The Diamagnetic Study of the Nature of the Association of Acetic Acid. II. The Binary Systems of Acetic Acid with Triethylamine, Pyridine and Aniline

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The interpretation of the observed magnetic susceptibility of carboxylic acids in different solvents is complicated by the fact that they are mostly in polymeric forms in the pure state and tend to associate in some solvents but to ionize in others. In an earlier communication,[1] the authors investigated the nature of the association of acetic acid in solvents like benzene, carbon tetrachloride, toluene, and cyclohexane, all of the non-interacting type, and also with dioxan and ethyl acetate, which have powerful anionoid centres. The reaction of protonic acids with bases leads to the formation of ion-pair salts associated through a hydrogen bond, or if the solvent base is weak, the proton may remain covalently bonded to the acid itself and the base will be associated with the hydrogen through an electrostatic attraction. Various physico-chemical studies of liquid mixtures of acetic acid with bases like aniline, pyridine and triethylamine[2-6] have indicated many singularities in the property-concentration relationship. The intermolecular complex formation between the acetic acid and bases employed has been held responsible for such singularities by different workers.[7-10] However, Suriyanarayana and Venkatesan[11] have shown that the equivalent conductivity, viscosity, volume contraction and refractive index

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1) S. Sriraman and V. Shanmugasundaram, This Bulletin, **37**, 395 (1964).

2) M. G. Andre, *Compt. rend.*, **125**, 1187 (1897); **126**, 1105 (1898).

3) A. E. Dunstan and F. B. Thole, *J. Chem. Soc.*, **95**, 1556 (1934).

4) C. G. Balachandran, *J. Indian Inst. Sci.*, **36**, 10 (1954).

5) Laxmanan, ibid., **36**, 97 (1954).

6) L. Swearingen and R. F. Ross, *J. Phys. Chem.*, **38**, 395 (1934).

7) S. Venkataraman, *J. Indian Chem. Soc.*, **17**, 297 (1940).

8) A. S. Naumova, *Zhur. Obshchei Khim.*, **19**, 1216 (1964); **19**, 1222 (1949).

9) M. Bokhovkin, ibid., **27**, 856 (1957).

10) R. Mierzecki, *Acta Phys. Polon.*, **12**, 26 (1953).

11) C. V. Suryanarayana and V. K. Venkatesan, *J. Phys. Chem.*, **60**, 777 (1956).

TABLE I

Solvent	Mol.% of acetic acid	Wt. fraction of acetic acid W	Density ρ	$\chi_{obs.}$	$\chi_{additive}$	$\Delta\chi$	$\frac{\Delta\chi}{W}$
	100	1.00	1.042	0.533	—	—	—
	90	0.8576	1.039	0.582	0.573	+0.009	+0.0105
Triethylamine	80	0.7134	1.020	0.625	0.614	+0.011	+0.0154
	70	0.5856	0.9915	0.654	0.650	+0.004	+0.0068
	66.66	0.5381	0.9757	0.666	0.663	+0.003	+0.0056
	60	0.4721	0.9430	0.683	0.682	+0.001	+0.0021
	Triethylamine	—	0.721	0.815	—	—	—
	80	0.8074	1.068	0.562	0.553	+0.009	+0.0111
	66.66	0.6984	1.054	0.575	0.563	+0.012	+0.0171
Pyridine	50	0.4859	1.021	0.587	0.581	+0.006	+0.0123
	40	0.3839	1.007	0.596	0.589	+0.007	+0.0182
	33.33	0.3265	1.001	0.599	0.593	+0.006	+0.0183
	20	0.1682	0.9845	0.607	0.605	+0.002	+0.0119
	Pyridine	—	0.9757	0.616	—	—	—
	80	0.7202	1.079	0.577	0.573	+0.004	+0.0056
	66.66	0.5676	1.076	0.598	0.594	+0.004	+0.0071
Aniline	50	0.3718	1.054	0.628	0.622	+0.006	+0.0162
	30	0.2210	1.037	0.640	0.644	−0.005	−0.0181
	20	0.1266	1.025	0.653	0.658	−0.005	−0.0395
	Aniline	—	1.015	0.675	—	—	—

of the acetic acid - pyridine system exhibit maxima at 83 mol.% of the acid and pointed out the possibility of the ionisation of the acetic acid molecule. A similar conclusion was obtained by Isobe et al.[12] on the basis of proton magnetic resonance studies of the acetic acid - aniline system. The present investigation was undertaken with a view of elucidating the nature of the association of acetic acid with sufficiently strong bases, such as triethylamine, pyridine and aniline.

