction, and steep slopes should arise. The naphthoic acids were included for completeness, and inspection of the Table I shows that the  $\alpha$ -acid (416, 332) has the steep

\* Part XVIII, *J.*, 1959, 1441.

<sup>1</sup> Dippy, Hughes, and Rozanski, *J.*, 1959, 1441.

<sup>2</sup> Ingold, "Structure and Mechanism in Organic Chemistry," Bell and Sons, London, 1953, p. 744.

<sup>3</sup> Hetzer and Davis, *J. Res. Nat. Bur. Stand.*, 1958, **60**, 569.

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slope associated with steric hindrance of carboxyl whereas the slope of the  $\beta$ -acid (320, 242) is characteristic of a normal unhindered acid.

TABLE I.  
 $\delta pK(\delta(1/D))$   
between

Acid	pK values in			water and soln. A and soln. B		Wynne Jones comparison		Hammett comparison		M. p.
	H <sub>2</sub> O *	Soln. A †	Soln. B †	(slope -1)	(slope -2)	X ‡	Y ‡	$\delta pK_1$	$\delta pK_2$	
Benzoic .....	4.203	4.454	4.996	257	282	—	—	-0.001	+0.044	122°
<i>o</i> -Toluic .....	3.908	4.304	4.895	405	307	-148	-25	+0.144	+0.093	105
<i>m</i> -Toluic .....	4.272	4.486	5.040	219	288	+38	-6	-0.038	+0.056	112.5
<i>p</i> -Toluic .....	4.373	4.656	5.137	290	250	-33	+32	+0.031	-0.017	179.5
<i>o</i> -Nitrobenzoic .....	2.173	2.609	3.344	447	382	-190	-100	+0.184	+0.237	148
<i>m</i> -Nitrobenzoic .....	3.494	3.695	4.182	206	253	+51	+29	-0.051	-0.011	142
<i>p</i> -Nitrobenzoic .....	3.425	3.585	4.039	164	236	+93	+46	-0.092	-0.044	238.5
<i>o</i> -Hydroxybenzoic ...	2.996	3.161	3.547	170	200	+87	+82	-0.087	-0.112	159
<i>m</i> -Hydroxybenzoic	4.083	4.460	4.951	387	255	-130	+26	+0.125	-0.007	201.5
<i>p</i> -Hydroxybenzoic ...	4.530	4.928	5.352	408	220	-151	+62	+0.146	-0.074	214.5— 215.5
<i>o</i> -Methoxybenzoic ...	4.094	4.511	5.022	428	265	-171	+17	+0.165	+0.013	101.5
<i>m</i> -Methoxybenzoic...	4.088	4.311	4.830	228	269	+29	+13	-0.029	+0.021	106
<i>p</i> -Methoxybenzoic ...	4.471	4.813	5.203	350	203	-93	+79	+0.090	-0.108	184.5
<i>o</i> -Acetylbenzoic .....	4.126	4.242	4.536	120	153	+137	+129	-0.136	-0.204	115—116
<i>m</i> -Acetylbenzoic ...	3.827	4.062	4.565	241	261	+16	+21	-0.017	+0.005	165
<i>p</i> -Acetylbenzoic .....	3.701	3.925	4.458	229	277	+28	+5	-0.028	+0.035	208
<i>o</i> -Fluorobenzoic .....	3.267	3.796	4.394	542	310	-285	-28	+0.277	+0.100	124.5
<i>m</i> -Fluorobenzoic ...	3.867	4.064	4.620	202	289	+55	-7	-0.055	+0.058	124
<i>p</i> -Fluorobenzoic .....	4.142	4.305	4.796	168	255	+89	+27	-0.089	-0.007	184
<i>o</i> -Chlorobenzoic .....	2.943	3.334	4.020	401	356	-144	-74	+0.139	+0.188	142
<i>m</i> -Chlorobenzoic .....	3.830	4.043	4.565	219	271	+38	+11	-0.039	+0.024	156.5
<i>p</i> -Chlorobenzoic .....	3.977	4.207	4.698	235	255	+22	+27	-0.022	-0.007	239
$\alpha$ -Naphthoic .....	3.695	4.101	4.740	416	332	—	—	+0.154	+0.141	160.5
$\beta$ -Naphthoic .....	4.161	4.474	4.939	320	242	—	—	+0.061	-0.033	183.5
Phenylacetic .....	4.312	4.567	5.065	262	259	—	—	+0.003	0.000	76.5
<i>o</i> -Tolylacetic .....	4.306	4.625	5.146	327	270	-65	-11	+0.067	+0.023	88—89
<i>m</i> -Tolylacetic .....	4.363	4.660	5.133	304	246	-42	+13	+0.045	-0.025	63.5
<i>p</i> -Tolylacetic .....	4.370	4.523	5.160	157	331	+105	-72	-0.099	+0.139	92
<i>o</i> -Nitrophenylacetic	4.004	4.281	4.886	283	314	-21	-55	+0.025	+0.107	140.5
<i>m</i> -Nitrophenylacetic	3.967	4.207	4.660	246	235	+16	+24	-0.012	-0.045	117
<i>p</i> -Nitrophenylacetic	3.851	4.177	4.570	334	204	-72	+55	+0.074	-0.105	152.5

$$\delta pK_1 = pK_{\text{soln. A}} - pK_{\text{H}_2\text{O}}; \delta pK_2 = pK_{\text{soln. B}} - pK_{\text{soln. A}}$$

\* Refs. 4, 17, 20, 24. † Soln. A 10% acetone-water; Soln. B 25% acetone-water. ‡ X = Parent (slope -1) - acid (slope -1); Y = Parent (slope -2) - acid (slope -2).

