



ULTRASONIC STUDIES ON 1, 4-DIOXANE AND METHANOL BINARY LIQUID MIXTURES AT DIFFERENT TEMPERATURES

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ABSTRACT

Densities and ultrasonic velocities of binary mixtures of 1,4-dioxane with polar solvent viz methanol have been measured over entire composition range at 303.15, 308.15, 313.15 and 318.15 K. From experimental data, various properties viz isentropic compressibility (K_s), intermolecular free length (L_f), acoustical impedance (Z), and excess functions viz excess isentropic compressibility (K_s^E), excess intermolecular free length (L_f^E), excess acoustical impedance (Z^E) have been determined. Further theoretical values of ultrasonic velocities of the binary mixtures are calculated using Nomoto's Model. On the basis of values of various excess properties, the nature of molecular interactions between the components of mixtures has been explained.

Key words: Ultrasonic velocity, Thermoacoustical parameters, Binary mixture (1,4-dioxane and methanol), Nomoto's model, Excess functions.

INTRODUCTION

The studies of ultrasonic velocities are being increasingly used as tool for investigation of properties of pure components and the nature of intermolecular interaction between the liquid mixture constituents. The ultrasonic studies are extensively used to estimate the thermodynamic properties and to predict the intermolecular interactions. These properties found extensive applications in chemical engineering processes, solution thermodynamic and molecular dynamics.

We report ultrasonic velocities of pure 1,4-dioxane and methanol as well as binary mixtures of these two at different temperatures (303.15, 308.15, 313.15 and 318.15 K). From

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these experimental results, acoustical impedance (Z), isentropic compressibility (K_s), inter molecular free length (L_f), excess isentropic compressibility (K_s^E), excess acoustical impedance (Z^E) and excess inter molecular free length (L_f^E) were derived over entire mole fraction range.

The theoretical values of ultrasonic velocities are calculated by Nomoto's equation and compared with experimental values.

EXPERIMENTAL

1,4-dioxane and methanol were S.D. fine chemicals (spectroscopic HPLC, A.R. grade) were further purified according to standard procedures^{1,2}. The purity was checked by comparing their densities and ultrasonic velocities, with literature values. The densities of pure liquid and their binary mixtures were measured using single capillary pycnometer (made up of Borosil glass) having bulb capacity $8 \times 10^{-3} \text{ m}^3$. The thermostatically controlled water bath, whose temperature was maintained constant ($\pm 0.02^\circ\text{C}$) by circulating water through Julabo F25MP thermostat (made in Germany) was used.

Ultrasonic velocities

Speed of sound was measured by using variable path single crystal interferometer Mittal Enterprises, New Delhi at frequency (2 MHz). The interferometer was calibrated using double distilled water and different pure liquids. The interferometer cell was filled with the test liquids and water was circulated around the measuring cell from the thermostat. Before this all the liquids were kept on 4A molecular sieves for several days to reduce the water content.

RESULTS AND DISCUSSION

The acoustic impedance (Z), was calculated by the equation -

$$Z = u \cdot \rho \quad \dots(1)$$

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

The isentropic compatibility (K_s), was calculated by the equation -

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

The inter molecular free length (L_f), was calculated by the equation -

$$L_f = K / u^{1/2} \quad \dots(3)$$

Where K is Jacobson's constant³.

The excess properties (L_f^E , Z^E , Ks^E , n_D^E) were derived over the entire mole fraction range by using the general equation,

$$A^E = A - (x_1 A_1 + (1-x_1) A_2) \quad \dots(4)$$

Where A is corresponding parameter, (L_f , Z , Ks ,) of binary mixture and A_1 , A_2 are corresponding pure component values. X_1 and x_2 are mole fraction of the components.

The theoretical value of ultrasonic velocities in the mixtures of 1,4-dioxane and methanol were computed using Nomoto's equation,

$$U \text{ (NOM)} = (x_1 R_1 + x_2 R_2) / (x_1 v_1 + x_2 v_2) \quad \dots(5)$$

Where R_1 and R_2 are Rao's constants.

The theoretical values of ultrasonic speed obtained by this relation with the experimental speed and average parentage error in the calculated values were summarized for comparison with the experimental values.

