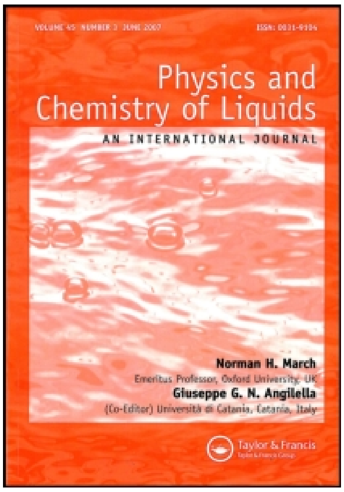

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ASSOCIATION AND SHAPE OF MOLECULES USING FREE LENGTH THEORY

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Traditionally workers engaged in calculation of the ultrasonic velocity in liquid mixtures using Jacobson's Free Length Theory (FLT) arrive at the conclusion that the predictions of FLT produce large deviations when compared with experimental velocities. 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. By introducing the association factor and deriving explicit expressions for different shapes of the molecules, the present work has demonstrated that FLT might be made to predict ultrasonic velocities in the mixtures better. Also this approach can very well be used to account for molecular associations and shapes.

Keywords: Molecular shape; mixtures; hydrogen bonding

1. INTRODUCTION

The second virial coefficient for hard non-spherical molecules is $B = bf$, where b is the second virial coefficient of hard-sphere of the same volume as the non-spherical molecules and $f > 1$, is a shape dependent factor [1]. Isihara [2, 3] and Kihara [4] have calculated the second virial coefficient for systems of elastic bodies of arbitrary shape. They have shown that for convex molecules, f is related to the volume, v, surface area, S, and mean radius of curvature, $\bar{R}$, of the molecule.

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Actually,

$$f = 1 + \left(\frac{\bar{R}S}{4v} - \frac{3}{4} \right). \tag{1}$$

$\bar{R}$, S and v for several shapes are given in [1] and are reproduced in Table I. Gibbons [5] using Scaled Particle Theory, has given expressions for second, third and nth virial coefficients in terms of $\bar{R}$, S and v and has concluded that the equation of state of hard non-spherical molecules is sensitive to the shape of the molecule. Also each shape of molecule produced a different relationship between the compressibility factor Z and the reduced density. Thus it is needless to emphasize the necessity of taking the shape of the molecules into account explicitly. That is why our previous work [6] was concerned with the determination of the shapes of component molecules in liquid mixtures (using Scaled Particle Theory).

Jacobson's Free Length Theory (FLT) [7, 8] has been employed by numerous workers, especially by those dealing with liquid mixtures, to predict the ultrasonic velocity in the mixture and in turn to compare FLT with other theories. Invariably the conclusion arrived at by them has been that Schaaffs' Collision Factor theory (CFT) is able to reproduce the sound velocity in mixtures better than FLT, as CFT deals with real, elastic molecules while FLT is concerned with hard molecules. All earlier workers seemed to have ignored the shape dependent parameter used by Jacobson himself in his FLT. Jacobson [8] also suggested that FLT could be used to determine the association of

TABLE I Shapes considered

No.	*Shape*	*Size*	$\bar{R}$	S	v
1	Sphere	radius = r	r	$4\pi r^2$	$4\pi r^3/3$
2	Cube	side = r	$3r/4$	$6r^2$	r^3
3	Tetrahedron	side = r	$3r\,(\arctan\sqrt{2})/2\pi$	$\sqrt{3}r^2$	$\sqrt{2}r^3/12$
		Discs: radius = r and depth = l			
4	Disc 1	$l = 2r$	$(\pi + 2)r/4$	$6\pi r^2$	$2\pi r^3$
5	Disc 2	$l = (3/2)r$	$(\pi + 1.5)r/4$	$5\pi r^2$	$1.5\pi r^3$
6	Disc 3	$l = r$	$(\pi + 1)r/4$	$4\pi r^2$	πr^3
7	Disc 4	$l = r/2$	$(\pi + 0.50)r/4$	$3\pi r^2$	$\pi r^3/2$
8	Disc 5	$l = r/4$	$(\pi + 0.25)r/4$	$5\pi r^2/2$	$\pi r^3/4$
9	Disc 6	$l = r/10$	$(\pi + 0.10)r/4$	$11\pi r^2/5$	$\pi r^3/10$

molecules in liquids. But this suggestion has not been given effect to, by the workers in the field. The present work is an attempt to apply FLT in its fullness to liquid mixtures.