The relatively low slopes (120, 153) found for *o*-acetylbenzoic acid can be explained on a basis similar to that used above. Bray, Dippy, and Hughes<sup>4</sup> attributed the small increase in acidity of benzoic acid in water, brought about by introduction of *o*-acetyl, to the preferential twisting of the less strongly conjugated acetyl group out of the plane of the ring. With less solvation of carboxyl, however, the acetyl substituent will assert its  $-M$  effect more readily and there will be less relative weakening of the acid by this effect, with a consequently smaller apparent dependence upon dielectric constant.

Salicylic acid (slopes 170, 200), whose abnormally high strength in water has long been attributed to stabilisation of this anion by intramolecular hydrogen bonding,<sup>5</sup> should be largely indifferent to solvation changes and it is not surprising that the slope is relatively small.

Although *ortho*-substituted phenylacetic acids do not show steep slopes, they have the greatest mean slopes of the three isomers, suggesting that small steric interactions are operative here.

<sup>4</sup> Bray, Dippy, and Hughes, *J.*, 1957, 265.

<sup>5</sup> Branch and Yabroff, *J. Amer. Chem. Soc.*, 1934, **56**, 2568.

The curvatures shown by slope alteration for *m*-hydroxy-, *p*-hydroxy-, and *p*-methoxybenzoic acids are consistent with previously observed effects of solvent on the acid-strength and reaction-rate influences of these substituents.<sup>6</sup> Hydrogen bonding with solvent molecules is probably an important factor here.<sup>7</sup>

The basic tendencies of the three solvents used by us increase with decreasing dielectric constant,<sup>8</sup> and of the opposing effects, *viz.*, decreased promotion of ionisation *versus* increased proton affinity, the Brønsted relationship takes account only of the former. Wynne-Jones's relationship attempted to compensate for basic tendency of the solvent by considering the increment in strength  $pK_u - pK$  in each medium (where  $K_u$  or  $K$  refer to parent and substituted acids, respectively). In Table 1 this comparison is made by the equivalent step of comparing (parent slope - slope) for the two pairs of media (columns 7 and 8). It will be seen that the fair linearity found for Wynne-Jones's relationship with pure solvents is not so well followed with mixed aqueous-organic solvents, but significant trends can be discerned: (i) Most of the *meta*- and *para*-substituted acids give a positive slope (of  $pK_u - pK$  with respect to  $1/D$ ) as predicted by Schwarzenbach and Egli's equation<sup>9</sup> which relates the polarity of a substituent to the acid strength. (ii) *ortho*-Substituted benzoic acids have negative slopes with the contrasting exceptions of *o*-acetylbenzoic and salicylic acids. (iii) The sharply varying slopes for *m*- and *p*-hydroxy- and *p*-methoxybenzoic acids confirm the significance of solvent-substituent interaction.

A notable feature of Wynne-Jones's relationship in the cases of the substituted phenylacetic acids is the consistent negative slope of ( $pK_u - pK$ ) with respect to  $1/D$  for the *ortho*-substituted acids, implying a steric effect.

Hammett's equation,  $\log k/k_u = \sigma_\rho$  was advanced originally<sup>10</sup> to correlate substituent effects on the velocity constants of reactions involving *meta*- and *para*-substituted benzene derivatives with the strengths of the related benzoic acids. In the majority of favourable cases, despite a reasonable degree of correlation between  $\log(K/K_u)$  and  $\log(k/k_u)$ , rigid linearity is rarely observed. The most serious deviations are to be found with *para*-substituents and these are attributed to variable mesomeric interaction with the functional group or reaction centre (foreshadowed by Dippy and Watson<sup>11</sup>). Hammett<sup>12</sup> later suggested alternative  $\sigma$  constants for some *para*-substituents and this duality of  $\sigma$ -constants has since been recognised by many workers,<sup>6,13</sup> although the more logical situation of having a multiplicity of  $\sigma$ -constants for all *para*-substituents has been recently demonstrated.<sup>14,15</sup>

We consider that the most favourable case for rigid applicability of the Hammett equation should be in the correlation of strengths for a series of *meta*- and *para*-substituted benzoic acids in related solvents having a small progressive difference in proton affinity. When confined to acid-strength data in different media the Hammett equation has the form  $pK_u - pK = \rho\sigma$  where  $\rho$  depends on the medium and is unity for water.

In columns 9 and 10 of Table 1 the conclusions to be drawn by plotting the  $pK$  values for a set of substituted benzoic acids in one medium against the corresponding values in another are summarised. This has been done by calculating the deviation of  $\delta pK$  (the acid weakening produced by a change of medium) from the straight line  $\delta pK = (\text{mean slope}) \times \delta(1/D)$ , using the mean values of this (selected for the unhindered acids) of 0.252 between water and 10% acetone-water and of 0.498 between 10 and 25% acetone-water.

