

## Prediction of ultrasonic velocity and intermolecular free-length and their correlation with interaction in binary liquid mixtures

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**Abstract.** The ultrasonic velocities of binary liquid mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane have been evaluated at 298·15 and 308·15 K using Schaaff's collision factor theory (CFT), Jacobson's free length theory (FLT), Nomoto's relation and Van Dael ideal mixing relation. The ideal mixing relation gives the minimum deviation for all the systems except with acetone. The intermolecular free length has also been evaluated using ultrasonic and thermodynamic methods and the limitations of both the methods have been discussed. The deviations in ultrasonic velocity and intermolecular free length are discussed in terms of weak interaction between unlike molecules.

**Keywords.** Nomoto relation; Van Dael ideal relation; intermolecular free-length; free-length theory; collision factor/non ideal behaviour.

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### 1. Introduction

Ultrasonic velocity has been a subject of active interest during the recent past. Attempts have been made to show the significance of thermodynamic properties derived from sound velocity and related data with intermolecular interactions in binary liquid mixtures by several workers (Reddy *et al* 1962; Deshpandey and Bhatgodde 1968; Hyderkhan and Subramanyam 1971; Sheshadri *et al* 1971; Jain *et al* 1974; Pandey *et al* 1977, 1978; Nath and Dubey 1980; Nath and Tripathi 1989; Shukla and Dubey 1984; Shukla *et al* 1985 and 1990). Nomoto (1958) and Bhimsenachar *et al* (1962) made successful attempts to evaluate sound velocity in binary liquid mixtures. Van Dael (1975) ideal mixing relation has also been employed successfully to investigate acoustical behaviour of binary liquid mixtures. Further the free length theory (FLT) of Jacobson (1951, 1952a, b) and Schaaff's (1939) collision factor theory (CFT) have been used to predict intermolecular interactions between unlike molecules of the mixtures by several workers (Pandey *et al* 1977, 1978; Shukla and Dubey 1984 and Shukla *et al* 1985, 1990). Sheshadri *et al* (1971) found that FLT is better than CFT for theoretical evaluation of sound velocity whereas Mishra and Pandey (1977, 1978) observed the CFT is better than FLT for the aforesaid purpose. Shukla and Dubey (1984) found that the Van Dael ideal mixing relation gives the minimum deviation. In the present communication all the above theories have been used to predict sound velocity in the above binary mixtures and they have been found to

yield satisfactory results. Further the concept of intermolecular free length has also been used to study the intermolecular interaction in the case of binary mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, *p*-xylene, acetone and cyclohexane at 298.15 and 308.15 K.

## 2. Theoretical

On assuming the additivity of molar sound velocity and no volume change on mixing, Nomoto (1958) established the following relation for sound velocity ( $U$ ) in binary liquid mixtures:

$$U = \left( \frac{R}{V} \right)^3 = \left( \frac{x_1 R_1 + x_2 R_2}{x_1 V_1 + x_2 V_2} \right)^3 \quad (1)$$

where the molar sound velocity  $R = (M/\rho)U^{1/3}$ .

Van Dael relation (1975) has been employed successfully in the study of acoustical behaviour of binary liquid mixtures. According to his assumption, the adiabatic compressibility ( $\beta_s$ ) of the mixture is given by the relation

$$\beta_{s(im)} = \phi_1 \frac{\gamma_1}{\gamma_{(im)}} \beta_{s(1)} + \phi_2 \frac{\gamma_2}{\gamma_{(im)}} \beta_{s(2)} \quad (2)$$

where  $\phi$  and  $\gamma$  represent the volume fraction and specific heats ratio respectively. To avoid complication, Richardson (1962) and Blandamer and Wadington (1970) assumed the following simple relation for  $\beta_{s(im)}$

$$\beta_{s(im)} = \phi_1 \beta_{s(1)} + \phi_2 \beta_{s(2)}. \quad (3)$$

But this relation is true only if the mixture is ideal and the condition  $\gamma_1 = \gamma_2 = \gamma_{(im)}$  is satisfied. Equation (3) can be transformed into a linear combination of mole fractions by assuming  $V_1 = V_2$

$$\beta_{s(im)} = x_1 \beta_{s(1)} + x_2 \beta_{s(2)}. \quad (4)$$

Following (3) and (4) we get the expression for sound velocity of mixtures as

$$\frac{1}{x_1 M_1 + x_2 M_2} \cdot \frac{1}{U_{(im)}^2} = \frac{x_1}{M_1 U_1^2} + \frac{x_2}{M_2 U_2^2}. \quad (5)$$

In (5),  $M_1$ ,  $M_2$  and  $U_1$ ,  $U_2$  are molecular weights and sound velocities of first and second components respectively.

