

Ultrasonic Velocity, Density and Viscosity of Binary Liquid Mixtures of Acetone with Toluene, Chlorobenzene and Nitrobenzene

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Abstract

We report the measurements of the speed of sound in the binary liquid mixtures of acetone with toluene, chlorobenzene and nitrobenzene measured at 303 K. The studies on ultrasonic velocity, density and viscosity in binary liquid mixtures have been used to evaluate the different thermo acoustical parameters along with the excess properties. It was found that in all the cases, the experimental data obtained fitted with the values correlated by the corresponding models very well. From the light of these parameters molecular interaction such as existence of strong molecular association and weak interaction among the participating liquids has been observed in the present study.

Keywords: Fractionalization, positive and negative deviation, ultrasonic velocity, excess properties.

Introduction

In the recent years, mixed solvents rather than pure solvents find practical application in most chemical processes as their properties are less known¹⁻². Ultrasonic technique has become a powerful tool for studying the molecular behaviour of liquid mixtures³. This is because of its ability of characterizing physico - chemical behaviour of liquid medium⁴⁻⁶. Binary liquid mixtures due to their unusual behaviour have attracted considerable attention⁷. Data on some of the properties associated with the liquids and

liquid mixtures like density, viscosity and ultrasonic velocity find extensive applications in chemical engineering process simulation, textile industries solution theory and molecular dynamics⁸. These measurements are used to study the molecular interactions in pure liquids, liquid mixtures and ionic interactions in solution comprising either single or mixed solutes⁹⁻¹⁰.

The studies on solution properties of liquid mixtures consisting of polar as well as non-polar components find applications in industrial and technological process¹¹. Acetone finds wide application in various industries as an organic solvent, its miscibility with numerous other solvents permits its use with them, thereby increasing their individual efficiency. It is used as a lacquer or varnish solvent; its vapour can be recovered by absorption in a suitable medium and then separated by fractionalization. Therefore in order to have a clear understanding of the intermolecular interaction between acetone - toluene, acetone -chlorobenzene, acetone - nitrobenzene molecules, an attempt has been made to measure density, viscosity and ultrasonic velocity for the mixtures over the entire composition range. The present investigation aims at understanding the molecular interactions based on thermodynamical parameters and their excess functions in the binary mixture at 303 K. Acetone belongs to the carbonyl compound series having functional group C=O and it has the ability to dissolve other materials, particularly polymers and adhesives, while toluene belongs to the hydrocarbons and chlorobenzene and nitrobenzene are compounds which possess electron withdrawing groups. From the experimental values, a few acoustical parameters such as, molar cohesive energy (MCE), isentropic compressibility (β_s), acoustical impedance (Z), molar sound velocity (R), Wada's constant (W), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), absorption coefficient (α/f^2) and viscous relaxation time (τ), ultrasonic velocity deviation (du), viscosity deviation ($d\eta$), isentropic compressibility deviation ($d\beta_s$), intermolecular free length deviation (dL_f), acoustical impedance deviation (dZ), degree of intermolecular attraction (α), excess volume (V^E) were derived over the entire mole fraction range. Ultrasonic velocities have also been evaluated theoretically with the help of Impedance relation, Nomoto relation, Van deal & Vangeal relation and Junjie relation. The suitability of these theories and equations were checked by comparing theoretical values of ultrasonic speeds with the values obtained experimentally. Literature survey showed that no measurements have been previously reported for the mixtures reported in this paper.

Materials and Methods

The chemicals used were of analytical grade and obtained from E.Merck company. Thermostatically controlled well-stirred water bath whose temperature was maintained to ± 0.01 K accuracy was used for all the measurements. Binary mixtures were prepared by weighing the liquids in airtight bottles. The possible uncertainty in the mole fraction was estimated to be less than ± 0.0001 .

Densities of pure liquids and their mixtures were determined by using a 1×10^{-5} m³ double arm pycnometer¹². The density values from triplicate replication at the temperature of 303 K were reproducible within $\pm 2 \times 10^{-2}$ kg m⁻³. The uncertainty in

density and excess molar volume values were found to be $\pm 4 \times 10^{-2} \text{ kg m}^{-3}$ and $\pm 0.001 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ respectively.

Ostwald's viscometer having capacity of about 15 ml and the capillary having a length of about 90 mm and 0.5 mm internal diameter has been used to measure the flow times of pure liquids and liquid mixtures and it was calibrated with benzene (density $\approx 0.8738 \text{ g cm}^{-3}$) and doubly distilled water (density $\approx 0.9970 \text{ g cm}^{-3}$) at 303 K. The flow time of pure liquids and liquid mixtures were repeated for five times. The uncertainty of viscosity was $\pm 0.005 \times 10^{-3} \text{ m Pas}$.

