The Diamagnetic Study of the Nature of Association in Acetic Acid

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A great deal of work has been done on the magnetic study of liquid mixtures, but comparatively very little work has been done on the influence of the hydrogen bond on the diamagnetism. The earliest report on this subject was by Angus and Hill,[1] who studied substances capable of forming a hydrogen bond in order to ascertain whether the formation of such bonds could be detected by magnetic methods. They confined their investigations to very dilute solutions. Their results showed that the formation of hydrogen bonds involving a ring closure decreases the susceptibility value. Ananthakrishnan and Varadachari,[2] on the basis of a critical analysis of the results on the subject, concluded that the formation of hydrogen bonds in certain cases where multiple linkages are involved should increase the susceptibility value. When Venkataramiah[3] studied the susceptibility of alcohohols in various solvents, his results indicated an increase in diamagnetism when the hydrogen bond is ruptured. However, the investigations of some organic compounds by Rumpf and Seguin[4] seem to show that no appreciable change occurs in the formation of hydrogen bonds. Later Venkateswarlu and Sriraman[5] studied the changes of susceptibility when benzoic, cinnamic, salicylic, and acetic acids are dissolved in a number of solvents with widely different proton-coordinating powers. Their results are in accordance with those of Angus and Hill.[1] Recently Deshpande and Pathki[6] studied magnetically acetic acid dissolved in pyridine at different concentrations. From their results they concluded that the maximum departures from the additive value at certain concentrations are due to the formation of complexes at those concentrations and that the formation or rupture of a hydrogen

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[1] W. R. Angus and W. K. Hill, *Trans. Faraday Soc.*, **36**, 923 (1940).

[2] S. V. Ananthakrishnan and P. S. Varadachari, *Proc. Indian Acad. Sci.*, **20A**, 128 (1944).

[3] H. S. Venketaramiah, *J. Mysore Univer., Sec. B*, Contrib. in Physics, 19, Pt. 4, 3, 1942.

[4] P. Rumpf and M. Seguin, *Bull. soc. chim. France*, **1950**, 542; ibid., **1950**, 177.

[5] K. Venkateswarlu and S. Sriraman, *Trans. Faraday Soc.*, **53**, 433 (1957).

[6] V. T. Deshpande and K. G. Pathki, ibid., **58**, 2134 (1962).

bond does not by itself appreciably affect the susceptibility value. In view of these divergent conclusions by different workers, it was considered desirable to study in detail some compounds in which the hydrogen bond is known to exist predominantly. Acetic acid, one such typical substance, has been chosen for study in the pure and dissolved states.

Experimental

The purification of the acid and the solvents was generally based upon the methods given by Vogel⁷⁾ and was continued until the acid and the solvents gave physical constants in good agreement with previously recorded values.

The susceptibility measurements were made by the Gouy method, using a large Pye magnet. The field strength had a range from 12 to 14 k. gauss for the different field currents used. For every measurement, observations were made with two experimental tubes of different cross-sections for the three field currents. Assuming the influence of the vapour to be negligible, the susceptibility values have been corrected for residual air in the space above the liquid by the manner described by Rao and Narayanaswami.⁸⁾ The densities of the liquids were found with a special type of stoppered, specific-gravity bottle assuming the density of water to be 0.9951 g. cm^{-3} at 32°C.

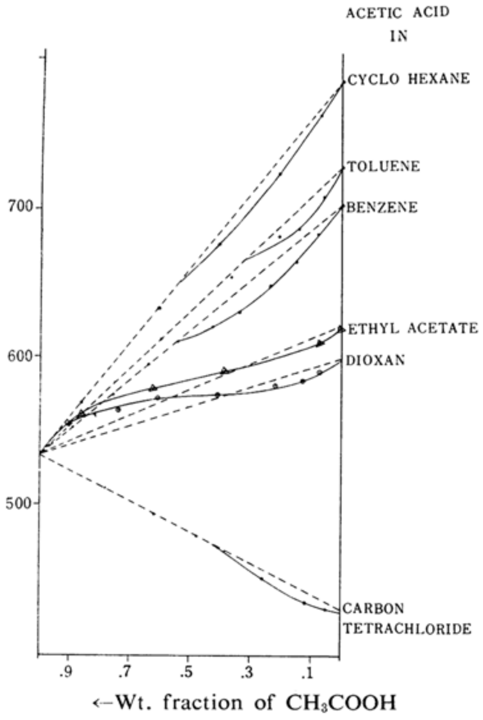

Fig. 1.

Results

The specific susceptibility values of the pure liquids and mixtures studied at different concentrations are given in the table with an experimental accuracy of ±0.5%. For mixtures, the χ values, calculated on the basis of the additive law, are also given. The values of χ are plotted against the weight fraction in Fig. 1. If χ_1 and χ_1' are the specific susceptibility values of the acetic acid in its pure and dissolved states respectively, and w_1, its weight fraction, then, according to Angus and Tilston ;⁹⁾

$$\chi_1' - \chi_1 = \frac{\chi_{(\text{observed})} - \chi_{(\text{additive})}}{w_1} = \frac{\Delta\chi}{w_1}$$

These values are calculated and plotted against the mole fraction in Fig. 2.