The values of densities (ρ), ultrasonic velocities (u), acoustic impedance (Z), isentropic compressibility (Ks), intermolecular free length (L_f), excess intermolecular free length (L_f^E), excess acoustical impedance (Z^E) and excess isentropic compressibility (Ks^E) for the binary liquid mixtures over entire composition range at 303.15, 308.15, 313.18 and 318.15 K. have been presented in Table 1.

A perusal of Table 1 show that ultrasonic velocity (U) decreases with increase in concentration of alcohol. Similarly L_f increases with increase in concentration of alcohol at all temperatures

On the basis of a model for sound propagation, proposed by Eyring et al.⁴, U (ultrasonic velocity) should decrease if L_f (intermolecular free length) increases and vice versa since mixing of the two components the intermolecular free length (L_f) mainly affect the sound velocity. The close packing of molecules, which in effect decrease the sound velocity. .

The isentropic compressibility (Ks) increases with mole fraction of alcohol. Showing strong molecular interaction (hydrogen bonding) between the component molecules and thus gives insight of the structure making and structure breaking property of components in binary mixtures⁵.

Table 1: Densities, (ρ), ultrasonic velocities (U), acoustic impedance (Z), isentropic compatibility (Ks), intermolecular free length (Lf) excess intermolecular free length (L_f^E) excess acoustical impedance (Z^E) and excess isentropic compressibility (Ks^E) of binary liquid mixtures of methanol and 1,4-dioxane at 303.15, 308.15, 313.15 and 318.15 K

Temp.	X	σ (g cm ⁻³)	U (ms ⁻¹)	Z (g cm ⁻² s ⁻¹)	Ks TPa ⁻¹	L _f (Å)	L _f ^E (Å)	Z ^E (g cm ⁻² s ⁻¹)	Ks ^E TPa ⁻¹
	0.0000	1.0204	1325.3	1341.00	558.00	0.4903	0.00	0.00	0.00
303.15	0.2341	1.0019	1317.3	1319.78	575.20	0.4978	84.83	-105.00	-105.00
K	0.4074	0.9777	1273.1	1244.71	631.06	0.5214	96.61	-139.61	-139.61
	0.6470	0.9241	1187.7	1097.54	767.14	0.5749	69.53	-128.60	-128.60
	0.8048	0.8723	1131.6	987.12	895.21	0.6210	38.20	-82.90	-82.90
	0.9166	0.8249	1104.7	911.23	993.46	0.6542	18.34	-43.01	-43.01
	0.9397	0.8139	1099.0	894.49	1017.23	0.6620	13.18	-31.30	-31.30
	0.9611	0.8031	1092.3	877.20	1043.69	0.6705	6.62	-16.01	-16.01
	1.0000	0.7823	1087.9	851.09	1080.00	0.6821	0.00	0.00	0.00
308.15	0.0000	1.0160	1315.2	1336.26	569.00	0.4996	0.00	0.00	0.00
K	0.2341	0.9966	1297.2	1292.80	596.29	0.5114	74.34	-101.69	-101.69
	0.4074	0.9725	1243.6	1209.41	664.88	0.5400	78.17	-128.59	-128.59
	0.6470	0.9184	1156.9	1062.52	813.49	0.5973	51.86	-112.00	-112.00
	0.8048	0.8669	1108.0	960.51	939.65	0.6420	29.25	-72.79	-72.79
	0.9166	0.8196	1083.6	888.14	1039.05	0.6751	13.15	-34.99	-34.99
	0.9397	0.8085	1078.9	872.29	1062.57	0.6827	8.92	-24.20	-24.20
	0.9611	0.7980	1075.1	857.89	1084.28	0.6896	5.29	-14.28	-14.28
	1.0000	0.7772	1071.8	833.03	1119.99	0.7009	0.00	0.00	0.00
	0.0000	1.0156	1295.2	1315.35	587.00	0.5120	0.0000	0.00	0.00
313.15	0.2341	0.9951	1266.7	1260.51	626.29	0.5288	-0.0325	62.91	-97.20
K	0.4074	0.9699	1206.3	1170.01	708.51	0.5625	-0.0354	59.58	-116.00
	0.6470	0.9150	1120.8	1025.53	870.01	0.6233	-0.0251	35.62	-94.20

