Summary

1. Data on the influence of phosphates, sulfates and arsenates on the dissolution of aged colloidal aluminum hydroxide in 0.2 N hydrochloric acid, have been presented.

2. Within certain limits, the amount of the hydroxide dissolved is a logarithmic function of the concentration of the electrolyte yielding bivalent and trivalent anions. The equations take the form $\chi = K \log a + C$.

3. The influence of the anion of higher valence is attributed to adsorption at the solid–liquid interface which produces a reduction in the electrical potential difference.

4. The findings are not in accord with the diffusion theory of reactions in heterogeneous systems.

SEATTLE, WASHINGTON

RECEIVED OCTOBER 17, 1932
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Relative Strength of Benzoic and Salicylic Acids in Alcohol–Water Solutions

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An earlier paper[1] presented measurements of the relative strength of a series of carboxylic acids in 50% ethyl alcohol and 60% butyl carbitol, determined by means of the antimony electrode. In those measurements, as in others,[2] the presence of a liquid junction between solutions in different solvents might be used as a basis for adverse criticism. It is therefore desirable to compare the results of a similar set of measurements with those obtained by an independent method. For this purpose the relative strength of benzoic and salicylic acids in a series of ethyl alcohol–water solutions has been determined with the antimony electrode and from the solubilities of the acids and their silver salts. The agreement justifies the assumptions of both procedures, and suggests that the earlier measurements in 50% alcohol, and, by inference, in 60% butyl carbitol, are more accurate than was originally claimed.

This result has an important bearing on the question of the variation of the relative strength of acids in different solvents. It seems reasonable, *a priori*, to assume that the relative ionization, in conformity with equilibria in general, should be conditioned by the solvent as well as by the acids. However, since the data which support this view were obtained exclusively by the use of cells with questionable liquid junctions, it could not be

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[1] Halford, THIS JOURNAL, **53**, 2944 (1931).

[2] Conant and Werner, *ibid.*, **52**, 4436 (1930); Hall, *Chem. Rev.*, **8**, 191 (1931); Michaelis and Mizutani, *Z. physik. Chem.*, **116**, 135, 350 (1925).

claimed to be firmly established. In fact, Hammett and Deyrup have based their general acidity[3] function on the assumption that relative strength does not vary with the solvent, and have supported their view by colorimetric comparisons of bases in strongly acidic solvents. They have suggested that the variations observed by others might be expressions of experimental error. Although this was improbable, since it involved the assumption that differences between nearly identical liquid junctions could be as large as 50 millivolts, it could not be definitely denied. The data presented here constitute reliable evidence of variable relative strength, at least for carboxylic acids in alcohol–water solutions.

Association.—Before proceeding with the presentation and discussion of the experimental data, the method of eliminating the possibly troublesome factor of association will be outlined. It is well known that the carboxylic acids show a strong tendency to associate in some solvents. The potentiometric titration curve of a dimolecular acid is not greatly different in appearance from that of the monomolecular acid, and might easily be mistaken for the latter unless a close examination is made. At the point of half neutralization, the dissociation constant of the monomolecular acid is equal to the hydrogen-ion concentration, so that, except for salt effects, the curves obtained with different initial acid concentrations should show the same potential at this point. With a dimolecular acid, this will not be true, and the hydrogen-ion concentration at half neutralization will be higher with the lower initial concentration.

The size of the effect is readily estimated. If the dissociation constant is expressed by the equation

$$K^2 = [\mathrm{H}^+]^2[\mathrm{A}^-]^2/[(\mathrm{HA})_2]$$

and if $2a$ is the concentration of the anion at half neutralization, then the concentration of associated acid is a, and

$$K^2 = [\mathrm{H}^+]^2\,\frac{4a^2}{a} = 4a[\mathrm{H}^+]^2$$

The error of observation, if the acid is wrongly interpreted as monomolecular, may be expressed as the ratio of the hydrogen-ion concentrations at this point, for two solutions whose initial concentrations differ by a factor of ten

$$\frac{[\mathrm{H}^+]_a}{[\mathrm{H}^+]_{0.1a}} = \sqrt{\frac{0.4a}{4a}} = \frac{1}{\sqrt{10}};\quad \Delta \log\,[\mathrm{H}^+] = -0.5$$

The strength of the acid would therefore appear greater, by 0.5 logarithmic unit (30 mv.), in the more dilute solution. In order to test for association, at least two measurements at different total concentrations are made. For the partially associated acid the effect will be smaller. If it lies within the experimental error, the acid may be considered to be monomolecular.

