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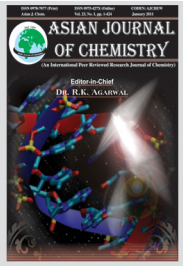

Extension and Comparision of Free Length Theory and Collision Factor Theory in the Binary Liquid Mixture

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In the present investigation, a comparison between the various theories of intermolecular free length, with their merits and demerits have been studied. Jacobson theory (FLT) and collision factor theory (CFT) have been extended to six binary liquid mixture of hexane-benzene, hexane-toluene, hexane-ethyl benzene, heptane-benzene, heptane-toluene, heptane-ethyl benzene at 313.15 K. The interaction between the components of binary mixture have also been studied on the basis of excess free length.

Key Words: Jacobson, Free-length, Shaffs, Excess function, Binary liquid.

INTRODUCTION

Intermolecular free length Lf, in pure liquids and their liquid mixtures are related to their sound velocity (U) and their density by the following equation[1]:

$$Lf = \frac{K}{U_{exp} \times \rho_{exp}^{1/2}} \quad (1)$$

where K is temperature dependent constant.

In pure liquids the intermolecular free length is given by the relation[2]:

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

In eqn. 2, $V_a = (V_T - V_o)$ is the available volume per mole and Y is the total surface area of the molecule present in one mole of liquid. The value of total surface area is given by the equation:

$$Y = (36\pi N V_o^2)^{1/3} \quad (3)$$

where N is the Avogadro's number. V_o is the molar volume at 0 K. The available volume V_a is given by the relation:

$$V_a = V_T - V_o \quad (4)$$

where V_T is the molar volume at Temp. K. Schaaffs[3,4] has shown that V_o = SB where S and B are the collision factor and geometerical volume respectively. Using this value of V_o, available volume is given by the relation:

$$V_a = V_T - V_B \quad (5)$$

Schaaffs[3,4] obtained the following equation for the available volume using ultrasonic method:

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

where U is the sound velocity and U_α is taken as equal to 1600 ms^{-1}.

Using the value of critical temperature T_c, the value of V_o evaluated thermodynamically

$$V_o = V_T\left(1 - \frac{T}{T_c}\right)^{0.3} \quad (7)$$

Thus, using eqn. 2 the value of the free length can be obtained from the following equation:

$$Lf = \frac{2(V_T - V_o)}{(36\pi N V_o^2)^{1/3}} \quad (8)$$

Thus, eqns. 2, 6 amd 8 give the value of the free length ultrasonically, whereas eqns. 2, 7 and 8 the value of free length can be obtained thermodynamically.

The excess free length Lf^E may be evaluated using the following relation:

$$Lf^E = Lf_{mix} - (X_1 Lf_1 + X_2 Lf_2) \quad (9)$$

where X_1 and X_2 are the mole fractions of the first and second component of the binary liquid mixture and Lf_1 and Lf_2 are the free length of the first and second component of the binary system obtained from Jacobsons, ultrasonic and thermodynamic relation.

RESULTS AND DISCUSSION

The interamolecular free length obtained from Jacobson relation (eqn. 1), thermodynamic methods (eqn. 7) and ultrasonic method (eqn. 6) for the six binary mixture hexane-benzene, hexane-toluene, hexane-ethyl benzene, heptane-benzene, heptane + toluene, heptane + ethyl benzene at 313.15 K, which has been tabulated in the column 4, 5 amd 6, respectively of the Table-1. The excess free length has also been obtained from these relation using (eqn. 9) which has been shown in the column 7, 8, 9 of the Table-1. The various parameter requires for the evaluation of free length were collected from the various sources[5,6].

Perusal of Table-1 reveals that the inter molecular free length of six binary system hexane-benzene, hexane + toluene, hexane + ethyl benzene, heptane + benzene, heptane-toluene, heptane + ethyl benzene at 313.15 K obtained, follow the same trend *i.e.* increases regularly with the increases of the first component, which are hexane and heptane. This shows that every method applied are giving good results, within the limits of experimental error.