<sup>6</sup> Jaffé, *Chem. Rev.*, 1953, **53**, 191; Ritchie and Lewis, *J. Amer. Chem. Soc.*, 1962, **84**, 591.

<sup>7</sup> Elliott and Kilpatrick, *J. Phys. Chem.*, 1941, **45**, 485.

<sup>8</sup> Braude and Stern, *J.*, 1948, 1976.

<sup>9</sup> Schwarzenbach and Egli, *Helv. Chim. Acta*, 1934, **17**, 1183.

<sup>10</sup> Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

<sup>11</sup> Dippy and Watson, *J.*, 1936, 436; cf. Dippy, *Chem. Rev.*, 1939, **25**, 197.

<sup>12</sup> Hammett, "Physical Organic Chemistry," McGraw Hill, 1940, p. 186.

<sup>13</sup> McGary, Okamoto, and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037.

<sup>14</sup> van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

<sup>15</sup> Knowles, Norman, and Radda, *J.*, 1960, 4885.

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If the hydroxy-group is omitted, the *meta*-substituents obey this relationship within 0.058 of a  $pK$  unit; if methoxy is also excluded (see above) the *para*-derivatives are seen to require a tolerance of 0.092 of a  $pK$  unit. As expected, the *ortho*-derivatives deviate widely in the positive sense when there is steric inhibition of the mesomerism of the carboxyl group, and in the negative sense by similar amounts for hydroxy and acetyl groups. In fact, if we exclude these two groups the remaining *ortho*-derivatives fit the relationships  $\delta pK_1 = 0.434$  and  $\delta pK_2 = 0.624$  within  $\pm 0.12$  of a  $pK$  unit although, as stated elsewhere,<sup>16</sup> we take leave to doubt that any useful additivity of *ortho*-substituent effects may be thereby implied.

It is seen, therefore, that even under the propitious conditions selected for this investigation no rigidly linear correlation between the  $pK$  values for a given acid is observed. Even when the alternative media differ only by the moderate changes in proton affinity employed here, significant deviations in  $\sigma$ -values occur for *meta*-substituents and marked deviations are found in the case of *para*-substituents (Table 2).

TABLE 2.

Substituent constants based on dissociation constants of substituted benzoic acids in three media at 25°.

Subst.	$\sigma = (pK_u - pK)/\rho$			Subst.	$\sigma = (pK_u - pK)/\rho$		
	H <sub>2</sub> O	10% COMe <sub>2</sub> -	25% COMe <sub>2</sub> -		H <sub>2</sub> O	10% COMe <sub>2</sub> -	25% COMe <sub>2</sub> -
	( $\rho = 1$ )	H <sub>2</sub> O ( $\rho = 1.05$ )	H <sub>2</sub> O ( $\rho = 1.15$ )		( $\rho = 1$ )	H <sub>2</sub> O ( $\rho = 1.05$ )	H <sub>2</sub> O ( $\rho = 1.15$ )
<i>m</i> -Me ...	-0.069	-0.031	-0.038	<i>p</i> -Me ...	-0.170	-0.193	-0.123
<i>m</i> -NO <sub>2</sub> ...	0.709	0.723	0.708	<i>p</i> -NO <sub>2</sub> ...	0.778	0.827	0.832
<i>m</i> -OH ...	0.120	-0.006	0.039	<i>p</i> -OH ...	-0.328	-0.452	-0.310
<i>m</i> -OMe ...	0.115	0.136	0.144	<i>p</i> -OMe ...	-0.268	-0.342	-0.181
<i>m</i> -Ac ...	0.376	0.373	0.375	<i>p</i> -Ac ...	0.502	0.504	0.467
<i>m</i> -F ...	0.336	0.371	0.327	<i>p</i> -F ...	0.061	0.141	0.174
<i>m</i> -Cl ...	0.373	0.391	0.374	<i>p</i> -Cl ...	0.226	0.235	0.259

The data given in Table 1 when analysed by the method of van Bekkum, Verkade, and Wepster<sup>14</sup> yield  $\rho$ -values of 1.05 and 1.15 for the 10 and 25% acetone-water mixtures, respectively, the variation of  $\rho$  with dielectric constant conforming to Jaffé's general rule.<sup>6</sup> Constants for *meta*- and *para*-substituents relating to the three media are listed in Table 2. The variation in  $\sigma$  for a given group between the three media, even in those cases free from excessive curvature ( $pK$  against  $1/D$ ), emphasises further that rigid compliance with the Hammett relationship is not general here.

Obviously, the foregoing parameters for aromatic substituents should not be extended to systems in which a fully saturated carbon atom separates the aromatic ring from the functional group; then parameters should be derived afresh from appropriate acid

TABLE 3A.

Substituent constants based on dissociation constants of substituted phenylacetic acids in water at 25°.

