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Ultrasonic Velocity Determination in Binary Liquid Mixtures

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ABSTRACT

Ultrasonic velocity, density and viscosity of binary liquid mixtures of acetone and carbon tetra chloride, Acetonitrile and aniline, acetone and iso-propyl alcohol, methyl ethyl ketone and Acetonitrile have been measured at room temperature 303K. Excess value of parameters such as adiabatic compressibility (β), internal pressure (π_i), acoustic impedance (Z), Excess volume (V^E), Excess viscosity (Δ_η) and Excess adiabatic compressibility (β^E) have been calculated. Ultrasonic velocities evaluated using Nomoto,Van Deal equation and Free length theory have been compared with Experimental values. It has been established that ultrasonic velocity increases with decrease in free length. Also Rao's constant shows a non linear variation confirming the associative nature of liquids.

Keywords: Ultrasonic velocity, binary mixtures, molecular interaction.

INTRODUCTION

A Knowledge of densities, viscosities and ultrasonic velocities of liquids and liquid mixtures is essential to understand interaction between molecules. Ultrasonic study plays an important role to analyse physio-chemical behavior of molecular interaction. A knowledge of variation of velocity with concentration provides vital information about molecular interaction.

The ultrasonic studies are extensively carried out to measure the thermodynamic properties and predict the intermolecular interaction of liquid mixtures. Ultrasonic data can be utilized to deduce some useful thermodynamic properties of liquid mixtures.

The present study deals with the study of the following binary liquid mixtures.

(i) Acetone + Carbon Tetra Chloride

(ii) Acetonitile + Aniline

A comparison has also been made between experimental and theoretical values of acoustical parameters evaluated at room temperature.

EXPERIMENTAL DETAILS

The liquids used were of pure analytical grade. The ultrasonic velocities(U)

were measured using ultrasonic interferometer at the frequency 1MHz. Densities of pure liquids and binary mixtures were found using specific gravity bottle. Viscosity measurements were made using Ostwald's viscometer.

THEORY AND CALCULATION

The equations which are relevant for our study are given below

Ultrasonic velocity

$$U = n\lambda \text{ m/s} \quad (1)$$

Adiabatic compressibility

$$\beta = 1/ (U^2\rho) \text{ ms}^2 \text{ kg}^{-1} \quad (2)$$

Acoustic impedance

$$Z = \rho U \text{ kg m}^{-2} \text{ s}^{-1} \quad (3)$$

Molar sound velocity or Rao's constant

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

Internal pressure

$$\Pi_i = b RT (k\eta/U)^{1/2} (\rho^{2/3} / M_{eff}^{7/6}) \text{ Nm}^{-2} \quad (5)$$

Excess volume

$$\Delta V = V - (X_1V_1 + X_2V_2) \quad (6)$$

Excess viscosity

$$\Delta\eta = \eta - (X_1\eta_1 + X_2\eta_2) \quad (7)$$

Excess adiabatic compressibility

$$\Delta\beta = \beta - (X_1\beta_1 + X_2\beta_2) \quad (8)$$

Vandael's equation for ultrasonic velocity

$$[1/ (X_1M_1 + X_2M_2)] [1 / U_{id}^2] = (X_1/M_1U_1^2) + (X_2 / M_2U_2^2) \text{ m/s} \quad (9)$$

Nomoto's equation for ultrasonic velocity

$$U = [(X_1R_1 + X_2R_2) / (X_1V_1 + X_2V_2)]^3 \text{ m/s} \quad (10)$$

WADA'S CONSTANT

$$W = \frac{M}{\rho\beta^{1/7}} \quad (11)$$

FREE LENGTH THEORY

$$U L_f \rho^{1/2} = K_T \quad (12)$$

where

U – ultrasonic velocity

n – the frequency of the ultrasonic wave in Hertz

λ – wavelength in metres

ρ – density in kg m $^{-3}$

R – Rao's constant

Meff – effective molecular weight.

Πi – internal pressure

b – packing factor assumed as two in liquid system

R – universal gas constant

T – temperature in Kelvin

k – 4.28 x 10^9 a constant which is independent of the nature of the liquids and temperature.

η – viscosity of the liquid mixture

V, V_1, V_2– molar volume of the mixture and the components

X_1, X_2– mole fraction of individual components

η_1 , η_2 – viscosity of pure liquids

β,β_1,β_2 – Adiabatic compressibility of binary mixture and the pure components

M_1, M_2 – molecular weight of the components

U_1 ,U_2 – ultrasonic velocity in the components

U_{id} – velocity of sound in the ideal mixture

R_1 , R_2 – molecular sound velocity of the individual components

W – Wada's constant

M – effective molecular weight of the components

L_{fmix} and ρ - free length and density of the mixture

K_T - temperature dependent Jacobson's constant, 200 x 10^{-8} at 303K.

