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Ultrasonic Study of Various Liquid State Models Using Protic and Aprotic Solvents from 298.15 to 318.15K

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Abstract:

Theoretical ultrasonic velocity was calculated for binary mixture of n-Dodecane and 1-Butanol from 298.15 to 318.15K over the entire composition range from the measured work of J. Peleterio. Collision factor theory (CFT), Free length theory (FLT), Nomoto relation (NOMO) and Van deal relation (VAN) have been used to evaluate the ultrasonic velocity and compare with the experimental values at different temperatures. Validity of these theoretical models and relations were explained with help of molecular interaction. Degree of molecular interactions were computed at different temperatures. Average absolute % deviation was the criteria of the success of the result. Collision factor theory (CFT) gave excellent results in comparison to other liquid state models.

Keywords **—Collision factor, Free length,Nomoto, Van Deal, Ultrasonic velocity.**

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I. INTRODUCTION

In past few years, ultrasonic study has become a subject of wide interest to show various thermophysical properties and acoustical parameters evaluated from ultrasonic velocity, which is basically depend on the intermolecular interaction. Several workers [1]-[8] have done an extensive theoretical study on acoustical properties based on intermolecular force of interactions and the free space that present between the weakly bounded like and unlike components of pureliquids and binary mixtures. In present investigation binary mixture of dodecane and 1-butanol has been taken from the measured work of J. Peleterio [9] and theoretical evaluation of ultrasonic velocity has been performed by using Schaaff's collision factor theory [10]-[11], Jacobson's free length theory [12]-[13], Nomoto relation [14] and van dael [15]-[16] ideal mixing relation. Degree of molecular interaction has also been calculated from temperature 298.15-318.15K.the main aim of this work to test the validity of various liquid state models applicable to different kind of liquids. which help to predict the different acoustical properties.

II. THEORETICAL MODELS

A. Collision factor theory.

W. Schaaf [10] derived a relation between ultrasonic velocity and space filling factor using collision factor and U_∞ in pure liquid is given below:

$$U = \left(\frac{B}{V_m}\right) U_\infty S (1)$$

Where S is collision factor,$U_\infty = 1600\ m/s$ $\left(\frac{B}{V_m}\right)$ is space filling factor, Vm is molar volume and B is actual volume of molecules per mole.

$$B = {}^{b}/_{4} = {}^{4}/_{3}\,\pi r^3 N \quad (2)$$

Where r and b are the molecular radius and Van der Waals constant respectively.

$$r = \left({}^{3b}/_{16\pi N}\right)^{1/3} (3)$$

The value of B has been used to calculate the collision factor S by the following equation

$$S = \left(\frac{U}{U_\infty}\right)\left(\frac{V_m}{B}\right) (4)$$

Nutsch-Kuhkies [11] modified the above Scharff's equation of ultrasonic velocity for binary system as

$$U_{CFT} = U_\infty \left\{\sum_{i=1}^{2} X_i S_i\right\}\left\{\frac{X_1 B_1 + X_2 B_2}{V_m}\right\} (5)$$

B. Free length theory

Jacobson [12] theoretical model which relates intermolecular free length (L_f) proposed by Eyring and Hirschfelder and ultrasonic velocity

$$U = \frac{K}{\left(L_f \rho^{1/2}\right)} (6)$$

Where K is temperature dependent constant. Its value lies in range (588-652) from temperature 273 to 323K.

According to Eyring [13] intermolecular free length depends on available volume (V_a) and surface area (Y) of molecule per mole

$$L_f = \left\{\frac{2V_a}{Y}\right\} \quad (7)$$

Put the value of L_f in equation (6)

$$U = \left\{\frac{KY}{\left(2V_a \rho^{1/2}\right)}\right\} (8)$$

Where $V_a = (V_m - V^0)$, V_m and V^0 are molar volume of individual component at observation temperature and absolute zero temperature respectively.

