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Evaluation of Intermolecular Free Length in Binary Liquid Mixtures

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Intermolecular free length has been evaluated in the binary mixture of cyclohexane-benzene, cyclohexane-toluene and cyclohexane-*p*-xylene at 30°C using three different approaches. Relative merits of every approach have been accessed. Furthermore, the study has been extended to obtain excess free length and to discuss intermolecular interaction within the components of the mixture.

Key Words: Evaluation, Intermolecular, Binary liquid mixtures

INTRODUCTION

Determination of intermolecular free length in liquids and liquid mixtures has been a subject of considerable interest in the recent past[1–14]. Recently Pandey *et al.*[15, 16] computed the temperature and pressure dependence of intermolecular free length in different liquids. Intermolecular free length has also been utilized to study the intermolecular interaction in binary[2, 16, 17] and ternary[10, 18, 19] liquid mixtures.

In the present paper an attempt has been made to compute intermolecular free length in the binary mixture of cyclohexane-benzene, cyclohexane-toluene and cyclohexane *p*-xylene using Jacobson's method, ultrasonic method and thermodynamic method.

Furthermore, the study has also been extended to study the intermolecular interaction in the aforesaid mixtures in terms of excess intermolecular free length along with a comparison of the methods giving better results.

Theoretical: A semi-empirical relation has been developed by Jacobson in between the ultrasonic velocity (u), density (ρ) and intermolecular free length (L_1) as follows:

$$uL_1\rho^{1/2} = K \qquad (1)$$

where K is a temperature dependent constant. In the above cases at 30°C the value of K = 631.

The intermolecular free length L_f in liquid may also be defind as

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$$L_f = \frac{2V_a}{Y} \tag{2}$$

where V_a is available volume, which is related with molar volume at absolute temperature (V_T) and molar volume at 0 K (V_0) by the equation

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

In equation (2), Y stands for the total surface area per mole and equals to $(36\pi NV_0^2)^{1/3}$, N being Avogadro's number.

Thermodynamically, the value of V_0 can be obtained from the following equation[4]:

$$V_0 = V_T\left(1 - \frac{T}{T_C}\right)^3 \tag{4}$$

Here, T_C is the critical temperature.

Recalling definitions, equation (2), L_1 may be expressed as

$$L_f = \frac{2(V_T - V_{0)}}{(36\pi NV_0^2)^{1/3}} \tag{5}$$

It has been shown by Schaffs[20] that

$$V_0 = SB \tag{6}$$

where S and B are collision factor and geometrical volume respectively. Thus from equations (3) and (6) one obtains

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

whereas the sound velocity u can be expressed as[20]

$$u = u_\alpha\left(\frac{SB}{V}\right) \tag{8}$$

Here u_α equal to 1600 m s^{-1}. From equations (7) and (8) one gets

$$V_a = V_T\left(1 - \frac{u}{u_\alpha}\right) \tag{9}$$

The free length of the mixtures has been calculated from the expression

$$L_{f\,(mix)} = \frac{2V_m - [x_1V_{01} - x_2V_{02}]}{x_1y_1 + x_2y_2} \tag{10}$$

Here V_m is the molar volume of the mixture.

The excess free length L_fE of the mixtures can be obtained by the relation

$$L_fE = L_{f\,(mix)} - \sum_{i=1}^{2} x_iI_{fi} \tag{11}$$

RESULTS AND DISCUSSION

The results of calculation of the intermolecular free length (from all the three methods) and the excess free length obtained have been shown in Table-1 .