Table 1. Properties of Binary Mixture (Acetone + Carbon Tetra Chloride) at 303k

Mole fraction of acetone (X_1)	Mole fraction of carbon tetra chloride (X_2)	Effective Molecular Weight x 10^{-3} kg	Density (Kg m^{-3})	Viscosity x 10^{-3} (Ns m^{-2})	Velocity (m s^{-1}) [Exp]	Velocity (m s^{-1}) [Van deal]	Velocity (m s^{-1}) [Nomoto]	Velocity (m s^{-1}) [Free Length Theory]	Internal pressure π_i x 10^6 (N m^{-2})
0.0000	1.0000	153.820	1642.3	0.707660	942.20	942.20	941.60	949.75	3.5153
0.1272	0.8728	141.641	1582.6	0.760777	956.40	942.41	963.64	964.06	3.8861
0.2470	0.7530	130.172	1503.6	0.830627	979.30	948.51	986.19	987.14	4.2798
0.3600	0.6400	119.353	1410.0	0.906052	997.60	959.80	1009.24	1005.59	4.6951
0.4666	0.5334	109.147	1326.6	0.964269	1005.60	975.91	1032.77	1013.65	5.1415
0.5675	0.4325	99.487	1298.6	1.092159	1024.40	996.79	1056.83	1032.60	5.9551
0.6631	0.3369	90.334	1142.6	1.319551	1090.80	1022.56	1081.43	1099.54	6.5193
0.7538	0.2462	81.651	1062.0	1.459132	1118.00	1053.58	1106.57	1126.95	7.2566
0.8400	0.1599	73.398	998.6	1.596109	1143.00	1090.47	1132.27	1152.15	8.1583
0.9219	0.0780	65.557	931.6	1.761220	1157.60	1113.07	1158.51	1166.87	9.2762
1.0000	0.0000	58.080	840.4	1.991394	1185.80	1185.80	1185.37	1195.30	10.4800

RESULTS AND DISCUSSION

The experimental values of density, viscosity, ultrasonic velocity and related acoustical parameters for different liquid mixtures are shown in tables (1 to 4). Further, figures (1 to 3) show the variation of ultrasonic velocity (U), Rao's constant (R), Internal pressure (π_i), at temperature 303K. Moreover the experimental values of ultrasonic velocity are compared with those calculated using Nomoto's, Vandeal's and Free length theory.

A close examination of velocity Table (1) for Acetone + Carbon tetra chloride shows that the variation of ultrasonic velocity is almost linear. This may be assumed due to the fact that when non-polar solvents are mixed there are only weak interactions between the liquid components and hence it is expected that ultrasonic velocity variation should be linear. Conversely the linear dependence in the ultrasonic velocity confirms the non-polar nature of carbon tetra chloride and acetone[1]. Since velocity and Adiabatic compressibility are inversely related, Adiabatic compressibility decreases as velocity increases. Rao's constant shows a non-linear variation (Fig. 1) confirming the associative nature of liquids.

The Ultrasonic velocity decreases with increase in concentration of acetonitrile. This is in accordance with the view that the ultrasonic speed increases with decrease in free length and vice versa [9]. Density is the measure of liquid-liquid interaction. Increase in density with increase in concentration of one of the components indicates solvent-solvent interactions while decrease in density indicates lesser-solvent interactions. It may be also be assumed that solvent-solvent interaction bring about a bonding between them. So the sizes of the molecules increase and hence there will be a decrease in density.