Speed of sound was measured by using a variable path, single crystal interferometer. (United scientific company, India), working at 2 MHz frequency. The interferometer was calibrated using toluene. Measurement of speed of sound through medium was based on the accurate determination of the wavelength of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell¹³. The interferometer cell was filled with the test liquid, and water was circulated around the measuring cell from a thermostat. The uncertainty was estimated to be 0.1 ms^{-1} . The change of speed of sound on mixing were calculated by the equation

$$du = u - (x_1 u_1 + x_2 u_2) \quad (1)$$

Where u is the speed of sound in the mixture and u_1 and u_2 are the speed of the sound in the pure compounds.

The isentropic compressibility (β_s) was calculated by the equation

$$\beta_s = 1 / \rho u^2 \quad (2)$$

Where ρ is the density of mixture and u is the ultrasonic velocity of the mixture.

The acoustical impedance (Z) was calculated by the equation,

$$Z = \rho u \quad (3)$$

Where ρ is the density of mixture and u is the ultrasonic velocity of the mixture.

The molar sound velocity (R) was calculated by the equation

$$R = (M_{\text{eff}} / \rho) u^{1/3} \quad (4)$$

Where u is the ultrasonic velocity of the mixture.

The molar compressibility or Wada's constant (W), was calculated by the equation

$$W = (M / \rho) \beta_s^{-1/7} \quad (5)$$

Where M is the relative molar mass and β_s is the isentropic compressibility.

The intermolecular free length (L_f) was calculated by the equation

$$L_f = k \beta_s^{1/2} \quad (6)$$

Where $K = 1.98 \times 10^{-6}$, the Jacobson constant (Jacobson 1952).

The Free volume was calculated by the equation

$$V_f = (M_{\text{eff}} U / K \eta)^{3/2} \quad (7)$$

Where $K = 4.28 \times 10^9$ for all liquids which is a temperature independent constant. The internal pressure was calculated by the equation

$$\pi_i = \{bRT / (V^2 V_f)^{1/3}\} \quad (8)$$

b is a packing factor, R is a gas constant, V_f is free volume & T is temperature. The absorption coefficient was calculated by the equation

$$(\alpha/f^2) = (8\pi^2\eta/3\rho U^3) \quad (9)$$

η is viscosity of the mixture & ρ is the density of the mixture.

The viscous relaxation time was calculated by the equation

$$\tau = (4\eta/3\rho U^2) \quad (10)$$

η is viscosity of the mixture and ρ is the density of the mixture.

The degree of intermolecular attraction (α) was calculated by the equation

$$\alpha = (u^2 / u_{im}^2) - 1 \quad (11)$$

Where $u_{im}^2 = 1 / \{(x_1M_1 + x_2M_2)(x_1/M_1u_1^2 + x_2/M_2u_2^2)\}$

The dU , dL_f , dZ , $d\beta_s$ and $d\eta$ were derived over the entire mole fraction range by using the general equation

$$A^E = A - (X_i A_1 + (1-X_i) A_2) \quad (12)$$

Where A is the corresponding parameters (U , L_f , Z , β_s & η) of binary mixture and A_1 and A_2 are the corresponding pure component values.

Excess volume was calculated by the equation

$$V^E = \{(X_1M_1 + X_2M_2)/\rho_M\} - (X_1M_1/\rho_1 + X_2M_2/\rho_2) \quad (13)$$

The sound velocity can be correlated with the relation called Impedance relation which is represented as

$$U_{IM} = (X_1Z_1 + X_2Z_2) / (X_1\rho_1 + X_2\rho_2) \quad (14)$$

where X , Z , ρ denote the mole fraction, acoustic impedance and density of the component respectively.

Nomoto¹⁴ derived an empirical formula for the sound velocity in binary liquid mixture. It is given by the equation.

$$U_{NR} = [R/V]^3 = \left\{ \frac{(X_1R_1 + X_2R_2)}{(X_1V_1 + X_2V_2)} \right\}^3 \quad (15)$$

Where X , R , V denote the mole fraction, molar sound velocity & molar volume at temperature T of the component.

