[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, RUSH MEDICAL COLLEGE.]

THE VOLATILITY WITH STEAM OF LOWER FATTY ACIDS IN DILUTE AQUEOUS SOLUTIONS.

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Received August 4, 1919.

In some tests of the volatility of the lower α-hydroxy aliphatic acids in dilute aqueous solutions of formic, acetic, propionic or butyric acids, it was again observed[1] that the behavior of the fatty acids in this respect is contrary to the laws of simple mixtures. The 4 fatty acids in dilute aqueous solutions show an increasing volatility with increasing molecular weight. It is proposed here to give briefly a few experimental data and to indicate how these relationships, which are commonly stated to be abnormal, are to be expected on the basis of existing knowledge of the molecular state and hydration of these acids in aqueous solution.

The experiments were done as follows: 2 g. of formic acid (by titration) and the corresponding molecular amounts of the 3 other acids, were each made up to 200 cc. with water. Five cc. of the solutions were pipetted off and titrated with 0.1 *N* sodium hydroxide solution in order to confirm the concentration of the solution. The remaining 195 cc. was transferred to a common distilling flask (500 cc.) and distilled off slowly in 20 cc. fractions correct to within one drop. The receiver (a calibrated test-tube) was emptied and rinsed. The fractions were then titrated separately with 0.1 *N* sodium hydroxide solution. Typical data are given in the table.

TABLE I.

Relative Volatility of Lower Fatty Acids. (Cc. 0.1 *N* NaOH).

	Fraction. Cc.	Formic. Cc.	Acetic. Cc.	Propionic. Cc.	Butyric. Cc.
	5	10.80	10.82	10.78	10.81
1	20	16.70	29.33	52.87	81.92
2	20	19.07	30.85	52.10	71.35
3	20	20.36	32.36	50.10	62.98
4	20	22.65	33.80	47.94	53.77
5	20	24.40	35.63	45.60	44.62
6	20	28.48	38.40	43.00	36.30
7	20	33.76	41.45	39.90	28.39
8	20	42.17	46.70	36.60	20.34
9	20	59.45	56.00	33.03	13.36
Residue		155.88	79.05	24.40	6.58
Total		422.92	423.57	424.54	419.61
Calculated		421.20	421.98	420.42	421.59

The above results are given graphically in Fig. 1.

It appears clearly that there is a gradually increasing volatility of

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[1] Duclaux, *Ann. chim. phys.*, **2**, 289 (1874); *Ann. inst. Pasteur*, **9**, 265 (1895); cf. also Upson, Plum and Schott, THIS JOURNAL, **39**, 731–42 (1917).

these 4 acids of the aliphatic series with increasing molecular weight, although the boiling points of the acids rise gradually from 101° for formic to 162° for butyric acid. Thus the first fractions contain 3.94% of the formic, 6.92% of the acetic, 12.4% of the propionic, and 19.5% of the butyric acid used, respectively. For the last fractions this order is reversed as shown, and the acid remaining in the distilling flask is as follows: formic acid 36.8%, acetic 18.6%, propionic 5.7%, butyric 1.4%, respectively, of the acid taken.

