

Evaluation of Sound Velocities in Mixtures of *n*-Alkanols + *n*-Heptane

T RAMANJAPPA*, K V SIVAKUMAR & E RAJAGOPAL

Department of Physics, Sri Krishnadevaraya University, Anantapur 515 003

Received 4 August 1983; revised and accepted 14 November 1983

Sound velocities in binary mixtures of *n*-alkanols with *n*-heptane have been calculated theoretically based on free length theory (FLT) of Jacobson and collision factor theory (CFT) of Schaaffs. The results have been compared with the experimental values of Benson *et al.* [*J chem Thermodyn*, 9(1977) 1189; 10(1978) 967; 11(1979) 861]. The molecular interactions are discussed in terms of the concentration dependence of intermolecular free length and a term signifying relative interaction which has been evaluated making use of molar sound velocity data in these mixtures.

n-Alkanol + *n*-alkane mixtures have been studied extensively from the view point of their ultrasonic and thermodynamic behaviour by various workers in order to understand and interpret the modification of structure in the associated alcohols on the addition of alkanes¹⁻⁷. These studies are highly useful for understanding the molecular interactions when water is added to alcohols⁸⁻¹⁰. The intermolecular free length in liquid mixtures has been found to depend on the concentration, and molecular association or dissociation in binary nonelectrolyte liquid mixtures has been studied on the basis of this parameter^{11,12}. The free length theory of Jacobson¹³ (FLT) and the collision factor theory of Schaaffs¹⁴ (CFT) have been extensively employed to theoretically evaluate sound velocities in liquid mixtures. The results have been interpreted in terms of relative adaptability of each theory to the type of mixtures studied^{11,12,15-17} and thereby the nature of molecular interactions in liquid mixtures has been inferred. Our recent study on *n*-hexanol + *n*-alkane mixtures has indicated that the intermolecular free length depends on the relative size of the component molecules, and it is linearly related to mole fraction of alcohols for *n*-hexanol + *n*-hexane system wherein the sizes of the two components are equal. To study the effect of size of the alcohol molecule on the intermolecular free length of the *n*-alcohol + *n*-alkane systems, we have taken up the study of *n*-alcohol + *n*-heptane series in the present work. Eventhough FLT is not strictly applicable to the system wherein the component liquids are associated in nature, still a study of the extent of applicability of FLT would be useful and we have evaluated velocities in these mixtures using FLT apart from CFT.

Theory

The free lengths in liquids have been evaluated using Jacobson's equation¹³ (Eq. 1),

$$L_f = \frac{K}{u\rho^{1/2}} \quad \dots (1)$$

where K is a temperature dependent parameter and u and ρ are the ultrasonic velocity and density of the liquid.

Free lengths in the mixture are evaluated using the relation (2),

$$L_f^{M'} = \frac{K}{u_{\text{mix}} \cdot \rho_{\text{mix}}^{1/2}} \quad \dots (2)$$

The available volume has been evaluated using Eq. 3,

$$V_a = V_M - V_0 \quad \dots (3)$$

where V_M and V_0 are the molar volumes at the temperature T and at absolute zero respectively.

The surface area per mole of the liquid is given by Eq. 4,

$$Y = (36 \pi N V_0^2)^{1/3} \quad \dots (4)$$

From the knowledge of pure liquid parameters, the ideal free length can be evaluated using Eq. (5),

$$L_f^M = \frac{2V_a}{x_1 Y_1 + x_2 Y_2} \quad \dots (5)$$

where

$$V_a = (x_1 V_{m1} + x_2 V_{m2}) - (x_1 V_{01} + x_2 V_{02}) \quad \dots (6)$$

where x_1 and x_2 are mole fractions of the first and second components in the mixture.