The acoustical behaviour of binary liquid mixture was studied in detail by Van deal etal¹⁵. The expression for sound velocity (U_{IMR}) of binary liquid mixtures can be obtained from equation

$$U_{\text{IMR}} = \left\{ \frac{[1/(X_1M_1 + X_2M_2)]}{[X_1/M_1U_1^2 + X_2/M_2U_2^2]} \right\}^{1/2} \quad (16)$$

Where X, M & U are the mole fraction, molecular weight & sound velocity of component.

Junjie derived an empirical formula for the sound velocity in binary liquid mixture. It is given by the equation^{19,20}

$$U_{\text{jun}} = \left\{ \frac{(X_1V_1 + X_2V_2)}{(X_1M_1 + X_2M_2)^{1/2}} \left[\frac{X_1V_1}{\rho_1U_1^2} + \frac{X_2V_2}{\rho_2U_2^2} \right] \right\}^{-1/2} \quad (17)$$

Where X, V, M, ρ denote the mole fraction, molar volume, molecular weight and density of the components.

The percentage deviation of the experimental velocity from the theoretical value is given by the equation¹⁶

Percentage deviation in velocity =

$$\frac{U_{\text{Theo}} - U_{\text{Expt}}}{U_{\text{Theo}}} \times 100 \quad (18)$$

Results and Discussion

The density, ultrasonic velocity and viscosity data for the pure liquids at 303 K are given below:

Table1: Comparison of density, ultrasonic velocity and viscosity data for liquids at 303 K.

Compound	Density Kg/m ³		U m/s		Viscosity X 10 ⁻¹ Nsm ⁻²	
	Expt	Lit	Expt	Lit	Expt	Lit
Acetone	792	804 ¹⁷	1138	1145 ¹⁷	3.73	-
Toluene	862	862 ¹⁸	1284	1304 ¹⁸	5.64	5.50 ¹⁸
Chlorobenzene	1106	1100 ¹⁸	1360	1269 ¹⁸	16.1	7.55 ¹⁸
Nitrobenzene	1192	1198 ¹⁸	1424	1461 ¹⁸	19.1	17.9 ¹⁸

Table 2 gives the measured density (ρ), ultrasonic velocities (u), viscosity (η), radius (r) & molar cohesive energy (MCE) for the binary liquid mixtures of acetone with toluene, chlorobenzene and nitrobenzene over the entire composition range at

303 K. Table 3 gives the acoustic properties like isentropic compressibility (β_s), acoustical impedance (Z), molar sound velocity (R), molar compressibility (W), intermolecular free length (L_f) of acetone with toluene, chlorobenzene & nitrobenzene at 303 K. Table 4 gives the thermodynamic properties like free volume (V_f), internal pressure (π_i), absorption coefficient (α/f^2), viscous relaxation time (τ), degree of intermolecular attraction (α) of acetone with toluene, chlorobenzene and nitrobenzene at 303 K. Table 5 gives the experimental deviation factors like ultrasonic velocity deviation (dU), intermolecular free length deviation (dL_f), acoustical impedance deviation (dZ), isentropic compressibility deviation ($d\beta_s$), viscosity deviation ($d\eta$) & excess volume of acetone with toluene, chlorobenzene and nitrobenzene at 303 K. Table 6 gives the theoretical values of ultrasonic velocity calculated from Impedance, Nomoto, Van deal & Vangeal and Junjie's relation along with the experimental ultrasonic velocity and percentage error for acetone – toluene, acetone – chlorobenzene and acetone - nitrobenzene mixtures at 303 K.

Table2: Measured properties of binary mixtures at 303 K.

Mole fraction of acetone	Density Kg/m ³	U m/s	Viscosity X 10 ⁻¹ Nsm ⁻²	$r \times 10^{-9}$ m	MCE X 10 ⁵ atm m ³
Acetone - Toluene					
0.0000	862	1284	5.64	3.49	3.42
0.1388	856	1292	5.25	3.43	3.32
0.2642	851	1266	5.05	3.38	3.32
0.3837	832	1268	4.77	3.35	3.28
0.4859	836	1240	4.62	3.30	3.28
0.5908	828	1218	4.40	3.26	3.27
0.6855	820	1208	4.36	3.22	3.31
0.7703	813	1216	4.16	3.18	3.25
0.8535	805	1222	3.95	3.14	3.19
0.9307	798	1160	3.75	3.11	3.23
1.0000	792	1138	3.56	3.08	3.20
Acetone - Chlorobenzene					
0.0000	1106	1360	16.1	3.43	4.99
0.1287	1077	1336	15.0	3.39	4.95
0.2542	1046	1304	13.7	3.34	4.89
0.3682	1017	1302	12.5	3.30	4.77
0.4802	981	1232	10.8	3.27	4.68
0.5769	950	1228	5.83	3.24	3.51
0.6700	921	1188	5.28	3.20	3.47
0.7609	886	1168	4.71	3.17	3.39
0.8486	857	1164	4.21	3.13	3.28
0.9228	827	1160	3.72	3.10	3.16