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Temp.	X	σ (g cm ⁻³)	U (ms ⁻¹)	Z (g cm ⁻² s ⁻¹)	Ks TPa ⁻¹	L _f (Å)	L _f ^E (Å)	Z ^E (g cm ⁻² s ⁻¹)	Ks ^E TPa ⁻¹
	0.8048	0.8624	1079.9	931.31	994.30	0.6663	-0.0153	20.78	-61.91
	0.9166	0.8148	1059.5	863.26	1093.38	0.6987	-0.0065	8.96	-28.00
	0.9397	0.8034	1056.5	848.75	1115.24	0.7057	-0.0044	6.07	-19.60
	0.9611	0.7926	1053.8	835.25	1136.11	0.7122	-0.0023	3.33	-11.21
	1.0000	0.7721	1052.1	812.35	1170.00	0.7228	0.0000	0.00	0.00
318.15	0.0000	1.0112	1282.8	1297.13	601.00	0.5226	0.0000	0.00	0.00
K	0.2341	0.9907	1242.4	1230.88	653.90	0.5451	-0.0294	51.52	-92.00
	0.4074	0.9650	1178.6	1137.37	745.98	0.5823	-0.0308	45.20	-107.20
	0.6470	0.9110	1093.5	996.19	917.99	0.6459	-0.0203	24.56	-83.50
	0.8048	0.8586	1053.0	904.11	1050.37	0.6909	-0.0104	11.87	-48.79
	0.9166	0.8112	1037.4	841.53	1145.48	0.7215	-0.0046	5.54	-22.89
	0.9397	0.8002	1035.0	828.18	1166.66	0.7282	-0.0031	3.81	-16.00
	0.9611	0.7893	1033.3	815.54	1186.72	0.7344	-0.0016	1.94	-9.20
	1.0000	0.7692	1032.3	794.04	1219.99	0.7446	0.0000	0.00	0.00

Acoustical impedance (Z) decreases with increase in mole fraction of alcohol, suggesting strong specific interactions between the constituent molecules of binary mixtures. Decrease of U and Z and increase in L_f and Ks in binary mixtures of alcohols with 1,4-dioxane suggest the hetero association of the molecules and it deactivate more at higher temperature, probably due to more depolymerisation of aggregates of alcohols at higher temperatures^{6,7}.

The excess values may be affected by three factors¹¹⁻¹³:

- (i) Due to specific forces between the molecules, such as hydrogen bonds, charge transfer complexes, and complexes gives negative values of excess functions.
- (ii) Due to physical intermolecular forces, including electrostatic forces between the charged particle and between a permanent dipole and so on induction forces between a permanent dipole and an induced dipole and forces of attraction and repulsion between non-polar molecules.
- (iii) Due to structural characteristic of the component arising from geometrical fitting of one component into other structure due to the differences in shape and

size of the components and free volume. The molecular interactions in liquid mixture may also be due to interstitial accommodation leading to more compact structure giving negative values of excess functions. While positive values are an indicative of weak interaction involving weak dispersion forces¹¹.

Since all excess function (K_s^E , L_f^E , n_D^E) are negative, it shows strong interaction due to hydrogen bonding^{14,15}. Figs. 1-3 show variation of excess functions with mole fractions of methanol.

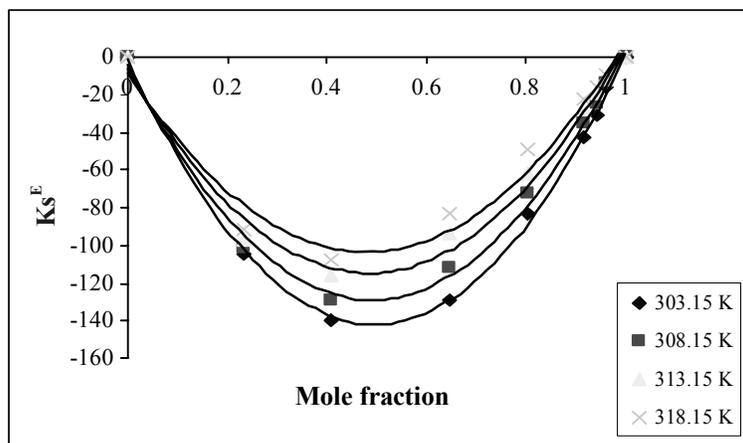


Fig. 1: Variation of excess isentropic compressibility (K_s^E) with mole fraction (x_1) for methanol (1) + 1,4-Dioxane (2) at 303.15, 308.15, 313.15 and 318.15 K

