Excess Intermolecular Free Length and Molecular Interaction for Some Binary Liquid Mixtures

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The concept of intermolecular free length has been applied to some binary liquid mixtures namely 1-chloro naphthalene + decane, 1-chloro naphthalene + dodecane, benzene + p-xylene and benzene + p-dioxane. The intermolecular interaction study was made through the excess free length for the systems under investigation. The free length (L_f) values obtained by the two methods have been compared. The results are consistent with the theories.

Key Words: Excess, Intermolecular, Free length, Molecular interaction, Binary liquid mixtures.

INTRODUCTION

Jacobson[1,2] suggested the following relation for the intermolecular free length (L_f):

$$L_f = \frac{K}{U\sqrt{\rho}} \qquad (1)$$

where K is a constant which is temperature dependent but independent of the nature of the liquid. Jacobson tabulated the value of K empirically between 0 to 50°C. The intermolecular free length in liquid is defined as

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

where V_a is the available volume per mol and Y is the total surface area of the molecule in one mole of the liquid. Eqn. (2) has been used by a number of workers[1-5] to determine the intermolecular free length. The free length theory has also been advanced[6,7] and compared with the collision factor theory of Schaafs[8,9]. Recently Pandey *et al.*[10] determined the available volume of a few liquids and binary mixtures by computing some of the thermo-acoustical parameters. In the present paper the concept of intermolecular free length has been applied to some of the binary liquid mixtures and the interaction studied in the mixtures has been made through excess intermolecular free length (L_f^E) using ultrasonic and thermodynamic approaches.

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Theoretical: The available volume V_a in eqn. (2) is given by

$$V_a = V_T - V_0 \tag{3}$$

where V_T and V_0 are molar volume at T K and 0 K respectively. It was shown by Schaafs that

$$V_0 = SB$$

where S and B are the collision factor and geometrical volume respectively. Thus

$$V_a = V_T - SB \tag{4}$$

and the sound velocity can be represented as

$$U = U_\infty \frac{SB}{V} \tag{5}$$

where U is the sound velocity and U_∞ was taken as equal to 1600 m/s by Schaafs. Using eqns. (4) and (5), one gets

$$V_a = V_T \left(1 - \frac{U}{U_\infty} \right) \tag{6}$$

Thermodynamically, V_a can be calculated from the following equation:

$$V_a = V \left(1 - \left\{ \frac{T}{T_c} \right\}^{0.3} \right) \tag{7}$$

The surface area per mol, Y, is given by

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

In the present study, T_c the critical temperature for mixtures has been assumed to be additive[11] and is calculated as

$$T_{c_{mix}} = X_1 T_{c_1} + X_2 T_{c_2} \tag{9}$$

The excess free length (L_f^E) is given by the relation

$$L_f^E = (L_f)_{mix} - (L_f)_{idl} \tag{10}$$

where $(L_f)_{idl} = X_1 L_{f_1} + X_2 L_{f_2}$.

RESULTS AND DISCUSSION

The intermolecular free length for binary mixtures namely 1-chloro naphthalene + decane, 1-chloro naphthalene + dodecane, benzene + *p*-xylene and benzene + *p*-dioxane and their pure components has been evaluated using ultrasonic and thermodynamic approach.

The computed value of L_f for the system by ultrasonic method (using eqns. 2, 6 and 8) are presented in column 4 of Table-2 while column 5 of Table-2 shows the value of L_f by thermodynamic method (using eqns. 2, 7, 8 and 9). Columns 6 and 7 of the table show the values of the excess intermolecular free length by two methods respectively. The necessary data required for the calculation have been taken from literature[12, 13]. The calculated values of free length from two methods for pure liquids are reported in Table-1 and the value for binary system are reported in Table-2. The excess free length (L_f^E) has been evaluated using eqn. (10) and the values of (L_f^E) are also recorded in Table-2.

In the calculation of free length from thermodynamic method a different approach has been used. Here we have first calculated $T_{c_{mix}}$ from eqn. (9) and then used $T_{c_{mix}}$ values in the calculation of V_a *vide* eqn. (7) which directly leads the V_0 values for the mixture. We have compared our values with those of ultrasonic method in Table-2.