Table 2. Properties of Binary Mixture (Acetone + Carbon Tetra Chloride) at 303k

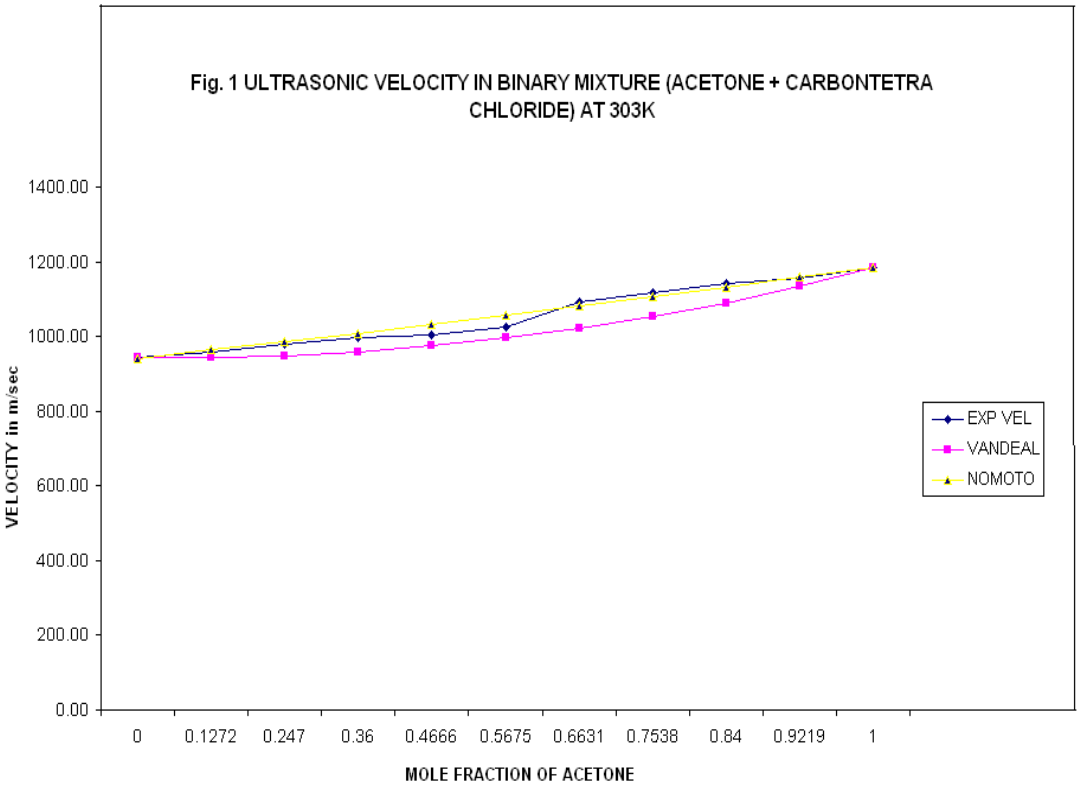
Rao's constant R x 10^{-4} m^3 $(m\ s^{-})^{1/3}$	Acoustic impedance (Z) (kg m^{-2} s^{-1})	Volume x 10^6 (m^3)	Free volume ml/mol	Excess volume ΔV x 10^6 m^3	Excess Viscosity $\Delta\eta$x 10^{-3} (Ns m^{-2})	Excess Adiabatic compressibility $\Delta\beta$x10^{-10} (m s^2 kg^{-1})	Wada constant	Adiabatic compressibility βx10^{-10} (m s^2 kg^{-1})
9.180	154737506.00	93.661	0.331002	0.00000	0.0000	0.0000	1908.38	6.85901
8.816	151359864.00	89.499	0.268346	-0.10388	-0.1101	-0.1549	1821.73	6.90960
8.595	147247548.00	86.574	0.214722	-0.10234	-0.1941	-0.3201	1761.20	6.93484
8.456	140661600.00	84.648	0.170135	-0.01748	-0.2637	-0.3098	1715.34	7.12636
8.241	133440296.00	82.276	0.137150	-0.00707	-0.3423	-0.1527	1656.59	7.45434
7.721	133028584.00	76.611	0.101804	-0.31169	-0.3440	-0.4307	1546.00	7.33813
8.137	124634808.00	79.061	0.072878	0.16794	-0.2393	-0.5666	1594.89	7.35556
7.978	118731600.00	76.884	0.055885	0.17299	-0.2162	-0.5341	1545.70	7.53341
7.683	114139980.00	73.501	0.043037	0.04631	-0.1898	-0.5407	1474.03	7.66507
7.387	107842016.00	70.371	0.031944	-0.06567	-0.1299	-0.3267	1402.39	8.01039
7.313	99654632.00	69.110	0.022970	0.00000	0.0000	0.0000	1366.51	8.46235

