

showed a strongly acid reaction. The hydrolytic adsorption accounts for the irregular change of the bromate adsorption at different salt concentrations as it will be a function of the pH of the solution in equilibrium with the solid.

TABLE VII
ADSORPTION OF BROMATE FROM CALCIUM BROMATE
10 g. of $BaSO_4$; 50 ml. of solution

Init. concn., molar $\times 10^3$	1	0.5	0.4	0.2
Final concn., molar $\times 10^3$	0.764	0.358	0.303	0.169
Adsorbed BrO_3^- in %	23.6	28.4	24.3	15.5
$x/m \times 10^5$	0.12	0.071	0.049	0.015

2. In Table VIII the relation is given between adsorbability from and solubility of the barium salts in 50% ethanol. The value of the constant a in the expression for the adsorption isotherm (equation 1) is taken as a measure of the adsorbability. From the experimental data, a and $1/n$ were calculated for four barium salts, an average value of 0.38 for $1/n$ being found. For the other

TABLE VIII
SOLUBILITY AND ADSORBABILITY

Barium salt	Order of adsorbability expressed in $a \times 10^4$	Relative solubility in 50% ethanol	Order of increasing solubility
1 Bromate	1.80	1	1
2 Formate	0.91	81	3
3 Nitrate	.69	33	2
4 Perchlorate	.59	1610	7
5 Chloride	.54	223	4
6 Bromide	.37	848	5
7 Iodide	.35	1477	6
8 Thiocyanate	.26	1663	8

barium salts, the adsorption of which was determined at one concentration only, the value of $1/n$ equal to 0.38 was used in the calculation of the " a " values.

It is seen that there is no close parallelism between adsorbability and solubility.⁹ Barium formate is adsorbed more strongly than the nitrate, although the latter is much less soluble. Particularly the perchlorate is out of place. Its adsorbability is of the same order as that of the chloride and much greater than that of the bromide or iodide, although its solubility in 50% ethanol is greater than that of the halides.

Summary

1. The adsorption of barium salts on barium sulfate and of salts not having an ion in common with the lattice is much greater from 50% ethanol than from water.

2. Contrary to the expectation, the adsorption of barium salts from 50% ethanol on barium sulfate follows the Freundlich adsorption isotherm.

3. No close parallelism has been found between adsorbability and solubility.

4. Potassium bromate gives an equivalent adsorption of cations and anions. Calcium bromate yields a hydrolytic adsorption and was found to be adsorbed in the form of $Ca(OH)(BrO_3)$.

(9) For a similar conclusion on the adsorption of silver salts on silver iodide compare the study of J. S. Beekley and H. S. Taylor, *J. Phys. Chem.*, **29**, 942 (1925).

MINNEAPOLIS, MINN.

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The Primary and Secondary Dissociation Constants of Malonic, Succinic and Glutaric Acids by Potentiometric Titration

BY WILLIAM L. GERMAN AND ARTHUR I. VOGEL

The primary thermodynamic dissociation constants at 25° of malonic, succinic and glutaric acids have been determined by conductivity methods by Jeffery and one of us¹ but it has not yet been found possible to calculate the true secondary dissociation constants satisfactorily from conductivity data alone. Attention was therefore directed to the potentiometric method for the simultaneous evaluation of both constants. Previous electrometric titrations for these three

(1) Jeffery and Vogel, *J. Chem. Soc.*, 21 (1935).

acids have been carried out by Britton² at 18°, Gane and Ingold³ at 25° for malonic acid; by Bjerrum⁴ at 18°, Auerbach and Smolczyk⁵ at 20°, Britton² at 18°, Kolthoff and Bosch⁶ at 18°, Gane and Ingold³ at 25°, Ashton and Partington⁷ at 25° for succinic acid; and by Gane and Ingold³ at 25°

(2) Britton, *ibid.*, **127**, 1906 (1925).

(3) Gane and Ingold, (a) *ibid.*, 1594 (1928); (b) 2158 (1931).

(4) Bjerrum, *Z. physik. Chem.*, **106**, 227 (1923); cf. Larsson, *Z. anorg. allgem. Chem.*, **123**, 291 (1925).

(5) Auerbach and Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924).

(6) Kolthoff and Bosch, *Rec. trav. chim.*, **47**, 861 (1928).

