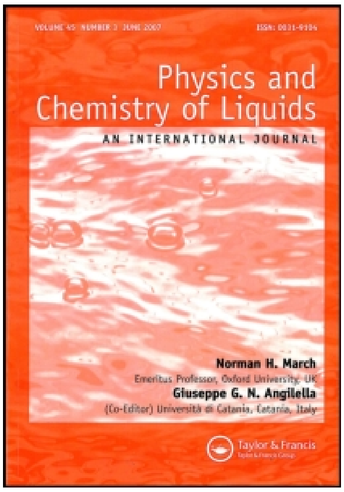

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MOLECULAR INTERACTIONS IN BINARY MIXTURES OF AQUEOUS METHYL VIOLET SOLUTIONS

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The ultrasonic behaviour of aqueous methyl violet solutions in the mixture form with different solutes namely methanol, formamide and dimethyl formamide (DMF), are studied at 30°C by evaluating various acoustical and thermodynamic parameters. The ultrasonic velocities are determined using a single crystal variable path interferometer working at 1 MHz with an accuracy of ±0.03%. The densities are measured using a pycnometer and viscosities with an Ostwald's viscometer. The related parameters are evaluated and the results are discussed in the light of the molecular interaction of the dye in aqueous form with different solutes.

KEY WORDS: Ultrasonic velocity, organic dyes and molecular interactions.

INTRODUCTION

Attempts have been made by several workers to study the behaviour of binary liquid mixtures by measuring the sound velocity and other related parameters. The variation of ultrasound velocity and isentropic compressibility is not always linear. The non-linearity may be explained on the basis of molecular dimensions and the forces acting between the molecules. Mikhailov[1] has pointed out that deviations from ideal behaviour of such a mixture should be useful for the study of structural variations and molecular interactions.

It has been found that ultrasonic velocity as such, has limited utility, in providing information about the nature and relative strength of various types of intermolecular interactions[2–5]. However numerous theoretical and experimental investigations have shown that a representation in terms of derived parameters from ultrasonic velocities such as adiabatic compressibility, molar volume, molecular sound and velocity and compressibility, together with their excess functions, provide a better insight into the mechanics of intermolecular process.

The acoustic properties of several binary mixtures have been computed with the related physico-chemical properties and from this the assessment of the molecular interaction between the components of the binary mixtures have been made. In the present study the various acoustical parameters are evaluated in the binary mixtures of aqueous methyl violet[6,7] solutions to understand the behaviour of the dye molecule in aqueous form with different solutes.

EXPERIMENTAL

The aqueous solutions of methyl violet (0.004 M) are prepared using triple distilled degassed water. The binary mixtures are prepared by adding the different solutes namely methanol, formamide and DMF to the aqueous dye solutions at the desired molefractions of the solutes. All the chemicals used are of high purity and are supplied by LOBA and Reidel-chemicals.

The ultrasonic velocities are evaluated in the solutions using a single crystal variable path interferometer working at 1 MHz, developed in our laboratory. The method of measurement of sound velocity and the details of the working of the interferometer are given in our earlier communications[8–10]. The interferometer technique used to evaluate sound velocity is accurate to $\pm 0.03\%$. The temperature of the test liquid was maintained constant to better than $\pm 0.002°C$ by immersing the interferometer in a water thermostat (VEB Prutgerate work, East Germany) whose temperature was maintained steady at any desired value using permanent heaters followed by "on and off" low wattage heaters.

The densities of the solutions are measured using a pycnometer and the viscosities with Ostwald's viscometer. The accuracy in density measurement is 2 parts in 10^5 and in viscosity is $\pm 1\%$. All the measurements were made in the low molefraction region only because the molecular interactions of these compounds with the solutes is well understood and studied effectively at low solute concentrations i.e., in the water rich region.

