

DIAMAGNETIC BEHAVIOUR OF BINARY LIQUID MIXTURES

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INTRODUCTION

DIAMAGNETIC susceptibilities of a large number of liquid mixtures have been measured by different workers (Selwood, 1956) and attempts are made to fit them to Wiedemann's law. It has also been pointed out by some workers (Angus and Tilston, 1940 and 1947) that deviations from this ideal behaviour are traceable to probable sources of error in measurements. In the physics laboratories of Sri Venkateswara University, we are engaged in a detailed study of the thermodynamic behaviour of liquid mixtures. A part of these studies, the ultrasonic behaviour of liquid mixtures of triethylamine with a number of liquids, have been reported in a recent note (Reddy and Subrahmanyam, 1962). The present communication deals with the diamagnetic behaviour of 10 liquid mixtures with triethylamine as a common component. It has been possible to establish a considerable amount of similarity in the ultrasonic and magnetic behaviours of these mixtures.

EXPERIMENTAL

Mixtures were prepared by mixing weighed amounts of extra pure liquids. Densities of the mixtures were determined by the hydrostatic method. Magnetic susceptibilities were measured by the Gouy method. Effect of magnetic impurities were eliminated by standard methods from measurements made at different field strengths in the range 4,000 to 10,000 Gauss. As a result of care taken in maintaining the fields steady, it was possible to realise an accuracy better than 1 per cent. in the value of susceptibilities.

RESULTS AND DISCUSSION

In this series of measurements it was noticed that the measured value of the susceptibility of the mixture deviated considerably from the value expected on the basis of the linear law. In order to bring out the nature of these differences with greater clarity, the excess susceptibility, χ^E defined as the difference between the experimental value and the linear law value, is

represented in Fig. 1 as a function of molar concentration n_2 of the second component, the molar concentration of the common component being n_1 . It is seen from these curves that aniline and *o*-Nitrotoluene mixtures conform to the linear law. In all other cases the deviation can be expressed by an empirical formula

$$\chi^E / n_1 n_2 = A + B(n_1 - n_2) + C(n_1 - n_2)^2.$$

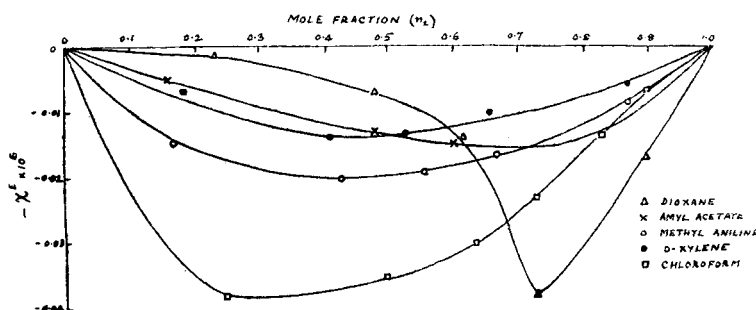


FIG. 1

The values of these constants are given in Table I.

TABLE I
Values of constants

System		$A \times 10^8$	$B \times 10^8$	$C \times 10^8$
Triethylamine-pyridine	..	-10.00	14.20	-14.90
„ -chloroform	..	-14.00	6.70	- 5.60
„ -dioxane	..	- 3.20	17.10	21.40
„ -diphenyl ether	..	-12.00	6.80	- 2.20
„ -methylaniline	..	- 7.20	- 2.60	- 3.44
„ - <i>o</i> -xylene	..	- 4.80	0	- 0.31
„ - <i>m</i> -xylene	..	- 4.80	1.56	2.05
„ -amyl acetate	..	- 6.40	0.17	6.90

We find that a correspondence in behaviour can be established by considering excess compressibility β^E and excess susceptibility χ^E . Table II brings out the essential features of this correspondence.

TABLE II

Component 2	Nature of β^E	Nature of χ^E	Concentration at which χ^E is maximum	Concentration at which χ^E is maximum
Dioxane	.. Linear	Concave	..	0.75
Diphenyl ether	.. Concave	Concave	0.48	0.32
Amyl acetate	.. Concave	Concave	0.51	0.68
Aniline	.. Concave	Linear	0.30	..
Pyridine	.. Concave	Concave	0.42	0.33
<i>o</i> -Xylene	.. Concave	Concave	0.45	0.50
<i>m</i> -Xylene	.. Concave	Concave	0.50	0.52
Chloroform	.. Concave	Concave	..	0.33
Methylaniline	.. Concave	Concave	0.40	0.44
<i>o</i> -Nitrotoluene	.. Linear	Linear

It is seen that the behaviours of χ^E and β^E are similar in all cases except the mixtures of dioxane and aniline. On the basis of this comparison Triethylamine-*o*-Nitrotoluene mixtures are to be regarded as ideal.

Departures from this ideal behaviour are often attributed to the formation of complexes. The concentration at which a maximum in β^E or χ^E occurs is to be taken as a measure of the molecular complex; thus $n_2 = 0.50$ means 1:1 complex, $n_2 = 0.33$ would mean a 2:1 complex, and $n_2 = 0.66$ indicates a 1:2 complex. From this point of view, it is seen that the same complex appears to control the magnetic and ultrasonic behaviour of *o*-Xylene, *m*-Xylene and methylaniline mixtures.

In other cases different complexes appear to control the magnetic and the ultrasonic behaviours of the mixtures; for example, in amyl acetate the ultrasonic behaviour indicates a 1:1 complex whereas the magnetic data indicate a 1:2 complex. These differences are engaging our further attention.

SUMMARY

Diamagnetic susceptibilities of 10 mixtures with triethylamine as the common component have been determined. Deviations from linearity

have been observed in all cases except in aniline and *o*-Nitrotoluene. The magnetic behaviour has been compared with the ultrasonic behaviour of these mixtures.

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