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(3) Hammett and Deyrup, THIS JOURNAL, **54**, 2721, 4239 (1932).

Relative Strength from Solubilities

The relation between relative strength and solubilities[4] is expressed by the equations

$$C^{\circ}_{\mathrm{Ag}} + pK_2 = pK_1 + \log \frac{a_2\, \sigma_1^2}{a_1\, \sigma_2^2} \tag{1}$$

and

$$\Delta pK\,(\mathrm{A}) - \Delta pK\,(\mathrm{B}) = \log \frac{a_2\, \sigma_1^2}{a_1\, \sigma_2^2}\,(\mathrm{A}) \qquad - \log \frac{a_2\, \sigma_1^2}{a_1\, \sigma_2^2}\,(\mathrm{B}) \tag{2}$$

where pK is a logarithmic measure of strength, ΔpK (A) refers to the difference of the strengths of the acid A in the two solvents distinguished by the subscripts 1 and 2, a is the activity of the acid in its saturated solution, and σ is the mean activity of the ions in a saturated solution of some salt of the acid with a univalent cation. The value of the constant in Equation 1 is determined by the acidity scales of the solvents, the charge on the acid, and the cation of the salts. The charge has been indicated by the superscript, the cation by the subscript. The data required for the accurate comparison of two acids in two solvents are the solubilities of the acids and the selected salts, and the information necessary to relate activity and concentration in the saturated solutions.

The use of Equation 1 requires knowledge of the strength of the acid in one solvent and the independent determination of the constant. It is interesting to note that if relative strength is assumed to be independent of the solvent, the left side of Equation 2 becomes zero, leaving a relation of solubilities.

Solubilities may be used to provide an independent check on the results of potentiometric and colorimetric measurements, when a question of reliability or accuracy is raised, and to determine acid strength indirectly in solvents in which other methods are less convenient. From the theoretical side, the fact that the effect is divided into two parts, associated, respectively, with the acid and the salt, may prove to be an advantage. On the other hand, the procedure will not, in general, be highly accurate, although there is no reason as yet to say that it is less accurate than other methods employed in non-aqueous solvents. The choice of experimental conditions is restricted, and inaccuracy may result from a very high or very low solubility in one of the solvents, an effect which is more serious with the acid than with the salt, since an appropriate cation may be selected. The discrepancy between activity and concentration, especially with the acid, may be evaluated only in favorable cases, where solvents melting near room temperature, or with easily measured vapor pressures, are employed. Where mixed solvents are used, such as the otherwise convenient alcohol–water solutions, no practical method of activity measurement is known, and the use of the solubility procedure requires

(4) Ref. 1, p. 2939.

the assumption that activities may be replaced by concentrations. This is the principal weakness of the method, but it should not be serious in the comparison of acids of similar structure and roughly equivalent solubilities.

Solubilities of the Acids.—The saturated solution was obtained by shaking an excess of the acid with the solvent for twenty-four hours in a thermostat at 25 ± 0.05°. The salicylic acid measurements were run in pairs, the second solution being supersaturated by heating before immersion in the oil-bath. The values from undersaturation for benzoic acid checked so closely with those of Seidell[5] that further measurements appeared unnecessary. The titration of the acid, with sodium hydroxide standardized against benzoic acid, was carried out electrometrically with the quinhydrone electrode. In Table I the first row shows the weight per cent. of alcohol in the solvent, the second the solubility, in moles per liter of solution, of benzoic acid, the third the specific gravity, the fourth and fifth the solubility of salicylic acid from undersaturation (u) and supersaturation (s), and the last the corresponding specific gravity.

