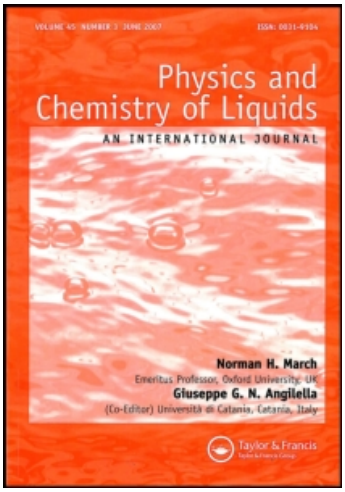

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KALIDOSS–JACOBSON FREE LENGTH THEORY APPLIED TO BINARY LIQUID MIXTURES OF CCl_4 + TOLUENE/ANILINE/ *o*-CRESOL/*m*-CRESOL/*p*-CRESOL

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Ultrasonic velocities and intermolecular free lengths in binary liquid mixtures of CCl_4 with toluene, aniline, *o*-cresol, *m*-cresol and *p*-cresol have been calculated theoretically, at different compositions and at temperature 298 K, based on Free Length Theory as revised recently by Kalidoss. It is observed that there is a close agreement of calculated velocities with experimental ones. The shape and thermostatic state picture built up in this formulation could be considered as a good representation of molecular state.

Keywords: Binary liquid mixtures; Free length theory; Molecular shape; Association

1. INTRODUCTION

Ultrasonic velocity and related data of liquid mixtures are found to be the most powerful tools in testing the theories of liquid state. In recent years, successive attempts have been made by large number of workers to evaluate theoretically the ultrasonic velocity in pure liquids and binary liquid mixtures using Free Length Theory (FLT), Collision Factor Theory, Nomoto's Relation and Van Deal's ideal mixing relation. Some workers [1, 2] have also compared the relative merits of these theories. They arrive at the conclusion that compared with other

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theories, FLT results in larger deviation of calculated velocities from experimental values. Such workers seemed to have ignored the necessity of incorporating two parameters in FLT as originally suggested by Jacobson himself: one, to account for the association and the other, for the shape of the component molecules in the mixture. Recently Kalidoss [3, 4] incorporated both shape factor and thermostatic state into FLT and found close agreement with experimental results.

The present paper reports the results of the application of the different thermostatic state and shape factors based on the FLT as revised by Kalidoss to binary liquid mixtures of CCl_4 with toluene, aniline, *o*-cresol, *m*-cresol and *p*-cresol at different mole fractions at 298 K.

2. THEORY

If the volume and surface area of one liquid molecule be written in terms of shape parameters a and b as

$$v = ar^3 \quad and \quad S = br^2 \tag{1}$$

then, the surface area of all the molecules in one mole of a pure liquid can be written as [3, 4],

$$Y = Nbr^2 = F(36\pi NV_0^2)^{1/3}$$
$$\text{where,} \quad F = \frac{b}{(36\pi a^2)^{1/3}} \tag{2}$$

Here, N is the Avogadro's number, F is the shape factor giving the relation between the surface of the molecules and the imagined spherical surface which enclosed the same volume as the volume of the molecules. The different shapes considered [5] in this work are given in Table I.

Jacobson himself observed that for liquids of low molecular weights, $F = 1$, and for those with high molecular weights, which are highly asymmetrical, F is considerably greater than unity.

V_o is the volume of pure liquid at 0 K and is given by,

$$V_o = V_T[1 - (T/T_c)]^{0.3} \tag{3}$$

TABLE I Shapes considered

Shape	*Size*	$\bar{R}$	S	v	a	b	F
Sphere	radius $= r$	r	$4\pi r^2$	$4\pi r^3/3$	4.1888	12.5664	1.0000
Cube	side $= r$	$3r/4$	$6r^2$	r^3	1.0000	6.0000	1.2407
Tetra	side $= r$	$(3r(\tan^{-1}\sqrt{2})/2\pi)$	$\sqrt{3}r^2$	$\sqrt{2}r^3/12$	0.1179	1.7321	1.4900
Cylinders: radius $= r$ and length $= l$							
Cyr n	$l = nr$	$((\pi+n)r/4)$	$2(1+n)\pi r^2$	$n\pi r^3$	$n\pi$	$2(1+n)\pi$	$(2(1+n)/36+n^2)$
$n = 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 5, 6, 7$							

where, T_c is the critical temperature and V_T is the molar volume at T K.

According to Kalidoss [3,4], if A_i and F_i are respectively the association and shape factor of the ith liquid molecule, then the expression for the intermolecular free length for the binary mixture becomes,

$$L_{KJ} = \frac{2\left[\left(\sum x_i A_i M_i/\rho\right) - \sum x_i A_i V_{0i}\right]}{\sum x_i A_i F_i Y_i} \tag{4}$$

where x_i and M_i are the mole fraction and the molecular weight respectively of the ith liquid. $A_i = 1$ and 2 refer to the monomeric and dimeric state of the molecules. With $A_i = 1$ and $F_i = 1$, the above equation reduces to that originally proposed by Jacobson.

From this value of L_{KJ} and density of the mixture, the sound velocity in the binary liquid mixture can be calculated using the relation,

$$U_{KJ} = \frac{k}{\rho^{1/2} L_{KJ}} \tag{5}$$

where, k is the Jacobson's temperature dependent constant.