A perusal of Tables 1 and 2 as well as the graphs shows that the values of free length increases with temperature. Table-2 shows that the values of free length due to both the methods in the case of all binary mixtures decreases with the increase in mole fraction of the first named component, except in case of benzene + p-xylene, where the free length value by ultrasonic method increases with the decrease in mole fraction of first named component. Probably it will be due to the empirical value of U_∞. The excess free length (L_f^E) for the system benzene + p-xylene is found to be positive from both methods at both the temperatures. For the system benzene + p-dioxane the L_f^E values are negative for both the systems.

The L_f^E values for the system 1-chloro naphthalene + decane and 1-chloro naphthalene + dodecane are found to be negative for both the systems.

The ultrasonic method however has the limitation that the sound velocity U should be less than U_∞ because in case when $U \geq U_\infty$, the ratio U/U_∞ will be either greater than one or zero and in either case, it will give negative values. Therefore the ultrasonic method fails when the value of sound velocity is more than 1600 m s^{-1}. It is to be noted that the value of L_f obtained by the ultrasonic method is greater than those obtained by thermodynamic method. The thermodynamic method involves the ratio T/T_c, then gives direct values of V_a while the ultrasonic method involves the ratio of sound velocity to an empirical value of 1600 m s^{-1}.

The sign excess free length clearly indicates the presence of intermolecular interaction in the systems.

TABLE-1

PARAMETERS OF PURE COMPONENTS

Components	T (K)	T_c (K)	ρ (g cm^{-3})	U (m s^{-1})	L_f (Å)	
					Ultrasonic	Thermodynamic
1-Chloronaphthalene	298.15	785.0	1.1882	1480.0	0.2114	0.3763
Decane	298.15	617.9	0.7267	1224.0	0.7637	0.5823
Dodecane	298.15	658.9	0.7466	1284.0	0.6565	0.5503
Benzene	298.00	562.0	0.8722	1297.8	0.4812	0.5167
	313.00	562.0	0.8564	1229.3	0.6008	0.5619
p-Xylene	298.00	618.0	0.8552	1309.4	0.5052	0.4991
	313.00	618.0	0.8422	1248.2	0.6216	0.5397
p-Dioxane	298.00	585.0	1.0266	1344.4	0.3978	0.4790
	313.00	585.0	1.0091	1297.9	0.5064	0.5196