TABLE I

SOLUBILITIES OF BENZOIC AND SALICYLIC ACIDS IN ALCOHOL–WATER SOLUTIONS AT 25°

Wt. % alc.		0	18.8	37.5	56.2	75.0	93.8
Benzoic acid	u	0.0275	0.0703	0.6050	1.591	2.455	2.729
	sp. g.	1.010	.974		0.939	0.934	0.918
Salicylic acid	u	0.0153	.0388	.332	1.070	1.806	2.194
	s	.0153	.0389	.329	1.063	1.802	2.192
	sp. g.	1.011	.982	.950	0.949	0.949	0.922

Solubilities of the Silver Salts.—The silver salts were prepared by precipitation from solutions of the sodium salts. Silver benzoate was recrystallized from water; silver salicylate was washed with water, then with alcohol. The saturated solutions were obtained by following the procedure used with the acids. A tendency to produce metallic silver in small quantity was observed, but it may be assumed from the agreement of the results from supersaturation with those from undersaturation that no serious error was introduced. The concentration in the saturated solution was determined by titration with sodium chloride, standardized against silver nitrate, to an end-point with the silver electrode. Table II shows the solubilities, in millimoles per liter.

TABLE II

SOLUBILITIES OF SILVER BENZOATE AND SILVER SALICYLATE IN ALCOHOL–WATER SOLUTIONS AT 25°

Wt. % alc.		0	18.8	37.5	56.2	75.0	93.8
Silver benzoate	u	11.18	8.57	7.34	5.82	3.05	0.97
	s	11.63	8.48	7.45	5.84	3.21	.97
Silver salicylate	u	4.18	3.86	4.83	4.43	2.60	.80
	s	4.18	4.01	4.75	4.40	2.61	.80

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(5) Seidell, "Solubilities," D. Van Nostrand Co., New York, 1919, p. 134.

Variation of Relative Strength.—The solubilities may be used to determine the function log $(a_2\ \sigma_1^2)/a_1\ \sigma_2^2)$, if the assumption is made that activities may be taken as equal to the concentrations. This function, according to Equation 2, is directly related to the variation of relative strength, which is obtained from the difference of these terms for the two acids. The value of a is obtained by subtracting from the acid solubility an estimated concentration of the ionized acid, using the dissociation constants of Bradley and Lewis,[6] for salicylic acid. This correction, which is smaller with benzoic acid, may be obtained with sufficient accuracy by assuming constant relative strength. For more accurate work, this would be the first of a series of approximations, but here the second approximation is not required. In Table III, column one shows the weight per cent. of alcohol, columns two and five the concentration of undissociated acid, columns three and six the values selected for σ from the salt solubilities, columns four and seven, the function log $(a_2\ \sigma_1^2)/a_1\ \sigma_2^2)$, and the last column the variation of relative strength in logarithmic or *pK* units, referred to water as a comparison standard. The variation is the difference of the logarithmic terms, a positive value denoting greater relative strength of salicylic acid. The maximum error, neglecting the activity assumption, should be less than 0.1 unit.

TABLE III

VARIATION OF THE RELATIVE STRENGTH OF BENZOIC AND SALICYLIC ACIDS IN ALCOHOL–WATER SOLUTIONS AT 25°

	Benzoic acid			Salicylic acid			
Wt. % alc.	a	σ	Log $\frac{a_2\ \sigma_1^2}{a_1\ \sigma_2^2}$	a	σ	Log $\frac{a_2\ \sigma_1^2}{a_1\ \sigma_2^2}$	Variation
0	0.0262	11.40	0	0.0119	4.18	0	0
18.8	.0686	8.53	0.68	.0341	3.93	0.50	0.18
37.5	.6022	7.40	1.73	.323	4.79	1.31	.42
56.2	1.588	5.83	2.36	1.058	4.42	1.89	.47
75.0	2.453	3.13	3.09	1.799	2.60	2.59	.50
93.8	2.728	0.97	4.16	2.191	0.80	3.70	.46

Relative Strength from Cell Potentials with the Antimony Electrode.—The test solution was prepared by adding weighed amounts of the acid and of sodium carbonate to a small volume of the solvent, and diluting to the desired concentration after the reaction had subsided. After one minute of stirring, the solution was allowed to stand until equilibrium was reached (one to two hours). A filter paper plug in a 1-mm. tube was used in the construction of the liquid junction. Except for these points, the procedure was the same as that previously used. Reproducibility, within three mv., was demonstrated by repeating the initial measurement with a new solution after nine intervening determinations covering a period of several days. The error in relative strength, neglecting the liquid

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(6) Bradley and Lewis, *J. Phys. Chem.*, **29**, 782 (1925).

junction, should not, therefore, be greater than 0.1 logarithmic unit. To increase conductance and minimize the salt effect, an ionic strength of 0.1 was maintained by means of lithium chloride. To test for association, measurements were made at three concentrations. The difference between the values at 0.05 *m* and 0.005 *m* in 75% alcohol might be due either to association or to a salt effect, but, since this difference appears with both acids, the relative strength is not seriously affected.