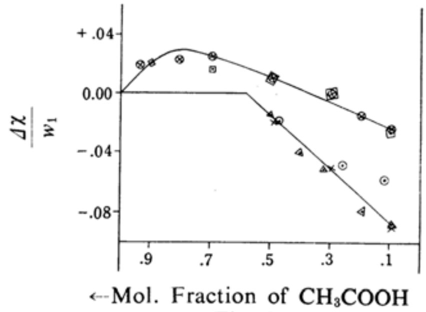

Fig. 2.

△ Benzene
⊙ Carbon tetrachloride
× Cyclohexane
⊗ Dioxan
▣ Ethyl acetate

Discussion

It has been generally assumed by earlier workers⁵,¹⁰⁾ that acetic acid in the pure liquid state exists in a cyclic hydrogen-bonded dimer. However, the existence of a non-zero dipolemoment indicates that a portion of the dimeric units should be non-cyclic. Pohl et al.,¹¹⁾ on the basis of their studies of electric polarisation, concluded that chains of molecules are also present. Recent studies relating to the mechanism of association in acetic acid by the Raman effect,¹²⁾ the dipole moment,¹³⁾ and proton magnetic resonance¹⁴⁾ reveal that the

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8) S. R. Rao and A. S. Narayanaswami, *Proc. Indian Acad. Sci.*, **9A**, 35 (1939).

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11) H. A. Pohl, M. E. Hobbs and P. M. Cross, *J. Chem. Phys.*, **9**, 408 (1941).

12) M. I. Batuev, *Doklady Akad. Nauk S. S. S. R.*, **59**, 1170 (1948).

13) M. Blinc and R. Blinc, *J. Polymer Sci.*, **32**, 506 (1958).

14) L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, **54**, 314 (1958).

TABLE I.

Solvent	Mol. frac.	Wt. %	Density ρ_4^{32}	χ* Solution		$\frac{\Delta\chi}{w_1}$
				Calcd.	Obs.	
Benzene	1.00	—	1.043	—	0.533	—
	0.91	89.00	1.019	0.551	0.550	—
	0.80	75.84	0.991	0.574	0.574	—
	0.70	64.13	0.968	0.594	0.593	—
	0.61	54.50	0.948	0.610	0.610	—
	0.50	43.70	0.929	0.628	0.621	−0.017
	0.40	34.03	0.914	0.644	0.631	−0.039
	0.32	24.13	0.899	0.661	0.649	−0.051
	0.19	15.17	0.888	0.676	0.665	−0.075
	0.10	7.86	0.877	0.689	0.682	−0.088
	0	—	0.876	—	0.702	Taken as standard
Cyclohexane	0.89	85.88	0.985	0.569	0.568	—
	0.69	61.16	0.903	0.633	0.632	—
	0.49	40.64	0.847	0.685	0.677	−0.019
	0.30	21.10	0.808	0.735	0.725	−0.047
	0.10	6.80	0.780	0.772	0.766	−0.088
	0	—	0.772	—	0.790	
Toluene	0.70	60.34	0.970	0.610	0.611	—
	0.50	37.24	0.908	0.655	0.655	—
	0.30	20.90	0.882	0.687	0.683	−0.019
	0.20	12.37	0.870	0.704	0.700	−0.024
	0.10	5.98	0.864	0.716	0.714	−0.033
	0	—	0.860	—	0.728	
Carbon tetrachloride	0.90	77.93	1.132	0.510	0.511	—
	0.80	61.70	1.191	0.493	0.493	—
	0.70	47.94	1.251	0.479	0.480	—
	0.48	26.18	1.374	0.457	0.452	−0.019
	0.26	12.15	1.472	0.442	0.436	−0.049
	0.12	5.15	1.534	0.435	0.432	−0.058
	0	—	1.581	—	0.430	—
Ethyl acetate	0.90	86.14	1.018	0.545	0.562	+0.019
	0.70	61.69	0.979	0.566	0.575	+0.016
	0.50	39.34	0.947	0.585	0.590	+0.012
	0.30	22.23	0.933	0.600	0.600	0.000
	0.10	7.53	0.902	0.612	0.610	−0.026
	0	—	0.892	—	0.619	
Dioxan	0.94	91.96	1.045	0.538	0.556	+0.019
	0.81	74.18	1.044	0.549	0.565	+0.021
	0.70	61.05	1.040	0.557	0.572	+0.024
	0.50	40.94	1.035	0.570	0.575	+0.012
	0.30	21.90	1.030	0.582	0.582	0.000
	0.20	12.91	1.028	0.588	0.586	−0.015
	0.10	6.66	1.023	0.592	0.590	−0.030
	0	—	1.028	—	0.596	

* All the susceptibility values in this paper are expressed in 10^{-6} c.g.s. units.

association is a mixture of non-polar dimer association and polar chain association.