TABLE-1
INTERMOLECULAR FREE LENGTH (L_f) AND EXCESS FREE LENGTH (L_fE) OBTAINED FROM JACOBSON'S RELATION, ULTRASONIC RELATION AND THERMODYNAMIC RELATION

x_1	ρ_{mix} (g mL^{-1})	u_{mix} (m s^{-1})	L_fE (Å) (eq 1)	L_f (Å) (eq 2, 9)	L_f (Å) (eq 2, 10)	L_fE (Å) (eq 11)	L_fE (Å) (eq 11)	L_fE (Å) (eq 11)
				Cyclohexane-Benzene (30°C)				
0.0000	0.8679	1277	0.5304	0.5149	0.5316	0.0000	0.0000	0.0000
0.1009	0.8544	1262	0.5409	0.5473	0.5392	0.0051	0.0128	0.0033
0.2002	0.8410	1250	0.5504	0.5748	0.5548	0.0091	0.0192	0.0133
0.3008	0.8294	1242	0.5578	0.5947	0.5627	0.0110	0.0226	0.0162
0.3991	0.8185	1235	0.5647	0.6128	0.5704	0.0125	0.0248	0.0189
0.5014	0.8480	1230	0.5705	0.6309	0.5756	0.1270	0.0292	0.0238
0.6009	0.7992	1226	0.5757	0.6392	0.5797	0.1240	0.0254	0.0181
0.7007	0.7908	1224	0.5797	0.6472	0.5821	0.0109	0.0231	0.0155
0.8007	0.7829	1225	0.5821	0.6489	0.5836	0.0078	0.0156	0.0120
0.9005	0.7765	1227	0.5835	0.6480	0.5808	0.0009	0.0100	0.0042
1.0000	0.7693	1229	0.5853	0.6476	0.5817	0.0000	0.0000	0.0000
				Cyclohexane-Toluene (30°C)*				
0.0000	0.8574	1284	0.5307	0.5325	0.5209	0.0000	0.0000	0.0000
0.1017	0.8471	1272	0.5389	0.5568	0.5308	0.0027	0.0090	0.0038
0.2004	0.8377	1263	0.5458	0.5755	0.5388	0.0043	0.0145	0.0058
0.2995	0.8284	1254	0.5528	0.5940	0.5465	0.0059	0.0200	0.0075
0.3989	0.8192	1246	0.5595	0.6108	0.5540	0.0071	0.0239	0.0089
0.4988	0.8101	1239	0.5558	0.6258	0.5611	0.0080	0.0264	0.0100
0.5989	0.8011	1234	0.5713	0.6365	0.5680	0.0080	0.0247	0.0108
0.6995	0.7925	1230	0.5762	0.6452	0.5735	0.0074	0.0224	0.0102
0.8004	0.7843	1226	0.5811	0.6538	0.5776	0.0068	0.0213	0.0082
0.8983	0.7766	1226	0.5840	0.6540	0.5808	0.0044	0.0129	0.0054
1.0000	0.7693	1229	0.5853	0.6476	0.5817	0.0000	0.0000	0.0000
				Cyclohexane-*p*-Xylene (30°C)*				
0.0000	0.8530	1289	0.5300	0.5490	0.5147	0.0000	0.0000	0.0000
0.1012	0.8442	1279	0.5369	0.5677	0.5250	0.0014	0.0055	0.0036
0.2000	0.8359	1270	0.5434	0.6690	0.5337	0.0024	0.0954	0.0057
0.2999	0.8269	1262	0.5498	0.5985	0.5441	0.0033	0.0140	0.0094
0.4007	0.8183	1253	0.5567	0.6149	0.5524	0.0046	0.0164	0.0110
0.5024	0.8096	1246	0.5628	0.6271	0.5604	0.0051	0.0145	0.0121
0.6015	0.8012	1240	0.5685	0.6369	0.5673	0.0035	0.0172	0.0124
0.7012	0.7927	1235	0.5738	0.6448	0.5738	0.0053	0.0153	0.0123
0.8015	0.7842	1231	0.5788	0.6503	0.5792	0.0051	0.0118	0.0109
0.8991	0.7763	1233	0.5822	0.6492	0.5830	0.0045	0.0038	0.0081
1.0000	0.7693	1229	0.5853	0.6476	0.5817	0.0026	0.0000	0.0000

*In case of toluene and *p*-xylene, the values of L_f (Å) have been calculated using eqn. (3).