RESULTS AND DISCUSSIONS

The ultrasonic velocity and related parameters of aqueous methyl violet with methanol, formamide and DMF at 30°C are given in the Table 1. The ultrasonic velocity in all the three systems studied is increasing and the compressibility (β_s) decreasing with the solute composition. The molar volume (V) increases and intermolecular free-length (L'_f), internal pressure (π_i) values decrease with the increase of solute concentration. The free volume (V_f) increases for the formamide system and decreases for the remaining two systems, i.e., methanol and DMF. These are shown clearly in the Figures 1 to 6.

From the results it can be observed that the molecular sound velocity (R), acoustic impedance (Z) and Van der Waals constant (b) are increasing where as molar compressibility (W) decreasing with solute composition for all the systems. The ultrasonic velocity in the binary mixtures of aqueous methyl violet with DMF, shows much variation than the remaining two systems. Similarly the variation of adiabatic *compressibility* with the solute composition for all the three systems shows that, the

Table 1 Various acoustical and thermodynamical parameters in the binary mixtures of aqueous Methyl violet at 30°C

$X^2 \times 10^{-2}$	*Umt/sec.*	$\beta_\delta \times 10^{12}$ $cm^2/dyne$	V *ml/mole*	$Vf \times 10^{-2}$ *ml/mole*	$Lf \times 10^{-2}$ Å	$\Pi \times 10^3$ *atmp.*	$Z \times 10^5$	R	W	b
					(*a*) *Methanol*					
02.3	1524.76	43.51	18.56	1.97	41.62	26.252	1.507	213.61	560.74	68.56
04.7	1539.64	42.97	19.03	1.91	41.36	26.089	1.511	219.78	576.10	19.03
07.3	1550.78	42.63	19.52	1.82	41.19	26.057	1.513	225.99	591.63	19.52
09.9	1562.38	42.27	20.04	1.74	41.02	25.985	1.514	232.59	608.13	20.04
12.9	1567.72	42.25	20.59	1.17	41.01	25.694	1.509	239.26	624.84	20.59
16.0	1570.42	42.40	21.19	1.64	41.08	25.531	1.502	246.32	642.63	21.19
					(*b*) *Formamide*					
02.3	1536.08	42.82	18.60	2.28	41.29	24.976	1.530	214.17	563.33	18.59
04.8	1539.56	41.76	19.12	2.37	40.77	24.209	1.555	220.78	581.09	19.12
07.4	1550.01	40.92	19.68	2.45	40.36	23.498	1.576	227.77	599.88	19.68
10.1	1556.86	40.27	20.27	2.42	40.04	23.118	1.595	234.94	619.26	20.27
13.1	1565.10	39.59	20.91	2.53	39.70	22.328	1.614	242.75	640.28	20.90
16.2	1570.96	39.06	21.57	2.62	39.44	21.612	1.629	250.81	661.98	21.57
					(*c*) *DMF*					
01.2	1533.08	42.76	18.79	2.12	41.26	25.405	1.525	216.64	569.06	18.54
02.5	1555.16	41.57	19.52	2.06	40.68	25.025	1.547	226.15	593.60	19.27
03.9	1577.38	40.42	20.32	2.02	40.12	24.513	1.568	236.53	620.41	20.07
05.5	1589.84	39.83	21.20	1.90	39.82	24.325	1.579	247.42	648.63	20.94
07.2	1607.10	38.98	22.145	1.89	39.39	23.657	1.596	259.39	679.67	21.89
09.1	1630.32	37.85	23.19	1.92	38.82	22.828	1.619	272.98	614.72	22.93