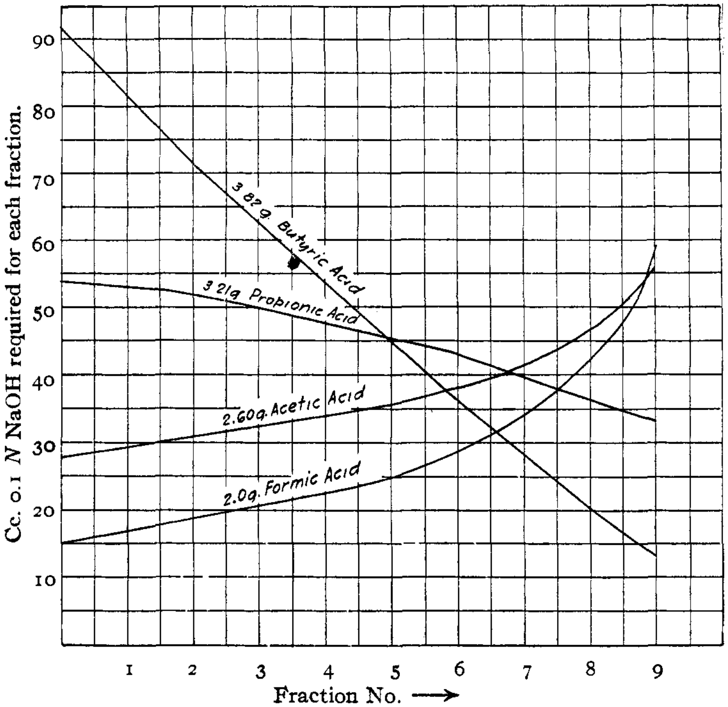

Fig. 1.—Relative volatility of the lower fatty acids from boiling aqueous solutions.

The interpretation of these data on the basis of existing knowledge may be briefly stated as follows:

(1) That along with their clearly demonstrated powers of molecular association[1] these 4 acids form hydrates with water.

(2) The hydration, as well as the molecular association of these acids, varies in amount and stability.[2]

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[1] Jones, *Carnegie Inst. Publications*, 1915, 210; cf. summary and list of earlier publications at the end. Turner, "Molecular Association," Longmans, Green & Co. (1915).

[2] Cf. Turner, *Loc. cit.* for review; Roscoe, *Ann.*, 125, 320 (1863); Peddle and Turner, *J. Chem. Soc.*, 89, 1439 (1907); Colles, *Ibid.*, 89, 1246 (1906); Jones, *Loc. cit.*, p. 148.

(3) The hydrates of greatest stability appear to occur with formic acid (cf. Roscoe, Colles) and this stability appears to diminish with increase in the molecular weight of the 4 fatty acids. It seems evident that this greater stability is due to affinities of the carboxyl group and that the diminishing stability is associated with the increasing hydrocarbon function.[1]

(4) That the hydrates of these acids presumably have the power of lowering the partial vapor pressure of the acid in dilute solutions was definitely established, at least for formic acid, by Roscoe.[2]

(5) It is because of this capacity of the hydrates to lower the partial vapor pressure of the acid that the volatility of these acids in dilute aqueous solution presents a reverse picture as compared with what would be expected if the solutions were simple physical mixtures of the two ingredients. When the decreasing stability of the hydrates at the boiling point of the mixture is considered it appears that the behavior of these acids from the standpoint of simple mixtures tends to become less anomalous on passing from formic to butyric acid. Accordingly, hydration phenomena probably have less influence on the volatilization of higher fatty acids (stearic acid) with steam than on those here discussed.

(6) The behavior of dilute solutions of these acids on distillation apparently constitutes evidence of hydration of these compounds since it agrees with all the other data on this subject.

Of the above statements (5) and (6) are perhaps novel.

The Effect of Neutral Salts.

From the existing data regarding the effects of salts on the hydration of another salt in the same solution[3] as well as from Kolossovsky's[4] observations of the influence of salts on the partition of acetic acid between ether and water, the addition of a neutral salt, to such solutions as were used above should produce an increase in the volatility of the fatty acid. This increase in volatility should be greater the greater the concentration of the salt used. That this is true is shown by the data represented in Fig. 2, which were obtained by the same method used above, except that the acetic and formic acids used were weighed. In a 0.5 M solution of magnesium chloride (III) the 15 cc. of residue remaining in the distilling flask contains no acetic acid. In (II) this residue consumes 22.65 cc. of 0.1 N sodium hydroxide solution, and in (I) it requires 55.75 cc.

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[1] This statement is also supported by Auwer's generalizations on the relation of constitution of solvent and solute to the molecular weight of the latter (*Z. physik. Chem.*, **15**, 33 (1894); **18**, 595 (1895); **30**, 529 (1899); **42**, 513, 542 (1903)) provided the reasonable assumption is made that the ethyl and propyl groups come first beyond the methyl group in this series.