Subst.	$\sigma$	Subst.	$\sigma$	Subst.	$\sigma$	Subst.	$\sigma$
<i>m</i> -Me .....	-0.051	<i>m</i> -Cl .....	0.171	<i>p</i> -Me .....	-0.058	<i>p</i> -Cl .....	0.121
<i>m</i> -NO <sub>2</sub> .....	0.345	<i>m</i> -Br .....	0.172	<i>p</i> -NO <sub>2</sub> .....	0.461	<i>p</i> -Br .....	0.124
<i>m</i> -F .....	0.181	<i>m</i> -I .....	0.152	<i>p</i> -F .....	0.066	<i>p</i> -I .....	0.134
						<i>p</i> -OMe .....	-0.049

strength data. Values of  $\sigma$  calculated from data for substituted phenylacetic acids in water<sup>17</sup> are listed in Table 3A, and the few available for the acetone-water media studied here, based on the above  $\rho$ -values are in Table 3B. The variation of  $\sigma$  from one medium to the other is once again to be noted.

<sup>16</sup> Dippy and Hughes, *Tetrahedron*, 1963, 1527.

<sup>17</sup> Dippy, *Chem. Rev.*, 1939, 25, 151.

TABLE 3B.

Substituent constants based on dissociation constants of substituted phenylacetic acids in aqueous acetone media at 25°.

	Subst.:	<i>m</i> -Me	<i>m</i> -NO <sub>2</sub>	<i>p</i> -Me	<i>p</i> -NO <sub>2</sub>
10% COMe <sub>2</sub> -H <sub>2</sub> O ( $\rho = 1.05$ )	.....	-0.088	0.343	0.042	0.372
25% COMe <sub>2</sub> -H <sub>2</sub> O ( $\rho = 1.15$ )	.....	-0.059	0.353	-0.083	0.430

It is noteworthy that Taft and Lewis,<sup>18</sup> and Norman and Radda *et al.*<sup>19</sup> have already claimed that such parameters give better correlations for side-chain reactions in which no primary resonance interaction is possible between substituent and the reacting group. However, it is fair to state that the fit of the rate constants for alkaline hydrolysis of *N*-acylbenzanilides obtained by Lamberton and Standage<sup>20</sup> provides no evidence in favour of a change from benzoic to phenylacetic acid data.

Our general observations serve to emphasise how sensitive  $\sigma$  constants are to environment and consequently how rare any rigid compliance with Hammett's equation will be. The obstacles presented to a comprehensive quantitative theory of substituent effects have recently been reviewed elsewhere.<sup>21</sup>

### EXPERIMENTAL

*Preparation and Purification of Acids.*—The carboxylic acids used in this investigation were purchased, with the exception of those described below.

*o*-Acetylbenzoic acid was obtained by the hydrolysis of the product formed by interacting phthalic anhydride and maleic acid in warm pyridine<sup>22</sup> whilst *m*- and *p*-acetylbenzoic acid were derived from the corresponding aminoacetophenones by diazotisation, cyanolysis, and hydrolysis.

*o*-Methoxybenzoic acid was prepared by the methylation of salicylic acid, and *m*-nitrophenylacetic acid by treatment of *m*-nitrobenzyl chloride with potassium cyanide and subsequent hydrolysis.

*p*-Tolylacetic acid was obtained from *p*-tolualdehyde which was converted into the  $\alpha$ -azlactone of  $\alpha$ -benzylamino- $\beta$ -*p*-tolylacrylic acid; hydrolysis and subsequent oxidation of this yielded a mixture of benzoic and *p*-tolylacetic acids which was separated by fractional distillation of the methyl esters.

When possible the acids were recrystallised from conductivity water, and the final specimens stored over silica gel for at least 3 weeks before use. The melting points and equivalent weights of the purified acids were determined, and the former are shown in Table I.

*Solvents.* The acetone used in this work was purified as outlined by Dippy, Hughes, and Rozanski.<sup>1</sup> The water content of the unwetted acetone was determined by using the density relationships given by Hughes.<sup>23</sup>

Mixed solvent, prepared by weight ( $\pm 0.01\%$ ), was kept overnight in capped flasks before use. The specific conductivities of 10 and 25% aqueous acetone solutions were 0.5–0.6 and 0.2–0.3 gemmho, respectively, at 25°. The conductivity water used in preparing the mixed solvent possessed a specific conductivity of 0.4–0.8 gemmho.

TABLE 4.

Physical constants of the solvents.

	$d_4^{25}$	$\eta_0^{25}$	$D_{25}$
10% (w/w) acetone–water	0.9832	0.01105	73.0
25% (w/w) acetone–water	0.9618	0.01335	64.0
H <sub>2</sub> O			78.6

*Conductivity Measurements and Calculations.*—Conductivity measurements followed earlier procedures<sup>24</sup> except for the cells used and their calibration. The cells were of the conical-flask

<sup>18</sup> Taft and Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.

<sup>19</sup> Norman, Radda, Brimacombe, Ralph, and Smith, *J.*, 1961, 3247.

<sup>20</sup> Lamberton and Standage, *J.*, 1960, 2957.

<sup>21</sup> Dewar and Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539.

<sup>22</sup> Yale, *J. Amer. Chem. Soc.*, 1947, **69**, 1547.

<sup>23</sup> Hughes, *J.*, 1956, 988.

<sup>24</sup> Dippy, Hughes, and Laxton, *J.*, 1954, 1470.

TABLE 5.  
Conductivities ( $C$  in equiv./l.  $\Lambda$  in mho cm.<sup>-2</sup>).