Jacobson (1951, 1952a, b) was first to introduce the concept of intermolecular free-length given by Eyring and Hirschfelder (1937) to evaluate sound velocity in pure liquid and liquid mixtures. According to Eyring *et al*, intermolecular free-length ( $L_f$ ) is given by the relation

$$L_f = \frac{2V_a}{Y} \quad (6)$$

where  $V_a$  is available volume and  $Y$  is surface area per mole.  $V_a$  and  $Y$  can be expressed as

$$V_a = V_T - V_0 \tag{7}$$

$$Y = (36\pi N V_0^2)^{1/3} \tag{8}$$

In (7)  $V_T$  and  $V_0$  are molar volume at temperature  $T$  and zero degree absolute respectively.  $N$  stands for Avagadro's number in (8).  $V_0$  can be obtained from the following relation using critical temperature ( $T_c$ )

$$V_0 = V_T(1 - T/T_c)^{0.3} \tag{9}$$

Assuming additivity of surface area, the intermolecular free-length in the mixture is given by

$$L_f = 2[V_T - \{x_1 V_{0(1)} + x_2 V_{0(2)}\}]/(x_1 Y_1 + x_2 Y_2) \tag{10}$$

The value of  $L_f$  so obtained is known as thermodynamic  $L_f$ . On the basis of above relations, Jacobson (1951, 1952) obtained the following expression for sound velocity in liquid mixtures:

$$U_{\text{mix}} = \frac{K}{L_{f(\text{mix})} \rho_{\text{mix}}^{1/2}} \tag{11}$$

Jacobson constant  $K$  is only temperature dependent. Its value at 298.15 and 308.15 K are 623.34 and 633.71 respectively. Although (6) is valid for many liquids, it is essentially empirical. Due to an uncertain value of  $L_f$ , there is uncertainty in its exact applicability to a particular liquid or liquid mixtures.

It is evident from (6), (7) and (8) that  $L_f$  can be in error due to an error in  $V_a$ , the available volume (caused by an error in computing  $V_0$ ) and to an error in estimating the surface area per mole, or due to both. Jacobson observed that  $V_0$  cannot be computed with an accuracy better than 0.5% by means of (9) even when the correct value of critical temperature  $T_c$  is known. Since the difference ( $V_T - V_0$ ) is 20–30% of  $V_T$ , even a small error in  $V_0$  has relatively large effect on free-length. So it is not possible to calculate  $L_f$  with accuracy greater than 2%. As regards the error in  $Y$ , the greatest uncertainty is in the relation  $Y = (36\pi N V_0^2)^{1/3}$  itself, which is theoretically valid for spherical molecules only. Schaaffs (1939) gave the following relation for available volume

$$V_a = V_T[1 - (U/U_\infty)] \tag{12}$$

The limitation of this equation is that  $U_\infty$  has been equalled to 1600 ms<sup>-1</sup> by Schaaffs. The ultrasonic value of  $L_f$  can now be obtained by using (6), (8) and (12). Schaaffs equation for sound velocity was extended by Nutsch–Kuhkies (1963) to binary liquid mixtures as

$$U_{\text{mix}} = U_\infty(x_1 S_1 + x_2 S_2) \frac{[(x_1 B_1 + x_2 B_2)]}{V_m} \tag{13}$$

where  $S$  and  $B$  represent collision factor and geometrical volume respectively. The actual volume of the molecule per mole can be calculated by the relation

$$B = \frac{4}{3}\pi r_m^3 \quad (14)$$

Here  $r_m$  stands for molecular radii. Its value has been evaluated by Shukla *et al* (1990). The value of  $B$  thus obtained has been used to compute  $S$  by the relation

$$S = \frac{UV}{BU_\infty} \quad (15)$$

### 3. Results and discussion

The deviation of ultrasonic velocity  $(\Delta U/U)\%$  from experimental values evaluated by four different methods alongwith thermodynamic and ultrasonic values of  $L_f$  are recorded in table 1. The necessary data required for the evaluation of  $L_f$  and sound

