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Research Article

ULTRASONIC INVESTIGATIONS ON BINARY MIXTURE OF ACETOPHENONE WITH N-BUTANOL AT TEMPERATURES 303.15 K – 323.15 K

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ABSTRACT

Ultrasonic velocity, density and viscosity values are measured in a binary mixture of acetophenone with n-butanol at temperatures T = (303.15, 308.15, 313.15, 318.15 and 323.15) K over the entire mole fraction range. The experimental data is used to calculate various thermo acoustic parameters like Adiabatic compressibility (β), intermolecular free length (L_f), molar volume (V_m), free volume (V_f), internal pressure (π), enthalpy (H), acoustic impedance (Z), Rao's constant (R) and Wada's constant (w). The results are explained in the light of molecular interactions.

Keywords: Acetophenone, n-butanol, acoustic parameters, ultrasonic velocity.

INTRODUCTION

Properties of liquid–liquid mixtures are thermodynamically very important as part of studies of the thermodynamic, acoustic and transport aspects. The compositional dependence of thermodynamic properties has proved to be very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interaction between components. This type of study is powerful means of characterizing the various aspects of physico-chemical behavior of liquid mixtures and studying the interaction between molecules[1,2].

Ultrasonic investigations find extensive application in characterizing physico-chemical behavior of liquid mixtures. The non-ideal behavior has been studied by several researchers[3-5].Compressibility (β) and Viscosity (η) are static and transport properties of liquid respectively and are the most important amongst the properties of liquid. The various models of the liquid states relate these properties to strength of molecular interaction[6]; the study of temperature dependence of these properties of some liquid mixtures has been carried out by few groups with some liquid mixtures[7-9]. Though a considerable number of recent investigations on ultrasonic velocities and related parameters in a variety of liquid mixtures with variation of composition and temperature are available in literature, still there is a lot of scope to carry out the detailed investigations along these lines. The temperature dependence of the parameters gives important information about the molecular interaction between the components of the mixtures. In the present work, an attempt has been made by studying the temperature dependence of different parameters to throw some light on the strength of molecular interactions of some organic liquid mixtures.

THEORY

From the experimental data of density, viscosity and ultrasonic velocity, various thermo acoustic parameters are evaluated using the following standard equations:

Values of adiabatic compressibility β, were calculated using the following relation:

$$\beta = 1/\rho u^2 \qquad (1)$$

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

Inter molecular free length

$$L_f = K_T \beta^{1/2} \quad (2)$$

Where K_T is the temperature dependent constant.

The values of V_m were obtained from the relation:

$$V_m = M_{eff} / \rho \quad (3)$$

M_{eff} is given by $M_{eff} = (x_1M_1 + x_2M_2)]$, where M_1 and M_2 are the molar masses of pure components.

Free volume

$$V_f = \left(\frac{M_{eff} u}{K\eta} \right)^{3/2} \quad (4)$$

Where M_{eff} is the effective molecular weight and K is proportionality constant, which is sensitive to molecular phenomenon.

Internal pressure

$$\pi = bRT \left(\frac{k\eta}{u} \right)^{1/2} \left(\frac{\rho^{2/3}}{M^{7/6}} \right) \quad (5)$$

Where b is a packing factor, k is a dimensionless constant independent of temperature and nature of liquids and its value is 4.28 x 10^9 and η is the viscosity. The other symbols have their usual meaning.

Enthalpy

$$H = V_m \pi \quad (6)$$

Where V_m is the molar volume and π is the internal pressure.

The acoustic impedance is given by the product of ultrasonic velocity and density as shown below:

$$Z = U \times \rho \quad (7)$$

Rao[10] related the sound velocity (U) and molar volume (V) of liquids by the formula,

$$R = U^{1/3}.V \quad (8)$$

Where R is a constant called Rao's constant, which is independent of temperature.

Wada[11] derived a relation between adiabatic compressibility (β) and molar volume (V) of liquids, which is given by the formula,

$$W = V.\beta^{-1/7} \quad (9)$$

Where W is a constant called Wada's constant, which is independent of temperature and pressure.

PROCEDURE

The solvents are of AR grade samples and these were purified by usual methods [12,13]. Their boiling points agreed with literature values indicating that the liquids used in the present study are of high purity.

In order to carry out experiment on ultrasonic interferometer for ultrasonic velocity, specific gravity bottle for density, Oswald viscometer apparatus for coefficient of viscosity, the apparatus are standardized first with pure water and then with benzene, the results obtained are found to be good agreement with reported values.

