

Theoretical evaluation of ultrasonic velocities of binary liquid mixtures of 1-bromopropane in chlorobenzene at 303.15, 308.15, 313.15 and 318.15 K

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ABSTRACT

Theoretical velocities of binary liquid mixtures of 1-bromopropane with chlorobenzene at 2 MHz and four different temperatures 303.15, 308.15, 313.15 and 318.15 K, have been evaluated as a function of concentration and temperature. The experimental values are compared with theoretical models of liquid mixtures such as Nomoto, Van Dael-Vangeel, Impedance Relation, Rao's Specific Velocity Method, Junjie's relations and Free Length Theory. In the chosen system there is a good agreement between experimental and theoretical values calculated by Nomoto's theory. The deviation in the variation of U_{2exp}/U_{2imx} from unity has also been evaluated for explaining the non ideality in the mixtures. The results are explained in terms of intermolecular interactions occurring in these binary liquid mixtures.

Keywords: ultrasonic velocities; molecular interactions; 1-bromopropane and chlorobenzene

1. INTRODUCTION

The ultrasonic velocity measurement plays an important role in understanding the molecular interaction between the components of the mixture and provides an insight into the physicochemical properties of liquid mixtures such as molecular association and dissociation as well as the strength of interaction between the components [1-5]. Several relations, semi-empirical formulae and theories of Nomoto, Van Deal and Vangeel ideal mix relations, impedance relation, Rao's Specific velocity, Junjie and Free length theory are available for the theoretical computation of ultrasonic velocity in liquid and liquid mixtures [6-11].

This investigation presents the evaluation of ultrasonic velocity using above theoretical relations for 1-bromopropane with chlorobenzene at temperatures of 303.15-318.15 K with intervals of 5 K. An attempt has been made to study the molecular interactions from the deviation values in U_{2exp}^2/U_{2imix}^2 from unity based on earlier studies [12-13].

2. EXPERIMENTAL SECTION

The chemicals used in the present investigation are of Analar grade (with purity >0.995) and are further purified by employing the standard methods mentioned in literature [14-15]. Ultrasonic velocity (U) was measured using an ultrasonic interferometer working at 2 MHz with an accuracy of $\pm 0.05\%$ (Model F-81, Mittal enterprises, India).

The measured speeds of sound have a precision of $0.8 \text{ m}\cdot\text{sec}^{-1}$. The temperature stability was maintained with $\pm 0.01 \text{ K}$. By circulating water bath around the measuring cell through a pump.

The densities, ρ , of the pure liquids and their mixtures are determined using a 10^{-5} m^3 double-arm pycnometer, and the values from triplicate replication at each temperature are reproducible within $2 \times 10^{-1} \text{ kg}\cdot\text{m}^3$ and the uncertainty in the measurement of density is found to be 2 parts in 10^4 parts. The reproducibility in mole fractions was within ± 0.0002 .

3. THEORETICAL DETAILS

The following are relations/theories used for the prediction of ultrasonic velocity in the binary liquid mixtures.

3.1. Nomoto's relations (U_{NOM}):

On assuming the additivity of molar sound velocity (R) and no volume change on mixing, Nomoto established the following relation for a liquid mixture

$$R = \frac{M}{\rho U^3} \quad (1)$$

where U and ρ are determined experimentally and M is the mean molecular weight in a binary liquid mixture

$$M = (X_1 M_1 + X_2 M_2) \quad (2)$$

where M_1 and M_2 are molecular weights of constituent components. Simple manipulation yields the following relation

$$U_{\text{NOM}} = \left[\frac{(X_1 R_1 + X_2 R_2)}{(X_1 V_1 + X_2 V_2)} \right]^3 \quad (3)$$

3.2. Junjie's method (U_J):

$$U_J = \frac{X_1 M_1 / \rho_1 + X_2 M_2 / \rho_2}{\left[\{X_1 M_1 + X_2 M_2\}^{1/2} \{X_1 M_1 / \rho_1 U_1^2 + X_2 M_2 / \rho_2 U_2^2\}^{1/2} \right]} \quad (4)$$

where M_1 and M_2 are molecular weights of constituent components. ρ_1 and ρ_2 are the densities of constituent components.