Table 3. Properties of Binary Mixture (Acetonitrile + Aniline) at 303k

Mole fraction of acetonitrile (X_1)	Mole fraction of aniline (X_2)	Effective Molecular Weight x 10^{-3} kg	Density (Kg m^{-3})	Viscosity x 10^{-3} (Ns m^{-2})	Velocity (m s^{-1}) [Experim -ental]	Velocity (m s^{-1}) [Van deal]	Velocity (m s^{-1}) [Nomoto]	Adiabatic compressibility βx10^{-10} (m s^2 kg^{-1})	Internal pressure π_i x 10^6 (N m^{-2})
0.0000	1.0000	93.130	1080.4	0.306131	1601.70	1601.70	1599.04	3.6078	2.4093
0.1616	0.8384	84.713	1063.2	0.333492	1569.60	1386.29	1557.45	3.8710	2.8069
0.3025	0.6975	77.375	1045.6	0.386613	1556.50	1283.22	1516.76	3.9470	3.3359
0.4265	0.5735	70.917	1023.6	0.445499	1430.30	1228.04	1476.93	4.7754	4.0773
0.5364	0.4636	65.194	998.8	0.521987	1403.20	1198.37	1437.96	5.0848	4.8358
0.6345	0.3655	60.085	972.4	0.625843	1399.00	1184.16	1399.84	5.2543	5.7296
0.7225	0.2775	55.502	961.2	0.760315	1392.40	1180.24	1362.59	5.3660	6.8907
0.8019	0.1981	51.367	933.2	0.910337	1386.00	1183.62	1326.18	5.5782	8.1104
0.8741	0.1259	47.606	887.6	1.077427	1339.30	1192.53	1290.51	6.2809	9.4864
0.9398	0.0602	44.185	863.6	1.404924	1252.00	1205.80	1255.68	7.3871	12.001
1.0000	0.0000	41.050	809.2	1.897409	1222.70	1222.70	1221.59	8.2661	14.726

Table 4. Properties of Binary Mixture (Acetonitrile + Aniline) at 303k

Rao's constant R x 10^{-4} m^3 (m s^{-1})$^{1/3}$	Acoustic impedance (Z) (kg m^{-2} s^{-1})	Volume x 10^6 (m^3)	Free volume ml/mol	Excess volume ΔV x $10^6 m^3$	Excess Viscosity Δη x 10^{-3} (Ns m^{-2})	Excess Adiabatic compressibility Δβx10^{-10} (m s^2 kg^{-1})	Wada constant	Free Length x 10^{-11} m	Velocity (m s^{-1}) [Free Length Theory]
10.0800	173047668.00	86.200	1.214729	0.00000	0.00000	0.0000	1925.17	3.76869	1614.53
9.2580	166879872.00	79.678	0.899128	-0.07880	-0.22978	-0.54300	1765.21	3.87674	1582.17
8.5740	162747640.00	74.001	0.620942	-0.14703	-0.40087	-1.06965	1631.62	3.94214	1568.97
7.8046	146405508.00	69.283	0.388006	-0.17920	-0.53931	-0.81749	1486.60	4.33582	1441.76
7.3061	140151616.00	65.273	0.262022	-0.19038	-0.63770	-1.02962	1388.05	4.47409	1414.44
6.9096	136038760.00	61.791	0.175798	-0.19042	-0.68995	-1.31677	1307.86	4.54803	1410.21
6.4464	133837488.00	57.743	0.115732	-0.28329	-0.69554	-1.60685	1218.52	4.59613	1403.55
6.1360	129341520.00	55.044	0.078109	-0.27166	-0.67183	-1.76685	1155.15	4.68612	1397.10
5.9110	118876268.00	53.636	0.051413	-0.15556	-0.61964	-1.40330	1106.67	4.97253	1350.03
5.5130	108122720.00	51.164	0.027905	-0.17052	-0.39669	-0.59946	1031.50	5.39266	1262.03
5.4230	98940884.00	50.729	0.015365	0.00000	0.00000	0.00000	1006.43	5.70448	1232.49