1.0000	792	1140	3.40	3.08	3.13
Acetone - Nitrobenzene					
0.0000	1192	1424	19.0	3.45	5.09
0.1358	1153	1392	17.0	3.40	4.98
0.2532	1120	1308	16.0	3.35	5.10
0.3729	1077	1348	14.3	3.31	4.87
0.4769	1037	1312	11.5	3.28	4.53
0.5686	1002	1276	8.2	3.24	3.97
0.6660	957	1240	7.0	3.21	3.84
0.7661	914	1220	5.9	3.17	3.68
0.8462	974	1204	5.5	3.03	3.54
0.9270	831	1164	3.9	3.11	3.22
1.0000	790	1136	3.3	3.08	3.13

Table3: Acoustic properties of binary liquid mixtures at 303 K.

Mole fraction of acetone	$\beta_s \times 10^{-10}$ kg^{-1}m^2	$Z \times 10^5$ $\text{Kg m}^{-2}\text{s}^{-1}$	R	W	$L_f \times 10^{-11}$ m
Acetone - Toluene					
0.0000	7.04	11.06	1.16	2.17	5.26
0.1388	7.00	11.05	1.11	2.07	5.25
0.2642	7.33	10.77	1.06	1.97	5.37
0.3837	7.48	10.54	1.03	1.91	5.42
0.4859	7.78	10.36	0.97	1.81	5.53
0.5908	8.14	10.08	0.92	1.73	5.66
0.6855	8.36	9.90	0.89	1.66	5.74
0.7703	8.32	9.88	0.86	1.61	5.72
0.8535	8.32	9.83	0.83	1.55	5.72
0.9307	9.31	9.25	0.79	1.48	6.05
1.0000	9.75	9.01	0.76	1.42	6.20
Acetone - Chlorobenzene					
0.0000	4.89	15.0	1.13	2.18	4.39
0.1287	5.20	14.4	1.08	2.08	4.53
0.2542	5.62	13.6	1.03	1.98	4.70
0.3682	5.80	13.2	0.99	1.90	4.78
0.4802	6.72	12.1	0.94	1.80	5.14
0.5769	6.98	11.7	0.91	1.74	5.24
0.6700	7.69	10.9	0.87	1.66	5.50
0.7609	8.27	10.3	0.85	1.59	5.71
0.8486	8.61	9.9	0.81	1.53	5.82
0.9228	8.99	9.5	0.79	1.48	5.95

1.0000	9.72	9.0	0.77	1.42	6.18
Acetone - Nitrobenzene					
0.0000	4.14	16.97	1.16	2.26	4.04
0.1358	4.48	16.04	1.11	2.15	4.20
0.2532	5.22	14.64	1.04	2.02	4.53
0.3729	5.11	14.51	1.01	1.95	4.49
0.4769	5.60	13.60	0.97	1.86	4.70
0.5686	6.13	12.78	0.93	1.78	4.91
0.6660	6.80	11.86	0.89	1.70	5.17
0.7661	7.35	11.15	0.85	1.62	5.38
0.8462	7.08	11.72	0.741	1.42	5.28
0.9270	8.88	9.67	0.79	1.48	5.91
1.0000	9.81	8.97	0.76	1.42	6.21

Table4: Thermodynamic properties of binary liquid mixtures at 303 K.

Mole fraction of acetone	$V_f \times 10^{-7}$ $m^3 mol^{-1}$	$\pi_l \times 10^6$ Pa.	$\alpha/f^2 \times 10^{-12}$ $m^{-1}s^2$	$t \times 10^{-10}$ sec	$\alpha \times 10^{-1}$ m
Acetone - Toluene					
0.0000	3.43	3.20	8.13	5.29	0
0.1388	3.56	3.25	7.48	4.90	0.96
0.2642	3.40	3.40	7.69	4.94	1.14
0.3837	3.45	3.45	7.39	4.75	1.64
0.4859	3.27	3.63	7.62	4.79	1.44
0.5908	3.17	3.76	7.74	4.78	1.27
0.6855	2.97	3.94	7.93	4.86	1.23
0.7703	3.02	4.01	7.48	4.61	1.45
0.8535	3.08	4.08	7.07	4.38	1.60
0.9307	2.88	4.26	7.93	4.66	0.43
1.0000	2.85	4.37	8.03	4.63	0
Acetone - Chlorobenzene					
0.0000	1.05	4.90	15.2	10.5	0
0.1287	1.03	5.05	15.3	10.4	1.1
0.2542	1.03	5.19	15.5	10.3	1.67
0.3682	1.07	5.25	14.6	9.65	2.41
0.4802	1.10	5.31	15.5	9.70	1.62
0.5769	2.52	4.11	8.7	5.43	1.84
0.6700	2.53	4.20	8.9	5.41	1.23
0.7609	2.64	4.22	8.7	5.20	0.89
0.8486	2.81	4.24	8.1	4.83	0.75
0.9228	3.05	4.19	7.5	4.46	0.55