**Table 1.** Percentage deviation of sound velocity evaluated by different methods and intermolecular free-length.

$x_1$	$U_{\text{expt}}$ $\text{ms}^{-1}$	$(\Delta U/U)\%$ (Nomoto)	$(\Delta U/U)\%$ (Van Dael)	$(\Delta U/U)\%$ (FLT)	$(\Delta U/U)\%$ (CFT)	$L_f/\text{\AA}$ Ultra- sonic	$L_f/\text{\AA}$ Thermo- dynamic
CHCl <sub>2</sub> -CHCl <sub>2</sub> + benzene							
Temp. 298.15							
0.0665	1276	1.02	-0.39	-0.65	1.46	0.5141	0.5104
0.1858	1243	2.06	-1.22	-1.00	3.10	0.5763	0.5003
0.1860	1243	2.01	-1.22	-1.06	3.09	0.5764	0.5006
0.2606	1227	2.33	-1.74	-1.24	1.70	0.6086	0.4940
0.4252	1201	2.40	-2.47	-1.83	4.13	0.6661	0.4809
0.5705	1181	2.33	-2.43	-2.02	4.05	0.7134	0.4702
0.6562	1172	2.10	-2.18	-2.18	3.68	0.7372	0.4643
0.7000	1168	1.95	-2.00	-2.26	3.42	0.7484	0.4613
0.8679	1160	0.79	-1.40	-2.95	1.59	0.7790	0.4505
0.9337	1158	0.26	-0.96	-3.20	0.69	0.7891	0.4463
Temp. 308.15							
0.1003	1224	1.20	-0.91	-0.97	1.92	0.6162	0.5579
0.1944	1200	1.98	-1.44	-0.87	3.21	0.6641	0.5280
0.2000	1199	2.01	-1.52	-0.90	3.25	0.6662	0.5270
0.2859	1183	2.31	-2.07	-1.24	3.88	0.7009	0.5193
0.5407	1149	2.29	-2.68	-1.98	4.17	0.7840	0.4978
0.6835	1135	1.97	-2.25	-2.18	3.60	0.8231	0.4867
0.8539	1128	0.84	-1.62	-2.90	1.78	0.8533	0.4744
CHCl <sub>2</sub> -CHCl <sub>2</sub> + toluene							
Temp. 298.15							
0.2623	1237	2.20	-0.32	1.51	2.78	0.6151	0.4837
0.4200	1212	2.30	-0.83	0.58	3.03	0.6654	0.4754
0.4364	1207	2.50	-4.58	0.16	3.24	0.6746	0.4748

(Continued)

Table 1. (Continued)