The free length obtained from Jacobson's method, ultrasonic method and thermodyanmic method for the above system have been shown in columns 4, 5 and 6 respectively of the table. The excess free lengths obtained form the three methods have been shown in columns 7, 8 and 9 respectively. The essential data required from the calculation have been taken from literature[22, 23].

In the Jacobson method the free lengths for the mixture have been calculated from eqn. (1). In the ultrasonic method V_a is directly obtained by using eqn. (9).

The value of V_a so obtained from eqn. (9) in turn have been used to obtain the value of L_f of pure liquids from eqn. (2). Thermodynamically the values of L_f of mixtures have been calculated from eqn. (10) using the value of V_0 of pure liquids as obtained from eqn. (4). Ultrasonically the values of pure liquids have been calculated from eqn. (3) using the value of V_a as obtained from eqn. (9) and these values of V_0 of pure liquids so obtained in turn have been employed to compute the values of L_f of mixtures ultrasonically with eqn. (10). The values of excess free length of the mixtures have been calculated from eqn. (11) .

A perusal of Table-1 reveals that the L_f values as obtained from the above three methods are very close to each other which verify the validity of the equations and the assumptions on which their derivation is based. In the same way all the values of L_fE of mixtures are also in good agreement in sign and magnitude with each other. A thorough examination of Table-1 also reveals that the excess free length values for all the systems are positive under the present investigation. Their magnitude is also low. A positive excess function is an indication of weak interaction, which is also obvious from the physical nature of the liquids taken under investigation.

The excess free length values which are positive in all the systems further show a similar behaviour of molecular interaction in the system.

A very interesting thing in all the above investigation has been observed which is the increasing trend of free length values with the increase of mole fraction of cyclohexane in every system. This may be explained on the basis that cyclohexane has no planar structure but exists in 'chair' and 'boat' form. Contrary to this, benzene has a planar structure. When the concentration of cyclohexane is increased in benzene, the tilted ends of the molecules of the former keep the molecules of the latter farther. Due to this more space is created as evidence from excess values of intermolecualr free length values. This has also been confirmed by other workers[21], on the basis of molar volume (V), available volume (V_a) and free volume(V_f) and adiabatic compressibility (β_s).

In case of cyclohexane-toluene and cyclohexane-*p*-xylene, all the positive values may be explained on the same line as in the case of cyclohexane-benzene. The positive values of free length are minimum in the system cyclohexane-*p*-xylene and maximum in cyclohexane benzene.

The lower excess free length in the latter two systems may be explained as due to adjustment of tilted ends of cyclohexane molecules, in the space created due to hindrance caused by methyl group of toluene and xylene molecules.

According to Fort and Moore[21] the positive values occur mainly due to dispersion forces and as the positive value tends towards negative, the strength of interaction increases. In all the systems reported here the excess values are

positive. It is obvious that there is weak interaction between the unlike molecules. However, strength of interaction in the system cyclohexane-toluene is greater than in cyclohexane-benzene but less than in cyclohexane-*p*-xylene.

Thus we can conclude that the method given by Jacobson, the ultrasonic method and the thermodynamic method hold good in the evaluation of the values of free length of the liquid mixtures.

The ultrasonic method and the thermodynamic method have their limitations. The ultrasonic method will completely fail when the ultrasonic velocity in pure liquid exceeds 1600 ms^{-1}. The thermodynamic method is not good when $T_C \ll T$ since at this time a very low value of L_f will be obtained. Since the T_C of pure liquids under the present investigation is close to T, the values of L_f obtained from the thermodynamic relation is lower than the ultrasonic method.

It is also concluded that the extent and magnitude of interaction between the components of the mixture can be studied on the basis of free length and excess free length values when the property of the liquid other than density, sound velocity and critical temperature (T_C) is not known.

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