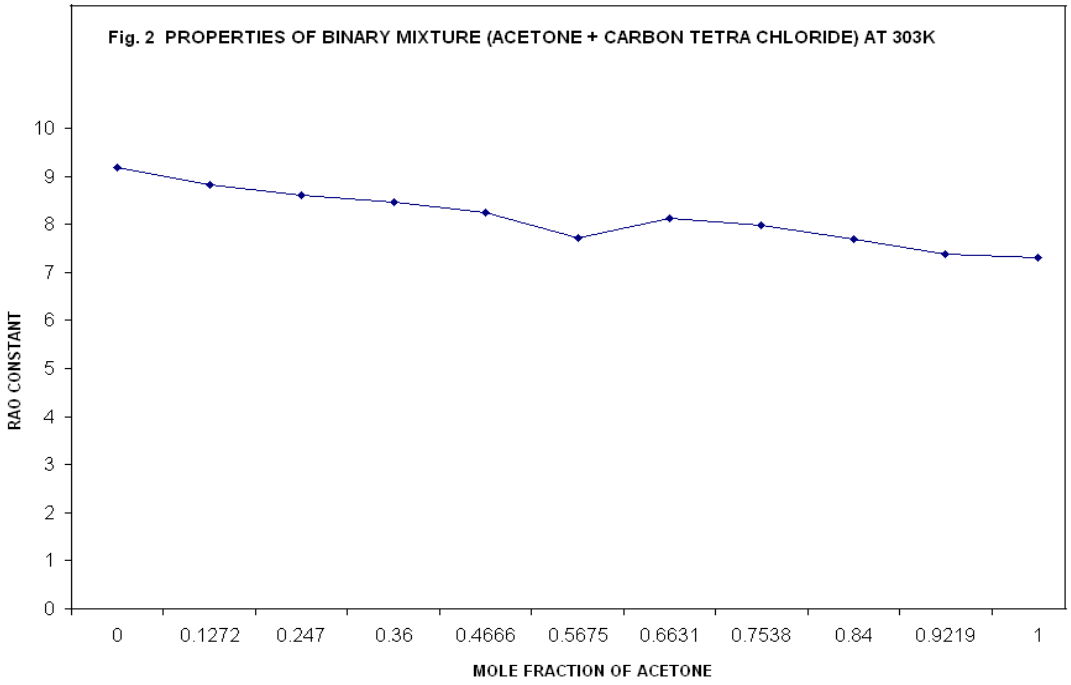


Fig. 2 PROPERTIES OF BINARY MIXTURE (ACETONE + CARBON TETRA CHLORIDE) AT 303K
RAO CONSTANT
0
1
2
3
4
5
6
7
8
9
10
0
0.1272
0.247
0.36
0.4666
0.5675
0.6631
0.7538
0.84
0.9219
1
MOLE FRACTION OF ACETONE

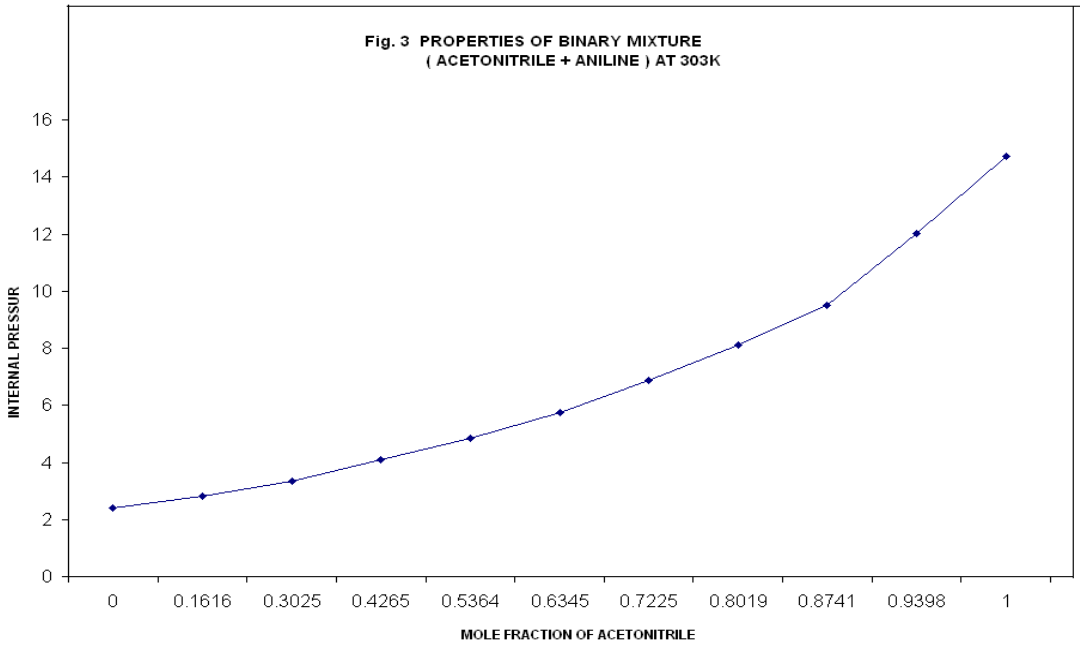


Fig. 3 PROPERTIES OF BINARY MIXTURE
(ACETONITRILE + ANILINE) AT 303K
INTERNAL PRESSUR
0
2
4
6
8
10
12
14
16
0
0.1616
0.3025
0.4265
0.5364
0.6345
0.7225
0.8019
0.8741
0.9398
1
MOLE FRACTION OF ACETONITRILE

CONCLUSION

Ultrasonic velocity has been determined in Binary liquid mixtures of Acetone + Carbon Tetra Chloride and Acetonitrile + Aniline. The molecular interaction has been analysed in terms of acoustical parameters.

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