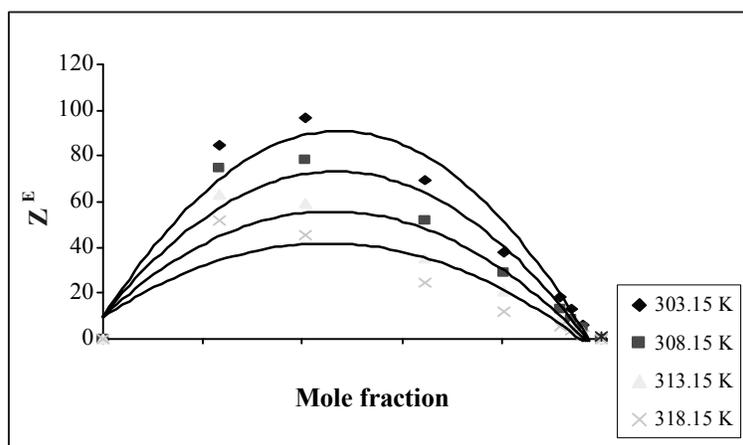


Fig. 2: Variation of excess acoustical impedance (Z^E) with mole fraction (x_1) for methanol (1) + 1,4-Dioxane (2) at 303.15, 308.15, 313.15 and 318.15 K

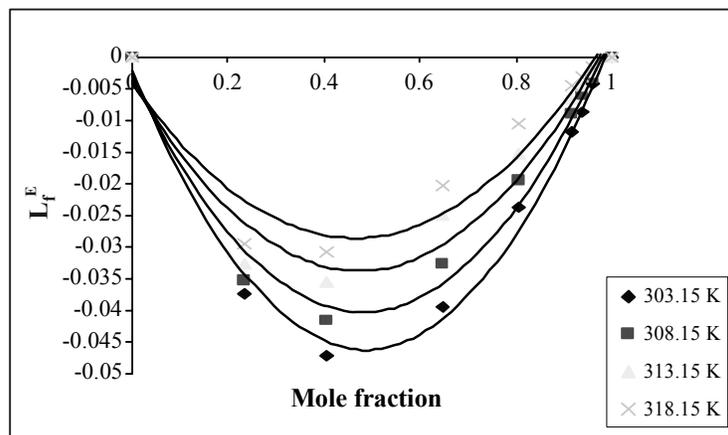


Fig. 3: Variation of excess intermolecular free length (L_f^E) with mole fraction (x_1) for methanol (1) + 1,4-Dioxane (2) at 303.15, 308.15, 313.15 and 318.15 K

It can be seen from Table 2 that the theoretical values of ultrasonic velocity computed by Nomoto's theory¹⁶ show little deviation from experimental values. It is due to the limitations and approximations incorporated in this theory, which are responsible for it. In Nomoto's theory, it is assumed that all the molecules are spherical in shape, which is not true every time. It is also supposed that the volume does not change on mixing and therefore, there is no interaction between the component of the liquid mixtures and it has not taken into account. Thus, the observed deviation of theoretical values of sound velocity from the experimental values shows that the strong molecular interaction is taking place between the molecules in the liquid mixtures^{17,18}.

Table 2: Theoretical values of ultrasonic velocity calculated from Nomoto's relation along with experimental ultrasonic velocity and percentage of error for 1,4-dioxane and methanol binary mixtures at 303.15, 308.15, 313.15 and 318.15 K.

Temperature (K)	Mole fraction	Experimental value (ms^{-1})	Nomoto's value (ms^{-1})	% of error
303.15	0.0000	1325.25	1325.25	0.00
	0.2341	1317.28	1293.407	0.49
	0.4074	1273.1	1263.895	3.06
	0.6470	1187.69	1210.882	0.73
	0.8048	1131.63	1164.643	-0.09

Cont...