3. 3. Ideal Mixture Relation (U_{IMR}):

Van Deal and Vangeel suggested the following relation for the velocity of sound:

$$\frac{1}{(X_1M_1 + X_2M_2) * U_{mix}^2} = \frac{X_1}{M_1U^2} + \frac{X_2}{M_2U^2} \quad (5)$$

where U_{mix} is the ideal mixing ultrasonic velocity in liquid mixture, and U_1 and U_2 are the velocities of the individual components.

3. 4. The Rao's specific velocity method relation (U_{RAO}):

$$U = (\sum X_i r_i \rho)^3 \quad (6)$$

$$r_i = U_i^{1/3} / \rho_i$$

where X_i mole fraction, U_i is the ultrasonic velocity, ρ_i is the density of the mixture, r_i is the Rao's specific sound velocity and Z_i is the acoustic impedance.

3. 5. The Impedance dependence relation (U_{IDR}):

$$U_{IDR} = \frac{\sum_{i=1}^n X_i Z_i}{\sum_{i=1}^n X_i \rho_i} \quad (7)$$

where X_i is the molefraction, Z_i is the acoustic impedance and ρ_i is the density of the components in the mixture.

3. 6. Free Length Theory (U_{FLT}):

$$U_{FLT} = \frac{K}{L_{mix} d_{exp}^{1/2}} \quad (8)$$

where

$$L_{mix} = 2 \left[\frac{V_m - (X_1V_{01} + X_2V_{02})}{X_1Y_1 + X_2Y_2} \right]$$

Molar volume at absolute zero,

$$V_{01} = \frac{V_1 U_1}{U_\infty} \quad V_{02} = \frac{V_2 U_2}{U_\infty}$$

Surface area per mole;

$$y_1 = \frac{2(V_1 - V_{01})}{L_{f_1}} \quad y_2 = \frac{2(V_2 - V_{02})}{L_{f_2}}$$

3. 7. Percentage deviation

The percentage deviation in sound velocity between the experimental and computed values are calculated as

$$\left(\frac{\Delta U}{U} \right) \% = \left(\frac{U_{\text{exp}} - U_{\text{theory}}}{U_{\text{exp}}} \right) \cdot 100 \quad (9)$$

4. RESULTS AND DISCUSSIONS

The experimentally measured ultrasonic velocity and the estimated ultrasonic velocity from the various theoretical models like Nomoto, Van Dael-Vangeel, Impedance Relation, Rao's Specific Velocity Method, Junjie's relations and Free Length Theory for the binary mixture of 1-bromopropane with chlorobenzene at four different temperatures are summarized in the Table 1.

Table 1. Values of experimental and theoretical ultrasonic velocity (U) at four different temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K.

Mole Fraction X	U _{EXP} ms ⁻¹	U _{NOM} ms ⁻¹	U _J ms ⁻¹	U _{FLT} ms ⁻¹	U _{IDR} ms ⁻¹	U _{IMR} ms ⁻¹	U _{RAO} ms ⁻¹
303.15 K							
0	1249.20	1249.20	1249.20	1249.20	1249.20	1249.20	1249.20
0.1824	1198.65	1196.37	1187.59	1184.05	1186.02	1179.14	1216.92
0.3581	1149.22	1145.06	1131.97	1128.34	1129.68	1120.27	1177.79
0.5273	1100.10	1095.23	1081.49	1080.72	1079.13	1069.96	1133.64
0.6905	1051.23	1046.88	1035.44	1032.71	1033.52	1026.39	1076.76
0.8480	1002.44	999.96	993.26	991.28	992.15	988.22	1017.05
1	954.47	954.47	954.47	954.47	954.47	954.47	954.47
308.15 K							
0	1225	1225	1225	1225	1225	1225	1225
0.1824	1175.96	1173.26	1164.65	1162.23	1163.27	1156.49	1193.47
0.3581	1127.72	1123.01	1110.17	1108.52	1108.15	1098.85	1155.84
0.5273	1079.54	1074.21	1060.72	1061.43	1058.63	1049.57	1112.39

