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THEORETICAL PREDICTION OF ULTRASONIC VELOCITY OF BINARY LIQUID MIXTURES

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ABSTRACT
Experimental and theoretical ultrasonic velocity of the binary mixtures of alcohols with carbon tetrachloride systems have been find at 303K, The following theoretical methods such as, Nomotos relation, Van Dael relations , Impedance relations , Junjies relation , Impedance relations, Rao relations are used to calculate the theoretical ultrasonic velocity . Theoretical values are compared with experimental values to find the merits of the relations and check the validity of theses theoretical models by using percentage error and average percentage deviations. The results are discussed in terms of inter molecular interactions occurring in the systems.
Key words: Ultrasonic velocity, mixing model, binary, sound velocity, percentage deviation.

INTRODUCTION

Ultrasonic velocity gives the information about the molecular interactions of the pure liquid and liquid mixtures.[1-3] The various theoretical models are employed by many authors,[3-6] for the ultrasonic velocity of pure, binary, ternary mixtures etc. Many workers checked the validity of the theoretical ultrasonic model for the solution by different models[7-16] like Nomoto[17], Van Dael and Vangel[18], impedance relation[19], Rao's specific velocity[20] and Junjie[21]. In the present investigation study the ultrasonic velocity of the binary mixtures of alcohols with carbon tetrachloride systems.

EXPERIMENTAL

The ultrasonic velocity was measured using a single crystal interferometer with an accuracy of 0.001 m/s operating frequency at 2 MHz. The chemicals methanol, ethanol, propanol and carbon tetrachloride were used without further purification.

Theory

The following theoretical relations are used to the find the ultrasonic velocity in the binary mixtures. Nomotos (NR) established the mixtures relation by assuming molar sound velocity-

$$u = \left[\frac{\sum x_i R_i}{\sum x_i V_i} \right]^3 \quad (1)$$

Where x is the mole fraction of specie and R is the molar sound velocity related to the molecular weight and density i.e,

$$R_i = \left[\frac{m_i}{\rho_i} \right]^3 u^{1/3} = v_i u_i^{1/3} \quad (2)$$

The molar volume is given by $V_i = \frac{m_i}{\rho_i}$

Van Dael *et al* (VVR) obtained the relation for ultrasonic velocity in the liquid mixtures as-

$$\left[\frac{1}{m_1x_1+m_2x_2}\right]\left[\frac{1}{u^2}\right]=\frac{x_1}{m_1u_1^2}+\frac{x_2}{m_2u_2^2} \quad (3)$$

Junjies relations (JR) given by-

$$u_{JM}=\left[\frac{\sum x_iv_i}{(x_im_i)^{1/2}}\right]\left[\frac{x_iv_i}{\rho_iu_i^2}\right] \quad (4)$$

Impedance relation (IR) written as-

$$u=\frac{\sum x_iZ_i}{\sum x_i\rho_i} \quad (5)$$

Z is the acoustic impedance

From the Rao Realations (RR) obtained the ultrasonic velocity of the mixtures -

$$R_i=\left[\frac{m_i}{\rho_i}\right]u^{1/3}=v_iu_i^{1/3}$$

$$u=\left[\frac{x_i\rho_iR_i}{m_i}\right]^3=\left(\frac{x_iR_i}{V_i}\right)^3$$

X, V, m, and ρ are the mole fraction, molar volume, molecular weight and density of constituent's species.

RESULTS AND DISCUSSION

The experimental ultrasonic velocity along with calculated theoretical ultrasonic velocity using the following relations, Nomotos, Van Dael and Vangeel, Junjes theory, Impedance relation, and Rao specific sound velocity of methanol, ethanol, and propanol with carbon tetrachloride at 303 K are given in Table 1 to 3 and also reported the percentage deviations of all the binary mixtures. The Table 4 is presented to check the validity of the theoretical relation in terms of average percentage deviation for alcohols with carbon tetrachloride mixtures.

It can be seen from Table-1 to 3 that the theoretical values of ultrasonic velocity computed by various relations shows the deviation from experimental values. The limitation and approximations incorporated in these relations are responsible for it. It is assumed that all the molecules are in spherical shape which is not true every time. In Nomotos relations, it is supposed that the volume does not change on mixing, there is no interaction between the components of liquid mixtures has taken into account.

Similarly, the assumption for the formation of ideal mixing relation is that the ratios of specific heat of ideal mixtures and the volume are equal. Again no molecular interaction is taken into account. But on mixing more than one liquids, the interaction between two liquids taken place because of the presence of various type of forces such as dispersion forces, charge transfer, hydrogen bonding, dipole-dipole, dipole-induced dipole interaction, thus the observed deviation of theoretical ultrasonic velocity from experimental values shows that the molecular interactions is taking place between the unlike molecule in the liquid mixtures.

