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Study of Interactions in Some Binary Systems by Ultrasonic Velocity Measurements

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The ultrasonic velocity measurements were carried out for the binary mixtures of ethanol/methanol with the ketones such as acetone, ethyl methyl ketone, acetophenone, cyclohexanone. To study the intermolecular interactions in the components chosen, the observed excess ultrasonic velocity values are compared with the calculated values. When excess ultrasonic velocity is plotted against mole fraction the curve shows maximum at almost 50% by mole fraction. Ethanol shows stronger interaction with the ketones relative to methanol as indicated from ultrasonic data.

Key Words: Binary systems, Interactions, Ultrasonic Velocity.

The study of molecular interactions plays an important role in understanding the structure and properties of various liquids and gases. The forces, which arise due to these molecular interactions, can be broadly classified as (1) Long-range forces and (2) Short-range forces. The long-range forces are the electrostatic induction and dispersion forces and arise when the interacting molecules come close together without the overlap of their electron clouds. The short-range forces arise when the molecules come close enough together for their electron clouds to overlap and are often highly directional.

The hydrogen bonding interaction is due to the short-range interaction. From the fact that the H-bond distance is smaller than the van der Waals' radii, the short-range interactions are mainly responsible for the hydrogen bonding[1-4]. Among the non-spectroscopic methods in the study of molecular interactions, the ultrasonic velocity measurements find extensive applications owing to their ability to characterize physico-chemical behaviour of liquid systems from speed data. In the case of liquid mixtures the data obtained from the ultrasonic velocity measurements and their variation with concentration of components help to understand the nature of the molecular interactions in terms of some physical parameters.

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EXPERIMENTAL

The alcohols methanol and ethanol were purified by fractional distillation. Acetone, cyclohexanone, acetophenone, ethyl methyl ketone were purified by distillation.

Binary mixtures containing about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 mole fractions of methanol/ethanol with various ketones, such as acetone, ethyl methyl ketone, acetophenone and cyclohexanone were prepared.

The densities of pure liquids as well as mixtures were measured using a 10 mL specific gravity bottle. The ultrasonic velocity of the waves in the liquid was measured by using a multi-frequency ultrasonic interferometer. The ultrasonic frequency produced by the interferometer is 4MHz with a tolerance of ±0.005%. The capacity of the measuring cell is 17 mL. The measuring cell is connected to the output terminal of high frequency generator through a shielded cable.

The sound waves are generated by applying an alternating field or suitable frequency to a quartz crystal, which is thereby set into resonant longitudinal oscillations. Ultrasonic waves are generated from the surface of such an oscillating crystal and their wavelengths can be measured by setting up standing waves in the liquid between the crystal surface and a parallel reflector. The wavelength and the velocity of the ultrasonic waves in the liquid and the velocity of ultrasonic waves in the liquid can be calculated using the formulae

$$\mu = 2d/n$$

$$U = \lambda f$$

where f is the frequency of the generator. In understanding the molecular interactions in binary mixtures, the excess volume, heat capacity and internal pressure are very much useful.

Calculation

The ultrasonic velocity of an ideal mixture[5, 6] is

$$U_{id} = \left[\frac{X_1R_1 + X_2R_2}{X_1V_1 + X_2V_2}\right]^3 \quad (1)$$

$$U_{id} = \frac{U_1U_2}{U_1\phi_2} + U_2\phi_1 \quad (2)$$

$$U_{id} = \frac{1}{(\beta_{id}\rho_{id})^2} \quad (3)$$

$$U_{id} = \left[\frac{V_{id}}{\beta_{id}(X_1M_1 + X_2M_2)}\right]^2 \quad (4)$$

In the above expressions X_1, X_2; ϕ_1, ϕ_2 and U_1, U_2 represent mole fractions, volume fractions and ultrasonic velocities of the solvent and solute respectively. The various functions of ideal mixtures may be calculated as

$$V_{id} = X_1V_1 + X_2V_2 \quad (5)$$

$$\rho_{id} = \phi_1P_1 + \phi_2P_2 \quad (6)$$

$$\beta_{id} = \phi_1\beta_1 + \phi_2\beta_2 \quad (7)$$

where V_1, V_2, ρ_1, ρ_2 and β_1, β_2 represents molar volumes, densities and adiabatic compressibility of solvent and the solute respectively.