Rearranging the equation (8) to get the value of Y of individual component

$$Y = \left\{\frac{2UV_a \rho^{1/2}}{K}\right\} (9)$$

Available volume (V_a) can be calculated for pure component having $U < U_\infty (1600 ms^{-1})$ by the following equation:

$$U = V_{m,T}\left(1 - \frac{U_{Exp}}{U_\infty}\right) (10)$$

For binary system equation (8) can be written as:

$$U_{FLT} = \left\{\frac{K(X_1 Y_1 + X_2 Y_2)}{2\left[V_{M,T} - (X_1 V_1^0 + X_2 V_2^0)\right]}\right\}\left\{{}^{1}/_{\rho^2}\right\} (10)$$

Where $V_{M,T}$ is molar volume of binary system can be calculated by the following relation

$$V_{M,T} = \frac{(X_1 M_1 + X_2 M_2)}{\rho_{mix}} (11)$$

Put the value of Y_1 and Y_2 calculated from equation (9) to equation (10), we get the value of ultrasonic velocity for binary system

$$U_{Fl} = \left\{\frac{\left(X_1\left(V_{m,T}^1 - V_1^0\right)U_1\rho_1^2 + X_2\left(V_{m,T}^2 - V_2^0\right)U_2\rho_2^2\right)}{2\rho_{Mix}^2\left[V_{M,T} - (X_1 V_1^0 + X_2 V_2^0)\right]}\right\} (12)$$

Where U_1&U_2 are ultrasonic velocity of liquid 1 and 2 respectively, ρ_1&ρ_2 are density of liquid 1 and 2 respectively.

C. Nomoto Relation

Nomoto [14] proposed an empirical relation, which was used to determine the ultrasonic velocity of liquid mixtures by assuming the linear dependence of molar sound velocity (R) and ideal volume of mixing.

$$U^{NOMO} = \left\{\left(\sum_{i=1}^{2} \frac{X_i R_i}{X_i V_i}\right)^3\right\} (13)$$

Where R is molar sound velocity can be determined by the following relation

$$R = \left({}^{M_i}/_{\rho_i}\right) U^{1/3} (14)$$

M_i and ρ_i are molecular weight of individual component.

D. Van Deal Relation

Vandeal [15] proposed an empirical relation to determine the ultrasonic velocity in ideal system, based on adiabatic compressibility, volume fraction and ratio of specific heat.

$$\beta_s^{IM} = \sum_{I=1}^{2} \frac{\emptyset_i \gamma_i \beta_{s(i)}}{\gamma^{IM}} (15)$$

Where Φ_i and γ_i are volume fraction and specific heat ratio of individual components.

If binary system is ideal and $\gamma_i = \gamma^{IM}$, then equation (15) can be written as:

$$\beta_s^{IM} = \sum_{i=1}^{2} \emptyset_i \beta_{s(i)} (16)$$

If $V_1=V_2$ then equation (16) will be converted into the following equation:

$$\beta_s^{IM} = \sum_{i=1}^{2} X_i \beta_{s(i)} \quad (17)$$

Where x_i is the mole fraction of individual component.

On the basis of above equation (16) and (17), ultrasonic velocity [16] of binary system can be determined by the following relation:

$$U^{VAN} = \left\{ \left(\sum_{i=1}^{2} \frac{1}{\sqrt{X_i M_i}} \right) \left(\sum_{i=1}^{2} \left(\frac{X_i}{M_i U_i} \right)^{-1/2} \right) \right\} \quad (18)$$

III. RESULT AND DISCUSSION

Table1 represent the density of binary system, experimental ultrasonic velocity, theoretical ultrasonic velocity calculated from collision factor theory, free length theory, Nomoto relation and van dael relation of ideal mixing from eq. (5), eq. (12), eq. (13) and eq. (18) respectively and their respective absolute % deviation. Average absolute % deviation calculated for all the theoretical models from temperature 298.15 to 318.15K are presented in table 2. Degree of molecular interaction(α) at different temperatures are presented in table 3.A close observations of table1 reveals that % absolute deviation for CFT,Nomotoand van dael relation decreases with increase in temperature while in case of free length theory its value increases with increase in temperature. Average absolute % deviation