The Table-1 shows that, in the systems of methanol with carbon tetrachloride, there is good agreement between the experimental and theoretical values of Nomotos relations. Here ideal mixing relation provides better results than the results of Nomotos relation. However, higher values are observed in Van Dael and Vangeel Relations, Junjies relation, Impedance relation, Rao Relations.

Table-1: Experimental, theoretical ultrasonic velocity and percentage deviations of methanol in carbon tetrachloride system

X_2	u_{Exp}	Theoretical ultrasonic velocity (U m/s)					Percentage deviation				
		NR	VVR	JR	IR	RR	NR	VVR	JR	IR	RR
0	848	848	848	848	848	848	0	0	0	0	0
0.1	862	865	844	859	863	875	0.05	2.39	0.73	0.19	1.12
0.2	880	883	846	871	880	902	0.01	4.23	1.36	0.30	2.13
0.3	900	903	852	885	899	930	0.02	5.65	1.96	0.40	2.95
0.4	923	926	864	902	921	958	0.04	6.72	2.57	0.56	3.45
0.5	948	951	882	922	945	987	0.01	7.29	3.01	0.61	3.77
0.6	976	979	907	947	973	1016	0.02	7.37	3.28	0.62	3.81
0.7	1008	1011	941	977	1005	1046	0.04	6.92	3.32	0.59	3.49
0.8	1045	1048	987	1016	1042	1077	0.02	5.79	3.01	0.53	2.76
0.9	1088	1091	1051	1068	1087	1108	0.04	3.70	2.10	0.39	1.57
1	1140	1140	1140	1140	1140	1140	0.00	0.00	0.00	0.00	0.00

Table-2: Experimental, theoretical ultrasonic velocity and percentage deviations of ethanol in carbon tetrachloride system

X_2	U_{Exp}	Theoretical ultrasonic velocity (U m/s)					Percentage deviation				
		NR	VVR	JR	IR	RR	NR	VVR	JR	IR	RR
0	848	848	848	848	848	848	0	0	0	0	0
0.1	872	874	864	866	868	881	0.02	1.09	0.88	0.73	0.78
0.2	899	901	883	887	889	914	0.04	1.95	1.58	1.30	1.49
0.3	929	931	905	910	914	949	0.00	2.78	2.29	1.87	1.93
0.4	961	963	930	936	941	984	0.03	3.40	2.85	2.31	2.21
0.5	995	997	959	965	972	1021	0.01	3.76	3.20	2.56	2.36
0.6	1032	1034	994	999	1007	1058	0.02	3.90	3.36	2.65	2.28
0.7	1072	1074	1034	1039	1047	1096	0.03	3.72	3.25	2.52	2.01
0.8	1115	1117	1082	1086	1094	1134	0.01	3.10	2.73	2.07	1.57
0.9	1162	1164	1141	1144	1149	1174	0.02	1.94	1.73	1.28	0.88
1	1215	1215	1215	1215	1215	1215	0.00	0.00	0.00	0.00	0.00

Table-3: Experimental, theoretical ultrasonic velocity and percentage deviations of propanol in carbon tetrachloride system

X_2	U_{Exp}	Theoretical ultrasonic velocity (U m/s)					Percentage deviation				
		NR	VVR	JR	IR	RR	NR	VVR	JR	IR	RR
0	848	848	848	848	848	848	0	0	0	0	0
0.1	858	858	812	854	861	871	0.02	5.40	0.48	-0.36	1.52
0.2	870	870	790	861	876	894	0.02	9.25	1.04	-0.65	2.81
0.3	883	883	779	869	892	918	0.02	11.83	1.53	-1.02	3.99
0.4	898	899	777	880	910	942	0.08	13.44	2.01	-1.37	4.95
0.5	917	917	786	893	931	967	0.01	14.31	2.60	-1.53	5.47
0.6	939	939	805	910	955	992	0.00	14.27	3.05	-1.68	5.67
0.7	965	966	837	933	982	1018	0.08	13.22	3.27	-1.77	5.47
0.8	999	999	888	966	1014	1044	0.01	11.12	3.31	-1.51	4.48
0.9	1041	1041	967	1015	1052	1070	0.02	7.14	2.50	-1.03	2.8
1	1097	1097	1097	1097	1097	1097	0.00	0.00	0.00	0.00	0.00

From the Table-2, it is observed that in the system of ethanol with carbon tetrachloride, there is good agreement between the experimental and theoretical values of Nomotos relations followed by impedance relations. However, higher values are observed in Junjies relation, Impedance relation, Rao Relations.
The Table 3 shows that, in the systems of propanol with carbon tetrachloride, there is good agreement between the experimental and theoretical values observed in Nomotos relations followed by impedance relations, where as higher deviation observed in Van Dael and Vangeel Relations, Junjies relation, Rao Relations. There is no significant deviation in Junjies relation, Rao relation in all the binary mixtures.
The good agreement between theoretical and experimental values of Nomotos relations in all the binary mixtures, suggests that R is additive property in all the systems.