Ultrasonic velocity can also be evaluated using Schaaffs' collision factor theory¹⁴. According to this theory velocity in a pure liquid is given by Eq. 7,

$$u = u_\infty S Y_f = u_\infty S \frac{B}{V_M} \quad \dots (7)$$

where V_M is the molar volume, Y_f is the space filling factor, S is the collision factor and B is the actual volume of the molecule per mole and is given by Eq. 8,

$$B = 4/3 \pi r^3 N \quad \dots (8)$$

The molecular radius r may be evaluated by the formula due to Schaaffs¹⁴. Nutsch-Kuhnckies¹⁸ extended this theory for binary mixtures and showed that,

$$u_{\text{mix}} = \frac{u_{\infty}(x_1 S_1 + x_2 S_2)(x_1 B_1 + x_2 B_2)}{V_{\text{mix}}} \quad \dots (9)$$

The relative interaction of the two components in a binary liquid mixtures has been studied^{19,20} in terms of the experimental and ideal molar sound velocities, and the magnitude of the relative interaction (I_R) is given by Eq. 10,

$$I_R = \frac{R_{\text{exp}}}{R_{i_d}} \quad \dots (10)$$

where $R_{i_d} = x_1 R_1 + x_2 R_2$.

Results and Discussion

The theoretically evaluated ultrasonic velocity data using FLT and CFT are presented graphically alongwith the experimental data for the systems n -alcohols + n -heptane in Fig. 1. The necessary experimental data have been taken from the work of Benson *et al.*^{3,21,22}. Intermolecular free length $L_r^{M'}$, evaluated using experimental ultrasonic velocity and density data, is plotted against the concentration of n -alcohol (x_1) in Fig. 2. The term I_R signifying the relative interaction is plotted against x_1 in Fig. 3. In view of high accuracy in the measurement of velocity data, I_R is accurate to ± 1 in 10^4 .

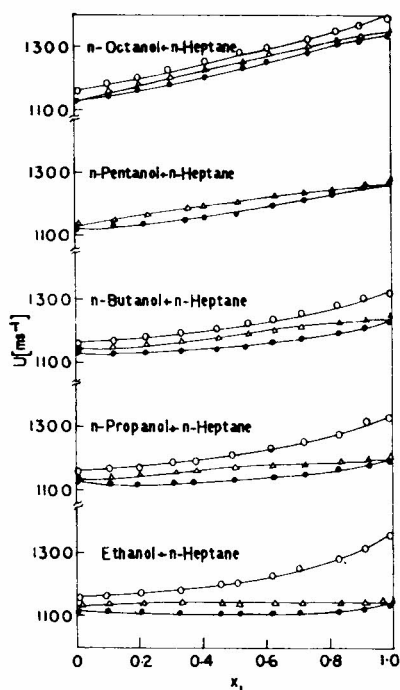


Fig. 1—Variation of ultrasonic velocity (u) versus concentration (x_1) of n -alcohol in n -heptane [—●—, experimental; —○—, FLT; —△—, CFT]

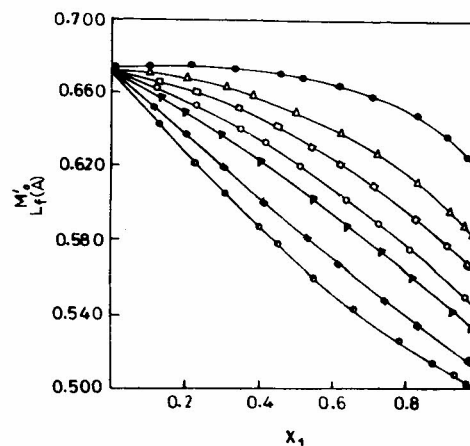


Fig. 2—Variation of intermolecular free length ($L_r^{M'}$) versus concentration (x_1) of n -alcohol in n -heptane

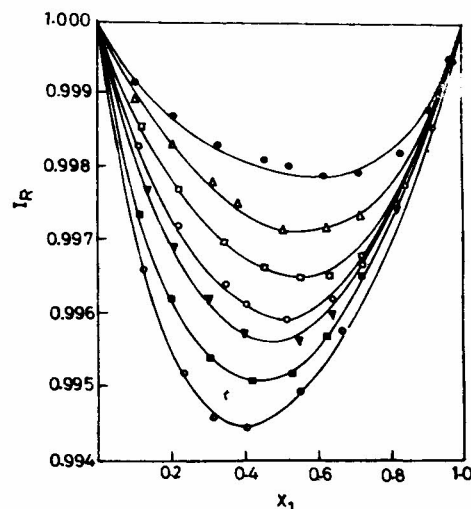


Fig. 3—Variation of relative interaction (I_R) versus concentration (x_1) of n -alcohol in n -heptane [—●—, Ethanol; —△—, n -propanol; —□—, n -butanol; —○—, n -pentanol; —▽—, n -hexanol; —■—, n -octanol; —●—, n -decanol]

An examination of the data presented in Fig. 1 indicates that the velocity data evaluated using CFT are close to the experimental data in comparison with the data evaluated using FLT. In view of the limitations of the theory, the agreement may be taken to be good. The result that CFT has an edge over FLT is in conformity with the results of the earlier studies, where these two theories have been tested for a larger number of liquid mixtures.

