Diamagnetism of Azeotropic Binary Liquid Mixtures

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(Received October 29, 1957)

A large amount of work has been reported on the diamagnetism of organic liquid mixtures. Ranganathan⁽¹⁾ investigated the mixtures benzene-carbon tetrachloride, acetone-chloroform, acetone-water, and ethanol-water and found small deviations from additivity, the deviations being least in mixtures of two non-polar liquids. Molecular deformation by dipole-dipole interaction and compound formation was invoked to explain the deviation. Rao and his collaborators[2-6] studied a large number of mixtures of liquids having large electric moments and having molecules of different shapes and concluded that in the cases studied there were no variations from additive law. Kido[7] reported that in all the mixtures investigated by him there were no departures from the additive law. Broersma[8] from his study of a few organic liquid mixtures concluded that the departures from the additive law are not appreciable. The work of Farquharson[9] and Angus and Hill[10] suggests a method of explaining small deviations from additivity observed by some authors, on the basis of hydrogen bond formation.

Though a large amount of work has been done on the subject, the reports published so far regarding the behavior of such mixtures from the point of view of the additive law have not been unanimous. Probably more accurate data on a larger number of liquids may help to arrive at some definite conclusions. It was with this object the present investigations were undertaken. All the mixtures chosen for study are azeotropic mixtures. None of the previous workers have chosen binary mixtures from this point of view though a few mixtures studied might come under this category. The results obtained regarding the magnetic measurements in the case of the mixtures studied are reported in this paper.

Experimental

Thorough purification of the liquids studied and the adoption of a magnetic method which could give reliable and consistant results were the chief guiding features of this investigation. The procedure adopted for the purification of the liquids was generally based upon Weissberger, 'Organic Solvents', Interscience, New York, 1956.

The determination of the specific susceptibility was made by a perfected form of Gouy method. The pole faces of the large PYE electromagnet used were 3 cm. in diameter and the air gap had a width of 1.2 cm.

Measurements were made with two ground glass stoppered tubes of slightly different cross-sections and at different field strengths ranging from 12 to 15 kilogauss. The experimental tube which was about 30 cm. long and 0.8 cm. in diameter was suspended from one arm of a sensitive balance and was arranged to be vertical with the liquid meniscus symmetrically situated between the pole faces. The field at the lower end of the liquid column was negligible. By a preliminary experiment the position of exact compensation for the glass tube was determined. Pure benzene was taken as the standard.

Assuming the influence of the vapor of the liquid to be negligible, the susceptibility values have been corrected for the residual air in the space above the liquid in the manner described by Rao and Narayanaswamy[5]. The refractive indices of the mixtures were measured with an Abbe refractometer made by Hilger's firm. The densities of the mixtures were found with a special type of stoppered specific gravity bottle.

Results

The mixtures were prepared by weight and due care was taken to minimise any possible change in concentration by evaporation. In Table I are given the values of the density, refractive index and specific susceptibility of the pure liquids and of the mixtures studied at various concentrations. The observed values of the density, refractive index, and magnetic susceptibility of the pure liquids are in good agreement with the previously

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[1] Ranganathan, *Indian J. Physics*, **6**, 421 (1931).
[2] Rao and Sivaramakrishnan, ibid., **6**, 509 (1932).
[3] Rao, ibid., **8**, 483 (1934).
[4] Rao and Varadachari, *Proc. Indian Acad. Sci.*, **1A**, 77 (1934).
[5] Rao and Narayanaswamy, ibid., **9A**, 35 (1939).
[6] Rao and Sriraman, *J. Annamalai Univ.*, **7**, 187 (1938).
[7] Kido, *Sci. Rep. Tohoku Imp. Univ.*, **21**, 385 (1932).
[8] Broersma, *J. Chem. Phys.*, **17**, 873 (1949).
[9] Farquharson, *Trans. Faraday Soc.*, **32**, 219 (1935).
[10] Angus and Hill, ibid., **36**, 923 (1940).