RESULTS AND DISCUSSION

The measured densities and ultrasonic velocity values of pure solvents and ketones are listed in Table-1.

TABLE-1
DENSITY AND ULTRASONIC VELOCITY VALUES OF THE LIQUIDS AT 318 K

Liquids	m.w.	Density (kg/m^3)	Ultrasonic velocity (m/sec)
Methanol	32.01	782.0	1200.00
Ethanol	46.02	810.7	1286.34
Acetophenone	120.00	1006.7	1396.00
Cyclohexanone	98.06	911.7	1303.56
Acetone	58.03	762.2	1097.50
Ethyl methyl ketone	72.04	779.4	1192.00

For the binary system of methanol with ethyl methyl ketone the sound velocities were calculated using equations (1)–(4) and compared with the measured values. From the comparison of values excess ultrasonic velocities are calculated and these values are listed in Table-2. Table-3 illustrates the comparison of experimental and calculated ultrasonic velocities of binary system of ethanol-acetophenone. In a similar manner the ultrasonic velocities were calculated for the remaining binary systems.

TABLE 2
EXCESS ULTRASONIC VELOCITY VALUES OF
METHANOL-ETHYL METHYL KETONE SYSTEM

Mole fraction of ethanol	Experiment ultrasonic velocity (m/sec)	Ideal Ultrasonic velocity (m/sec)				Excess ultrasonic velocity (m/sec)			
		By eqn. (1)	By eqn. (2)	By eqn. (3)	By eqn. (4)	By eqn. (1)	By eqn. (2)	By eqn. (3)	By eqn. (4)
.0.000	1192.0	—	—	—	—	—	—	—	—
0.123	1194.0	1193.6	1192.5	1192.4	1192.1	0.4	1.5	1.6	1.9
0.132	1195.0	1193.6	1192.8	1192.9	1192.6	1.4	2.2	2.1	2.4
0.358	1197.0	1195.2	1193.4	1193.3	1192.9	1.8	3.6	3.7	4.1
0.652	1199.2	1197.2	1193.9	1193.9	1193.0	2.0	5.3	5.3	6.2
0.664	1205.0	1197.3	1194.5	1194.5	1193.8	7.7	10.5	10.5	11.2
0.729	1205.5	1198.0	1195.2	1195.3	1194.5	7.5	10.3	10.2	11.0
0.737	1205.6	1198.2	1196.2	1196.1	1195.6	7.4	9.4	9.5	10.0
0.804	1205.8	1198.9	1197.2	1197.3	1198.3	6.9	8.6	8.5	7.5
0.810	1205.9	1199.0	1198.5	1198.4	1198.3	6.9	7.4	7.5	7.6
1.000	1200.0	—	—	—	—	—	—	—	—

TABLE-3
EXCESS ULTRASONIC VELOCITY VALUES OF ETHANOL-ACETOPHENONE SYSTEM

Mole fraction of methanol	Experiment ultrasonic velocity (m/sec)	Ideal Ultrasonic velocity (m/sec)				Excess ultrasonic velocity (m/sec)			
		By eqn. (1)	By eqn. (2)	By eqn. (3)	By eqn. (4)	By eqn. (1)	By eqn. (2)	By eqn. (3)	By eqn. (4)
0.000	1396	—	—	—	—	—	—	—	—
0.117	1391	1389.5	1390.1	1387.0	1388.1	1.5	0.9	4.0	2.9
0.187	1389	1386.8	1383.9	1377.8	1375.2	2.2	5.1	11.2	13.8
0.301	1382	1377.6	1376.2	1367.1	1367.0	4.4	5.8	14.9	15.0
0.392	1376	1370.6	1364.3	1352.7	1353.5	5.4	11.7	23.3	22.5
0.491	1374	1362.1	1358.8	1345.3	1344.1	11.9	15.2	28.7	29.9
0.583	1360	1353.0	1348.1	1333.5	1330.7	7.0	11.9	26.5	29.3
0.716	1344	1337.6	1336.1	1321.5	1323.9	6.4	7.9	22.5	20.1
0.814	1330	1324.0	1322.2	1309.3	1311.8	6.0	7.8	20.7	18.2
0.899	1312	1310.1	1305.6	1297.2	1296.1	1.9	6.4	14.8	15.9
1.000	1286.34	—	—	—	—	—	—	—	—

From the ultrasonic velocity data, the compressibility values were calculated using the equation $\beta_{id} = U^2\rho^{-1}$. The calculated values have been compared with the observed values and the comparison is displayed in Table-4.