Table 1 Ultrasonic velocity and Absolute % deviation

X_1	P^{mix}(g/cc)	U^{exp}(m/s)	U^{FLT} (eq. (5))	U^{CFT} (eq. (12))	U^{NOMO} (eq. (13))	U^{VAN} (eq. (18))	$\%\Delta^{FLT}$ (Abs)	$\%\Delta^{CFT}$ (Abs)	$\%\Delta^{NOM}$ (Abs)	$\%\Delta^{VAN}$ (Abs)
T=298.15K										
0.02749	0.74549	1275.72	1278.04	1275.83	1246.82	1263.40	0.18	0.01	2.27	0.97
0.08048	0.74651	1272.60	1277.41	1271.36	1246.03	1238.28	0.38	0.10	2.09	2.70
0.19017	0.74912	1267.38	1275.74	1262.51	1244.23	1198.30	0.66	0.38	1.83	5.45
0.28812	0.75204	1263.17	1273.82	1255.16	1242.38	1173.83	0.84	0.63	1.65	7.07
0.38654	0.75551	1259.03	1271.55	1248.44	1240.24	1158.11	0.99	0.84	1.49	8.02
0.44097	0.75773	1256.85	1270.09	1245.06	1238.90	1152.85	1.05	0.94	1.43	8.27
0.4835	0.75962	1255.23	1268.85	1242.62	1237.78	1150.36	1.08	1.00	1.39	8.35
0.58849	0.76509	1251.40	1265.26	1237.47	1234.63	1150.11	1.11	1.11	1.34	8.09
0.61515	0.76672	1250.47	1264.19	1236.39	1233.74	1151.38	1.10	1.13	1.34	7.92
0.69605	0.77204	1247.52	1260.74	1233.82	1230.72	1158.64	1.06	1.10	1.35	7.12
0.79594	0.7802	1244.06	1255.48	1232.44	1226.23	1175.04	0.92	0.93	1.43	5.55
0.90295	0.79157	1240.79	1248.26	1233.98	1220.15	1202.91	0.60	0.55	1.66	3.05
0.95321	0.79815	1239.77	1244.15	1236.16	1216.68	1220.28	0.35	0.29	1.86	1.57
T=308.15K										
0.02749	0.73818	1237.32	1239.78	1237.73	1213.11	1225.69	0.20	0.03	1.96	0.94
0.08048	0.73913	1234.00	1239.30	1233.77	1212.41	1201.70	0.43	0.02	1.75	2.62
0.19017	0.74167	1228.68	1237.90	1225.95	1210.82	1163.52	0.75	0.22	1.45	5.30
0.28812	0.74451	1224.60	1236.27	1219.46	1209.18	1140.19	0.95	0.42	1.26	6.89
0.38654	0.74793	1220.59	1234.29	1213.52	1207.29	1125.27	1.12	0.58	1.09	7.81
0.44097	0.75012	1218.52	1233.02	1210.54	1206.11	1120.33	1.19	0.66	1.02	8.06
0.4835	0.752	1217.02	1231.92	1208.38	1205.12	1118.02	1.22	0.71	0.98	8.13
0.58849	0.7574	1213.58	1228.77	1203.83	1202.34	1118.04	1.25	0.80	0.93	7.87
0.61515	0.75903	1212.77	1227.81	1202.88	1201.54	1119.34	1.24	0.82	0.93	7.70
0.69605	0.76436	1210.28	1224.72	1200.62	1198.87	1126.56	1.19	0.80	0.94	6.92

0.79594	0.7725	1207.63	1220.02	1199.41	1194.90	1142.69	1.03	0.68	1.05	5.38
0.90295	0.78388	1205.58	1213.52	1200.78	1189.52	1169.97	0.66	0.40	1.33	2.95
0.95321	0.79048	1205.26	1209.80	1202.72	1186.45	1186.94	0.38	0.21	1.56	1.52
				T=318.15K						
0.02749	0.7308	1199.74	1201.98	1200.05	1179.68	1188.41	0.19	0.03	1.67	0.94
0.08048	0.73165	1196.12	1201.67	1196.58	1179.08	1165.54	0.46	0.04	1.42	2.56
0.19017	0.73412	1190.76	1200.53	1189.72	1177.69	1129.15	0.82	0.09	1.10	5.17
0.28812	0.73686	1186.70	1199.20	1184.04	1176.27	1106.94	1.05	0.22	0.88	6.72
0.38654	0.7402	1182.73	1197.54	1178.85	1174.62	1092.81	1.25	0.33	0.69	7.60
0.44097	0.74236	1180.76	1196.44	1176.24	1173.60	1088.18	1.33	0.38	0.61	7.84
0.4835	0.74423	1179.44	1195.49	1174.36	1172.74	1086.07	1.36	0.43	0.57	7.92
0.58849	0.74954	1176.25	1192.78	1170.40	1170.32	1086.36	1.41	0.50	0.50	7.64
0.61515	0.75118	1175.56	1191.91	1169.58	1169.63	1087.68	1.39	0.51	0.50	7.48
0.69605	0.75646	1173.49	1189.21	1167.62	1167.30	1094.87	1.34	0.50	0.53	6.70
0.79594	0.76459	1171.64	1185.05	1166.61	1163.85	1110.73	1.14	0.43	0.66	5.20
0.90295	0.77598	1170.77	1179.25	1167.89	1159.17	1137.43	0.72	0.25	0.99	2.85
0.95321	0.7826	1171.10	1175.92	1169.64	1156.50	1154.00	0.41	0.12	1.25	1.46