Ultrasonic velocity of Acetophenone and n-Butanol were measured using multi frequency ultrasonic interferometer at a frequency of 2 MHz (Mittal enterprises-Model F-80X) the accuracy in measurement of ultrasonic velocity (U) was within ±0.01%. The densities of these liquids were measured using 25ml specific gravity bottle in electronic balance precisely within ±0.0001gms.

Oswald viscometer is used to measure viscosities of the pure liquids. The accuracy of the apparatus is 0.002%.

In all the above apparatus the temperature was maintained constant at 303.15K, 308.15K, 313.15K, 318.15 K and 323.15K using proportional temperature controller of accuracy ±0.01^{0}C.

RESULTS AND DISCUSSION

Ultrasonic velocity, density, viscosity were measured at a fixed frequency of 2MHz for the whole composition at four temperatures 303.15, 308.15, 313.15, 318.15K and 323.15K and are given in Table 1. The other physical properties such as Adiabatic compressibility (β), Intermolecular free length (L_f), Molar volume (V_m), Free volume (V_f), Internal pressure (π), Enthalpy (H), acoustic impedance (Z), Rao's constant (R) and Wada's constant (w) are calculated and presented in Tables 2-4.

At a temperature as mole fraction of n-butanol increases the sound velocity and density of binary mixture decreases totally. Also for a mole fraction of n-butanol as temperature increases the ultrasonic velocity, density and viscosity of the mixture decreases. This suggests that dipole-induced dipole attractions are stronger than induced dipole-induced dipole attraction.

The adiabatic compressibility and free length increases with increasing concentration of n-butanol in the binary mixture. Such an increase in β as well as L_f suggests that the hydrogen bonded association of alcohols breaks up gradually with addition of n-butanol. The increase in the value of L_f and β with the increase in temperature clearly reveals that the interaction becomes weaker at high temperatures[14].

The molar volume and free volume are decreases with increase of mole fraction of n-butanol. But as the temperature increases the above values are observed to be increased. The value of internal pressure increases uniformly with increase in the mole fraction of

n-butanol, suggesting that strength of the interaction increases with increase in mole fraction of n-butanol[15,16]. The values obtained for internal pressure are less in magnitude. The increase in the internal pressure in the mixture indicates that addition of n-butanol increases the cohesive force of acetophenone at all temperatures. As temperature increases the cohesive forces weaken and hence there is a fall in internal pressure is observed.
With the increase of mole fraction of n-butanol the enthalpy values increases and acoustic impedance values decreases[17]. The Rao's constant and Wada's constant values are also observed to be decreasing with increase of mole fraction of n-butanol.

CONCLUSIONS

Ultrasonic velocity, density, viscosity values are determined experimentally. By using these values various thermo acoustic parameters like adiabatic compressibility, free length, molar volume, free volume, internal pressure, enthalpy, acoustic impedance, Rao's constant and Wada's constant are calculated by using the standard equations. It is observed that the interactions are present between the molecules of binary mixture acetophenone + n-butanol and these interactions are observed to be increasing with increase of mole fraction of n-butanol and decrease with increase of temperature.

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Table 1: ultrasonic velocity, density and viscosity values of binary mixture acetophenone + n-butanol at different temperatures.