10% acetone-water			25% acetone-water			10% acetone-water			25% acetone-water		
10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K
<i>o</i> -Toluic acid						<i>o</i> -Nitrobenzoic acid					
3.641	90.38	4.94	6.017	24.79	1.27	2.556	281.5	245	2.095	171.6	45.3
5.361	77.12	4.96	8.452	21.18	1.27	2.897	278.5	246	3.163	157.0	45.3
6.648	70.46	4.98	10.65	19.03	1.28	4.113	269.6	248	4.208	146.3	45.4
7.966	65.21	4.98	11.80	18.13	1.27	5.183	262.4	248	5.128	138.7	45.4
9.372	60.74	4.96	13.30	17.13	1.28	6.042	256.8	247	6.745	128.0	45.4
11.69	55.00	4.97	15.62	15.86	1.27	7.762	247.4	247	8.444	119.4	45.4
15.02	49.20	4.97	17.88	14.88	1.27	8.927	241.4	246	10.00	112.9	45.3
						10.70	233.5	245	12.76	105.3	45.3
	$\Lambda_0$ 292.6		$\Lambda_0$ 181.8			$\Lambda_0$ 309.4			$\Lambda_0$ 230.5		
	10 <sup>5</sup> K 4.97		10 <sup>5</sup> K 1.275			10 <sup>5</sup> K 246			10 <sup>5</sup> K 45.3		
<i>m</i> -Toluic acid						<i>m</i> -Nitrobenzoic acid					
3.740	70.46	3.27	5.604	22.53	0.910	2.506	181.2	20.2	3.051	89.01	6.58
6.743	54.58	3.26	9.408	17.84	0.912	3.875	158.7	20.2	5.413	70.96	6.59
8.917	48.07	3.28	11.59	16.18	0.916	5.641	140.1	20.3	8.463	58.89	6.59
11.10	43.65	3.27	13.78	14.87	0.916	8.115	122.8	20.3	10.96	52.69	6.59
14.29	38.81	3.27	17.45	13.30	0.910	9.775	114.4	20.3	12.73	49.38	6.59
16.65	36.23	3.26	19.10	12.73	0.916	10.87	109.7	20.2	16.53	44.00	6.59
18.34	34.56	3.26	22.95	11.60	0.916	14.58	97.74	20.2	18.18	42.12	6.57
21.80	32.06	3.28				16.60	92.52	20.1	20.16	40.23	6.58
	$\Lambda_0$ 274.1		$\Lambda_0$ 188.1			$\Lambda_0$ 311.4			$\Lambda_0$ 239.5		
	10 <sup>5</sup> K 3.27		10 <sup>5</sup> K 0.913			10 <sup>5</sup> K 20.2			10 <sup>5</sup> K 6.58		
<i>p</i> -Toluic acid						<i>p</i> -Nitrobenzoic acid					
3.338	66.75	2.20	9.176	16.26	0.730	2.292	204.9	26.1	1.942	111.7	9.14
6.058	51.32	2.20	11.20	14.79	0.730	3.670	191.5	26.1	3.104	94.98	9.19
8.408	44.22	2.20	13.18	13.69	0.730	4.695	167.8	26.0	4.488	82.66	9.17
9.362	42.10	2.20	14.27	13.17	0.730	5.420	155.2	26.1	6.742	70.23	9.12
10.76	39.50	2.21	15.17	12.79	0.730	6.500	148.4	25.9	8.292	64.67	9.16
12.71	36.58	2.21	17.86	11.83	0.730	6.994	139.0	26.0	9.458	61.14	9.13
14.14	34.80	2.21	21.36	10.85	0.730	8.099	129.2	26.1	11.51	56.29	9.13
19.84	29.69	2.20							13.20	53.12	9.14
	$\Lambda_0$ 293.3		$\Lambda_0$ 189.0			$\Lambda_0$ 298.2			$\Lambda_0$ 226.7		
	10 <sup>5</sup> K 2.21		10 <sup>5</sup> K 0.730			10 <sup>5</sup> K 26.0			10 <sup>5</sup> K 9.14		
<i>o</i> -Hydroxybenzoic acid						<i>o</i> -Chlorobenzoic acid					
4.711	215.9	68.9	2.972	146.6	28.3	4.393	195.5	46.5	2.373	104.1	9.53
6.443	199.8	69.0	4.909	133.9	28.3	5.262	185.9	46.4	5.392	77.05	9.58
7.836	189.4	69.0	6.251	117.2	28.4	7.958	164.4	46.4	6.532	71.39	9.57
9.771	177.8	69.1	8.729	104.6	28.4	8.840	159.1	46.5	8.470	64.17	9.55
11.89	167.4	69.1	10.57	97.64	28.5	9.814	153.4	46.2	9.280	61.84	9.56
13.29	161.6	69.1	13.40	89.38	28.4	10.74	148.8	46.2	10.31	59.19	9.56
14.31	157.7	69.0	14.68	86.33	28.4	11.59	145.1	46.3	11.90	55.70	9.55
15.78	152.7	69.0	17.38	80.88	28.4	12.59	141.1	46.2	13.76	52.32	9.54
	$\Lambda_0$ 315.4		$\Lambda_0$ 238.3			$\Lambda_0$ 309.9			$\Lambda_0$ 223.1		
	10 <sup>5</sup> K 69.0		10 <sup>5</sup> K 28.4			10 <sup>5</sup> K 46.3			10 <sup>5</sup> K 9.56		
<i>m</i> -Hydroxybenzoic acid						<i>m</i> -Chlorobenzoic acid					
4.617	74.32	3.46	3.056	34.97	1.12	5.835	96.64	9.05	1.455	76.21	2.69
6.615	63.55	3.46	5.295	27.23	1.12	7.681	86.54	9.08	2.518	61.31	2.72
8.333	57.38	3.46	8.197	22.21	1.12	8.927	81.23	9.05	3.836	51.33	2.72
11.32	50.00	3.46	9.799	20.42	1.12	10.42	76.01	9.02	5.688	43.26	2.73
13.39	46.35	3.47	10.44	19.86	1.12	11.38	73.37	9.06	7.410	38.37	2.72
16.84	41.71	3.46	12.39	18.27	1.12	13.38	68.46	9.06	9.385	34.52	2.72
19.44	39.06	3.47	13.37	17.65	1.11				11.86	31.00	2.71
21.79	37.01	3.46							15.35	27.51	2.72
	$\Lambda_0$ 308.7		$\Lambda_0$ 199.8			$\Lambda_0$ 295.8			$\Lambda_0$ 218.2		
	10 <sup>5</sup> K 3.47		10 <sup>5</sup> K 1.12			10 <sup>5</sup> K 9.05			10 <sup>5</sup> K 2.72		