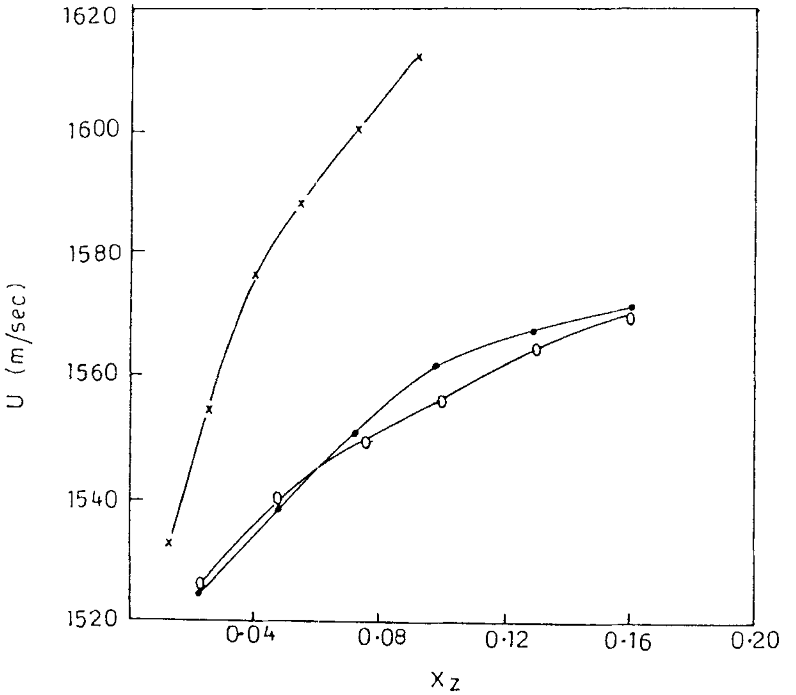

Figure 1 Variation of ultrasonic velocity (V) with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

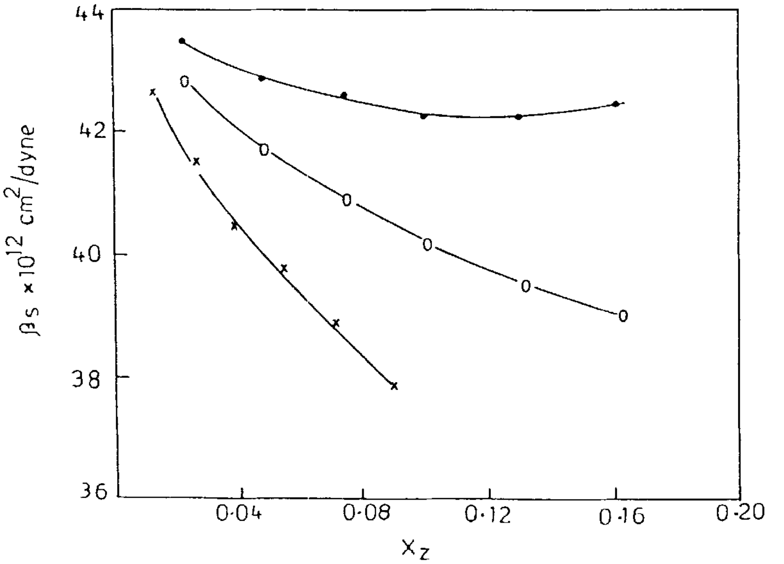

Figure 2 Variation of adiabatic compressibility (β_s) with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