x_1	u (m . s^{-1})					ρ (Kg . m^{-3})					η (m. pa. s)				
	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15 K	318.15 K	323.15K
0.0000	1455.99	1452.09	1449.09	1446.00	1441.09	1019.4	1014.1	1008.8	1003.9	999.08	1.3479	1.3186	1.2815	1.1864	1.1538
0.1239	1450.98	1432.98	1411.98	1390.98	1371.00	1032.0	1032.0	1031.9	1031.8	1030.3	1.3524	1.2098	0.9981	0.8188	0.7367
0.2415	1419.99	1401.00	1390.98	1374.99	1348.05	1032.8	1031.7	1031.5	1031.4	1030.0	1.3958	1.2750	1.1539	0.9511	0.6875
0.3532	1416.00	1401.99	1386.00	1365.99	1350.00	1010.7	1010.3	1010.3	1009.7	1009.5	1.4004	1.2868	1.1625	0.9544	0.6765
0.4596	1377.99	1359.00	1344.75	1325.25	1310.25	984.3	984.1	983.4	980.0	976.3	1.4275	1.2995	1.2182	1.0568	1.0290
0.5606	1359.00	1345.05	1331.25	1314.00	1290.75	962.3	961.8	961.2	957.4	954.8	1.4892	1.3374	1.2529	1.1596	1.1010
0.6570	1332.99	1317.99	1303.05	1286.25	1269.00	940.9	940.1	939.3	937.4	934.6	1.6076	1.4621	1.2835	1.1641	1.1363
0.7483	1312.98	1306.05	1287.75	1277.25	1264.05	913.1	912.8	911.4	910.1	908.7	1.7882	1.5668	1.4028	1.2398	1.1496
0.8364	1305.75	1287.75	1272.75	1260.00	1242.75	894.8	893.8	892.1	891.0	888.7	1.9728	1.7585	1.5083	1.3230	1.2219
0.9205	1282.05	1264.05	1252.00	1240.05	1227.75	885.6	883.8	882.5	878.6	875.0	1.9860	1.7954	1.6161	1.4150	1.2733
1.0000	1242.75	1233.00	1227.75	1215.75	1201.05	807.1	806.2	805.6	797.1	796.7	2.0116	1.7769	1.5805	1.3617	1.2643

Table 2: Adiabatic compressibility (β), Intermolecular free length (L_f) and Molar volume (V_m) values of binary mixture acetophenone + n-butanol at different temperatures

x_1	β x 10^{-10} (m^2 . N^{-1})					L_f (A)					V_m (m^3. mol^{-1})				
	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15 K	318.15 K	323.15K
0.0000	4.63	4.67	4.71	4.76	4.81	0.1357	0.1376	0.1391	0.1412	0.1441	0.1179	0.1185	0.1191	0.1197	0.1202
0.1239	4.60	4.72	4.86	5.01	5.16	0.1354	0.1383	0.1395	0.1448	0.1493	0.1109	0.1109	0.1109	0.1109	0.1111
0.2415	4.80	4.94	5.01	5.13	5.34	0.1383	0.1415	0.1427	0.1465	0.1518	0.1056	0.1057	0.1057	0.1057	0.1059
0.3532	4.93	5.04	5.15	5.31	5.44	0.1402	0.1428	0.1441	0.1491	0.1532	0.1028	0.1028	0.1028	0.1029	0.1029
0.4596	5.35	5.50	5.62	5.81	5.97	0.1460	0.1493	0.1506	0.1559	0.1605	0.1006	0.1006	0.1007	0.1010	0.1014
0.5606	5.63	5.74	5.87	6.05	6.29	0.1497	0.1525	0.1539	0.1591	0.1647	0.0980	0.0981	0.0981	0.0985	0.0988
0.6570	5.98	6.12	6.26	6.45	6.64	0.1543	0.1575	0.1589	0.1643	0.1693	0.0955	0.0956	0.0957	0.0959	0.0962
0.7483	6.35	6.42	6.62	6.74	6.88	0.1590	0.1612	0.1628	0.1679	0.1724	0.0939	0.0939	0.0940	0.0942	0.0943
0.8364	6.55	6.75	6.92	7.07	7.29	0.1616	0.1654	0.1669	0.1720	0.1773	0.0912	0.0914	0.0915	0.0916	0.0919
0.9205	6.87	7.08	7.22	7.40	7.58	0.1654	0.1693	0.1709	0.1760	0.1809	0.0878	0.0880	0.0881	0.0885	0.0889
1.0000	8.02	8.16	8.23	8.49	8.69	0.1787	0.1818	0.1834	0.1885	0.1937	0.0918	0.0919	0.0920	0.0930	0.0930

Table 3: Free volume (V_f), internal pressure (π) and enthalpy (H) values of binary mixture acetophenone + n-butanol at different temperatures