0.6905	1031.63	1026.83	1015.63	1014.42	1013.91	1006.86	1056.96
0.8480	939.88	980.87	974.31	973.26	973.32	969.43	998.23
1	936.31	936.31	936.31	936.31	936.31	936.31	936.31
313.15 K							
0	1214	1214	1214	1214	1214	1214	1214
0.1824	1134.57	1161.28	1152.11	1150.27	1151.41	1143.79	1181.97
0.3581	1115.49	1110.11	1096.51	1095.22	1095.45	1085.02	1143.28
0.5273	1066.49	1060.47	1046.21	1047.12	1045.11	1034.95	1098.88
0.6905	1017.72	1012.33	1000.51	999.73	999.58	991.68	1042.92
0.8480	969.04	965.67	958.76	957.96	958.21	953.86	983.36
1	920.46	920.46	920.46	920.46	920.46	920.46	920.46
318.15 K							
0	1198	1198	1198	1198	1198	1198	1198
0.1824	1149.06	1145.38	1136.05	1135.24	1135.77	1127.83	1166.41
0.3581	1100.33	1094.33	1080.49	1080.48	1080.05	1069.17	1127.92
0.5273	1051.44	1044.85	1030.35	1032.06	1029.85	1019.25	1083.25
0.6905	1002.67	996.83	984.83	985.12	984.40	976.16	1027.99
0.8480	954.15	950.32	943.32	943.03	943.06	938.51	968.17
1	905.29	905.29	905.29	905.29	905.29	905.29	905.29

It is observed that the experimental values show less deviation with the theoretical values of ultrasonic velocities which confirms the existence of molecular interactions. For all molefractions ultrasonic velocity is found in good agreement with Nomoto theory it is supposed that the volume does not change on mixing. Therefore, no interaction between the components of liquid mixtures has been taken into account. Similarly less deviation observed in Impedance and Junjie is due to the presence of weaker Interaction in binary liquid mixtures. The maximum deviation in Van Deal and Vangeel (IMR) theory and Rao's specific velocity method relation are due to the associated and non-associated components present in the mixture of different size components. The reason may be the limitations and approximations incorporated in these theories [16-19]. Thus, the observed deviation of theoretical values of velocity from the experimental values shows that the molecular interactions are taking place [20-21] between the unlike molecules in the liquid mixture. In general, the predictive ability of various ultrasonic theories depends upon the strength of interactions that exist in a binary system. In case strong interactions exist between the molecules of the mixtures, there is much deviation in theoretical prediction of velocity than the molecules of the mixture where less interactions are present. The validity of different theoretical formulae is checked by percentage deviation at all the temperatures and is given in Table 2.

Table 2. Percentage deviation between experimental and theoretical values of velocity at four different temperatures 303.15 K, 308.15 K, 313.15 K and 318.15 K.