$x_1$	$U_{\text{expt}}$ $\text{ms}^{-1}$	$(\Delta U/U)\%$ (Nomoto)	$(\Delta U/U)\%$ (Van Dael)	$(\Delta U/U)\%$ (FLT)	$(\Delta U/U)\%$ (CFT)	$L_f/\text{\AA}$ Ultra- sonic	$L_f/\text{\AA}$ Thermo- dynamic
0.4586	1202	2.64	-4.50	0.34	3.38	0.8846	0.4727
0.5325	1190	2.70	-0.34	0.08	3.46	0.7094	0.4683
0.6841	1175	2.11	-0.51	-1.02	2.79	0.7447	0.4596
0.9001	1159	0.76	-0.35	-2.59	1.00	0.7872	0.4480
Temp. 308.15							
0.0837	1243	0.78	-0.32	1.24	1.02	0.6117	0.5269
0.1517	1230	1.03	-0.82	0.81	1.42	0.6369	0.5211
0.1545	1230	0.99	-0.82	0.72	1.40	0.6370	0.5208
0.1648	1227	1.11	-0.82	0.09	1.54	0.6426	0.5200
0.3050	1198	1.83	-1.01	0.82	2.47	0.6996	0.5089
0.4565	1170	2.36	-0.76	0.00	3.10	0.7479	0.4984
0.6876	1141	2.08	-0.53	-1.15	2.69	0.8231	0.4838
0.7971	1133	1.45	-0.53	-1.94	1.90	0.8451	0.4772
CHCl <sub>2</sub> ·CHCl <sub>2</sub> + <i>p</i> -xylene Temp. 298.15							
0.0926	1282	1.15	0.31	2.72	1.14	0.5555	0.4945
0.2279	1253	1.91	0.32	2.18	1.85	0.6081	0.4856
0.2927	1239	2.27	0.40	1.65	2.12	0.6342	0.4834
0.4536	1209	2.76	0.58	1.24	3.14	0.6898	0.4724
0.4964	1202	2.80	0.66	0.96	2.64	0.7032	0.4704
0.5000	1201	2.84	0.66	0.38	2.57	0.7059	0.4732
0.5654	1193	2.67	0.58	0.48	2.51	0.7208	0.4664
0.6447	1181	2.64	0.67	2.07	2.47	0.7441	0.4621
0.7785	1168	1.93	0.43	2.18	1.79	0.7709	0.4401
Temp. 308.15							
0.0870	1248	0.98	0.24	2.22	0.91	0.6292	0.5227
0.0956	1245	1.12	0.32	2.28	1.06	0.6347	0.5221
0.3489	1192	2.56	0.58	1.53	2.43	0.7341	0.5045
0.4724	1171	2.83	0.68	0.94	2.67	0.7748	0.4971
0.7489	1136	2.27	0.70	-0.53	2.16	0.8454	0.4790
0.9500	1124	0.49	0.09	-2.56	0.47	0.8740	0.4671
0.9900	1122	0.07	-0.09	-3.09	0.06	0.8773	0.4653
CHCl <sub>2</sub> ·CHCl <sub>2</sub> + Acetone Temp. 298.15							
0.0604	1154	0.77	-2.67	-2.52	1.78	0.7140	0.5516
0.0713	1152	0.93	-3.04	-2.65	2.09	0.7184	0.5493
0.2374	1137	2.03	-8.29	-4.40	4.95	0.7583	0.5143
0.4599	1133	2.15	-11.63	-2.72	5.76	0.7869	0.4818
0.4964	1135	1.95	-11.93	-2.28	5.54	0.7874	0.4773
0.6507	1138	1.56	-11.13	-1.04	4.67	0.7974	0.4617
0.9267	1146	0.66	-3.34	-1.71	1.54	0.8101	0.4442
Temp. 308.15							
0.0595	1109	0.99	-2.40	-6.04	2.00	0.8094	0.5853
0.1965	1098	1.99	-7.12	-4.37	4.55	0.8412	0.5600
0.2857	1093	2.45	-9.19	-3.59	4.57	0.8589	0.5372
0.4883	1099	1.93	-12.26	-2.21	4.98	0.8739	0.5069

(Continued)

Table 1. (Continued)

$x_1$	$U_{\text{expt}}$ $\text{ms}^{-1}$	$(\Delta U/U)\%$ (Nomoto)	$(\Delta U/U)\%$ (Van Dael)	$(\Delta U/U)\%$ (FLT)	$(\Delta U/U)\%$ (CFT)	$L_f/\text{\AA}$ Ultra- sonic	$L_f/\text{\AA}$ Thermo- dynamic
0.4972	1100	1.84	-12.36	-1.93	5.36	0.8687	0.5053
0.6003	1104	1.50	-12.31	-1.14	4.79	0.8720	0.4924
0.7001	1106	1.33	-10.82	-0.38	4.17	0.8782	0.4819
0.7712	1109	1.06	-9.26	-0.00	3.44	0.8799	0.4755
CHCl <sub>2</sub> ·CHCl <sub>2</sub> + Cyclohexane							
Temp. 298.15							
0.0537	1238	0.85	-0.24	-0.79	0.83	0.6243	0.5624
0.3000	1181	0.49	-0.60	-2.09	3.53	0.7328	0.5395
0.4164	1162	4.12	-0.52	-2.90	4.21	0.7703	0.5257
0.5000	1154	4.11	-0.61	-1.07	4.64	0.7840	0.5035
0.6904	1150	2.89	-1.05	-0.88	3.02	0.8009	0.4903
0.8832	1152	1.10	-0.88	-3.00	1.15	0.8033	0.4567
0.7139	1152	0.83	-0.61	-3.79	0.87	0.8042	0.4561
Temp. 308.15							
0.2161	1154	3.10	-0.35	-1.70	3.12	0.7973	0.5786
0.4035	1125	4.20	-0.45	-2.61	4.27	0.8564	0.5561
0.4706	1111	4.22	-0.54	-2.90	4.31	0.8697	0.5472
0.7244	1108	3.29	-0.45	-2.92	3.39	0.8980	0.5704
0.8680	1113	1.76	-0.45	-3.22	1.81	0.8930	0.4875
0.9000	1115	1.33	-0.45	-3.55	1.37	0.8902	0.4822