Calculated forCollision factor theory, Nomoto and Van Dael decreases with increase in temperature whereas average absolute % deviation for free length theory increases with increase in temperature. Degree of molecular interaction (α) calculated from eq. (19) decreases with increase intemperate as shown in figure 1. Degree of molecular interaction increases with increase in concentration of dodecane then decreases for all temperatures.

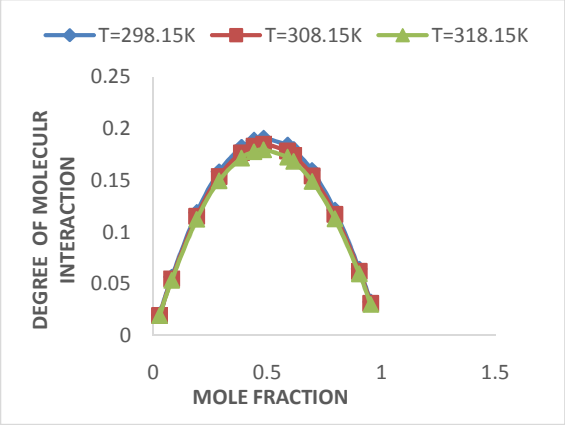

Fig. 1 variation of (α) with mole fraction

Degree of molecular interaction increases up to 19.06% ,18.49%, 17.39% for temperature 298.15,308.15,318.15K respectively at (X_1 =0.4835). density of binary system is used to predict the nature of solvent-solvent interaction. Since the density of the binary system was increasing linearly which confirm the weak intermolecular interaction between the like and unlike molecules but with increase in temperatures, density was decreasing which confirm the intermolecular association become very small at high temperature as shown in figure 1.

Table 2 Average absolute % deviation

Average absolute% deviation				
T/K	U^{FLT}	U^{CFT}	U^{NOMO}	U^{VAN}
298.15	0.7949	0.6938	1.6247	5.7037
308.15	0.8934	0.4880	1.2498	5.5462
318.15	0.9909	0.2940	0.8748	5.3909

$$\alpha = \left\{\left(\frac{U_{Exp}^2}{U_{IM}^2}\right) - 1\right\} (19)$$

where α is degree of molecular interaction, $U_{Exp}$and $U_{IM}$are measured ultrasonic velocity and calculated ultrasonic velocity from ideal mixing relation respectively.

Table 3 Calculated values of (α) from 298.15 to 318.15K

X_1	$\alpha^{298.15K}$	$\alpha^{308.15K}$	$\alpha^{318.15K}$
0.02749	1.96%	1.91%	1.92%
0.08048	5.62%	5.45%	5.32%
0.19017	11.86%	11.51%	11.21%

0.28812	15.80%	15.35%	14.93%
0.38654	18.19%	17.66%	17.13%
0.44097	18.86%	18.30%	17.74%
0.4835	19.06%	18.49%	17.93%
0.58849	18.39%	17.82%	17.23%
0.61515	17.95%	17.39%	16.81%
0.69605	15.93%	15.41%	14.88%
0.79594	12.09%	11.69%	11.27%
0.90295	6.40%	6.18%	5.95%
0.95321	3.22%	3.11%	2.99%

Table1 and 2 clearly indicate that Collision factor theory gave an excellent result in comparison to other liquid state models. Order is as follows Van Dael $<$ $Nomoto$ $<$ FLT $<$ CFT.

IV. CONCLUSIONS

Liquid state models are excellent tool which helps to determine various thermodynamic properties and acoustical parameter in absence of experimental data. In above discussion it is concluded that Collision factor theory gave an excellent result in comparison to other liquid state models.

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