Experimental

All the solvents and the acid were of B.D.H.A.R. quality and were distilled in an all-glass apparatus before use. The acid and the solvents gave physical constants in good agreement with the previously-recorded values.

The magnetic susceptibilities of the pure liquids and the mixtures were determined by the Gouy method described in the earlier paper.[1] Benzene was used as the standard, its susceptibility being taken as 0.702.*

Results

The specific susceptibility values of the pure liquids and mixtures studied at different concentrations are given in Table I with an experimental accuracy of ±0.5%. For mixtures, the χ values, calculated on the basis of the additive law, are also given in that table. If W is the weight percentage of the acid and $\Delta\chi = \chi_{(observed)} - \chi_{(additive)}$, the values of $\Delta\chi/W$ are as given in the last column of Table I.

Discussion

From Table I it can be seen that, for acetic acid - pyridine and acetic acid - triethylamine, the $\Delta\chi/W$ value is positive at all concentrations. In the case of acetic acid - pyrridine, Desphande and Pathki[13] have explained these positive exaltations as arising from the stabilization of monomers, neglecting the effect of hydrogen bonding on magnetic susceptibilty. Our results also confirm such positive deviation from additivity. However, the question arises of whether the effect of the hydrogen bond on magnetic susceptibility can be completely neglected. The recent precision magnetic measurements by Jatkar et al.[14] of several binary systems capable of forming intermolecular hydrogen bonding showed considerable deviations from linearity. Also, it has been shown by other physico-chemical studies that the species resulting from the reaction of acetic acid with pyridine and triethylamine is not completely an electrostatic complex but,

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12) I. Isobe, T. Ikenoue, and G. Hazato, *J. Chem. Phys.*, **30**, 1371 (1959).

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

13) V. T. Deshpande and K. G. Pathki, *Trans. Faraday Soc.*, **58**, 2134 (1962).

14) S. K. K. Jatkar, V. S. Jatkar and A. J. Mukhedekar, *Indian J. Chem.*, **1**, 465 (1963).

rather, is partially ionic, resulting in the formation of pyridinium and triethyl ammonium ions respectively. Barrow's infrared measurements[15] indicated the formation of such ions in at least the case of triethylamine. The maximum value of the equivalent conductivity observed by Suryanarayana and Venkatesan[11] at 83 mol.% of acid in the acetic acid - pyridine system has been explained as arising from the maximum ionisation at that concentration. According to them, the progressive fall of conductivity beyond 83% represents only the extent of ionisation. The degree of such deprotonation of acid will depend upon the energy required to break the bond, the stabilisation of the anion, and the strength of the base employed. The mixtures of acetic acid with triethylamine, pyridine and aniline are typical systems in which the bases are strong enough to produce ion-pair salts. The formation of such ion pairs results in an increased diamagnetism as a result of the release of constraints. Accordingly, it may be presumed that the positive exaltations of magnetic susceptibility observed in these cases only indicate the extent of ionisation, and that the maximum deviations observed at different concentrations in these three systems may be taken as indications of the maximum ionisation at these concentrations.

The behaviour of the acetic acid - aniline mixture is quite interesting. When acetic acid is diluted with aniline, there is a marked increase in $\Delta\chi/W$ at the initial dilutions, but the value decreases on further dilutions. In the free aniline molecule, the trivalent nitrogen can resonate with the phenyl group, and such resonance is held responsible for the negative exaltation of the magnetic susceptibility observed[16] in pure aniline. From the proton magnetic resonance study[12] of this system, it is found that such resonance is more pronounced in very dilute concentrations of the acid. This may be responsible for the negative exaltation at low acid concentrations. As more acid is added to the base, the aniline molecule is slowly converted into the anilinium ion, accompanied by a fast proton exchange reaction which gives rise to a positive exaltation.

Summary

The diamagnetic susceptibilities of three binary systems have been studied using the Gouy method. Deviations of the observed diamagnetic susceptibility values from Wiedemann's additive law have been discussed in the light of the partial ionisation of acetic acid with the solvent bases.

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[15] G. Barrow, *J. Am. Chem. Soc.*, 76, 5211 (1954).

[16] S. Sriraman and R. Sabesan, *Trans. Faraday Soc.*, 58, 1080 (1962).