[2] *Loc. cit.*

[3] Jones and Stine, *Am. Chem. J.*, **39**, 313 (1908).

[4] *Bull. Soc. chim. belg.*, **25**, 183 (1911); *Bull. Soc. chim.*, [4] **9**, 632 (1911).

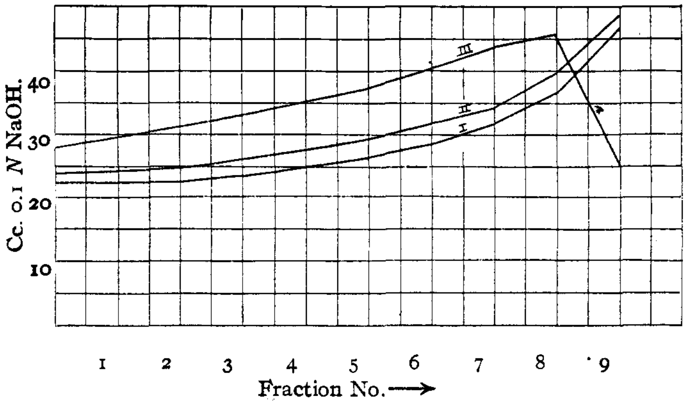

Fig. 2.—Effect of dissolved magnesium chloride on the volatility of acetic acid from boiling aqueous solutions.

2.0 g. acetic acid in 200 cc. { I—H_2O.
II—0.1 *M* $MgCl_2$.
III—0.5 *M* $MgCl_2$.

In Fig. 3 similar results for formic acid are given.

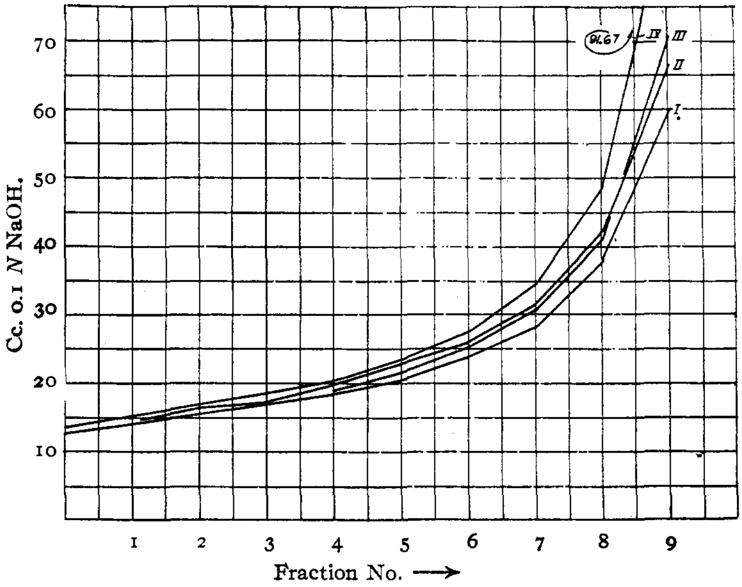

Fig. 3.—Effect of dissolved potassium and magnesium chlorides on the volatility of formic acid from boiling aqueous solutions.

2 g. formic acid in 200 cc. { I—H_2O.
II—0.1 *M* $MgCl_2$.
III—0.5 *M* KCl.
IV—0.25 *M* $MgCl_2$.

That this increased volatility is not solely a function of the concentration of the salt is suggested by the results for (II) and (III) in Fig. 3. For (III), in which the molecular salt concentration is 5 times greater than in (II), the increase in volatility over (I) averages less than for (II). This apparently indicates that 5 molecules of potassium chloride have a little less positive influence on the volatility of formic acid in this solution than one molecule of magnesium chloride. In experiments with acetic acid, not described here, in a 0.5 *M* potassium chloride solution, the volatility was just a little greater than in a 0.1 *M* magnesium chloride solution.

These results are relatively just what would be expected from our knowledge of the hydration of these salts and thus give further confirmation to the interpretation of the volatility of these acids given above.