TABLE I

ρ, μ AND χ FOR THE PURE LIQUIDS AND MIXTURES

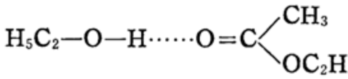
Component A	Component B	wt. % of A	$\rho_{4°}^{32°}$	μ	χ_1 Observed	χ_2 Calcd.	$\chi_2-\chi_1$
Ethanol	Benzene	100.0	0.782	1.3545	0.727		
		80.0	0.800	1.3810	0.721	0.722	+0.001
		60.0	0.813	1.4053	0.718	0.717	−0.001
		40.0	0.830	1.4330	0.712	0.712	0.000
		32.4	0.835	1.4431	0.711	0.710	−0.001
		20.0	0.845	1.4621	0.706	0.707	+0.001
		0.0	0.870	1.4925	0.702		
	Carbon tetra-chloride	80.0	0.872	1.3610	0.667	0.669	+0.002
		60.0	0.980	1.3792	0.610	0.611	+0.001
		40.0	1.121	1.3923	0.553	0.552	−0.001
		20.0	1.311	1.4205	0.495	0.494	−0.001
		15.8	1.353	1.4263	0.481	0.482	+0.001
		0.0	1.577	1.4540	0.436		
	Ethyl acetate	80.0	0.800	1.3590	0.702	0.705	+0.003
		60.0	0.812	1.3609	0.677	0.683	+0.006
		40.0	0.838	1.3629	0.656	0.660	+0.004
		30.8	0.851	1.3638	0.648	0.650	+0.002
		20.0	0.863	1.3650	0.636	0.638	+0.002
		0.0	0.889	1.3777	0.616		
	n-propyl bromide	80.0	0.864	1.3668	0.687	0.688	+0.001
		60.0	0.940	1.3751	0.647	0.649	+0.002
		40.0	1.037	1.3889	0.610	0.611	+0.001
		20.5	1.147	1.4012	0.574	0.573	−0.001
		0.0	1.310	1.4257	0.533		
	Chloroform	80.0	0.880	1.3670	0.679	0.681	+0.002
		60.0	0.974	1.3788	0.634	0.635	+0.001
		40.0	1.095	1.3927	0.587	0.589	+0.002
		20.0	1.269	1.4142	0.544	0.543	−0.001
		7.0	1.393	1.4302	0.511	0.513	+0.002
		0.0	1.473	1.4393	0.497		
Methanol	Chloroform	100.0	0.791	1.3285	0.686		
		80.0	0.870	1.3386	0·648	0.648	0.000
		60.0	0.995	1.3505	0.609	0.610	+0.001
		40.0	1.097	1.3695	0.574	0.573	−0.001
		20.0	1.256	1.4042	0.533	0.535	+0.002
		12.6	1.325	1.4165	0.520	0.521	+0.001
		0.0	1.473	1.4393	0.497		
	Carbon tetra-chloride	80.0	0.879	1.3340	0.637	0.636	−0.001
		60.0	0.982	1.3460	0.587	0.586	−0.001
		40.0	1.127	1.3790	0.534	0.536	+0.002
		20.6	1.304	1.4110	0.485	0.486	+0.001
		0.0	1.577	1.4540	0.436		
	Benzene	80.0	0.805	1.3475	0.688	0.689	+0.001
		60.0	0.820	1.3663	0.693	0.692	−0.001
		39.6	0.837	1.4215	0.695	0.696	+0.001
		20.0	0.854	1.4601	0.698	0.699	+0.001
		0.0	0.870	1.4945	0.702		