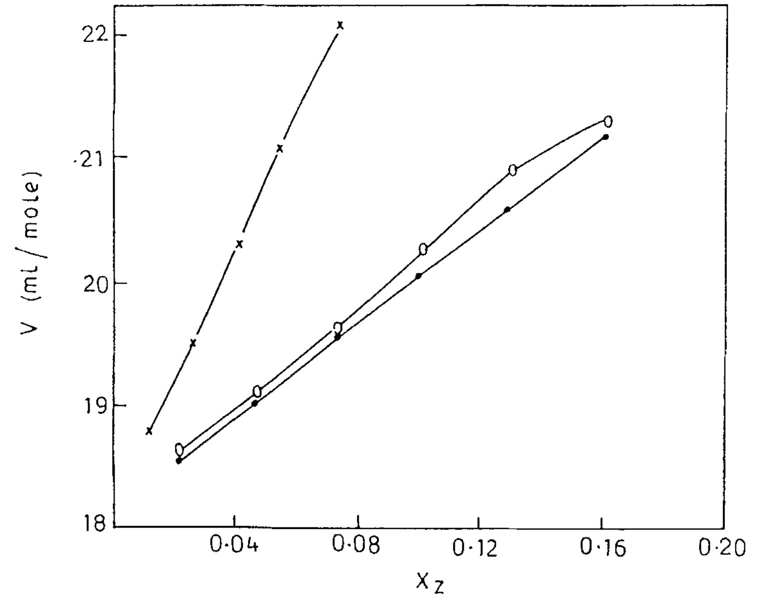

Figure 3 Variation of Molar Volume (V) with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

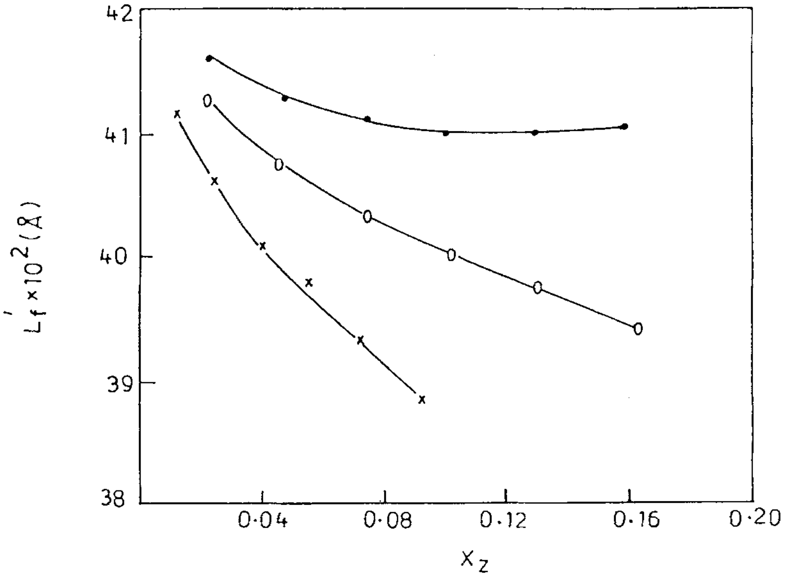

Figure 4 Variation of intermolecular free length (L_b') with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

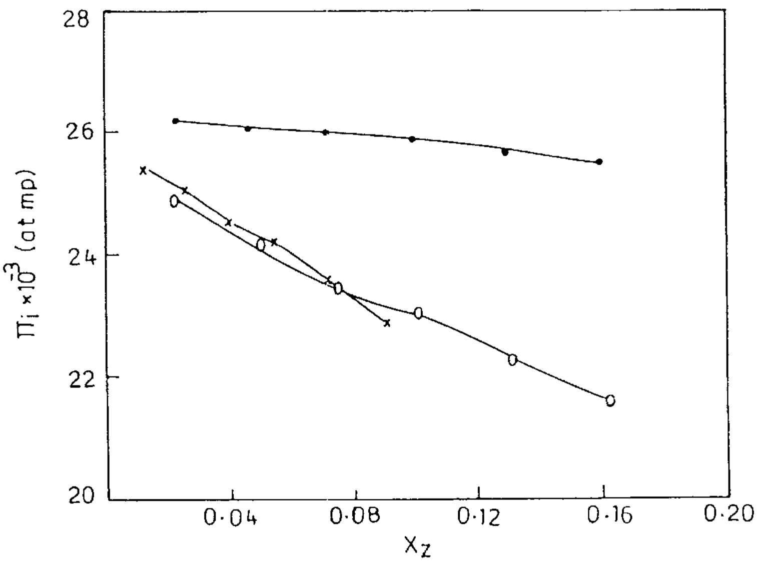

Figure 5 Variation of internal pressure (π_i) with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

decrease in β_s is more in DMF, less in formamide and very low in methanol when compared (Figure 2).