TABLE-4
ADIABATIC COMPRESSIBILITY AND INTERACTION COEFFICIENT AT ALMOST EQUIMOLAR CONCENTRATIONS OF ALCOHOL-KETONE SYSTEM

Alcohol	Ketone	Adiabatic compressibility β			Interaction coefficient (α)
		Experimental $\times10^9\ m^2\ N^{-1}$	Additive $\times10^9\ m^2\ N^{-1}$	Excess compressibility $\times10^9\ m^2\ N^{-1}\ \beta_{ad}^E$	
Ethanol	Acetone	0.0884777	0.0906054	–0.002	0.0318
	Ethyl methyl ketone	0.0806003	0.0826598	–0.002	0.0258
	Acetophenone	0.0535592	0.0625606	–0.009	0.0449
	Cyclohexanone	0.0689950	0.0692960	–0.003	0.0294
Methanol	Acetone	0.0974351	0.0993275	–0.002	0.0209
	Ethyl methyl ketone	0.0882940	0.0892932	–0.001	0.0188
	Acetophenone	0.0689418	0.0706332	–0.002	0.0141
	Cyclohexanone	0.0757363	0.0768319	–0.001	0.0146

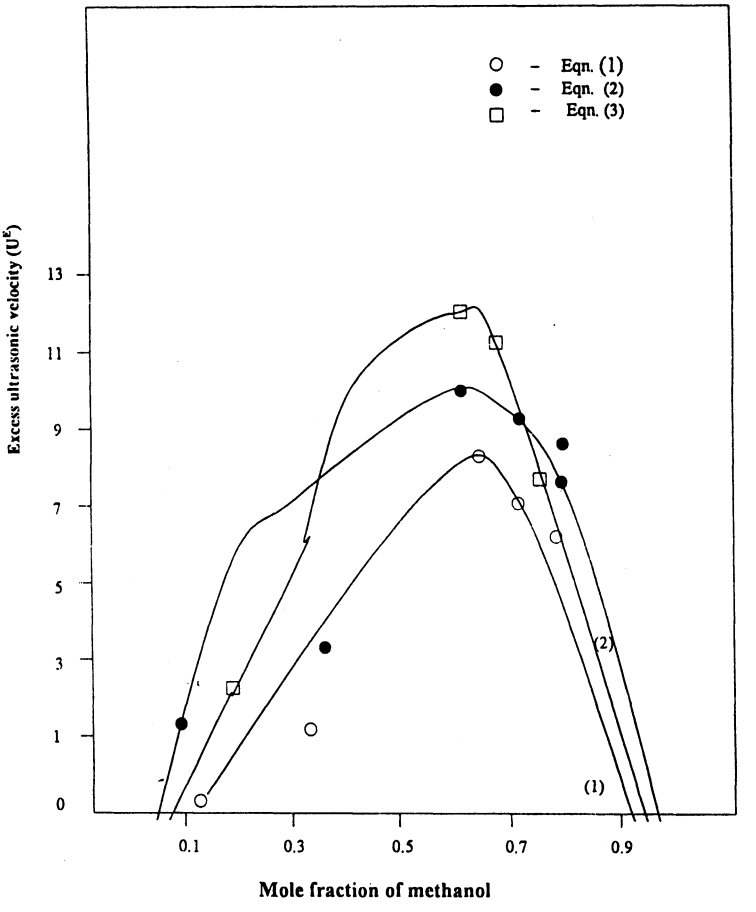


Fig. 1. Methanol-ethyl methyl ketone system (U^E *vs.* mole fraction of methanol)

The excess compressibility is plotted against the mole fraction. Figs. 1 and 2 represent the plot of excess ultrasonic velocity against mole fraction of alcohol for the systems methanol-ethyl methyl ketone and ethanol-acetophenone systems respectively. The interaction co-efficient can be calculated using the relation

$$\alpha = \left[\frac{U_{exp}^2}{U_{ideal}^2} - 1 \right] \tag{8}$$

and these values are also listed in Table-4.

In all these systmem studied the excess compressibility is negative and exhibits minimum at almost equimolar concentration which may be attributed to the presence of 1 : 1 complex formation through H-bonding between the interacting components.