1.0000	3.07	4.26	7.6	4.41	0
Acetone - Nitrobenzene					
0.0000	0.99	4.93	14.5	10.5	0
0.1358	1.02	5.03	14.4	10.1	1.68
0.2532	0.91	5.36	16.8	11.2	1.62
0.3729	1.01	5.31	14.3	9.7	3.45
0.4769	1.22	5.10	12.9	8.5	3.41
0.5686	1.75	4.62	10.4	6.7	3.06
0.6660	1.88	4.61	10.2	6.3	2.54
0.7661	2.06	4.59	9.4	5.8	2.17
0.8462	2.01	5.07	8.6	5.2	1.75
0.9270	2.89	4.26	7.8	4.6	0.77
1.0000	3.06	4.26	7.7	4.4	0

Table5: Experimental deviation factors of Binary liquid mixtures like dU , dL_f , dZ , $d\beta_s$, $d\eta$ and v^E at 303 K.

Mole fraction of acetone	dU m/s	$dL_f \times 10^{-12}$ m	$dZ \times 10^3$ $\text{kgm}^{-2}\text{s}^{-1}$	$d\beta_s \times 10^{-11}$ kg^{-1}m^2	$d\eta \times 10^{-2}$ Nsm^{-2}	$V^E \times 10^4$ $\text{m}^3\text{mol}^{-1}$
Acetone - Toluene						
0.0000	0	0	0	0	0	0
0.1388	28	-1.44	27.6	-4.15	-1.0	-1.2
0.2642	21	-1.37	24.8	-4.22	-0.50	-3.3
0.3837	40	-1.96	27.0	-6.02	-0.80	10.23
0.4859	27	-1.82	29.6	-5.75	-0.20	-1.7
0.5908	20	-1.53	23.1	-4.99	-0.10	-0.88
0.6855	24	-1.66	24.6	-5.39	0.010	0.053
0.7703	44	-2.59	40.1	-8.08	0.010	0.20
0.8535	63	-3.36	52.3	-10.03	0.80	0.98
0.9307	12	-0.75	10.1	-2.49	0.50	0.80
1.0000	0	0	0	0	0	0
Acetone - Chlorobenzene						
0.0000	0	0	0	0	0	0
0.1287	4	-0.92	12.1	-3.08	5.0	-1.10
0.2542	0	-1.39	12.7	-4.93	8.0	-1.73
0.3682	23	-2.70	4.14	-8.65	10.0	-3.47
0.4802	-22	-1.08	-6.83	-4.90	9.0	-0.43
0.5769	-5	-1.82	9.32	-6.93	-30.0	0.34
0.6700	-25	-0.88	-7.15	-4.29	-20.0	-1.36
0.7609	-25	-0.47	-11.8	-2.88	-20.0	1.22
0.8486	-9	-0.89	3.63	-3.72	-10.0	-2.43

0.9228	3	-0.97	10.0	-3.57	-7.0	-2.13
1.0000	0	0	0	0	0	0
Acetone - Nitrobenzene						
0.0000	0	0	0	0	0	0
0.1358	7	-1.34	16.2	-4.3	0.8	-1.24
0.2532	-43	-0.54	-29.9	-3.5	10.0	-5.274
0.3729	31	-3.63	52.7	-11.4	10.0	-3.91
0.4769	25	-3.78	44.6	-12.4	-1.0	-2.77
0.5686	16	-3.62	36.0	-12.3	-2.0	-3.97
0.6660	8	-3.14	22.1	-11.2	-2.0	-0.743
0.7661	17	-3.25	30.5	-11.3	-1.0	-2.94
0.8462	24	-5.99	15.2	-18.5	-2.0	-8.20
0.9270	7	-1.42	11.4	-5.1	-6.0	-0.87
1.0000	0	0	0	0	0	0