These methods are subjected to some limitations. In Jacobson relation availability of K is a must and it does not work below 0 ºC. The method is no doubt, very convenient, when density and sound velocity data are available along with value of Jacobson constant K.

The thermodynamic method seems not very reliable near to the critical temperature and accuracy increases as the difference between T_c and T becomes larger, as also noted by some other worker[7-9].

TABLE-1
ULTRASONIC VELOCITY (u), DENSITY (ρ), INTERMOLECULAR FREE LENGTH (Lf) AND EXCESS FREE LENGTH (Lf^E) Of BINARY LIQUID MIXTURES FROM VARIOUS RELATION AT 313.15 K

X_1 (Ref 10)	U (ms^{-1}) (Ref 10)	P (g/cc) (Ref 10)	Lf (Å) (eqn. 1)	Lf (Å) (eqn. 7)	Lf (Å) (eqn. 6)	Lf^E (Å) (eqn. 9)	Lf^E (Å) (eqn. 9)	Lf^E (Å) (eqn. 9)
Hexane (1) + Benzene (2)								
0.0000	1230.0	0.8574	0.5636	0.5621	0.6072	0.0000	0.0000	0.0000
0.0378	1214.8	0.8453	0.5748	0.5723	0.6357	0.0024	0.0027	0.0040
0.1009	1191.1	0.8258	0.5931	0.5896	0.6836	0.0062	0.0075	0.0109
0.1986	1158.5	0.7979	0.6203	0.6150	0.7556	0.0110	0.0135	0.0196
0.2979	1129.8	0.7722	0.6466	0.6385	0.8259	0.0145	0.0173	0.0254
0.4020	1104.3	0.7477	0.6723	0.6612	0.8967	0.0162	0.0193	0.0287
0.6024	1063.9	0.7063	0.7180	0.7000	1.0259	0.0159	0.0183	0.0279
0.7014	1047.7	0.6882	0.7386	0.7171	1.0865	0.0138	0.0158	0.0242
0.8010	1033.2	0.6714	0.7583	0.7329	1.1451	0.0106	0.0118	0.0182
0.9083	1020.2	0.6549	0.7776	0.7474	1.2047	0.0052	0.0050	0.0083
0.9464	1015.9	0.6492	0.7843	0.7529	1.2261	0.0031	0.0030	0.0049
1.0000	1010.3	0.6414	0.7934	0.7606	1.2559	0.0000	0.0088	0.0000
Hexane (1) + Toluene (2)								
0.0000	1240.7	0.8480	0.5619	0.5497	0.6217	0.0000	0.0002	0.0000
0.1032	1208.5	0.8229	0.5856	0.5714	0.6852	-0.0001	0.00008	-0.0019
0.1980	1180.8	0.8005	0.6076	0.5921	0.7447	-0.00004	0.0007	-0.0025
0.2997	1153.5	0.7775	0.6312	0.6138	0.8086	-0.0001	0.0010	-0.0032
0.4027	1127.5	0.7551	0.6552	0.6359	0.8736	0.0001	0.0013	-0.0034
0.5005	1104.6	0.7346	0.6781	0.6569	0.9359	0.0003	0..0017	-0.0032
0.5998	1083.1	0.7147	0.7011	0.6776	0.9988	0.0003	0.0014	-0.0032
0.6987	1063.3	0.6955	0.7239	0.6985	1.0623	0.0003	0.0015	-0.0025
0.7984	1044.5	0.6770	0.7470	0.7189	1.1258	0.0002	0.0008	-0.0023
0.9042	1026.3	0.6581	0.7711	0.7403	1.1934	-0.0001	0.0000	-0.0017
1.0000	1010.3	0.6414	0.7934	0.7606	1.2559	0.0000	0.0000	0.0000
Hexane (1) + Ethyl benzene (2)								
0.0000	1256.9	0.8492	0.5542	0.5400	0.6167	0.0000	0.0000	0.0000
0.0465	1243.8	0.8394	0.5633	0.5484	0.6419	-0.0020	-0.0018	-0.0045
0.0771	1235.0	0.8328	0.5696	0.5545	0.6592	-0.0030	-0.0024	-0.0067
0.2010	1200.8	0.8065	0.5953	0.5788	0.7298	-0.0070	-0.0054	-0.0153
0.3015	1173.9	0.7852	0.6171	0.5996	0.7894	-0.0092	-0.0068	-0.0199
0.3990	1148.5	0.7647	0.6392	0.6202	0.8488	-0.0104	-0.0077	-0.0229
0.5092	1121.1	0.7417	0.6649	0.6441	0.9179	-0.0111	-0.0081	-0.0242
0.6010	1098.9	0.7226	0.6872	0.6649	0.9776	-0.0107	-0.0076	-0.0232
0.7012	1075.7	0.7020	0.7123	0.6878	1.0442	-0.0096	-0.0068	-0.0206
0.7999	1054.1	0.6819	0.7375	0.7108	1.1116	-0.0080	-0.0055	-0.0163
0.8993	1031.8	0.6617	0.7649	0.7352	1.1822	-0.0044	-0.0031	-0.0093
0.9534	1020.3	0.6508	0.7799	0.7486	1.2213	-0.0023	-0.0016	-0.0047
1.0000	1010.3	0.6414	0.7934	0.7606	1.2559	0.0000	0.0000	0.0000