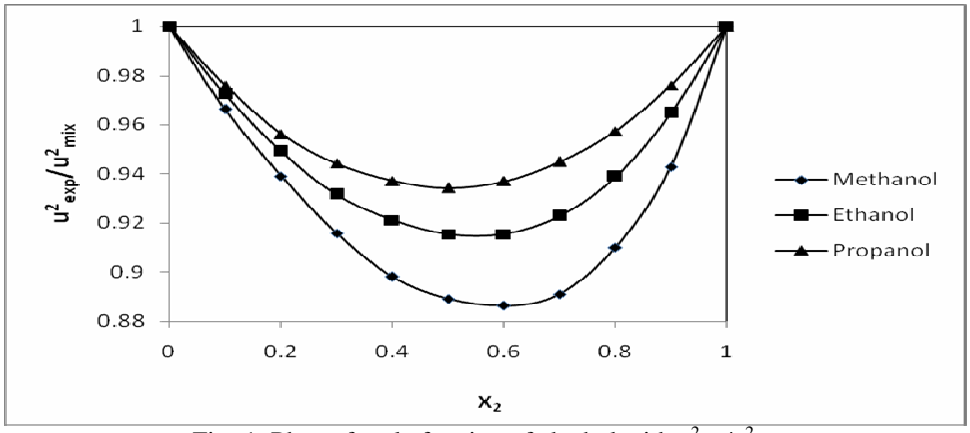

Fig.-1: Plots of mole fraction of alcohol with $u^2_{exp}/u^2_{mi.}$

Table-4: Average percentage deviations of alcohols in carbon tetrachloride systems

System	NR	VVR	JR	IR	RR
Methanol	0.05	9.09	1.8	0.99	3.38
Ethanol	0.04	4.55	1.94	0.38	2.28
Propanol	0.05	2.19	1.35	0.83	1.05

The higher deviation in some intermediate concentration range suggests the existence of strong tendency for association between the component molecules, in this concentration range as a result of hydrogen bonding. These values vary non-linearly with the composition suggesting that there is association in some composition. The percentage deviation shows maxima at an intermediate concentration in all the binary mixtures. Figure--1 represents the variation u^2_{Exp} / u^2_{Mix} with the mole fraction of methanol, ethanol and propanol. It is observed to be similar for all the systems.
The deviation of the ratio u^2_{Exp} / u^2_{Mix} from unity and its variation as a function of methanol or ethanol or propanol in a direct measure of non ideality of the systems as a consequence of association or other type of interaction. The Figure- 1 shows the interaction parameter and variation of u^2_{Exp} / u^2_{Mix} with the values of mole fraction of methanol or ethanol or propanol with carbon tetrachloride. From the Figure- it is observed that maximum positive deviations are observed at 0.5. The ratio of u^2_{Exp} / u^2_{Mix} is an important component to measure the non ideality in the mixtures especially in such cases where the perhaps other than the sound velocity are known.
Figure- 1 represents the variation of u^2_{Exp} / u^2_{Mix} with the mole fraction of alcohols for three binary mixtures. It is positive for the system and infers strong interaction between the mixing molecules. The negative value indicates the dominance of dispersion forces arising from breakage of hydrogen bonds in the associates. The positive value of the systems clearly indicates the evidence of strong tendency for the formation of association in mixtures through dipole-dipole interaction.

The high values of percentage deviation points out the maximum departure of the particle theory from experiment at the particular concentrations and finally determine the overall validation of these theories. The percentage deviations are given in Table-3. On the whole, all the theoretical models fairly close to the experiment values for the binary mixtures represents in this work thus showing the validity of theoretical models for the binary mixtures. The order of percentage deviations of theoretical models are Nomotos relations < Impedance relations < rao relations < Junjies relations <Impedance relations.

The prediction ability of various ultrasonic theories discussed above depends on the strength of interaction providing in a system. These theories are generally a tool to predict accurately the ultrasonic velocity where strong interaction are supposed to exist and average absolute percentage relation deviation is small in system where the interaction are less or nil.

CONCLUSIONS

From the experimental and theoretical ultrasonic velocity discuss about the solute-solvent interaction is in the order of methanol<ethanol< propanol. When increasing alcohol chain length decrease the solute-solvent interactions. Different theoretical methods used to evaluate the ultrasonic velocity of the binary mixture also predict the percentage deviations. From these values, the validity of these relations is checked. Nomotos relation is a best method compare than the other theoretical methods.

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