Mole Fraction X	U_{NOM}	U_{J}	U_{IDR}	U_{FLT}	U_{IMR}	U_{RAO}
303.15 K						
0	0	0	0	0	0	0
0.1824	-0.1898	-0.9230	-1.0536	-1.2182	-1.6275	1.5238
0.3581	-0.3619	-1.5013	-1.7001	-1.8171	-2.5194	2.4863
0.5273	-0.4423	-1.6921	-1.9062	-1.7613	-2.7397	3.0491
0.6905	-0.4142	-1.5018	-1.6849	-1.7615	-2.3629	2.4289
0.8480	-0.2473	-0.9155	-1.0262	-1.1133	-1.4187	1.4571
1	0	0	0	0	0	0
308.15 K						
0	0	0	0	0	0	0
0.1824	-0.2294	-0.9619	-1.0795	-1.1679	-1.6560	1.4889
0.3581	0.4184	-1.5561	-1.7357	-1.7021	-2.5596	2.4937
0.5273	-0.4948	-1.7429	-1.9366	-1.6775	-2.7757	3.0430
0.6905	-0.4654	-1.5514	-1.7175	-1.6681	-2.4006	2.4551
0.8480	-0.3056	-0.9727	-1.0733	-1.0798	-1.4685	1.4588
1	0	0	0	0	0	0
313.15 K						
0	0	0	0	0	0	0
0.1824	-0.2826	-1.0696	-1.1299	-1.2277	-1.7837	1.4939
0.3581	-0.4821	-1.7026	-1.7969	-1.8167	-2.7313	2.4910
0.5273	-0.5646	-1.9013	-2.0052	-1.8162	-2.9573	3.0370
0.6905	-0.5299	-1.6916	-1.7823	-1.7677	-2.5582	2.4764
0.8480	-0.3482	-1.0613	-1.1172	-1.1434	-1.5666	1.4721
1	0	0	0	0	0	0
318.15 K						
0	0	0	0	0	0	0
0.1824	-0.3198	-1.1322	-1.1563	-1.2026	-1.8475	1.5097
0.3581	-0.5450	-1.8029	-1.8434	-1.8044	-2.8319	2.5071
0.5273	-0.6295	-2.0060	-2.0532	-1.8434	-3.0613	3.0259
0.6905	-0.5829	-1.7786	-1.8217	-1.7506	-2.6440	2.5254
0.8480	-0.4011	-1.1346	-1.1622	-1.1655	-1.6389	1.4691
1	0	0	0	0	0	0

The percentage deviations of the ultrasonic velocity are both negative and positive. Such deviations indicate the nonideal behaviour of liquid mixtures. The limitations and approximations incorporated in these theories are responsible for the deviations between theoretical and experimental values. The variation of ultrasonic velocity with the molefraction of 1-bromopropane at different temperatures is shown in Figure 1.

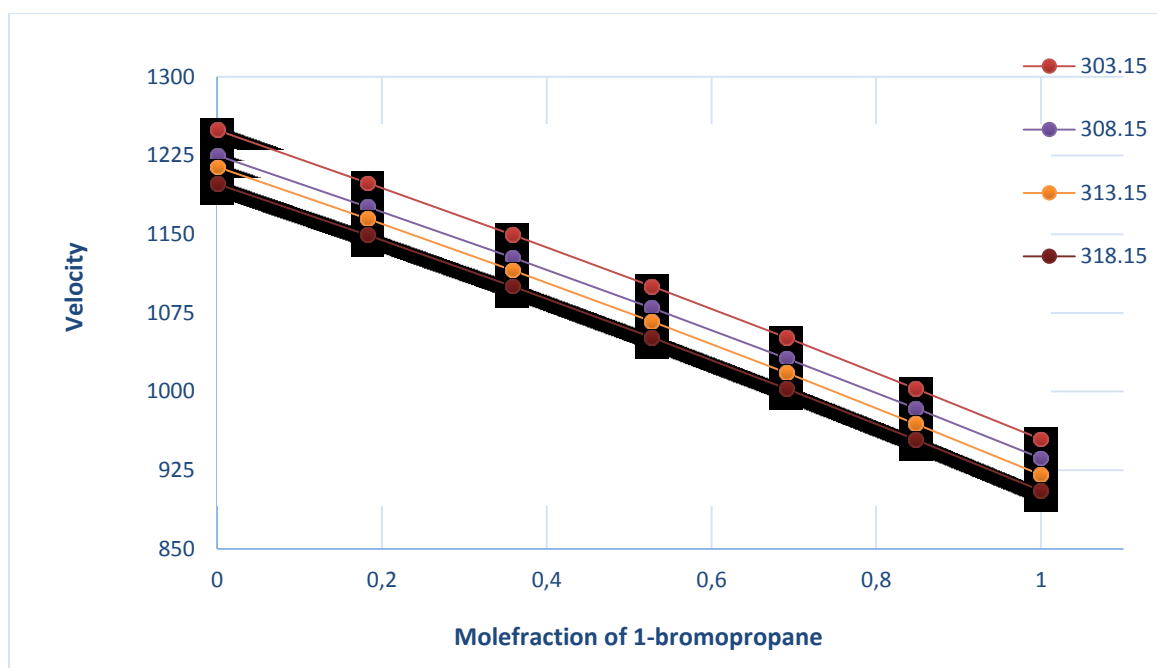


Fig. 1. Variation of Velocity with molefraction of 1-bromopropane in chlorobenzene.