Table6: Theoretical values of ultrasonic velocity calculated from Impedance, Nomoto, Van deal & Vangeal and Junjie's relation along with the experimental ultrasonic velocity and percentage error for acetone – toluene, acetone – chlorobenzene and acetone – nitrobenzene at 303 K

Mole fraction of acetone	U m/s					% Error			
	Experimental velocities	Imp	Nom	Van Deal & Vangeal	Junjies	Imp	Nom	Van Deal & Vangeal	Jungies
Acetone – Toluene									
0.0000	1284	1284	1284	1284	1284	0.000	0.000	0.000	0.000
0.1388	1292	1265	1269	1234	1265	-2.121	-1.818	-4.713	-2.121
0.2642	1266	1248	1254	1200	1248	-1.460	-0.940	-5.523	-1.462
0.3837	1268	1231	1239	1175	1231	-3.016	-2.335	-7.904	-3.021
0.4859	1240	1216	1225	1159	1216	-1.962	-1.211	-6.967	-1.970
0.5908	1218	1201	1210	1147	1201	-1.436	-0.671	-6.160	-1.447
0.6855	1208	1187	1195	1140	1186	-1.801	-1.079	-5.958	-1.814
0.7703	1216	1174	1181	1136	1174	-3.597	-2.964	-7.021	-3.611
0.8535	1222	1161	1166	1135	1161	-5.256	-4.777	-7.681	-5.267
0.9307	1160	1149	1152	1136	1149	-0.962	-0.714	-2.149	-0.969
1.0000	1138	1138	1138	1138	1138	0.000	0.000	0.000	0.000
Acetone - Chlorobenzene									
0.0000	1360	1360	1360	1360	1360	0.000	0.000	0.000	0.000
0.1287	1336	1339	1338	1268	1318	0.2221	0.127	-5.341	-1.382
0.2542	1304	1317	1315	1207	1281	0.975	0.804	-8.008	-1.826
0.3682	1302	1295	1292	1169	1250	0.523	-0.756	-11.39	-4.151
0.4802	1232	1272	1269	1143	1223	3.176	2.913	-7.780	-0.728
0.5769	1228	1251	1248	1129	1202	1.863	1.582	-8.790	-2.149
0.6700	1188	1230	1236	1121	1184	3.387	3.116	-5.970	-0.322
0.7609	1168	1207	1204	1119	1169	3.239	2.997	-4.360	0.067
0.8486	1164	1184	1182	1122	1156	1.679	1.491	-3.710	-0.682
0.9228	1160	1163	1162	1129	1147	0.259	0.145	-2.740	-1.113

1.0000	1140	1140	1140	1140	1140	0.000	0.000	0.000	0.000
Acetone - Nitrobenzene									
0.0000	1424	1424	1424	1424	1424	0.000	0.000	0.000	0.000
0.1358	1392	1397	1393	1288	1358	0.346	0.075	-8.062	-2.492
0.2532	1308	1371	1365	1213	1309	4.606	4.146	-7.802	0.073
0.3729	1348	1343	1334	1162	1265	-0.403	-1.065	-15.972	-6.534
0.4769	1312	1316	1305	1133	1232	0.268	-0.501	-15.794	-6.463
0.5686	1276	1290	1279	1116	1207	1.064	0.248	-14.289	-5.722
0.6660	1240	1260	1250	1107	1184	1.592	0.783	-12.000	-4.759
0.7661	1220	1227	1218	1106	1164	0.557	-0.171	-10.325	-4.822
0.8462	1204	1198	1191	1111	1151	-0.502	-1.084	-8.398	-4.584
0.9270	1164	1167	1163	1121	1142	0.222	-0.107	-3.812	-1.960
1.0000	1136	1136	1136	1136	1136	0.000	0.000	0.000	0.000

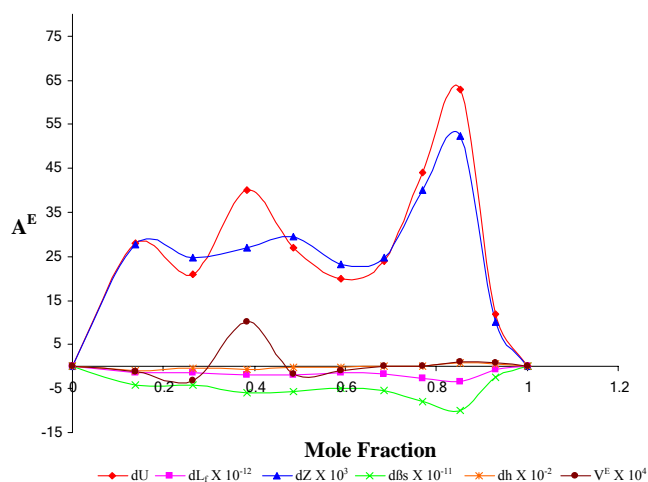


Figure1: Excess Values of Acetone and Toluene Mixtures.