(7) Ashton and Partington, *Trans. Faraday Soc.*, **30**, 598 (1934).

for glutaric acid. The large differences between the results of the various investigators for succinic acid cannot be attributed solely to the varying concentration and temperatures at which the titrations were performed; a particularly large discrepancy is that for succinic acid obtained by Gane and Ingold with the hydrogen electrode and by Ashton and Partington with the quinhydrone electrode. Gane and Ingold^{3b} (p. 2153) remark in connection with the correction of their data for interionic effects that "the application of the Debye and Hückel equation for activities of electrolytes . . . involves practical difficulties" and they have accordingly employed an empirical method involving the determination of "*K*" at a series of concentrations and extrapolating to zero concentration. We have carried out new potentiometric titrations of malonic, succinic and glutaric acids against sodium hydroxide with the quinhydrone electrode at 25° and have calculated the thermodynamic dissociation constants by the method described recently by German, Jeffery and Vogel.⁸ Table I summarizes our results: the conductivity values of Jeffery and Vogel¹ and Gane and Ingold's figures calculated by their empirical method, are included for purposes of comparison.

TABLE I

Acid	K_1 therm. $\times 10^3$ (Cond.)	Authors		Gane and Ingold	
		K_1 therm. $\times 10^3$	K_2 therm. $\times 10^3$	K_1 therm. $\times 10^3$	K_2 therm. $\times 10^3$
Malonic	139.7	143	2.20	149	2.03
Succinic	6.626	6.37	2.54	6.41	3.33
Glutaric	4.535	4.46	3.77	4.53	3.80

It will be noted that the agreement of our potentiometric with the conductivity values for K_1 is within 2.5, 4 and 2% for malonic, succinic and glutaric acids, respectively.

Calculation shows that an error of one millivolt will cause a variation of *ca.* 5% in both K_1 and K_2 . Our measurements were in general reproducible to 0.2–0.3 millivolt so that no greater accuracy than 1–2% could be expected in the final figures for K_1 and K_2 . The somewhat greater difference for K_1 actually found must be attributed to the inherent disadvantages of the method of calculation. It would appear therefore that no greater accuracy than 2–4% can be realized in the determination of K_1 and K_2 by potentiometric titration with the quinhydrone electrode under the experimental conditions that we have employed.

(8) German, Jeffery and Vogel, *J. Chem. Soc.*, 1624 (1935).

The mean values of the true dissociation constants together with the intercarboxylic distances, expressed in Å., calculated after Bjerrum⁴ (A) and Gane and Ingold^{3b} (p. 2161) (B) are collected in Table II. Gane and Ingold's values^{3b} (p. 2153) (G. and I.) for these acids are added for comparison.

TABLE II

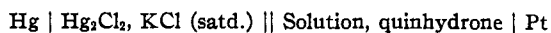
Acid	K_1 therm. $\times 10^3$	K_2 therm. $\times 10^3$	<i>r</i> (A)	<i>r</i> (B)	<i>r</i> (G. and I.)
Malonic	143	2.20	1.39	3.47	3.43
Succinic	6.37	2.54	3.89	5.13	5.58
Glutaric	4.46	3.77	6.60	7.15	7.11

Experimental

Preparation of Materials. Acids.—The details have been described by Vogel⁹ and by Jeffery and Vogel¹ (p. 23). Kahlbaum pure malonic acid was recrystallized twice from benzene–ether–light petroleum (b. p. 60–80°) and melted at 136° (dec.). Kahlbaum pure succinic acid was recrystallized from acetone and melted at 185–185.5°. Glutaric acid was prepared from the nitrile, b. p. 149–150° (14 mm.), and after crystallization from chloroform melted at 97.5–98°.

Sodium Hydroxide Solutions.—These were prepared by the electrolysis of chemically pure sodium chloride solution with a mercury cathode as described by Jeffery and Vogel¹⁰ and were standardized immediately before use with constant b. p. hydrochloric acid.¹¹ All dilutions were carried out with equilibrium water prepared in a "Vogel" still.¹² The quinhydrone and calomel were prepared as detailed by German and Vogel.¹³

Apparatus.—Full details have been given by German and Vogel¹³ and by German, Jeffery and Vogel.⁸ An electrically-controlled oil thermostat maintained at 25 ± 0.01° was used. Stirring was effected with purified nitrogen. All titrations are accurate to 0.01 cc. The cell employed was



The liquid junction potential was assumed to be negligible. Standardization was effected before and after each titration against at least two independent 0.1 *N* calomel cells¹⁴ for which a value of 0.3376 volt was assumed,^{15,16} and also against 0.05 *M* potassium hydrogen phthalate (chemically

(9) Vogel, *ibid.*, 336 (1934).(10) Jeffery and Vogel, *Phil. Mag.*, **15**, 400 (1932).(11) Jeffery and Vogel, *J. Chem. Soc.*, 409 (1932).(12) Vogel, *ibid.*, 1201 (1931).(13) German and Vogel, *ibid.*, 913 (1935).(14) Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

(15) Clark, "The Determination of Hydrogen Ions," 1928, p. 487.

