

## 542. *The Composition of Acetic Acid-Water Mixtures.*

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An analysis, based on density data, gives the approximate composition of aqueous solutions of acetic acid in terms of the mole-fractions of water and of monomeric and dimeric acetic acid over the complete concentration range. It is assumed that the monomer is present mainly in the hydrated form, as is suggested by the Raman spectra. The results are used in a further analysis, which is based on the law of mass action equations for the equilibria of dimerisation and hydration of monomeric acetic acid. This treatment gives the mole-fractions of hydrated and unhydrated monomer separately.

It has long been known that the density of aqueous solutions of acetic acid is not a linear function of either volume or weight concentration, the curves showing a maximum at about 77% acetic acid by weight at room temperature. A similar maximum is also found in the curves for viscosity and refractive index. Krishnamurti (*Nature*, 1931, **128**, 639; *Indian J. Physics*, 1930, **6**, 401) has investigated the Raman spectra of these solutions. On dilution of glacial acetic acid, a new line appears which he attributed to the formation of a hydrate,  $\text{CH}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ . He noted that in 75% solution, this line had completely replaced the characteristic line given by glacial acetic acid, and drew attention to the fact that the hydrate contains 77% of acetic acid by weight, corresponding to the solution of maximum density. Holmes (*J.*, 1906, 1774) had earlier pointed out that for aqueous solutions of formic, propionic, and *n*-butyric acids, as well as for acetic acid, the contractions in the percentage volumes occupied by the acids is greatest (at 20°) for a 1:1 molecular ratio, water:acid.

From our present knowledge of hydrogen bonding, it might be expected that monomeric acetic acid would form hydrogen bonds with water (to give a hydrate) and with itself (to give the dimer) to comparable extents, in so far as an O—H---O bond would be involved in each case. The postulate of a monomer hydrate, already familiar in the case of ammonia and its derivatives, has also been made for benzoic and salicylic acids (Szyszkowski, *Z. physikal. Chem.*, 1927, **131**, 175). The existence of acetic acid hydrate has been questioned by Koteswaram (*Z. Physik*, 1938, **110**, 118), but has been re-affirmed after a more detailed investigation by Traynard (*Bull. Soc. chim.*, 1947, 316).

The Raman spectra referred only to a few chosen concentrations, and did not cover the complete range of concentration. In view of this, we have attempted (for a single temperature, 20°) a semiquantitative analysis in order to give a more detailed picture of the compositions of solutions of all concentrations. The approach is in two stages. In each case it is assumed that glacial acetic acid exists almost entirely as the dimer at 20°. This is in accordance with the findings of MacDougall (*J. Amer. Chem. Soc.*, 1936, **58**, 2585) for acetic acid vapour at 25°. It is also assumed, on the basis of the results of Krishnamurti and of Traynard, that the breakdown of dimer on dilution of acetic acid gives mainly the hydrated monomer, with very little unhydrated monomer.

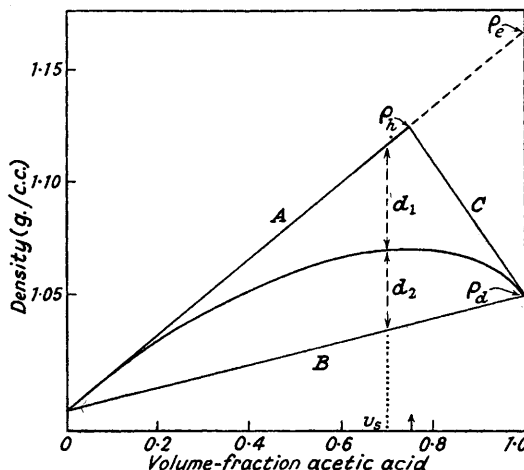
*First Stage.*—The initial approach uses the density curve, plotted in terms of volume fractions. In dilute solutions of acetic acid, the dimer is likely to be present in vanishingly small concentrations. The tangent (*A* in Fig. 1) to the curve at 0% acetic acid may therefore be taken as *approximating* to the density curve which would be given if the system consisted only of hydrated monomer and water. This line can be used, for the purposes of calculation, only up to the volume fraction (about 0.75) corresponding to the composition of the hydrate,  $\text{CH}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ , at which the density is  $\rho_{\text{h}}$ . The line *B* is taken as *approximating* to that which would be given if the system consisted only of dimeric acid

and water. Then for ideal behaviour in respect of volume additivity, it can be shown that, for any given solution :

$$m_h/m_d = d_2\rho_e/d_1\rho_d$$

where  $m_h$  and  $m_d$  are the masses of monomer hydrate and dimer respectively, and  $d_1$ ,  $d_2$ ,  $\rho_d$ , and  $\rho_e$  have the significance shown in Fig. 1. A similar expression can be used, in relation to the line C, for the concentrated solutions (volume fraction > 0.75). (It would be