2. FREE LENGTH THEORY (FLT) REVISITED

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

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

At absolute zero a liquid has a molar volume V_0 and the molecules have their closest packing so as to make the void space between the molecules negligible. Therefore,

$$Nar^3 = V_0 \tag{3}$$

where N is the Avogadro number and so,

$$r = \left[\frac{V_0}{Na}\right]^{1/3} \tag{4}$$

Thus the total surface area of all the molecules in one mole is,

$$\begin{aligned} Y &= Nbr^2 = Nb\left[\frac{V_0^2}{N^2a^2}\right]^{1/3} \\ i.e., Y &= \frac{b}{(36\pi a^2)^{1/3}}(36\pi NV_0^2)^{1/3} \\ &= F(36\pi NV_0^2)^{1/3} \end{aligned} \tag{5}$$

where,

$$F = \frac{b}{(36\pi a^2)^{1/3}}, \tag{6}$$

is the shape factor giving the ratio between the surface of the molecule and the imagined spherical surface which encloses the same volume as the volume of the molecule. Hereafter the total surface area of molecules in one mole of the ith liquid will be written as F_iY_i, where,

$$Y_i = [36\pi NV_{0i}^2]^{1/3}.$$

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. It is important at this juncture to note that f of Eq. (1) is different from F of Eq. (5); F is determined using Eq. (6) for the different shapes listed in Table I and are given in Table II.

Equation (5) includes the zero volumes V_0. This can be obtained in two ways. V_0 can be theoretically computed for any chemical compound of known composition and structure by the addition of atomic and structural constants. Greater accuracy of V_0 is obtained, however, if the critical temperature T_C is known and Sugden's [9] formula can be used, which gives the variation of molar volume with temperature as,

$$V_0 = V_T(1 - T/T_C)^{0.3} \tag{7}$$

where T_C is the critical temperature and the molar volume at T is V_T. It is to be noted that the maximum temperature limit of the above equation is T_C and that the temperature of study has to be considerably lower than T_C for the equation to yield V_0 values without appreciable error. At a temperature T, the liquid as a whole expands without the molecules themselves undergoing any expansion. If the

TABLE II Shape factors

Shape	*a*	*b*	*F*
Sphere	4.1888	12.5664	1.0000
Cube	1.0000	6.0000	1.2407
Tetrahedron	0.1179	1.7321	1.4900
Disc 1	6.2832	18.8496	1.1447
Disc 2	4.7124	15.7080	1.1556
Disc 3	3.1416	12.5664	1.2114
Disc 4	1.5708	9.4248	1.4422
Disc 5	0.7854	7.8540	1.8079
Disc 6	0.3142	6.9115	3.0924

available volume at T is V_a, then the free length, L, between the surfaces of the molecules is given by [7, 8],

$$L = \frac{2V_a}{Y} = \frac{2(V_T - V_0)}{Y} \tag{8}$$

The advantage of the Eq. (8) is that it does not necessarily require spherical molecules. The presence of F in Eq. (5) makes it possible to compute L for different shapes of molecules. Jacobson noted [8] that the deviation in the computed values of L is due in part but probably not wholly to the difficulty of determining V_0 exactly. Even if the error in V_0 for the different pure liquids forming the liquid mixture amounts to one or two percent, nevertheless it is possible to compute very accurate values for L with different concentrations. This was demonstrated by him for the case of 53 non-associated liquids and 16 mixtures (for which, he obtained a mean deviation of 0.8 percent in the value of L).

3. MOLECULAR ASSOCIATION

Computation of ultrasonic velocity using FLT is of special significance for associated liquids and this was highlighted by Jacobson [8]. Considering the fatty acids as dimers, he demonstrated the agreement between the free length values calculated from adiabatic compressibility data and those from Eq. (8). However this initiative was not followed up by other workers. In the present work, the possibility for the existence of molecules as monomers and dimers is also considered.

To this end, two parameters are ascribed to the molecules: one, to account for its association, and the other, for its shape. If A_i and F_i are respectively the association and shape factors of the ith liquid molecule, then Eq. (8) is extended to liquid mixtures as,

$$L = \frac{2\left[(\Sigma x_i A_i M_i/\rho_{\text{mix}}) - \sum x_i A_i V_{0i}\right]}{\Sigma x_i A_i F_i Y_i} \tag{9}$$

where, x_i is the mole fraction and M_i, molecular weight of the ith component liquid of the mixture. $A_i = 1$ and 2 refers to the monomeric and dimeric state of the molecules. Once free length L is thus known, the sound velocity in the liquid mixture is calculated using,

$$U = \frac{K_J}{L\rho_{\text{mix}}^{1/2}}, \tag{10}$$

where K_J is a temperature dependent constant [10]. Researchers so far assumed monomeric as well as spherical molecules (with $A_i = 1$ and $F_i = 1$ in Eq. (9)) resulting in poor agreement between FLT-predicted and experimental ultrasonic velocity in mixtures.