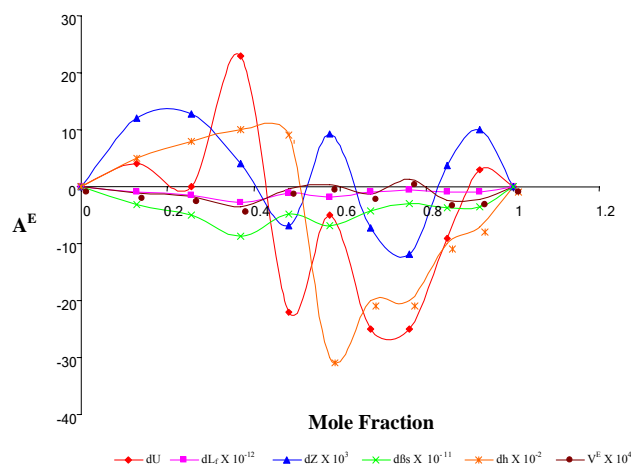


Figure2: Excess Values of Acetone and Chlorobenzene Mixtures.

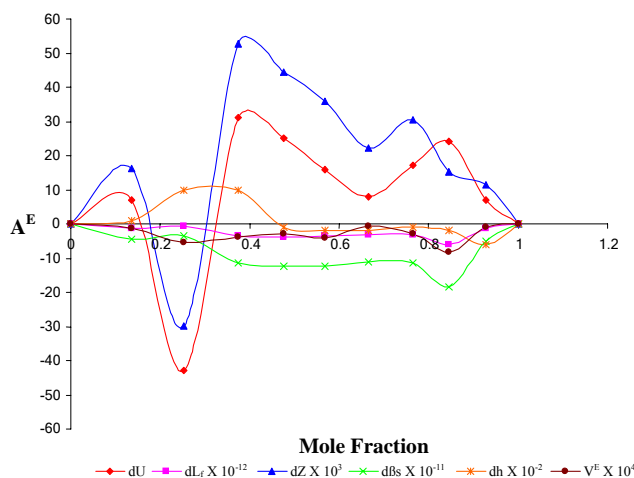


Figure3: Excess Values of Acetone and Nitrobenzene Mixtures.

In acetone, the carbonyl carbon atom is in a state of sp^2 hybridisation. CO sigma bond is produced by overlap of a sp^2 orbital of the carbonyl carbon with a p orbital of oxygen. The π bond of the C = O group is formed by the lateral overlap of p orbitals of carbon and oxygen atoms. Since oxygen is more electronegative than carbon, it is the oxygen of the carbonyl group that will attract electrons towards itself and hence will make the carbonyl group polarize. Thus we can expect that any positively charged species (electrophiles) will add on to the oxygen and any negatively charged species (nucleophiles) will attack the carbon of the carbonyl group. Since positively charged carbon is less stable than negatively charged oxygen due to higher electronegativity of oxygen than that of carbon, it is the nucleophile that will preferentially attack the carbonyl carbon. Thus carbonyl group will undergo nucleophilic addition reactions much more rapidly than electrophilic addition. It also shows that the greater the extent of positive charge on the carbonyl carbon, the easier will it be for a nucleophile to add. In acetone – toluene system, the nucleophilic addition is inhibited since the methyl group decreases the electron density at the carbonyl carbon of acetone by means of inductive effect. In acetone – chlorobenzene and acetone – nitrobenzene systems, the presence of electron withdrawing group in nitrobenzene readily react with the positive charge of carbon in acetone which favours nucleophilic addition reaction among which acetone – nitrobenzene shows stronger interaction than acetone – chlorobenzene which is also confirmed by maximum ultrasonic velocities. It may be due to the presence of nitro group in nitrobenzene that may act as both electrophile (NO_2^+) and nucleophile (NO_2^-), which may also lead to both electrophilic and nucleophilic reaction. Ultrasonic velocity is maximum for acetone -nitrobenzene when compared to other systems, It reveals that bigger the molecule greater will be the ultrasonic velocity. Ultrasonic velocity increases with mole fraction due to the interaction between unlike molecules that result in increase of relaxation strength. Acetone – nitrobenzene shows the greater density than acetone - chlorobenzene & acetone - toluene, as it shows large volume expansion and due to the