Component A	Component B	wt. % of A	$\rho_{4^\circ}^{32^\circ}$	μ	χ_1 Observed	χ_2 Calcd.	$\chi_2-\chi_1$
Methanol	Acetone	80.0	0.789	1.3337	0.666	0.665	−0.001
		60.0	0.787	1.3394	0.643	0.644	+0.001
		40.0	0.785	1.3454	0.626	0.624	−0.002
		20.0	0.783	1.3509	0.602	0.603	+0.001
		12.1	0.783	1.3524	0.593	0.595	+0.002
		0.0	0.782	1.3534	0.582		
n-propanol	Acetal	100.0	0.797	1.3815	0.750		
		80.0	0.800	1.3811	0.739	0.738	−0.001
		60.0	0.807	1.3806	0.725	0.725	0.000
		37.0	0.813	1.3793	0.712	0.711	−0.001
		20.0	0.816	1.3781	0.702	0.700	−0.002
		0.0	0.819	1.3761	0.688		
	Toluene	80.0	0.812	1.4019	0.746	0.745	−0.001
		60.0	0.823	1.4218	0.739	0.740	+0.001
		52.5	0.827	1.4298	0.737	0.738	+0.001
		40.0	0.834	1.4440	0.734	0.735	+0.001
		20.0	0.847	1.4662	0.731	0.730	−0.001
		0.0	0.856	1.4908	0.725		
Acetic acid	Toluene	100.0	1.041	1.3648	0.525		
		80.0	0.990	1.3937	0.567	0.565	−0.002
		60.0	0.950	1.4171	0.603	0.605	+0.002
		40.0	0.914	1.4417	0.644	0.645	+0.001
		34.0	0.905	1.4491	0.656	0.657	+0.001
		20.0	0.885	1.4666	0.686	0.685	−0.001
		0.0	0.856	1.4908	0.725		
	Chlorobenzene	80.0	1.048	1.3951	0.542	0.544	+0.002
		58.5	1.054	1.4253	0.563	0.564	+0.001
		40.0	1.067	1.4530	0.583	0.581	−0.002
		20.0	1.081	1.4849	0.600	0.600	0.000
		0.0	1.099	1.5198	0.618		
	Ethylene bromide	80.0	1.157	1.3843	0.502	0.504	+0.002
		60.0	1.302	1.4038	0.484	0.484	0.000
		55.0	1.340	1.4092	0.478	0.479	+0.001
		40.0	1.495	1.4312	0.465	0.463	−0.002
		20.0	1.761	1.4700	0.442	0.443	+0.001
		0.0	2.157	1.5332	0.422		
Formic acid	Diethyl ketone	100.0	1.206	1.3686	0.435		
		80.0	1.092	1.3722	0.482	0.482	0.000
		60.0	1.003	1.3770	0.531	0.530	−0.001
		33.0	0.904	1.3830	0.596	0.595	−0.001
		20.0	0.865	1.3855	0.624	0.625	+0.001
		0.0	0.811	1.3887	0.672		
	Methyl *n*-propyl ketone	80.0	1.091	1.3720	0.484	0.482	−0.002
		60.0	1.003	1.3761	0.528	0.529	+0.001
		40.0	0.922	1.3808	0.578	0.577	−0.001
		32.0	0.892	1.3821	0.594	0.595	+0.001
		20.0	0.859	1.3842	0.623	0.624	+0.001
		0.0	0.800	1.3871	0.671		
Acetone	Chloroform	100.0	0.782	1.3534	0.582		
		80.0	0.864	1.3639	0.564	0.565	+0.001
		60.0	0.964	1.3764	0.547	0.548	+0.001
		40.0	1.089	1.3922	0.532	0.531	−0.001
		20.4	1.247	1.4124	0.514	0.514	0.000
		0.0	1.473	1.4393	0.497		

recorded values. In the case of mixtures the values of χ calculated on the basis of additive law are also given for comparison. The values of the azeotropic concentrations are underlined.