3. COMPUTATIONAL ASPECTS

Using the literature value of T_c, experimental density, mole fraction and shape factor by considering various shapes and the two possible thermostatic state of both the liquid molecules as input data, the

TABLE II Shape and association in mixtures

Mixtures	χ^2 *value*		
CCl_4+	*JFLT*	*KJFLT*	*Shape-association*
Toluene	6.83	6.83	Sph–Monomer+Sph–Monomer
o-cresol	15.49	15.49	Sph–Monomer+Sph–Monomer
m-cresol	25.40	25.40	Sph–Monomer+Sph–Monomer
p-cresol	269.18	78.60	Cub–Dimer+Cub–Monomer
Aniline	134.02	12.41	Cyr 1.5–Dimer+Tetra–Monomer

JFLT: Jacobson Free Length Theory
KJFLT: Kalidoss–Jacobson Free Length Theory

intermolecular free length L_{KJ} and the u.s. velocity in the binary liquid mixture, U_{KJ} can be calculated. For a given mixture $16 \times 2 \times 16 \times 2 = 1024$ combinations of F_i and A_i values were considered. The set of F_i and A_i values which generates the minimum χ^2 gives the corresponding shape and themostatic state of the component liquid molecules in mixture. The results obtained are summarized in Table II.

4. RESULTS AND DISCUSSION

Table III gives the experimental and theoretical values of u.s. velocity and inter-molecular free length for the binary liquid mixtures of *p*-cresol and aniline with CCl_4. As mentioned in Section 2, *for spherical and monomeric state of the liquids*, there is no difference between Jacobson's Free Length Theory (JFLT) and Kalidoss–Jacobson's FLT (KJFLT). Hence the tables corresponding to the mixtures of CCl_4 + toluene, *o*-cresol and *p*-cresol are not given.

Toluene is neutral, while other liquids studied are basic (aniline is more basic than cresols). Again, toluene has plus inductive character whereas other liquids have negative inductive character. Even though (all) cresols belong to alcohol group, because of high sterric hindrance and high intra-molecular H-bonding, the reactivity of *o*-cresol is less than that of *m*- or *p*-cresols. Also because of high electron withdrawing nature of amino group, the reactivity of the liquids studied decreases as

$$\text{aniline} > p\text{-cresol} > m\text{-cresol} > o\text{-cresol} > \text{toluene}$$

Therefore, when CCl_4 is added to these liquids, the intermolecular forces increase in the reverse order. Thus the less-reacting toluene, *o*-cresol and *m*-cresol have spherical-monomeric state themselves, maintain the shape and polymeric state of CCl_4 as spherical-monomer. The more-reacting *p*-cresol and aniline assume cubical and tetrahedral shapes themselves respectively, while modifying that of CCl_4 to cubic-Dimer and Cylinder 1.5-Dimer respectively. Thus, when CCl_4 molecule goes into a mixture with other liquid molecules, it may or may not have same shape and thermostatic state in different mixtures [4, 6]. This only indicates that the relative strength of the AB-interaction is different in different systems studied.

TABLE III Experimental and calculated values of velocity and free length

		$U\ (m\,s^{-1})$			L_f (Å)		
x_1	$\rho\ (kg \cdot m^{-3})$	*Expt.*	*JFLT*	*KJFLT*	*Expt.*	*JFLT*	*KJFLT*
$CCl_4 + p$-cresol							
0.9	1525.0	943.12	968.63	1072.23	0.5366	0.5225	0.4720
0.8	1469.7	986.80	1029.92	1050.77	0.5224	0.5006	0.4906
0.7	1385.6	1027.59	993.62	960.62	0.5167	0.5344	0.5527
0.6	1353.8	1094.03	1137.96	1023.31	0.4910	0.4720	0.5249
0.5	1305.5	1132.35	1238.39	1058.70	0.4831	0.4417	0.5167
0.4	1246.4	1192.64	1288.01	1078.86	0.4694	0.4346	0.5189
0.3	1254.7	1256.60	1915.53	1447.99	0.4440	0.2913	0.3853
0.2	1140.1	1338.21	1454.60	1261.27	0.4374	0.4024	0.4641
0.1	1086.6	1402.94	1537.19	1463.28	0.4274	0.3900	0.4097
χ^2 value:			269.18	78.60			
CCl_4 + Aniline							
0.9	1538.0	964.09	985.89	955.37	0.5227	0.5112	0.5275
0.8	1486.1	1011.28	1044.22	982.90	0.5070	0.4910	0.5216
0.7	1447.5	1063.81	1166.42	1065.74	0.4883	0.4454	0.4874
0.6	1391.9	1121.20	1239.19	1107.09	0.4725	0.4275	0.4785
0.5	1337.3	1189.94	1332.05	1169.43	0.4542	0.4057	0.4622
0.4	1277.1	1258.65	1408.22	1227.30	0.4394	0.3927	0.4506
0.3	1218.0	1336.93	1506.44	1316.50	0.4236	0.3759	0.4302
0.2	1172.6	1425.89	1756.16	1549.46	0.4048	0.3287	0.3725
χ^2 value:			134.02	12.41			

x_1: mole fraction of CCl_4

Toluene, aniline, *o*-cresol, *m*-cresol, *p*-cresol all are polar liquids while CCl_4 is non-polar. Thus the AB interaction in all the four systems is dipole-induced dipole type.

5. CONCLUSION

The theoretical approach of revised free length theory is found to be applicable to the systems investigated and there is closer agreement with experimental results. The shape and thermostatic state picture built into this formulation could be considered as a good representation of molecular interaction in mixtures.

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