FIG. 1. Density of aqueous solutions of acetic acid.



expected that the monomer hydrate would have a higher density,  $\rho_h$ , than that of the dimer,  $\rho_d$ , in which there are two methyl groups).

Fig. 2 shows the results of this analysis for 20°, based on the critical compilation of density data in International Critical Tables, Vol. 3.

*Second Stage.*—The second stage is based on the law of mass action equations for the equilibria of dimerisation and hydration of monomeric acetic acid :

$$[\text{monomer}]^2/[\text{dimer}] = K_1 \quad \dots \quad (1)$$

$$[\text{hydrate}]/([\text{monomer}][\text{water}]) = K_2 \quad \dots \quad (2)$$

where the concentrations are in mole fractions. From these equations, it follows that :

$$[\text{hydrate}] = K_2[\text{water}]\sqrt{K_1[\text{dimer}]}$$

or 
$$[\text{hydrate}]^2 = K_1K_2^2[\text{water}]^2[\text{dimer}] \quad \dots \quad (3)$$

Also, 
$$[\text{dimer}] = 1 - [\text{water}] - [\text{monomer}] - [\text{hydrate}] \quad \dots \quad (4)$$

As we assume that the monomer will readily either dimerise or become hydrated, we can write as an approximation :

$$[\text{hydrate}]^2 = K_1K_2^2[\text{water}]^2(1 - [\text{water}] - [\text{hydrate}]) \quad \dots \quad (5)$$

For any selected value for the mole-fraction of water, this leads to a quadratic equation in  $[\text{hydrate}]$ , the positive root of which gives an approximate analysis of the system. This can be used in equation (2) to obtain an approximate value of  $[\text{monomer}]$ , which in turn can be used in equations (4) and (3) for further successive approximations.

The analysis can be made with these equations if it is assumed that water is present solely as monomeric water. This is an inadequate assumption, though it is difficult to find data on which to base a more realistic calculation. An attempt has, however, been made to show the effect to be expected from both the association of water and its change with concentration. For mathematical convenience, this has been done by treating the water as if it were  $(\text{H}_2\text{O})_2$ , dissociating according to the expression :

$$[\text{H}_2\text{O}]^2/[(\text{H}_2\text{O})_2] = K_3 \quad \dots \quad (6)$$

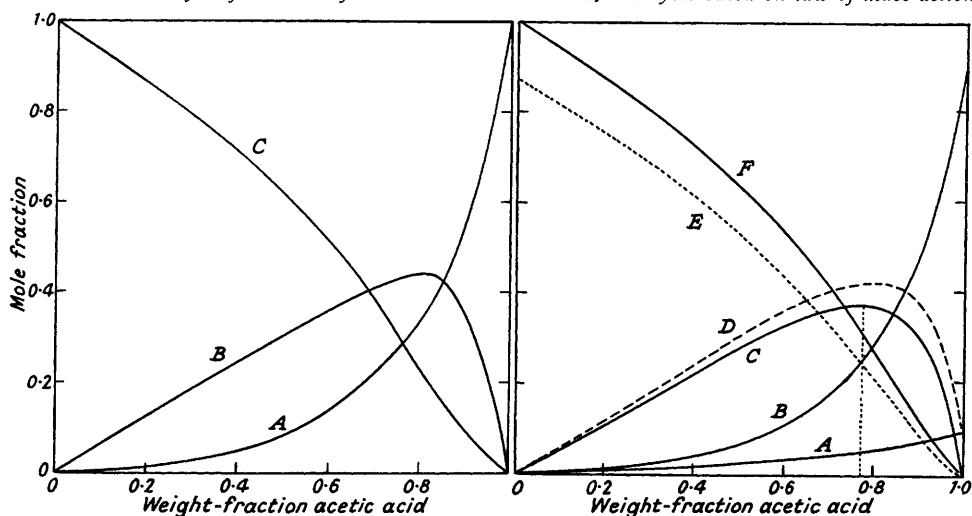
A given value of  $[(\text{H}_2\text{O})_2]$  then gives a value for  $[\text{H}_2\text{O}]$  which can be used for [water] in equation (2). Equation (5) becomes:

$$[\text{hydrate}]^2 = K_1 K_2^2 [\text{H}_2\text{O}]^2 \{1 - [\text{H}_2\text{O}] - [(\text{H}_2\text{O})_2] - [\text{hydrate}]\} \quad (7)$$

The analysis is shown in Fig. 3, for the following values of the constants:  $K_1 = 1/90$ ,  $K_2 = 100$ ,  $K_3 = 1/50$ . The value of  $K_1$  is chosen to give a rather higher degree of association in liquid acetic acid at  $20^\circ$  than was found in the vapour at  $25^\circ$  (MacDougall, *loc. cit.*). The values of  $K_2$  and  $K_3$  have been derived to give approximate agreement

FIG. 2. Composition of aqueous solutions of acetic acid; analysis from density data.

FIG. 3. Composition of aqueous solutions of acetic acid; analysis based on law of mass action.



A, Dimeric acetic acid. B, Total monomeric acetic acid. C, Water.

A, AcOH. B,  $(\text{AcOH})_2$ . C, Acetic acid hydrate. D, Total monomeric acetic acid. E,  $(\text{H}_2\text{O})_2$ . F, Total water.

TABLE 1.

(1) Solutions of water in acetic acid.

a	b	c	d	e	f	g	h	j
0.972	4.5°	4.67°	5.5°	0.846	5.5°	2.85°	2.92°	5.7°
0.981	3.2	3.50	3.8	0.891	3.8	1.94	1.98	3.89
0.992	1.5	1.53	1.64	0.951	1.63	0.82	0.83	1.65

a = Weight-fraction of acetic acid.

b = F. p. depression, Jones and Murray

c = " " Richmond and England } interpolated.

d = Calc. depression, analysis of Fig. 3.

e = Mole-fraction acetic acid (dimer and free monomer), analysis of Fig. 3.

f = Calc. depression for  $\text{H}_2\text{O}$  in  $(\text{AcOH})_2$ .

g = " "  $(\text{H}_2\text{O})_2$  in  $(\text{AcOH})_2$ .

h = " "  $(\text{H}_2\text{O})_2$  in AcOH.

j = " "  $\text{H}_2\text{O}$  in AcOH.

(2) Solutions of acetic acid in water.

k	m	n	o	p	q	r	s
0.876	4.35°	4.23°	0.9265	2.17°	2.15°	4.21°	4.29°
0.9114	3.1	2.95	0.9481	1.50	1.48	2.93	2.96
0.9650	1.2	1.09	0.9805	0.56	0.56	1.11	1.12

k = Weight-fraction of water.

m = F. p. depression, Jones and Murray, interpolated.

n = Calc. depression, analysis of Fig. 3.

o = Mole-fraction of water  $[\text{H}_2\text{O}]$  and  $(\text{H}_2\text{O})_2$ , analysis of Fig. 3.

p = Calc. depression, for  $(\text{AcOH})_2$  in  $\text{H}_2\text{O}$ .

q = " "  $(\text{AcOH})_2$  in  $(\text{H}_2\text{O})_2$ .

r = " " AcOH in  $(\text{H}_2\text{O})_2$ .

s = " " AcOH in  $\text{H}_2\text{O}$ .

between this analysis and that based on the density data (Fig. 2), particularly for the dilute solutions. For this purpose, Fig. 2 has been plotted on the assumption that the molecule of water is  $(H_2O)_2$  throughout. The value of  $K_3$  finds support in that the hydrogen bond is weaker in water than in acetic acid (Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York), but that polymeric water has considerable stability in organic solution such as acetone (Rao, *Phil. Mag.*, 1935, [vii], 20, 587). For the present system, we are guided especially by the spectroscopic evidence, which emphasises the stability of the hydrated acetic acid. This treatment of water, although artificial, gives a more adequate mathematical representation of the system, which is consistent over the whole concentration range, than any simpler assumption. This is seen by reference to the cryoscopic data given in Table 1 (Jones and Murray, *Amer. Chem. J.*, 1903, 30, 193; Richmond and England, *Analyst*, 1926, 51, 283). Table 1 shows values interpolated from experimental data for both ends of the concentration range, compared with theoretical values calculated from the equation:

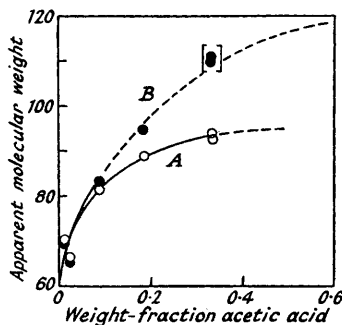
$$\Delta T = -(RT^2/l_1) \ln x_1 \quad \dots \quad (8)$$

where  $\Delta T$  is the depression of the freezing point, and  $x_1$  the mole-fraction of the solvent.

*Discussion.*—It is seen first that the two analyses give curves of the same form, especially if the curve for hydrated acetic acid in Fig. 2 is compared with the curve for total monomer in Fig. 3. This suggests that the postulate of a monomer hydrate is a useful one.

FIG. 4. Apparent molecular weight of acetic acid in benzophenone solution.

A, Calc. : Vandoni and Chazeau.  
B, Calc. : this paper.



Given that the analysis based on the law of mass action is qualitatively concordant with that based on density data, it can be seen that it has two advantages; first, in giving separately the mole-fractions of hydrated and unhydrated monomer at all concentrations; secondly, in giving an analysis for all molecular species in the region of high acetic acid concentrations, and one which is compatible with the cryoscopic measurements in this region. Although this region is small in terms of weight-fraction, it is probably of considerable importance in many studies of the complete system. The present treatment cannot be claimed to be quantitatively precise; in particular, the association of water is difficult to allow for. It can be shown, however, that the results of the law of mass action analysis are relatively insensitive to considerable changes in this factor. It is therefore to be expected that a more exact analysis might differ in detail, but not in form, from that given in Fig. 3.

In most solvents in which acetic acid has been studied, it exists almost entirely as the dimer (except in high dilution), without any sign of solvation. Recently, however, a cryoscopic study has been made of the solution in benzophenone (Vandoni and Chazeau, *Mem. Serv. Chim.*, 1948, 34, 97). The results are plotted in Fig. 4, curve A. From this it will be seen that the value of the molecular weight remains well below 120 (that of the dimer) up to quite considerable concentrations. Vandoni and Chazeau therefore concluded that dimerisation was being inhibited by solvation of the monomer through hydrogen bonding, similar to the effect which has been described above for aqueous solutions. Curve A, however, seems unlikely to rise, if continued, to a value near 120, which glacial acetic acid must have. It appears that the results have been calculated from the formula:

$$M_2 = RT^2w_2/l_1\Delta T w_1 \quad \dots \quad (9)$$

which is useful only in very dilute solutions. We have recalculated the results from the more exact equation (8) which, though strictly applicable only to dilute, ideal solutions, is probably less unsatisfactory than equation (9) in indicating the trend of molecular association. The new results are shown in Table 2 and are plotted as Curve *B* in Fig. 4.

TABLE 2.

Acetic acid,		F. p.	$\Delta T$	<i>M</i> (V & C)	<i>M</i> (K)
weight- fraction	mole- fraction				
0.0	0.0	19.62°	0.0°	—	—
0.0122	0.0241	18.64	0.98	70.3	69.4
0.0231	0.0453	17.65	1.97	66.4	65.3
0.0874	0.1607	13.55	6.07	81.3	82.6
(0.1870	0.3150	7.71	11.90	88.75	94.5)
(0.3362	0.5032	−0.70	20.32	93.48	110.7)
(0.3362	0.5032	−0.84	20.46	92.30	109.9)

It appears that the effect of solvation may be less than that claimed by Vandoni and Chazeau, but will be seen to be still significant, if this curve is compared with similar curves for non-polar solvents, *e.g.*, benzene.

We may therefore expect to find similar behaviour when acetic acid is dissolved in other liquids which offer the possibility of hydrogen bonding. This factor may be of considerable importance in physico-chemical studies, as it is hoped to show in a later paper.

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