Fig. 2 indicates that the intermolecular free length depends on the relative sizes of the component molecules. As the chain length of the alcohol molecule increases the convexity decreases and finally for higher alcohols the plot of intermolecular free length versus x_1 becomes concave in nature. This behaviour indicates that as the chain length of the alcohol molecules increases the structure breaking nature of the molecule increases. The rate at which the

intermolecular free length decreases with increase in concentration of *n*-heptane is slower in lower alcohols than that in the higher alcohols. From this behaviour one may infer that in lower alcohols the association is predominant whereas the higher alcohols are dissociative in nature in the environment of alkanes.

Fig. 3 indicates that the concentration at which I_R becomes minimum decreases with increase in the size of the alcohol molecule. Also, at any given concentration of *n*-heptane, I_R decreases with increase in the size of the alcohol molecule. This behaviour shows that the relative interaction of alcohol-alkane molecules in the mixture increases with increase in the size of the molecule. The destabilization of the hydrogen bonded structure of higher alcohols by *n*-heptane is more in comparison with the destabilization of the structure of lower alcohols by *n*-heptane. It may be mentioned here that I_R close to 1 indicates less interaction; and if $I_R = 1$, there exists no interaction between the two types of molecules in the mixture and the mixture behaves ideally. The results of the present study are in conformity with the volumetric and compressibility studies of Benson *et al.*^{3,21,22}.

References

- 1 Awwad A M & Pethrick R A, *J chem Soc Faraday Trans I*, **78** (1982) 3213.
- 2 Marsh K N & Burfitt C, *J chem Thermodyn*, **7** (1975) 955.
- 3 Kiyohara O & Benson G C, *J chem Thermodyn*, **11** (1979) 861.
- 4 Van Ness H C, Soczek C A & Kochar N K, *J Chem Engng Data*, **12** (1962) 346.
- 5 Staveley L A K & Spice B, *J chem Soc*, (1952) 406.
- 6 Diaz Pena M & Rodriguez Cheda D, *An R Soc Esp Fis Quim Ser B*, LXVI (1970) 637.
- 7 Swamy G N, Dharmaraju G & Raman G K, *Can J Chem*, **58** (1980) 229.
- 8 Emery J & Gasse S, *Acustica*, **43** (1979) 205.
- 9 Wishikawa S, Mashima M & Yasunaga T, *Bull chem Soc Japan*, **49** (1976) 1413.
- 10 Blandamer M J & Waddington D, *Adv Mol Relaxation Processes*, **2** (1970) 1.
- 11 Kaulgud M V, *Acustica*, **10** (1960) 316.
- 12 Ramanjappa T, Sivakumar K V & Rajagopal E, *Acustica*, in press.
- 13 Jacobson B, *Acta chem scand*, **6** (1952) 1485.
- 14 Schaaffs W, *Molekularakustik* (Springer Verlag, Berlin-Gohingen-Heidelberg) Chaps XI and XII (1963); *Z Phys*, **114** (1939) 110; *Z Phys*, **115** (1940) 69.
- 15 Kaulgud M V, *Indian J Phys*, **36** (1962) 577.
- 16 Kaulgud M V, *Z physik Chem (NF)*, **36** (1963) 365.
- 17 Kaulgud M V & Tarsekar V K, *Acustica*, **25** (1971) 14.
- 18 Nutsch-Kuhnies R, *Acustica*, **15** (1965) 383.
- 19 Van Dael W & Vangeal E, *Proc first int conf on calorimetry and thermodynamics*, Warsaw (1969) 55.
- 20 Van Dael W & Van Ittesbeek, *Physics of high pressure and condensed phases*, (John Wiley, New York) 1965, 350.
- 21 Treszczanowicz A J & Benson G C, *J chem Thermodyn*, **10** (1978) 967.
- 22 Treszczanowicz A J & Benson G C, *J chem Thermodyn*, **9** (1977) 1189.