Temperature (K)	Mole fraction	Experimental value (ms ⁻¹)	Nomato's value (ms ⁻¹)	% of error
	0.9166	1104.65	1123.976	2.89
	0.9397	1099.02	1114.54	2.25
	0.9611	1092.27	1105.437	1.56
	1.0000	1087.93	1087.93	0.00
308.15	0.0000	1315.22	1315.22	0.00
	0.2341	1297.21	1282.433	0.49
	0.4074	1243.61	609.5018	3.12
	0.6470	1156.93	1197.644	0.74
	0.8048	1107.98	1150.256	-0.09
	0.9166	1083.63	1108.65	2.93
	0.9397	1078.9	1099.006	2.28
	0.9611	1075.05	1089.706	1.58
	1.0000	1071.83	1071.83	0.00
313.15	0.0000	1295.15	1295.15	0.00
	0.2341	1266.72	1262.208	0.50
	0.4074	1206.32	1231.769	3.14
	0.6470	1120.8	1177.313	0.75
	0.8048	1079.91	1130.051	-0.09
	0.9166	1059.47	1088.668	2.98
	0.9397	1056.45	1079.09	2.32
	0.9611	1053.81	1069.859	1.61
	1.0000	1052.13	1052.13	0.00
318.15	0.0000	1282.76	1282.76	0.00
	0.2341	1242.43	1248.736	0.51
	0.4074	1178.62	1217.316	3.18

Cont...

Temperature (K)	Mole fraction	Experimental value (ms ⁻¹)	Nomato's value (ms ⁻¹)	% of error
	0.6470	1093.51	1161.151	0.76
	0.8048	1053.01	1112.458	-0.09
	0.9166	1037.39	1069.863	3.04
	0.9397	1034.97	1060.01	2.36
	0.9611	1033.25	1050.517	1.64
	1.0000	1032.29	1032.29	0.00

REFERENCES

1. A. Reddick and W. B. Bunger, Techniques in Chem. Organic Solvent, 12th, 4th Ed., Wiley, New York (1986).
2. A. Dean and S. Lange, Hand Book of Chemistry, 12th Ed., Mc Graw Hill, New York (1979).
3. B. Jacobson, Compressibility of Binary Mixtures, Acta, Chem. Scand., **6**, 485 (1952).
4. H. Eyring and J. F. Kincaid, J. Chem. Phys., **6**, 620 (1938).
5. V. Rajendran, Indian J. Pure Appl. Phys., **34**, 52 (1996).
6. A. Ali and A. Nain, J. Pure Appl. Ultrason., **24**, 27 (2002).
7. S. Jayakumar and V. Kannappan, Ind. J. Pure & Appl. Phys., **34**, 761 (1996).
8. P. J. Fiory, J. Am. Chem. Soc., **87**, 867 (1961).
9. M. R. Rao, Indian J. Phys., **14**, 109 (1940).
10. M. R. Rao, J. Chem. Phys., **9**, 682 (1941).
11. R. J. Fort and W. R. Moore, Trans. Faraday. Soc., (Gb) **61**, 2102 (1975).
12. K. Sheshadri and Reddy, Acoustica (Germany), **29**, 59 (1973).
13. M. V. Kaulgud and K. J. Patil, Ind. J. Pure Appl. Phys., **13**, 22 (1975).
14. M. Sakuri, Bull. Chem. Soc. Japan, **67**, 35 (1994).
15. C. V. Suryanarayan, J. Acoust. Soc. Ind., **7**, 13 (1979).

16. Nomoto, J. Phys. Soc. Japan, **13**, 1528 (1958).
17. O. Redlich and A. T. Kister, Ind. Eng. Chem., **40**, 345 (1984).
18. S. Anuradha, Prema and K. Rajagopal, Modern Applied Science, **2(5)**, 91 (2008).
19. S. Jayakumar and V. Kannappan, Ind. J. Pure & Appl. Phys., **34**, 761 (1996).
20. S. K. Satyaban, J. Chem. Thermodyn., **37**, 820 (2005).
21. T. P. Pandey, Ind. J. Pure Appl. Phys., **31**, 54 (1993).

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