Discussion

All the mixtures with an alcohol as one of the components, except ethanol-ethyl acetate show practically little or no deviation from the additive law, with regard to magnetic susceptibilities. However, in all the cases departures from additive law were observed in their densities and refractive indices. The Raman spectra of ethanol benzene mixture have been studied by Cennamo and Vitale[11] and Sundara Rao[12]. The former authors found evidence of the existence of association in the mixture and the results of the latter indicated no such association. Ethanol-ethyl acetate and methanol-acetone mixtures are cases of two polar liquids for the mixtures. The magnetic data for ethanol-ethyl acetate mixture show slight departures from additive law. The observed χ values are lower than the additive values, the maximum deviation being nearly 1% at a concentration of 60% of alcohol. Ethyl acetate is an electron donor with a strong anionoid center C=O. When this is mixed with ethanol, the two types of molecules may associate through a hydrogen bond, lowering the anionoid power of C=O. The variation of χ from additive values might be due to the formation of hydrogen bonds between ethanol and ester molecules as represented below.



$$H_5C_2\text{—}O\text{—}H\cdots\cdots O=C\begin{matrix}\diagup CH_3\\ \diagdown OC_2H_5\end{matrix}$$

Murthy and Seshadri[13] found from Raman spectra of this mixture a diffuseness in the C=O frequency towards the shorter wavelength and they have taken this as evidence for the formation of hydrogen bonds as shown above.

The Raman spectra of methanol-acetone have been studied by Koteswaram[14], Joerges and Nikuradse[15] and Murthy and Seshadri[16]. From a study of the infrared spectra of this mixture Gordy[17] reported a shift of the C=O frequency of acetone. Koteswaram[14] observed a perceptible shift of C=O line at 1712 cm.$^{-1}$ towards shorter frequency. In 1:1 mixture, the C=O line was found to have a structure with two peaks. Also he reported a shift of C—C line towards higher frequency. These he attributed to the formation of association complexes. Joerges and Nikuradse[15] have also suggested the possibility of the formation of complexes by hydrogen bonding.

Acetone has a strong anionoid C=O center and hence it is normal to expect the formation of such complexes in this mixture. Any large change in the C=O bond strength will normally manifest itself in a susceptibility change. But the magnetic data do not show any such change from additive law. Murthy and Seshadri[16] studied the Raman spectra of this mixture but did not find any shift in the C=O line of acetone at 1710, thus indicating no evidence for the formation of hydrogen bonds. They distinguished between an ordinary hydrogen bond and a true hydrogen bond by postulating that a true hydrogen bond is one where both the cationoid and the anionoid center (OH and CO group) are affected. In the weaker type the OH group only will be affected. Quite possibly this mixture belongs to the case where the weaker type of hydrogen bond is formed and hence no deviation from additive law is observed.

The case of *n*-propanol acetal mixture is similar to methanol acetone mixture. Acetal has two anionoid centers. Because of this, one can expect the formation of associated complexes through a hydrogen bond. But the negative charge on the oxygen atom is very weak and the hydrogen bond that might be formed will consequently be weak. That this might be the case is evidenced by the magnetic data which show that the mixture obeys additive law.

The magnetic data of all the five mixtures having for one of their components a fatty acid, either acetic or formic, show fairly good agreement with additive values. Both acetic and formic acid are known to exist as associated molecules.

From a study of Raman spectra of some liquid mixtures Koteswaram[14] has observed that certain general changes might be expected when a fatty acid is mixed with a polar solvent. According to him the

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11) Cennamo and Vitale, *Nuovo Cemento*, **13**, 465, (1936).

12) Sundara Rao, *J. Indian Chem. Soc.*, **22**, 260 (1945).

13) Murthy and Seshadri, *Proc. Indian Acad. Sci.*, **14A**, 593 (1941).

14) Koteswaram, *Indian J. Physics*, **14**, 341 (1940).

15) Joerges and Nikuradse, *Naturforsch*, **5A**, 25 (1950).

16) Murthy and Seshadri, *Proc. Indian Acad. Sci.*, **15A**, 154 (1942).

17) Gordy, *Phy. Rev.*, **50**, 1151 (1936).

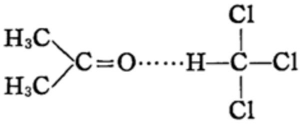
changes expected are (i) breaking up of associated molecules into simpler ones and (ii) the formation of complexes between the solvent molecule and the monomeric molecule. Hence in such a mixture the possibilities are three fold.