\*  $x_1$  refers to the mole fraction of first components.

velocity have been taken from literature (Nath and Tripathi 1989). The results of the present evaluation using various equations for sound velocity show that the agreement in all the cases is quite satisfactory. CFT, however, has the limitation that sound velocity  $U$  should be less than  $U_\infty$  (i.e.  $1600 \text{ mS}^{-1}$ ). It fails completely when the velocity of sound exceeds  $1600 \text{ mS}^{-1}$ . A perusal of table 1 shows values of  $L_f$  evaluated by ultrasonic method are greater than those obtained by thermodynamic method. The accuracy in the values of  $L_f$  depends upon accurate calculation of molar volume ( $V_0$ ) at zero temperature. The thermodynamic method involves the ratio  $T/T_c$  and gives direct value of  $V_0$  while on the other hand ultrasonic method involves the ratio of sound velocity to an empirical value of  $1600 \text{ mS}^{-1}$ . The thermodynamic method therefore gives comparatively more accurate values of  $V_0$ ,  $V_a$  and  $L_f$  provided  $T$  is not very close to  $T_c$ .

Table 1 indicates that percentage deviation  $(\Delta U/U)\%$  obtained by Nomoto's relation is positive for all the five systems studied. The limitation of this method is that it assumes no volume change on mixing and thus no account has been taken for interaction between the components of the liquid mixture. The ideal mixing relation of Van Dael has also some limitations. During its formulation it has been assumed that the ratio of specific heats of the components is equal to ratio of specific heats of ideal mixing (i.e.  $\gamma_1 = \gamma_2 = \gamma_{im}$ ) and also  $V_1 = V_2$ . Van Dael ideal mixing relation, however, gives the minimum deviation in all the systems except in CHCl<sub>2</sub>CHCl<sub>2</sub> + acetone where it gives maximum deviation up to  $-12.36\%$ . This may be due to strong specific interaction in this system. The CFT gives positive deviations in all systems

and Van Dael relation gives negative deviation except for the system  $\text{CHCl}_2\text{CHCl}_2 + p$ -xylene. By using FLT for evaluation of sound velocity, negative deviations are obtained in the systems  $\text{CHCl}_2\text{CHCl}_2 + \text{benzene}$ ,  $+ \text{acetone} + \text{cyclohexane}$  at both the temperatures. The negative deviations obtained by ideal mixing relation for the systems  $\text{CHCl}_2\text{CHCl}_2$  with benzene, toluene and acetone indicate existence of specific interaction leading to the formation of molecular complexes between the two components of the various systems in the liquid state. The highly negative deviation for  $\text{CHCl}_2\text{CHCl}_2 + \text{acetone}$  indicates the formation of strong complex between  $\text{CHCl}_2\cdot\text{CHCl}_2$  and acetone.

Table 1 indicates that the values of  $L_f$  obtained by thermodynamic method for the binary mixtures of 1,1,2,2-tetrachloroethane with aromatics follow the sequence

benzene > toluene >  $p$ -xylene.

This increase in  $L_f$  with an increased number of  $-\text{CH}_3$  group attached to the benzene ring is due to the increasing strength of interaction.

The various types of forces which are operating between molecules of different systems are dispersion forces and charge transfer, hydrogen bonding, dipole-dipole and dipole-induced dipole interaction. Dispersion forces are invariably present in all the systems and for a system in which more than one type of interactions are present between the components, the deviation of sound velocity would be net result of contributions from all types of interactions. The highly negative values of deviation of sound velocity for  $\text{CHCl}_2\cdot\text{CHCl}_2 + \text{acetone}$  gives evidence for the formation of strong molecular complexes between  $\text{CHCl}_2\cdot\text{CHCl}_2 +$  and acetone in the liquid state.

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