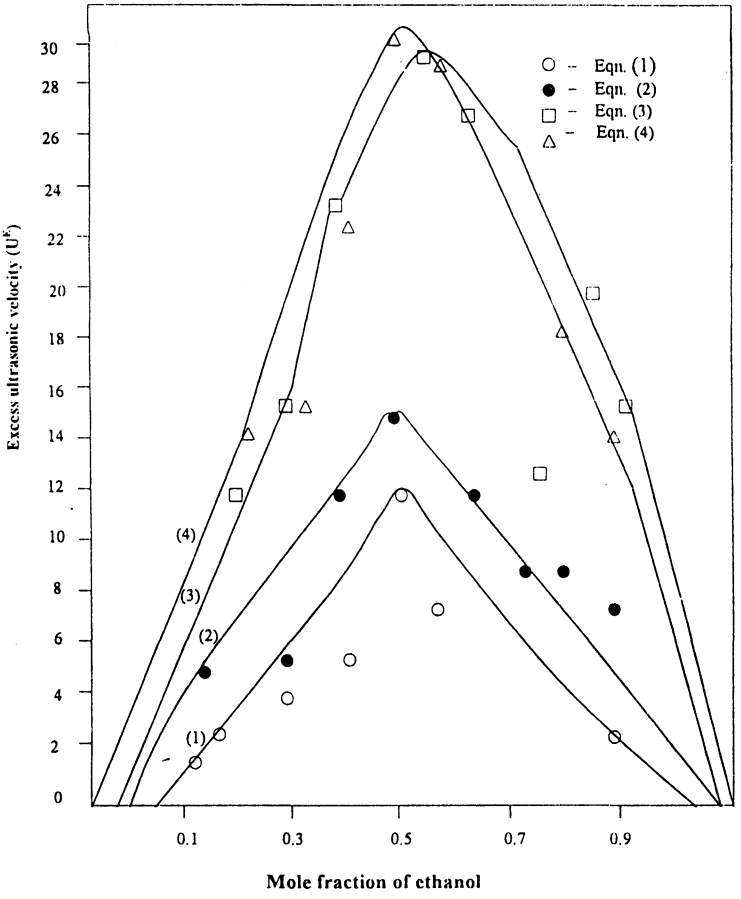
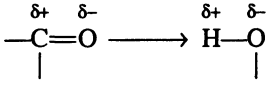
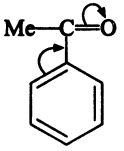


Fig. 2. Ethanol-acetophenone system (U^E *vs.* mole fraction of ethanol)

One can visualize the interaction between carbonyl group of ketones and hydroxyl group of alcohols in the following manner.



Groups which increase the electron density on carbonyl oxygen will strengthen the interaction. As we move from acetone to ethyl methyl ketone one of the methyl groups is replaced by ethyl group. This is reflected in the lower interaction coefficient at almost equimolar concentrations for the binary system of ethyl methyl ketone with alcohol when compared to that of acetone.



Acetophenone shows a stronger interaction with ethanol when compared to the other ketones. Here mesomeric effect (structure) and methyl group will increase electron density on carbonyl oxygen and so the interaction will be strong. The fact that the interaction of acetone with ethanol is less than that of acetophenone indicates that mesomeric effect is the dominant factor. It can be noted that as we move from acetophenone to cyclohexanone mesomeric effect is absent and so the interaction of cyclohexanone with ethanol is less which is indicated by the interaction coefficient. It can be noted that the interaction of methanol with the ketones is less when compared to that of ethanol as seen from the interaction coefficient (α). An examination of the adiabatic compressibility of alcohols shows that the compressibility of the alcohol decreases from lower member to higher member[7]. It is known that the hydrogen bond strength increases as we go from lower member of alcohol to higher member and hence it is possible to say that the compressibility can be related to hydrogen bond strength[8]. The change in the strength of H-bonding between the interacting components is reflected in the measured values of ultrasonic velocity also.

Thus, the present study provides evidence for the interaction of —C=O group of ketones with the —OH group of alcohols. The ultrasonic velocity data and compressibility data indicate the presence of 1 : 1 complex formation. The interaction may be ascribed to be due to H-bonding between the carbonyl group of ketones and the hydroxyl group of alcohol.

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