TABLE 5. (Continued.)

10% acetone-water			25% acetone-water			10% acetone-water			25% acetone-water		
10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K
<i>p</i> -Hydroxybenzoic acid						<i>p</i> -Chlorobenzoic acid					
3.349	54.29	1.18	8.515	12.84	0.444	1.626	133.4	6.21	2.830	49.81	2.01
6.934	38.85	1.18	11.89	10.94	0.445	1.918	125.7	6.20	4.845	39.30	2.00
8.371	35.62	1.18	15.79	9.533	0.444	3.342	102.1	6.22	5.905	35.95	2.00
11.80	30.29	1.18	18.46	8.829	0.444	3.675	98.32	6.22	6.877	33.64	2.01
16.53	25.83	1.18	23.40	7.881	0.445	4.930	87.42	6.23	7.969	31.45	2.01
18.78	24.29	1.18	28.70	7.136	0.445	6.625	77.31	6.22	9.051	29.58	2.00
22.06	22.51	1.18	31.61	6.805	0.445	7.730	72.34	6.20	11.34	26.71	2.01
24.14	21.55	1.18	33.46	6.617	0.444						
	$\Lambda_0$ 315.9			$\Lambda$ 182.9			$\Lambda_0$ 291.3			$\Lambda_0$ 212.1	
	10 <sup>5</sup> K 1.18			10 <sup>5</sup> K 0.445			10 <sup>5</sup> K 6.21			10 <sup>5</sup> K 2.00	
<i>o</i> -Fluorobenzoic acid						<i>o</i> -Methoxybenzoic acid					
2.486	166.8	16.0	1.794	83.25	4.02	3.704	76.96	3.08	3.209	30.00	0.949
4.731	134.5	16.0	2.666	71.39	4.04	5.459	65.08	3.08	6.749	21.30	0.951
6.266	121.6	16.0	3.925	61.01	4.05	6.706	59.46	3.09	10.57	17.24	0.950
7.490	113.7	16.0	5.366	53.44	4.04	8.944	52.25	3.08	12.99	15.63	0.950
8.398	108.7	16.0	8.387	44.00	4.04	10.15	49.35	3.08	14.46	14.86	0.951
9.999	101.5	16.0	10.78	39.35	4.04	12.86	44.37	3.08	16.24	14.05	0.950
11.07	97.44	16.0	13.00	36.14	4.03	13.95	42.71	3.09	18.64	13.15	0.950
12.58	92.56	16.0	14.42	34.50	4.04	15.62	40.53	3.08			
	$\Lambda_0$ 305.9			$\Lambda_0$ 221.0			$\Lambda_0$ 305.9			$\Lambda_0$ 188.9	
	10 <sup>5</sup> K 16.0			10 <sup>5</sup> K 4.04			10 <sup>5</sup> K 3.08			10 <sup>5</sup> K 0.950	
<i>m</i> -Fluorobenzoic acid						<i>m</i> -Methoxybenzoic acid					
2.310	132.6	8.64	1.100	83.05	2.41	2.038	109.6	4.89	0.9087	63.77	1.47
2.713	125.3	8.65	2.030	65.03	2.41	3.065	93.51	4.89	2.195	44.31	1.48
3.658	112.1	8.63	3.026	54.95	2.40	4.158	82.62	4.89	3.174	37.70	1.48
4.661	102.1	8.64	4.150	47.93	2.40	5.566	73.13	4.89	4.927	30.93	1.48
6.036	92.12	8.62	5.260	43.16	2.40	6.152	70.11	4.89	7.434	25.59	1.48
7.039	86.59	8.63	6.493	39.33	2.40	6.737	67.38	4.89	8.390	24.22	1.48
8.533	79.94	8.62	8.007	35.80	2.41	7.391	64.77	4.88	9.192	23.17	1.48
			9.151	33.68	2.41	8.730	60.24	4.89	11.03	21.31	1.48
	$\Lambda_0$ 291.5			$\Lambda_0$ 222.8			$\Lambda_0$ 283.7			$\Lambda_0$ 193.0	
	10 <sup>5</sup> K 8.63			10 <sup>5</sup> K 2.40			10 <sup>5</sup> K 4.89			10 <sup>5</sup> K 1.48	
<i>p</i> -Fluorobenzoic acid						<i>p</i> -Methoxybenzoic acid					
2.782	95.34	4.94	1.944	49.79	1.60	2.738	65.34	1.54	1.790	30.80	0.627
4.580	77.94	4.95	2.232	39.92	1.60	3.151	61.42	1.54	3.323	23.18	0.626
5.621	71.52	4.95	4.977	32.92	1.60	3.680	57.33	1.54	5.164	18.86	0.626
7.890	61.82	4.96	7.087	27.96	1.60	4.430	52.75	1.54	6.498	16.93	0.626
9.033	58.34	4.96	8.673	25.51	1.60	5.055	49.71	1.54	7.976	15.37	0.627
10.44	54.77	4.96	9.812	24.13	1.60	5.704	47.01	1.54	8.997	14.50	0.626
11.27	52.94	4.95	12.95	21.17	1.60	7.046	42.70	1.54	10.40	13.53	0.626
13.72	48.36	4.93	15.22	19.62	1.60	8.517	39.10	1.54			
	$\Lambda_0$ 277.1			$\Lambda_0$ 199.2			$\Lambda_0$ 308.5			$\Lambda_0$ 179.8	
	10 <sup>5</sup> K 4.95			10 <sup>5</sup> K 1.60			10 <sup>5</sup> K 1.54			10 <sup>5</sup> K 0.626	
<i>o</i> -Acetylbenzoic acid						$\alpha$ -Naphthoic acid					
4.438	74.46	5.75	4.241	31.97	2.93	2.189	132.4	7.96	1.492	57.01	1.82
5.599	67.45	5.71	6.113	27.13	2.91	3.020	117.6	7.91	3.431	39.94	1.82
7.345	60.10	5.73	8.089	23.93	2.91	4.088	104.8	7.91	4.282	36.20	1.82
8.710	55.98	5.70	10.04	21.74	2.92	5.219	95.27	7.94	5.333	32.81	1.82
10.72	51.10	5.72	11.42	20.52	2.92	5.842	90.93	7.92	6.512	29.97	1.82
12.47	47.85	5.73	12.82	19.47	2.92	6.620	86.42	7.92	7.962	27.34	1.82
15.11	43.99	5.75	14.22	18.56	2.92	7.749	81.04	7.94	9.267	25.51	1.82
						8.729	77.07	7.93	11.28	23.27	1.82
	$\Lambda_0$ 245.6			$\Lambda_0$ 137.6			$\Lambda_0$ 294.1			$\Lambda_0$ 193.0	
	10 <sup>5</sup> K 5.72			10 <sup>5</sup> K 2.91			10 <sup>5</sup> K 7.93			10 <sup>5</sup> K 1.82	