x_1	$V_f \times 10^{-10}$ ($m^3 . mol^{-1}$)					$\pi \times 10^{-15}$ ($N . m^{-2}$)					$H \times 10^{-16}$ ($J. m^{-1}$)				
	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15 K	318.15 K	323.15K
0.0000	0.2950	0.3000	0.3081	0.3405	0.3455	1.5000	1.4900	1.4600	1.3500	1.3300	1.7700	1.7600	1.7300	1.6200	1.6000
0.1239	0.2714	0.3108	0.4004	0.5209	0.5836	1.5300	1.3800	1.1400	0.9300	0.8460	1.6900	1.5300	1.2400	1.0300	0.9400
0.2415	0.2331	0.2582	0.2929	0.3803	0.5873	1.6200	1.5000	1.3700	1.1200	0.7930	1.7100	1.5800	1.4300	1.1800	0.8400
0.3532	0.2148	0.2371	0.2680	0.3484	0.5605	1.6100	1.4900	1.3600	1.1200	0.7670	1.6500	1.5300	1.3900	1.1500	0.7900
0.4596	0.1864	0.2074	0.2221	0.2658	0.2657	1.6600	1.5300	1.4600	1.2700	1.2600	1.6700	1.5400	1.4500	1.2800	1.2800
0.5606	0.1594	0.1821	0.1951	0.2124	0.2184	1.7400	1.5700	1.4900	1.4000	1.3700	1.7000	1.5400	1.4500	1.3800	1.3500
0.6570	0.1284	0.1437	0.1696	0.1902	0.1889	1.9100	1.7600	1.5500	1.4200	1.4200	1.8200	1.6800	1.4700	1.3600	1.3700
0.7483	0.0996	0.1190	0.1357	0.1594	0.1719	2.1500	1.8800	1.7100	1.5100	1.4200	2.0200	1.7700	1.5800	1.4200	1.3400
0.8364	0.0793	0.0910	0.1112	0.1318	0.1421	2.3900	2.1600	1.8500	1.6300	1.5300	2.1800	1.9700	1.6700	1.4900	1.4000
0.9205	0.0710	0.0798	0.0910	0.1082	0.1219	2.4400	2.2300	2.0200	1.7700	1.6000	2.1400	1.9600	1.7700	1.5700	1.4300
1.0000	0.0618	0.0726	0.0849	0.1034	0.1110	2.4000	2.1300	1.8900	1.6200	1.5300	2.2100	1.9600	1.7300	1.5100	1.4200

Table 4: Acoustic impedance (Z), Rao's constant (R) and Wada's constant (W) values of binary mixture acetophenone + n-butanol at different temperatures.

x_1	$Z \times 10^3$ ($Kg. m^{-2} .s^{-1}$)					R					W				
	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15K	318.15K	323.15K	303.15K	308.15K	313.15 K	318.15 K	323.15K
0.0000	1484.24	1473.39	1462.66	1451.64	1441.61	11.9383	11.9591	11.9800	11.9994	12.0158	2.5404	2.5502	2.5617	2.5689	2.5759
0.1239	1497.41	1478.84	1457.02	1435.21	1412.54	11.3245	11.3245	11.3248	11.3252	11.3307	2.3920	2.3835	2.3837	2.3637	2.3569
0.2415	1466.57	1445.41	1434.80	1418.17	1388.96	10.7863	10.7902	10.7909	10.7912	10.7961	2.2634	2.2567	2.2571	2.2453	2.2354
0.3532	1431.15	1416.43	1400.28	1379.24	1362.83	10.3522	10.3536	10.3536	10.3556	10.3563	2.1953	2.1898	2.1898	2.1747	2.1677
0.4596	1356.36	1337.39	1322.43	1298.75	1279.20	9.9514	9.9520	9.9544	9.9659	9.9785	2.1232	2.1151	2.1164	2.1075	2.1075
0.5606	1307.77	1294.10	1279.60	1258.02	1232.41	9.5556	9.5573	9.5593	9.5719	9.5806	2.0548	2.0499	2.0510	2.0441	2.0384
0.6570	1254.21	1239.04	1224.38	1205.73	1186.01	9.1744	9.1770	9.1796	9.1858	9.1950	1.9853	1.9803	1.9817	1.9714	1.9688
0.7483	1198.88	1192.57	1173.66	1162.43	1149.05	8.8337	8.8346	8.8392	8.8434	8.8479	1.9334	1.9312	1.9338	1.9237	1.9207
0.8364	1168.39	1150.99	1135.42	1122.66	1104.43	8.4732	8.4764	8.4817	8.4852	8.4925	1.8713	1.8657	1.8688	1.8591	1.8559
0.9205	1135.78	1117.57	1105.33	1089.90	1074.28	8.0984	8.1039	8.1079	8.1199	8.1310	1.7891	1.7850	1.7872	1.7842	1.7852
1.0000	1003.02	994.04	989.08	969.07	957.24	7.9609	7.9638	7.9658	7.9940	7.9953	1.8298	1.8274	1.8286	1.8378	1.8325