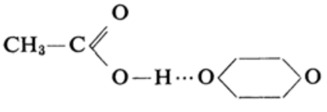
When acetic acid is diluted with non-interacting solvents, such as benzene, toluene, cyclohexane, and carbon tetrachloride, there is no possibility of the formation of hydrogen bonds between the solute and solvent molecules; any deviation from the additive law should arise only from the change in the mechanism of association of the acetic acid molecules. The results obtained for these mixtures in Fig. 1 show that the χ values of mixtures are strictly additive up to nearly equimolecular proportions; then a regular diminution of χ values occurs on further dilution.

The formation of hydrogen bonds between the hydrogen and carbonyl groups can be considered to be due to an electrostatic force, and the presence of such a force can be considered as equivalent to an electric field between the two groups and its contribution to the diamagnetism, to be paramagnetic. Therefore, the rupture of the hydrogen bond should give an increased χ value of the molecule. It is clear that the monomeric form of the acetic acid molecule should have a higher susceptibility value than the associated form.

The decrease in $\Delta\chi/w_1$ values at dilutions beyond equimolecular proportions can be explained in terms of polymer-dimer equilibria. The hydrogen bonds in the polar chain polymers are weaker than those in closed dimers. The effect of dilution is to break the polymers into monomers. The monomers are strongly polar and could not have stability as such. Hence, they probably combine to form closed dimers. The progressive diminution of $\Delta\chi/w_1$ in Fig. 2 at a higher dilution evidently indicates the progressive formation of ring dimers since such a formation of closed rings should result in a decrease in χ value.[1,5,15] The studies of the dilution shift of the proton resonance signal of the -OH group of acetic acid by Reeves and Schneider[14] indicate a shift to the low field up to a 0.1 mol. fraction of the acid and explains it as arising from the formation of dimers. The higher value of χ obtained by Deshpande and Pathki[6] for all the concentrations in an acetic acid-pyridine mixture has been explained as arising from the stabilization of monomers, even at a higher concentration. However, our results indicate positively that monomerization does not take place, even up to a 0.1 mol. fraction in solutions of non-interacting solvents.

Dioxan and ethyl acetate, both with powerful anionoid centres, are capable of breaking down the molecular aggregates of acetic acid.[5,10] When acetic acid is diluted with these solvents, there is a marked increase in χ at the initial dilutions but a regular decrease (Fig. 1) on further dilution. In these solutions the competition of the solvent molecule as a hydrogen-bonding base causes the dissociation of acetic acid dimers also. Therefore, even at a very low dilution the formation of a strong hydrogen bond of the hetero-molecular type is highly probable. This breaking of the non-polar dimeric units of acetic acid by donor solvents like acetone has been suggested by Huggins et al.[16] from the proton magnetic resonance study of these mixtures. The replacement of the -OH doublet of the cyclic dimer by a diffuse band in the Raman spectra of an acetic acid-dioxan mixture has been explained by Batuev[12] as being due to the breaking of ring dimers and to the formation of hydrogen-bonded chain complexes between acetic acid and dioxan. The contribution of this type of complex formation to the magnetic susceptibility may be in two forms: (1) an increased diamagnetism brought about by the release of constraints upon the breaking of the dimers, or (2) a paramagnetic contribution arising from the formation of a strong hydrogen bond with the solvent molecule. The observed increased value of χ on the initial dilution of the acid by dioxan and ethyl acetate may be the net effect of these two contributions.

The $\Delta\chi/w_1$ value of these mixtures at a high dilution causes a negative deviation (Fig. 2). The results are best explained in these cases with the predominant occurrence of a strong hydrogen-bonded addition compound of donor solvents with a monomeric acid molecule, as is shown below:



Batuev's report[17] of the complete disappearance of the lines at 1668 and 1710 cm⁻¹ characteristic of C=O in ring dimers and coordinated C=O respectively, lines which appeared in the Raman spectrum of pure acid, and of the exclusive appearance of the line (1740 cm⁻¹), which is characteristic of the C=O free from a hydrogen bond, with an increased intensity in weak dioxan solutions lends support to the above argument.

Summary

The magnetic susceptibilities of acetic acid in the pure and dissolved states have been investigated, and the results obtained have been attributed to the changes that take place in the association of acetic acid molecules.

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[15] J. Farquharson, ibid., 32, 219 (1935).

[16] C. M. Huggins and G. C. Pimental, *J. Phys. Chem.*, **60**, 1314 (1956).

[17] M. I. Batuev, *Comp. rend. acad. Sci., U. R. S. S.*, 53, 507 (1946).