4. COMPUTATIONAL ASPECTS

Literature values of T_C were used in Eq. (7) to calculate V_0. With the reported [6, 11 – 16], experimental mole fraction and density as inputs in Eqs. (9) and (10), the ultrasonic velocity in the liquid mixture, U_{cal}, is calculated; while doing so, F_i values of Table II were used along with A_i (= 1 and 2) values. Then χ^2 value, given by,

$$\chi^2 = \sum \frac{(U_{\text{exp}} - U_{\text{cal}})^2}{U_{\text{cal}}},$$

is calculated. The sum in the above equation covers all the combinations of concentrations of the liquids participating in the mixture. Thus for a given binary mixture, $2 \times 2 \times 9 \times 9 = 324$ combinations of F_i and A_i values were considered. The set of values of F_i and A_i values which produces minimum χ^2 value results in Table III, wherein the corresponding shapes and association factors are tabulated.

5. RESULTS AND DISCUSSION

1. Results of RFLT are found to be very sensitive to T_C values.
2. Triethylamine (TEA), Benzene, Toluene, Ethylbenzene, Cyclohexane and *o*,*p*,*m*-Xylenes are found to exist in monomeric spherical form, as expected. Interestingly, all spherical molecules are monomers.

TABLE III Shape and association in mixtures

No.	*Mixtures*			*Shape-assn.*			*Temp.* (*K*)
1	TEA	+	Benzene	$S-1$	+	$S-1$	308
2		+	Toluene	$S-1$	+	$S-1$	308
3		+	Ethyl Benzene	$S-1$	+	$S-1$	308
4		+	*o*-Xylene	$S-1$	+	$S-1$	308
5		+	*p*-Xylene	$S-1$	+	$S-1$	308
6		+	*m*-Xylene	$S-1$	+	$S-1$	308
7		+	*o*-Cresol	$S-1$	+	$S-2$	303
8		+	Phenol	$S-1$	+	$S-2$	303
9		+	Ethanol	$S-1$	+	$S-2$	303
10		+	Propanol	$S-1$	+	$S-2$	303
11		+	Butanol	$S-1$	+	$S-2$	303
12	Cyclo-hexane	+	Propanol	$S-1$	+	$S-2$	308
13		+	Butanol	$S-1$	+	$S-2$	308
14	DCE	+	Cyclohexane	$S-1$	+	$S-1$	308
15		+	Propanol	$S-1$	+	$S-1$	308
16		+	Butanol	$S-1$	+	$S-1$	308
17	Dioxane	+	DCE	$D3-1$	+	$D1-2$	308
18		+	Butanol	$S-1$	+	$S-1$	308
19	*n*-Hexane	+	Propanol	$S-1$	+	$S-1$	303
20		+	Butanol	$S-1$	+	$S-1$	303
21		+	Pentanol	$S-1$	+	$S-1$	303
22		+	Hexanol	$S-1$	+	$S-1$	303
23		+	Heptanol	$D1-1$	+	$S-2$	303
24		+	Octanol	$S-1$	+	$S-1$	303
25	TBP	+	Hexanol	$S-1$	+	$S-1$	303
26		+	Heptanol	$S-2$	+	$S-1$	303
27		+	Octanol	$S-1$	+	$S-1$	303
28		+	Decanol	$S-1$	+	$S-1$	303
29	CCl_4	+	Propanol	$S-1$	+	$S-1$	308
30		+	Butanol	$D2-1$	+	$S-1$	308
31		+	Benzene	$D1-1$	+	$S-1$	308

TEA: Triethylamine DCE: 1,2 Dichloroethane TBP: Tributyl Phosphate.

3. In the TEA mixtures, the less interacting partners have $S-1$ structure. But the structure is changed in the case of H-bonded partners because of strong molecular interactions between the lone pair electrons of nitrogen in TEA and the proton of the hydroxyl group. This was confirmed by dielectric [17] studies.
4. 1,4 Dioxane is found to have Disc 3 shape with 1,2 Dichloroethane (DCE) and spherical shape with Butanol. This may be due to the higher molecular weight of DCE. However it is monomeric in both the cases as it is not an associated liquid.

5. All alcohols, except Heptanol, listed in Table III have $S-1$ structure with *n*-Hexane; Heptanol alone is in $S-2$ structure.
6. Similarly, all alcohols have $S-1$ structures with Tributyl Phosphate (TBP). However the structure of TBP is $S-2$ only with Heptanol. In our earlier work [16] (using Scaled Particle Theory), TBP + Heptanol mixture was shown to be different from TBP + Hexanol, Octanol and Decanol mixtures. Also, ultrasonic as well as dielectric studies of Dash *et al.* [18] and Swain [19] showed that the interaction is maximum in TBP + Heptanol mixture only.
7. In the present study, Ethanol, Propanol and Butanol (with TEA and Cyclohexane) have the same Sph-dimeric state. But they are in $S-1$ structure with DCE and CCl_4.
8. This study confirms the major role of hydrogen bonding in deciding the shape as well as the polymeric state of the liquid molecules in the mixture. When a particular molecule goes into a mixture with other liquids, it may or may not have the same shape in different mixtures. This indicates that the relative strength of $A-B$ interaction is different in different mixtures. This was observed in the earlier work [6] too.

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