interaction of the molecules. Viscosity increases when acetone is added to nitrobenzene than with chlorobenzene & toluene because of greater molecular association in solution and due to non rupturing of components where as viscosity decreases when acetone is added to toluene, due to the weakening of the intermolecular interaction between the molecules. It has been observed that molecular interaction depends upon the size and shape of the molecules (R J Fort & W R Moore) when the substituted components like toluene, chlorobenzene and nitrobenzene are added to acetone, the molecular size shrinks, leading to molecular contraction. The radius of the molecule follows the order as

nitrobenzene > toluene > chlorobenzene.

In all three systems, isentropic compressibility increases, among this acetone - toluene shows the maximum value when compared to chlorobenzene and nitrobenzene. As free length and isentropic compressibility are interrelated, it shows that acetone - toluene has least molecular interaction which indicates the dispersion force (or) London type forces are present in the system. Similarly weak dipole-dipole interactions may be present in acetone - nitrobenzene and weak dipole-induced dipole interaction may be present in acetone - chlorobenzene. As we know that at lower concentration, molecules are not closer, therefore free length increases, similarly at higher concentration molecules come closer to each other which favours segment - segment interaction which shows decrease in free length, internal pressure & isentropic compressibility. In acetone - toluene, increase in free length is greater than in other systems which is also confirmed by isentropic compressibility values. It indicates that the dissociation between the molecules may be due to the increase in internal pressure. In acetone - nitrobenzene system, free length & isentropic compressibility between the molecules are less, which is indicated by the decrease in internal pressure that favours the interaction between the molecules leading to molecular association between acetone - nitrobenzene which is confirmed by maximum value of ultrasonic velocity.

In system acetone - nitrobenzene, thermodynamic values like L_f , β_s , π_l , α/T^2 , τ decreases which shows maximum molecular interaction that may be due to dipole - dipole interaction where as in system acetone - chlorobenzene, dipole - induced dipole interaction is seen and in acetone - toluene, as all these values are greater which reveals the dispersion force exist between the molecules. It follows the order

nitrobenzene > chlorobenzene > toluene

In Figure 1 & 2, it explains the experimental deviation values of acetone - toluene & acetone - chlorobenzene in which both positive and negative deviations are found that shows strong interaction are present in lower concentration & weak interaction are present in higher concentration . If both positive & negative deviation exists, it may be due to physical interaction such as dispersion force due to breaking of cohesive forces acting in like molecules & rupture of associated structure which dominates the interaction between like molecules. In Figure 3, it explains the experimental deviations in acetone - nitrobenzene. It has been observed that negative deviation occurs for excess values in acetone - nitrobenzene is greater when

compared to acetone – toluene & acetone - chlorobenzene, which shows that chemical forces may exist between the molecules. As greater the strength of interaction between the components, there is compressibility that may be qualitatively interpreted in terms of closer approach of unlike molecules leading to reduction in volume.

We infer that for acetone - toluene, acetone - chlorobenzene & acetone - nitrobenzene system, the theoretical ultrasonic values based on Impedance relation, Nomoto relation, Vandael & Vangeal relation & Jungie relation are given along with their error values. In all three systems, less percentage of deviation is observed for Impedance relation than Nomoto relation than Vandael & Vangeal relation than Junjie relation. On the whole, the entire theoretical model fairly predicts ultrasonic velocities are reasonably close to the experimental values and all the three binary mixtures reported in this work thus showing the validity of these theoretical models for binary mixtures.

Conclusion

The experimental values of density, viscosity and ultrasonic velocity for the binary mixtures of acetone - toluene, acetone - chlorobenzene and acetone - nitrobenzene at 303 K and different composition are measured. From these data, several thermodynamic excess functions have been calculated and correlated using standard relations like Impedance relation, Nomoto relation, Van deal& Vangeal & Junjie models. The sign and magnitude of these quantities have been discussed in terms of dipole – dipole interactions between the mixing components. In entire systems, negative deviation and positive deviations are observed for excess values which explain the molecular interaction between the components over entire range of mole fraction at 303 K. It is clear that experimental values for all the three binary mixtures reported agrees well with the theoretical values.

Acknowledgements

The authors thank the head of the department for providing necessary laboratory facilities.

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