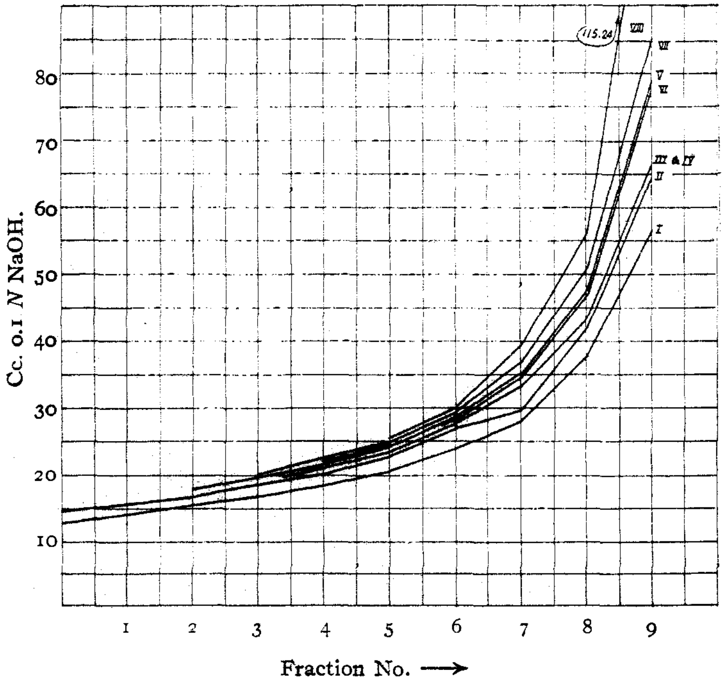

Fig. 4.—Influence of dissolved salts (0.25 *M*) on volatility.

2.0 g. formic acid in 200 cc.
I—H_2O.
II—KCl.
III—NaCl sol.
IV—$BaCl_2$ sol.
V—$SrCl_2$.
VI—$CaCl_2$.
VII—$MgCl_2$.
VIII—$AlCl_3$.

It was of interest to learn whether these relations could be extended in the manner suggested by the deductions of Poma and Albonico[1] regarding the neutral salt effect on the hydrolysis of esters. If their deductions were applicable here equimolecular amounts of metallic salts such as chlorides, for instance, should produce an increasing volatility with the decreasing electro-affinity of the metallic ion of the added salt. Experiments with 0.25 *M* solution of the chlorides of potassium, sodium, barium, strontium, calcium, magnesium, aluminum, manganese, iron and copper were carried out. The volatility was, slightly and progressively, a little increased for each member of this series over the preceding member up to and including aluminum, except in the case of strontium and calcium, for which the order given above should be reversed. The solutions of manganese, iron and copper chlorides showed anomalies and give increases in volatilities lower than aluminum chloride.

Part of the results are given in graphic form in Fig. 4. The results for sodium and barium chlorides are so nearly alike that the results for sodium chloride only were plotted (Curves III and IV).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE DEGREE OF IONIZATION OF VERY DILUTE ELECTROLYTES.

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Received August 16, 1919.

The ionic theory in its earlier days would have suffered greater criticism than it received if it had been generally known how great were the discrepancies between the actual behavior of electrolytes and that which was calculated so confidently from the various equations in common use. The failure of the mass law for strong electrolytes was recognized, but in the case of uni-univalent electrolytes, which were most commonly studied, this could be attributed to minor errors in the measurement of conductivity or in Kohlrausch's law of the constancy of ionic mobilities. However, as quantitative data accumulated regarding electromotive force, freezing points, solubilities and the like, it became increasingly evident that the equations generally employed lead to errors which were never trivial and which in some cases became enormous.

The equations in question were based in part upon a safe foundation of thermodynamics, but also in part upon two assumptions of doubtful validity. The first of these assumptions was that the concentration of the ions could be obtained from conductivity ratios. The second was the assumption that the ions and undissociated parts of an electrolyte

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[1] *Atti accad. Lincei*, **24**, I, 747, 979; II, 43 (1915).