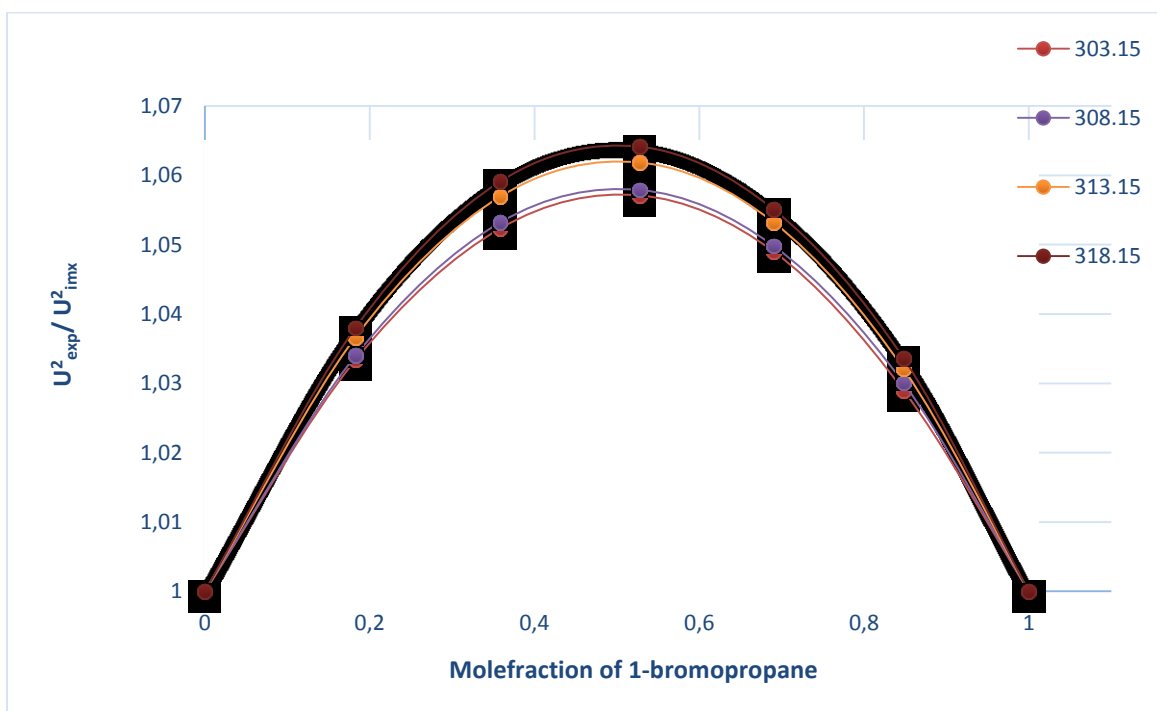


Fig. 2. Variation of U^2_{exp} / U^2_{imx} with molefraction of 1-bromopropane in chlorobenzene.

It is evident from the figure that the velocity decreases with increase in the concentration of 1-bromopropane and decreases with increase in temperature at any particular concentration. This is probably due to the fact that the thermal energy activates the molecule,

which would increase the rate of association of unlike molecules. Figure 2 represent the variation of $U_{\text{exp}}^2/U_{\text{imix}}^2$ with mole fraction of 1-bromopropane with chlorobenzene and it is observed that it is maximum at approximately 0.52 M.

5. CONCLUSION

Ultrasonic velocities predicted using six theories and relations were compared with experimentally measured velocity values at 303.15 K, 308.15 K, 313.15 K and 318.15 K in the binary mixture of 1-bromopropane with chlorobenzene gives satisfactory results. Thus, the linearity of molar sound velocity and additivity of molar volumes, as suggested by Nomoto's relation is in best suited with the experimental velocity values in all the temperatures for non-polar-polar liquid mixtures has also been emphasized by others [22-27].

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