The intermolecular free-length shows similar variation to that of β_s and variation of molar volume is similar to that of ultrasonic velocity. The variation of internal pressure for all the systems decreases but in methanol the variation is less. For the remaining systems the variation is high and almost equal. The free volume in all the three systems studied shows similar variation as that of π_i but the free volume values are decreasing in methanol and increasing in formamide. For the system DMF, it decreases up to 0.075 molefraction then increases afterwards.

It is well known that many aqueous solutions exhibit eccentric static and dynamic properties in the low concentration range of the solute. A widely accepted point of view relates this peculiar behaviour to the unique structural properties of water as a solvent and to the ability of the solute to promote such structure effects. The anomalous behaviour of aqueous solutions in many of the physical properties such as sound velocity, density, compressibility, heat capacity etc., which have been attributed to either promotion or disruption of the hydrogen bonded structure of water[11,12] by the solutes.

It has been already known that methanol forms aggregates with water[13] where as formamide and DMF are forming amide-water complexes[14,15] in water. The present study shows the effect of dye moleculer on these complexes through non-linear behaviour of the ultrasonic velocity and related parameters. Also the values of R, W and b are sensitive to the structure of molecules. These values give information on the formation of a complex and on the association or dissociation of the components.

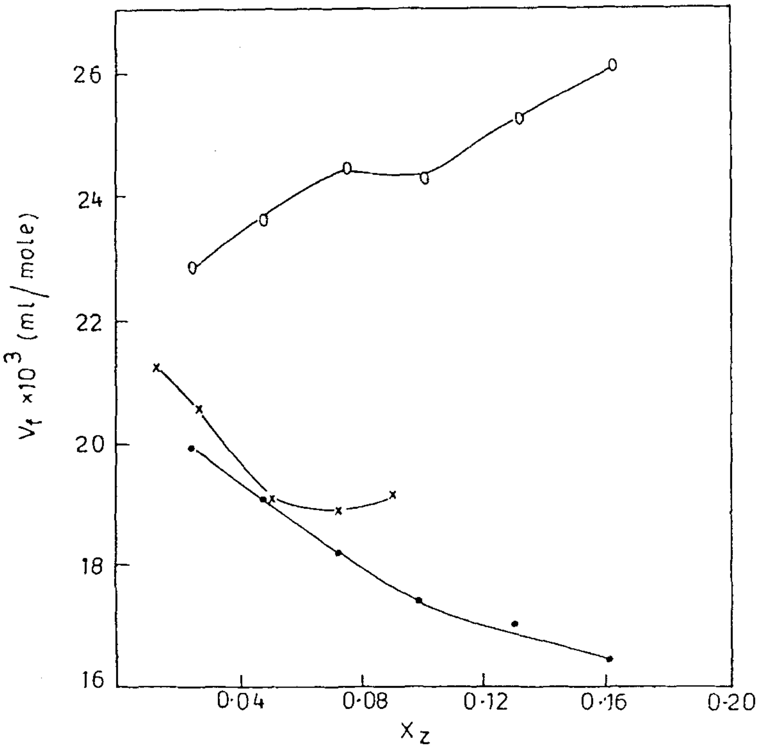

Figure 6 Variation of free volume (V_f) with molefraction (X_2) of (a) Methanol (●) (b) Formamide (○) and (c) DMF (×) in aqueous Methyl violet.

CONCLUSIONS

In the present study the effect of methanol on the aqueous dye solution is more when compared to formamide and DMF, but all the three solutes are strongly interacting with aqueous dye solution. The non- linear variation of ultrasonic velocity and other related parameters in these binary mixtures indicate the presence of heteromolecular interactions. It is difficult to separate out the role of specific interactions, however it may be expected that the excess parameters reveal the changes in the nature and the strength of specific interactions more prominently. Work is in progress to evaluate the excess parameters in these solutions and hence to study the nature of interactions in these binary mixtures more effectively.

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