Heptane (1) + Benzene (2)								
0.0000	1230.0	0.8574	0.5636	0.5621	0.6072	0.0000	0.0000	0.0000
0.0511	1210.9	0.8408	0.5782	0.5755	0.6444	0.0101	0.0059	0.0101
0.1025	1193.3	0.8252	0.5922	0.5884	0.6808	0.0197	0.0112	0.0192
0.1998	1165.5	0.7986	0.6163	0.6105	0.7469	0.0354	0.0190	0.0327
0.2987	1142.8	0.7750	0.6381	0.6296	0.8071	0.0486	0.0236	0.0414
0.3972	1124.4	0.7543	0.6574	0.6461	0.8635	0.0594	0.0256	0.0456
0.5013	1108.9	0.7349	0.6753	0.6611	0.9191	0.0683	0.0254	0.0460
0.5998	1096.8	0.7184	0.6905	0.6740	0.9687	0.0750	0.0237	0.0433
0.6980	1086.4	0.7037	0.7044	0.6847	1.0145	0.0804	0.0200	0.0369
0.8043	1077.8	0.6894	0.7173	0.6945	1.0606	0.0842	0.0143	0.0267
0.9013	1071.6	0.6777	0.7277	0.7017	1.0994	0.0861	0.0072	0.0140
0.9518	1068.8	0.6719	0.7328	0.7055	1.1193	0.0868	0.0036	0.0071
1.0000	1066.5	0.6666	0.7373	0.7090	1.1377	0.0871	0.0000	0.0000
Heptane (1) + Toluene (2)								
0.0000	1240.7	0.8480	0.5619	0.5497	0.6217	0.0000	0.0001	0.0000
0.0496	1225.2	0.8357	0.5732	0.5595	0.6505	0.0025	0.0020	0.0032
0.1037	1211.5	0.8228	0.5842	0.5699	0.6816	0.0041	0.0038	0.0064
0.2040	1185.7	0.8002	0.6052	0.5886	0.7381	0.0075	0.0065	0.0111
0.4060	1144.8	0.7594	0.6435	0.6236	0.8475	0.0104	0.0093	0.0162
0.5045	1127.8	0.7415	0.6610	0.6394	0.8986	0.0106	0.0094	0.0166
0.6016	1113.1	0.7249	0.6774	0.6545	0.9481	0.0100	0.0090	0.0159
0.7011	1099.4	0.7090	0.6935	0.6690	0.9972	0.0086	0.0076	0.0137
0.8029	1087.0	0.6937	0.7091	0.6832	1.0462	0.0063	0.0056	0.0102
0.9019	1075.9	0.6797	0.7237	0.6964	1.0927	0.0036	0.0031	0.0056
0.9517	1071.2	0.6730	0.7305	0.7027	1.1155	0.0017	0.0014	0.0027
1.0000	1066.5	0.6666	0.7373	0.7090	1.1377	0.0000	0.0000	0.0000
Heptane (1) + Ethyl benzene (2)								
0.0000	1256.9	0.8492	0.5542	0.5400	0.6167	0.0000	0.0000	0.0000
0.0494	1243.9	0.8385	0.5636	0.5490	0.6429	0.0003	0.0006	0.0002
0.1039	1229.8	0.8269	0.5740	0.5589	0.6713	0.0007	0.0014	0.0005
0.2025	1205.9	0.8067	0.5927	0.5760	0.7226	0.0014	0.0018	0.0003
0.3022	1183.7	0.7868	0.6114	0.5939	0.7751	0.0018	0.0028	0.0010
0.4038	1162.6	0.7672	0.6304	0.6121	0.8289	0.0022	0.0039	0.0018
0.5006	1144.6	0.7492	0.6480	0.6292	0.8801	0.0021	0.0046	0.0026
0.6003	1126.9	0.7316	0.6660	0.6454	0.9315	0.0019	0.0040	0.0020
0.7014	1109.8	0.7143	0.6844	0.6619	0.9838	0.0018	0.0033	0.0016
0.8048	1094.8	0.6973	0.7022	0.6781	1.0369	0.0006	0.0021	0.0008
0.9028	1079.9	0.6817	0.7200	0.6934	1.0872	0.0005	0.0009	0.0001
1.0000	1066.5	0.6666	0.7373	0.7090	1.1377	0.0000	0.0000	0.0000