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TABLE 5. (Continued.)

10% acetone-water			25% acetone-water			10% acetone-water			25% acetone-water		
10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K	10°C	$\Lambda$	10 <sup>5</sup> K
<i>m</i> -Acetylbenzoic acid						$\beta$ -Naphthoic acid					
3.249	119.5	8.64	4.642	47.19	2.73	1.920	102.3	3.34	2.454	37.63	1.15
4.060	110.1	8.67	6.812	39.80	2.72	3.114	84.41	3.37	3.310	32.88	1.15
8.960	80.10	8.68	9.366	34.52	2.73	3.733	78.20	3.36	5.105	27.21	1.15
10.44	75.19	8.69	11.52	31.39	2.72	4.770	70.41	3.36	6.590	24.00	1.15
11.19	72.92	8.68	13.43	29.29	2.73	5.775	64.83	3.37	7.573	22.51	1.15
13.37	67.46	8.65	15.31	27.60	2.73	7.234	58.62	3.35	8.744	21.04	1.15
15.94	62.52	8.65	16.97	26.25	2.72	8.302	55.10	3.35	10.24	19.52	1.15
			20.40	24.11	2.72				11.91	18.19	1.15
	$\Lambda_0$ 297.4		$\Lambda_0$ 217.8			$\Lambda_0$ 300.5			$\Lambda_0$ 192.1		
	10 <sup>5</sup> K 8.67		10 <sup>5</sup> K 2.72			10 <sup>5</sup> K 3.36			10 <sup>5</sup> K 1.15		
<i>p</i> -Acetylbenzoic acid											
2.359	147.3	11.9	1.623	82.42	3.46						
3.655	127.1	12.0	3.180	63.12	3.48						
4.598	116.7	12.0	4.417	55.04	3.49						
5.709	107.5	11.9	5.878	48.70	3.49						
7.358	97.29	11.9	8.998	40.29	3.49						
8.592	91.59	12.0	10.59	37.44	3.48						
9.881	86.47	11.9	12.91	34.24	3.48						
12.33	79.16	11.9	17.72	29.60	3.48						
	$\Lambda_0$ 292.6		$\Lambda_0$ 223.2								
	10 <sup>5</sup> K 11.9		10 <sup>5</sup> K 3.48								
<i>o</i> -Tolylacetic acid						<i>o</i> -Nitrophenylacetic acid					
2.234	82.44	2.36	5.577	21.27	0.714	6.695	73.75	5.24	5.175	31.89	1.30
3.697	60.57	2.37	8.588	17.36	0.715	8.479	66.64	5.24	7.826	26.33	1.30
5.322	56.72	2.37	11.45	15.16	0.717	10.78	60.00	5.25	11.04	22.42	1.30
6.564	51.65	2.37	15.48	13.10	0.715	12.35	56.47	5.24	14.14	19.94	1.30
7.583	48.41	2.37	18.89	11.89	0.713	14.09	53.25	5.24	18.03	17.80	1.30
9.322	44.03	2.37	20.92	11.34	0.716	16.00	50.34	5.25	20.17	16.66	1.30
11.21	40.46	2.37	22.29	11.01	0.717	18.99	46.56	5.24	23.85	15.56	1.30
13.46	37.18	2.37	24.88	10.43	0.716	21.94	43.56	5.24	26.65	14.76	1.30
	$\Lambda_0$ 296.5		$\Lambda_0$ 197.4			$\Lambda_0$ 300.4			$\Lambda_0$ 215.8		
	10 <sup>5</sup> K 2.37		10 <sup>5</sup> K 0.715			10 <sup>5</sup> K 5.24			10 <sup>5</sup> K 1.30		
<i>m</i> -Tolylacetic acid						<i>m</i> -Nitrophenylacetic acid					
2.515	75.75	2.19	13.02	14.03	0.736	3.957	95.26	6.22	5.429	35.75	2.18
2.524	75.72	2.19	16.56	12.52	0.738	6.199	79.33	6.23	7.203	31.58	2.19