1) The associated molecules are not affected by the presence of the solvent. If this is the case the magnetic susceptibility will be additive. 2) Depolymerisation may take place. This by itself will to some extent affect the susceptibility. 3) These simpler molecules may associate with the solvent molecules forming 'addition compounds'. This again may result in a change in the value in the reverse direction.

As all these five mixtures obey additive law, it might be inferred that the solvents used with these acids act merely as diluents without affecting the association in the acid molecules. If the association in the acid molecules is broken and the monomers form complexes with the solvent molecules, the two competing processes may compensate each other. But exact compensation is a remote possibility. Hence it may be taken that association between the acid molecules is not affected when the two acids are dissolved in the solvent used.

The acetone-chloroform mixture is of special interest. Its magnetic susceptibility, Raman spectrum and infrared spectrum have been studied by several workers. But the conclusions arrived at from these studies are not in agreement with one another. In view of the divergent views expressed regarding this mixture, the magnetic study has been repeated several times for each concentration. The data obtained show that the maximum departure from additive law is only about 0.2%. Even this small variation is not progressive. Hence the results may be taken to indicate that this mixture obeys additive law in conformity with the observations of Rao and his collaborators[2-4] and contrary to those made by Trifonov[18], Trew and Spencer[19], Buchner[20], Ranganathan[1] and Sibaiya and Venkataramiah[21].

Gordy[22] from a study of infrared spectra of this mixture has reported a shift of C=O absorption towards longer frequency in chloroform solution. A new absorption frequency at $4\mu(\Delta\nu=2500)$ was found and is attributed to a hydrogen bond between oxygen in C=O and hydrogen in C—H in chloroform as represented below.



$(H_3C)_2C=O\cdots H-CCl_3$

This he claimed[23] to be the first discovery of the direct spectrum of the hydrogen bond, all other evidences being indirectly based upon the changes in frequency.

Koteswaram[14] studied the Raman spectra of this mixture and found that even prolonged exposures did not give any trace of a line or band at $\Delta\nu=2500$. Even assuming that the band excited by the hydrogen bond is only infrared active, there must be a pronounced effect on the C=O frequency in acetone. No such effect was observed.

Murty and Seshadri[16] found no shift or diffuseness in the C=O line either. In the case of methanol-acetone and chloroform-acetone mixtures they found that the C=O frequency is not affected. If hydrogen bond existed, it should only be a weak one which could not affect the C=O group. If this group is affected, then it would produce a change from additivity. But these mixtures obey additive low. Hence in these mixtures either no hydrogen bonds are formed or the hydrogen bonds formed are so weak that the C=O group is not affected.

Though azeotropic mixtures have been specially chosen for this investigation, it has been found that the magnetic data in general seem to be unaffected even at the azeotropic concentrations. Hence any peculiarity that might be characteristic of the mixtures at the azeotropic concentrations could not be detected by the magnetic investigations.

From the present study and from previous literatures available, it may be concluded that, in general, binary organic liquid mixtures obey very closely additive law unless the bonds linked to the carbon atoms are affected.

Summary

An exhaustive study of the diamagnetic susceptibilities of the two types of azeotropic binary mixtures has been made

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[18] Trifonov, *Ins. Anal, Physico-Chem. Leningrad*, **3**, 434 (1923).

[19] Trew and Spencer, *Proc. Roy. Soc.*, **131A**, 209 (1931).

[20] Buchner, *Z. Physik*, **72**, 344 (1931).

[21] Sibaiya and Venkatramiah, *Indian J. Physics*, **7**, 393 (1932).

[22] Gordy, *J. Am. Chem. Soc.*, **60**, 605 (1938).

[23] Gordy, *Nature*, **142**, 831 (1938).

with a view to find out any correlation between the magnetic data and the azeotropic behavior of the mixtures. The results obtained in the case of seventeen mixtures show that in almost all the cases additive law is obeyed even at the azeotropic concentrations. The small deviation from additivity observed in the case of ethanol-ethyl acetate mixture is explained on the basis of the formation of hydrogen bonds. The magnetic data are not affected by the azeotropic nature of the mixtures.

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