(16) MacInnes and Belcher, *THIS JOURNAL*, **53**, 3325 (1931).

modynamic" dissociation constants²¹ were calculated from $pK_{1\text{therm.}} = pK_{1\text{incomp.}} + 0.505 \mu^{0.5}$ (i) and $pK_{2\text{therm.}} = pK_{2\text{incomp.}} + 1.515 \mu^{0.5}$ (ii), where $pK_{1\text{therm.}} = -\log K_{1\text{therm.}}$ etc., and the total ionic strength, which was deduced from the expression⁸

$$\mu = 0.5 \left(a + h + c \left\{ \frac{1}{(h/K_1 + 1 + K_2/h)} + \frac{4}{(h/K_2 + 1 + h^2/K_1K_2)} \right\} \right)$$

where c is total acid concentration, a is concentration of sodium hydroxide added, h is hydron concentration, and K_1 and K_2 are the "incomplete" (previously termed "classical") values.

The use of the approximate expressions (i) and (ii) over the concentration range ($\mu = 0.0015$ to 0.006) that we have employed is justified by the following considerations. Morton²² has deduced the equation

$$p_k = p\text{H} + \log [\text{Acid}]/[\text{Salt}] + \log f_a/f_s$$

in which f_a and f_s are the activity coefficients of

(21) It is appreciated that this term should be strictly confined to values obtained by experimental technique which does not involve uncertainties in liquid junction potentials and by strict thermodynamic methods, as in the precise work of Harned and co-workers. It is believed, however, that the approximations introduced are sufficiently precise for the ultimate accuracy of 2-3% which is claimed to justify the use of the term.

(22) Morton, *J. Chem. Soc.*, 1406 (1928).

the undissociated acid and of the salt anions or of the acid anions of lower and higher valency, respectively. This may be written in the form

$$pK_{1\text{therm.}} = pK_{1\text{incomp.}} + \log f_a/f_s \\ = pK_{1\text{incomp.}} + (n - 0.5)\mu^{0.5} - B\mu$$

since $\log f_a/f_s = (n - 0.5)\mu^{0.5} - B\mu$; n is the basicity of the acid. For phthalic acid, which is the acid most closely allied to those that we have studied, the highest value of B found by Morton was approximately 1 and this was in the presence of $M/3$ potassium sulfate. It can be readily shown that with $B = 1$ in the most concentrated solutions that we have employed, the maximum error introduced by the neglect of this term is ca. 1%. Actually the error will be much less than this.

Summary

The thermodynamic dissociation constants of malonic, succinic and glutaric acids have been determined by potentiometric titration with the quinhydrone electrode. The values for the primary dissociation constants agree within 2-4% with those determined by conductivity.

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β -Amoxyethyl Esters of *p*-Aminobenzoic Acid

BY H. V. ASHBURN, A. R. COLLETT AND C. L. LAZZELL

In continuation of our work on the β -alkoxyethyl esters of *p*-aminobenzoic acid,¹ we have prepared a series of six amoxyethanols, three of which are new, together with the corresponding *p*-nitro and *p*-aminobenzoates. The alcohols used were purified by fractional distillation, until a sample having a boiling point range of 0.5° or less was obtained.

β -Amoxyethanols

The β -amoxyethanols were prepared by heating the desired alcohol with ethylene oxide in the presence of a small amount of sulfuric acid as a catalyst² except in the case of the tertiary amoxyethanol, for which acid aluminum fluosilicate was used as a catalyst.³

The method was as follows: 20 to 30 moles of the alcohol, 7 moles of ethylene oxide, and 1 cc.

of concentrated sulfuric acid were placed in an autoclave and heated at 130 - 150° for eight to ten hours. The autoclave was then emptied and the contents fractionally distilled. The tertiary amyl compound was prepared by using acid aluminum fluosilicate as the catalyst and heating at 130 - 150° for twenty-five hours.

These compounds are all colorless, sweet smelling liquids, very soluble in alcohol and ether. The iso primary amyl, active primary amyl and tertiary amyl compounds are all appreciably soluble in water at 25° while the *n*-primary amyl, secondary amyl and active secondary amyl compounds are only slightly soluble.

Table I lists the yields and physical constants of all the amoxyethanols prepared, together with the analyses of the new compounds. The tertiary butoxyethanol has been prepared since the only physical property recorded in the literature is the boiling point, 150 - 153° . Its density is 0.8935

(1) Ashburn, Collett and Lazzell, *THIS JOURNAL*, **57**, 1862 (1935).

(2) German Patent 580,075, July 5, 1933; *C. A.*, **27**, 4814 (1933).

(3) French Patent 39,773, Feb. 17, 1931; *C. A.*, **26**, 4826 (1932).