5.770	52.80	2.20	18.07	11.99	0.736	9.141	67.05	6.18	9.104	28.38	2.19
7.710	46.29	2.20	20.56	11.27	0.736	11.27	61.33	6.21	11.90	25.10	2.19
9.526	41.96	2.19	23.07	10.67	0.738	13.03	57.62	6.23	14.05	23.19	2.18
11.22	38.95	2.20	24.79	10.30	0.737	14.67	54.57	6.20	15.96	21.86	2.19
12.23	37.42	2.19	26.56	9.958	0.736	16.52	51.84	6.22	17.76	20.80	2.19
13.85	35.32	2.19	29.78	9.423	0.737	18.57	49.16	6.22			
	$\Lambda_0$ 295.8		$\Lambda_0$ 191.7			$\Lambda_0$ 290.5			$\Lambda_0$ 195.6		
	10 <sup>5</sup> K 2.19		10 <sup>5</sup> K 0.737			10 <sup>5</sup> K 6.21			10 <sup>5</sup> K 2.19		
<i>p</i> -Tolylacetic acid						<i>p</i> -Nitrophenylacetic acid					
4.224	59.83	2.00	5.051	21.69	0.693	2.145	132.5	6.63	3.089	51.51	2.69
5.679	52.45	2.00	8.054	17.39	0.692	2.293	129.6	6.67	5.447	46.25	2.69
6.969	47.82	2.00	9.960	15.72	0.692	3.528	110.0	6.66	7.108	41.05	2.70
8.196	44.41	2.00	13.53	13.56	0.692	3.831	106.6	6.67	9.201	36.93	2.69
9.247	42.05	2.00	15.62	12.67	0.692	4.435	100.7	6.69	12.25	34.42	2.69
9.891	40.73	2.00	17.18	12.10	0.692	6.097	88.23	6.66	14.21	31.23	2.69
10.49	39.63	2.00	20.85	11.03	0.693	7.373	81.49	6.66	15.24	28.91	2.69
14.37	34.21	2.00	23.17	10.48	0.693	11.48	66.92	6.65	17.88	27.17	2.69
	$\Lambda_0$ 304.8		$\Lambda_0$ 194.9			$\Lambda_0$ 312.0			$\Lambda_0$ 203.0		
	10 <sup>5</sup> K 2.00		10 <sup>5</sup> K 0.692			10 <sup>5</sup> K 6.66			10 <sup>5</sup> K 2.69		

pattern suited to non-aqueous solvent work<sup>25,26</sup> and were of some 650-ml. capacity with side-chamber electrodes of bright platinum mounted so as to have cell constants in the range 0.05—0.07 cm.<sup>-1</sup>. These cells were calibrated both directly, by using the data of Gunning and

<sup>25</sup> Daggett, Blair, and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 799.

<sup>26</sup> Dippy and Hughes, *J.*, 1954, 953.



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Gordon<sup>27</sup> for aqueous potassium chloride solutions, and also by the indirect procedure used formerly,<sup>24</sup> complete agreement being obtained between the two methods.

Values of  $K$  and  $\Lambda_0$  were evaluated by the Fuoss extrapolation method<sup>28</sup> using the appropriate physical constants shown in Table 4.

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<sup>27</sup> Gunning and Gordon, *J. Chem. Phys.*, 1942, **10**, 126.

<sup>28</sup> Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.

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