

2. Flocculation values for a number of electrolytes were determined by the classical method.

3. The chloride-free ferric oxide sol prepared was found to differ from ferric oxide sols prepared and studied by other investigators in that it followed the Burton-Bishop coagulation rule. Furthermore, it gave uniformly lower flocculation values than did these sols. By adding chloride to this chloride-free sol its behavior could be made to conform to that displayed by similar sols prepared by other investigators. The conclusion was drawn that the striking behavior of this sol was due to the absence of detectable chloride. This behavior serves to emphasize the fact that the variation of the flocculation value of anions with dilution of the sol is a function of the purity of the sol; that is, the validity or invalidity of the Burton-Bishop rule is apparently determined by the purity of the sol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

### THE SOLUBILITY, SPECIFIC GRAVITY AND INDEX OF REFRACTION OF AQUEOUS SOLUTIONS OF FUMARIC, MALEIC AND *i*-MALIC ACIDS

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The stereoisomerism of these acids makes any data on them of theoretical interest. The physical properties are scattered throughout the literature, mostly as isolated observations; the latest and most comprehensive list of values are those reported by Weiss and Downs.<sup>1</sup> The present investigation was undertaken with a view of obtaining a more complete series of values—the solubility in water at rather close intervals of temperature, the density of aqueous solutions and the refractive index of aqueous solutions. The values for the solubility are in good agreement with those reported by Weiss and Downs with the exception of the solubility of maleic acid at 60°; the value at this temperature as reported by them was found to be very close to the solubility at 50°.

The acids used in these determinations were the commercial grades which were subjected to a further purification. After two crystallizations from water it was found that the melting points of maleic and fumaric acids remained constant. Malic acid, which is very soluble in water, was purified by a crystallization from water, filtering, digesting the crystals with hot acetone, cooling to room temperature, filtering and air drying at room temperature. The three acids were then dried *in vacuo* at room temperature; the melting points of maleic, fumaric and malic acids thus obtained were found to be 130, 284 and 128.5°, respectively. Weighed samples when dis-

<sup>1</sup> J. M. Weiss and C. R. Downs, *THIS JOURNAL*, **45**, 1003 (1923).

solved in water and titrated against standard 0.1 *N* sodium hydroxide solution (standardized against pure succinic acid) showed a purity of +99.8%. All of the data obtained in this work are based upon weights in air.

**Solubility in Water.**—The solubility determinations were made by suspending an excess of the acid in water contained in 100-cc. Soxhlet flasks which were then almost completely immersed in a water-bath which was maintained at the desired temperature within  $\pm 0.2^\circ$ . The temperature was determined by means of thermometers which had recently been calibrated by the U. S. Bureau of Standards. The contents of the flask was kept agitated by means of a glass stirrer. Samples of the solution were taken from the flask by means of a small pipet of about 5–6-cc. capacity (the low solubility of fumaric acid necessitated using larger pipets) which had previously been brought to the temperature of the solution under investigation. After removal of the cotton filter from the tip of the pipet, the weight of the sample in the pipet was determined, the sample transferred to a beaker for titration or to a volumetric flask for titration against standard 0.1 *N* sodium hydroxide solution with phenolphthalein indicator. The solubility equilibrium was approached from both temperature directions. Several successive samples were taken at each temperature to determine when equilibrium was attained and it was found that 12 to 14 hours of agitation was sufficient. Determinations were made at approximately  $5^\circ$  intervals of temperature and from these results a curve was plotted. The following equations express the solubility (*C*) of the acids in water at temperatures (*t*) between 5 and  $80^\circ$  in terms of grams of acid per 100 g. of solution. The solubility for maleic acid is nearly a straight line and the two equations for this acid as given below give values within the limits of experimental error.