The ultrasonic method does not work successfully if the sound velocity exceeds more then 1600 ms^{-1}. In such condition the available volume V_a in (eqn. 6) comes to be negative. This is one of the greatest draw back of this method. Moreover this method sometimes gives abnormal values.

Thus, the thermodynamic method is applicable over a wide range of temperature *i.e.* to say very near to the critical temperature.

Ultrasonic method has got restricted validity and is applicable to the liquid having $u_s < u$.

The Lf obtained for all the six binary mixtures from these relation are in the order ultrasonic > Jacobson > thermodynamic method, which are also observed by several workers[7-10]. Since the value of K in (eqn. 1) suggested by Jacobson refers to atmospheric pressure the intermolecular free length obtained from thermodynamic method seems to be more reliable than Jacobson equation.

Looking the values of excess free length Lf^E, obtained from these relations, using (eqn. 9) given in the column 7, 8 and 9, respectively of the Table-1, shows that positive and negative values of excess free length are indication of the interaction within the component of the mixture. Since its magnitude are very low, it shows that there is no specific interaction between the pairs of component molecules, except in the hexane + ethyl benzene system where a negative value of Lf has been observed. This may be due to formation of transient complex between the pairs of the components of the molecules, hexane + ethyl benzene as also obtained by Tiwari *et al.*[11] during their study in the binary mixture of of benzene + tetrahydrofuran, considering it as a non polar + nonpolar type of system.

Conclusion

Thus, it may be concluded that Jacobson relation, thermodynamic relation and ultrasonic relation can be used successfully to predict free length of binary liquid mixture, with in the limit of experimental error, with their limitaions. The excess free length Lf^E obtained may be used successfully as an important tool to access the magnitude and extent of interaction with in the component of binary system, revealing the physico chemical changes occuring in the system.

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