In Table IV the first column shows the weight per cent. of alcohol, the second the concentration of acid (and sodium salt), the third and fourth the potentials with benzoic and salicylic acids, the fifth the corresponding relative strength, assuming that a ten-fold change of hydrogen-ion concentration produces a 55-mv. potential change, and the last the variation of relative strength, obtained by subtracting the relative strength in water (1.19 units). The relative strength has not been calculated from the potentials obtained with the 0.0005 molal solutions, because in such dilute solutions, even in 75% alcohol, salicylic acid is no longer a typical weak acid.

The corresponding results of Michaelis and Mizutani,[2] who used the hydrogen electrode, are smaller by about 0.1 unit.

TABLE IV

VARIATION OF RELATIVE STRENGTH FROM CELL POTENTIALS AT 25°

Wt., % alc.	Acid concn.	*E* (benzoic)	*E* (salicylic)	Relative strength	Variation
37.5	0.05	0.275	0.190	1.55	0.37
	.005	.278	.189	1.62	.44
	.0005	.279	.203		
42[a]	.05	.285	.195	1.63	.45
56.2	.05	.308	.215	1.69	.51
	.005	.305	.214	1.64	.46
	.0005	.308	.221		
75.0	.05	.330	.238	1.67	.51
	.005	.323	.228	1.73	.55
	.0005	.320	.233		

[a] From the measurements previously published.

Ionization Constants.—By combining the data of Tables III and IV with the ionization constant of benzoic acid in water and that of salicylic acid in the alcohol–water solutions, the latter obtained from the conductance measurements of Bradley and Lewis, the ionization of benzoic acid in the alcohol–water solutions may be determined. In Table V the first row shows the weight per cent. of alcohol, the second the *pK* of salicylic acid by interpolation of the results of Bradley and Lewis, and the third and fourth the corresponding values for benzoic acid, from solubilities and cell potentials. As an example, the figure 4.57 (third row, second column) is the sum of the strength difference in water (1.18), the *pK* of salicylic acid in 18.8% alcohol (3.21), and the difference of relative strength (0.18).

TABLE V

IONIZATION OF BENZOIC ACID IN ALCOHOL–WATER SOLUTIONS AT 25°

Wt. % alc.	0	18.8	37.5	56.2	75.0	93.8
pK (salicylic)	3.00	3.21	3.70	4.20	4.82	6.20
pK (benzoic solubility)	(4.18)	4.57	5.30	5.85	6.50	7.84
pK (benzoic e. m. f.)			5.28	5.87	6.53	

These results are not strictly comparable with those of Michaelis and Mizutani, since their pK' values are obtained by an interpretation which is equivalent to the arbitrary assignment of the value zero to the normal hydrogen electrode potential in any alcohol–water solution. However, the qualitative agreement between their results and those of Table V shows that this condition is approximately fulfilled, so that their procedure may be used to obtain dissociation constants in alcohol–water solutions. A similar result has been obtained by Kuhn and Wassermann,[7] for 50% methyl alcohol, and a theoretical discussion of this point has been given by Schwarzenbach.[8]

Summary

The relative strength of benzoic and salicylic acids in a series of alcohol–water solutions, measured with the antimony electrode, is found to agree closely with that determined from the solubilities of the acids and their silver salts. The antimony electrode may be used in solutions of high alcohol content, against an aqueous calomel cell, to obtain reliable values of relative acid strength. The relative strength varies with the concentration of alcohol by as much as 0.5 logarithmic unit.

ANN ARBOR, MICHIGAN RECEIVED NOVEMBER 29, 1932
PUBLISHED JUNE 6, 1933

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[7] Kuhn and Wassermann, *Helv. Chim. Acta*, **11**, 17 (1928).

[8] Schwarzenbach, *ibid.*, **13**, 870 (1930).