$$\text{Fumaric acid } \log C = 0.01672t - 0.6362$$

$$i\text{-Malic acid } C = 0.438t + 47.04$$

$$\text{Maleic acid } C = 0.645t + 28.2 \text{ (for temperatures from } 5 \text{ to } 40^\circ), \text{ and}$$

$$C = 0.492t + 34.5 \text{ (for temperatures above } 40^\circ)$$

**Specific Gravity of Aqueous Solutions.**—The densities of the solutions at  $20/4^\circ$  were determined by dissolving the acid in water, filtering, diluting to different extents and determining the specific gravity of the various dilutions by means of a pycnometer; the concentration of acid in each of the various dilutions was determined by titration of weighed samples of solution against standard 0.1 *N* sodium hydroxide with phenolphthalein indicator. From these results a curve was plotted. The curves were exceedingly regular and that in the case of maleic acid was a straight line; the curve for *i*-malic acid is nearly a straight line, for which the following two equations of straight lines give values within the limits of experimental error. No values for the specific gravity of fumaric acid solutions are given because of the low solubility of this acid at  $20^\circ$ . The following equa-

tions express the concentration ( $C$ ) of acid in grams per 100 g. of aqueous solution corresponding to the specific gravity ( $d$ ) at 20° referred to water at 4°.

Maleic acid  $C = 276.78(d - 0.9982)$ , for values of  $d$  up to 1.071

*i*-Malic acid  $C = 244.55(d - 0.9982)$ , for values of  $d$  less than 1.108, and

$C = 216.17(d - 0.9839)$  for values of  $d$  from 1.108 to 1.169

**Index of Refraction.**—The index of refraction was determined at 20° on aqueous solutions prepared as described under specific gravity and the readings were made with a Zeiss immersion refractometer using the prism which gives a reading of 14.5 with distilled water at 20° ( $14.5 = n_D = 1.33301$ ). The following equations express the concentration of acid in grams per 100 g. of aqueous solution corresponding to the immersion refractometer reading ( $r$ ).

Fumaric acid g./100 g. of solution =  $0.263r - 3.814$  (for values of  $r$  from 14.5 to 16.3)

Maleic acid g./100 g. of solution =  $0.272r - 3.922$  (for values of  $r$  from 14.5 to 95)

Malic acid g./100 g. of solution =  $0.323r - 4.68$  (for values of  $r$  from 14.5 to 45.5), and  
g./100 g. of solution =  $0.289r - 3.132$  (for values of  $r$  from 45.5 to 95)

### Summary

The solubility, specific gravity and index of refraction of aqueous solutions of fumaric, maleic and *i*-malic acids have been determined; equations representing these values are given.

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## THE VELOCITY OF SAPONIFICATION OF ETHYL FORMATE BY AMMONIUM HYDROXIDE IN THE PRESENCE OF AMMONIUM SALTS

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In early work by Drs. Julius Stieglitz and Edith E. Barnard<sup>1</sup> of this Laboratory, it was found that although ethyl and methyl formates are hydrolyzed at immense speed in dilute solutions of strong bases,<sup>2</sup> the velocity of these reactions may be measured in suitable mixtures of ammonium hydroxide and ammonium salts. The present paper<sup>3</sup> represents a continuation of this work in the case of ethyl formate.

<sup>1</sup> The work referred to had been completed before 1911.

<sup>2</sup> Bibliography of published reports on the alkaline hydrolysis of methyl and ethyl formates: (a) Trautz and Volkmann, *Z. physik. Chem.*, **64**, 53 (1908); (b) Nernst, *Ber.*, **42**, 3178 (1909); (c) Handa, *ibid.*, **42**, 3179 (1909); (d) Eucken, *Z. physik. Chem.*, **71**, 550 (1910); (e) Skrabal and Sperk, *Monatsh.*, **38**, 191 (1917). Only the last reference contains data bearing on the present problem. Reference will be made to this later.

<sup>3</sup> The experimental work of this paper was completed in 1918 by Dr. Roberts in partial fulfilment of the requirements for the degree of Doctor of Philosophy at this University. See also Terry and Stieglitz, *THIS JOURNAL*, **49**, 2216 (1927).