TABLE-2

INTERMOLECULAR FREE LENGTH OF BINARY LIQUID MIXTURES

| X_1	ρ (g cm^{-3})	U (m s^{-1})	L_f (Å)		L_f^E (Å)	
			Ultrasonic	Thermo-dynamic	Ultrasonic	Thermo-dynamic
1-Chloro naphthalene (1) + decane (2) at 298.15 K						
0.0960	0.7593	1232.0	0.3683	0.5559	−0.3423	−0.007
0.1972	0.7962	1248.0	0.3461	0.5282	−0.3086	−0.013
0.2962	0.8343	1262.0	0.3272	0.5041	−0.2729	−0.017
0.3923	0.8737	1280.0	0.3053	0.4824	−0.2417	−0.019
0.4594	0.9027	1299.0	0.2843	0.4679	−0.2256	−0.020
0.5960	0.9650	1323.0	0.2561	0.4402	−0.1789	−0.019
0.6943	1.0142	1360.0	0.2185	0.4219	−0.1617	−0.017
0.7960	1.0680	1384.0	0.1936	0.4039	−0.1304	−0.014
0.8982	1.1263	1424.0	0.1555	0.3877	−0.1121	−0.009
1-Chloro naphthalene (1) + dodecane (2) at 298.15K						
0.1953	0.8037	1296.0	0.3100	0.5160	−0.3733	−0.0003
0.2927	0.8361	1304.0	0.2967	0.4960	−0.4001	−0.0033
0.3910	0.8722	1312.0	0.2834	0.4766	−0.4269	−0.0056
0.4954	0.9132	1322.0	0.2683	0.4574	−0.4564	−0.0067
0.5954	0.9560	1363.0	0.2244	0.4388	−0.5140	−0.0079
0.6916	1.0036	1377.0	0.2178	0.4217	−0.5339	−0.0082
0.8196	1.0723	1400.0	0.1807	0.4000	−0.5886	−0.0076
0.8922	1.1206	1440.0	0.1402	0.3868	−0.6383	−0.0070
Benzene (1) + p-Xylene (2) At 298K						
0.7501	0.8653	1296.9	0.4952	0.5132	0.0008	0.0004
0.5015	0.8607	1298.8	0.5036	0.5090	0.0105	0.0011
0.2617	0.8575	1302.8	0.5071	0.5045	0.0082	0.0008
Benzene (1) + p-Xylene (2) At 313K						
0.7501	0.8505	1230.6	0.6149	0.5582	0.0090	0.0019
0.5015	0.8467	1234.0	0.6218	0.5518	0.0107	−0.0418
0.2617	0.8441	1239.4	0.6248	0.5462	0.0087	−0.1299
Benzene (1) + Dioxane (2) At 298K						
0.7503	0.9103	1310.0	0.4590	0.5067	−0.0013	−0.0005
0.5005	0.9484	1321.0	0.4391	0.4972	−0.0004	−0.0006
0.2497	0.9872	1332.5	0.4186	0.4879	−0.0002	−0.0005
Benzene (1) + Dioxane (2) At 313K						
0.7503	0.8940	1242.2	0.5763	0.5507	−0.0009	−0.0006
0.5005	0.9319	1254.2	0.5532	0.5399	−0.0004	−0.0008
0.2497	0.9703	1266.8	0.5302	0.5296	−0.0003	−0.0005
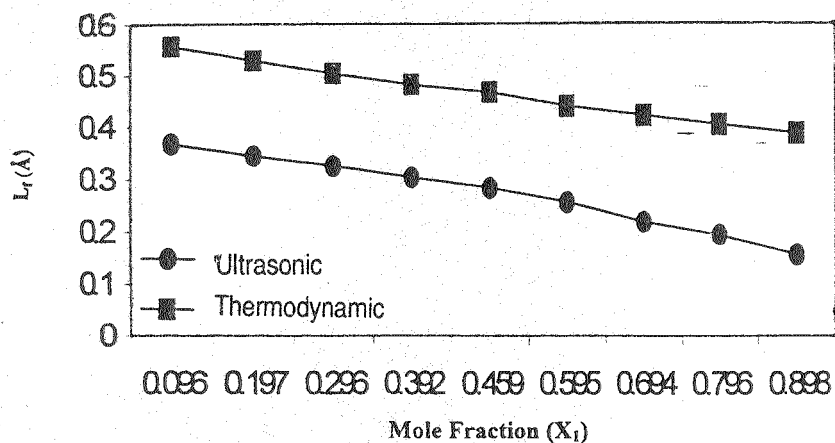
Fig. 1. Intermolecular free length *vs.* mole fraction of first component for 1-chloro naphthalene + decane
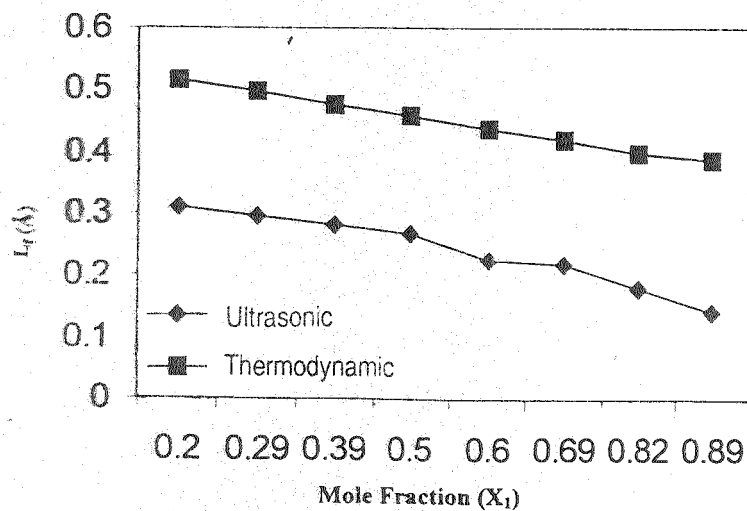

Fig. 2. Intermolecular free length *vs.* mole fraction of first component for 1-chloro naphthalene + dodecane

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