

## Sound velocity in binary liquid mixtures and the statistical mechanical theories

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**Abstract.** Sound velocity in three binary liquid mixtures benzene + cyclohexane (I), cyclohexane + carbontetrachloride (II) and benzene + carbontetrachloride (III) has been measured. Significant structure and Flory – Patterson theories have been employed to evaluate ultrasonic velocity in the systems. The values are in good agreement with the experimental ones. A comparative study of significant structure theory and Flory–Patterson Theory has been made. Both the theories give satisfactory results for the three liquid mixtures.

**Keywords.** Significant structure theory; ultrasonic velocity; binary liquid mixture; Flory–Patterson theory

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### 1. Introduction

The most widely used significant structure theory (SST) of liquids [1–4] has been employed by Choi and Jhon [5–6] for evaluating the sound velocity, internal pressure and van der Waals constant in pure liquids. Similar deductions were also carried out, recently, for molten salts [7–8] and liquid metals [9]. Although SST has been applied earlier to binary liquid mixtures [1, 10, 11] for calculating viscosity, surface tension and excess thermodynamic properties, its applicability for sound velocity in binary liquid mixtures has not, so far, been tested. Very recently [12] this theory has been applied quite successfully for transport properties in the case of ternary liquid systems. In the present paper SST has been applied for evaluating sound velocity in three different binary liquid mixtures. The results of theoretical calculations obtained from SST have been compared with those deducted from Flory–Patterson theory (FPT) [13–15], as well as the experimental values. The latter theory has recently been applied for estimating the sound velocity in varieties of liquid mixtures [16–21]. The three binary liquid mixtures considered for the present investigations are: benzene + cyclohexane (I), cyclohexane + carbontetrachloride (II), and benzene + carbon tetrachloride (III).

### 2. Experimental

Component liquids of BDH grade were distilled before use and their boiling points were recorded to ensure their purity [22]. Ultrasonic velocity was measured using an interferometer (supplied by M/S Mittal Enterprises, New Delhi, India) operating

at a frequency of 2.0 MHz. The density of liquids were measured by a precalibrated double stemmed pycnometer at a constant temperature of 298.15 K which was maintained by a thermostatically controlled bath to  $\pm 0.01^\circ\text{C}$ . The uncertainties in velocity and density measurements were  $\pm 0.1$  and  $\pm 0.0001$  respectively.

### 3. Theoretical

The velocity of sound,  $u$ , obeys the relation

$$u = \left( \frac{C_p V}{C_v \beta_T M} \right)^{1/2} = \left( \frac{\gamma}{\beta_T \rho} \right)^{1/2}, \quad (1)$$

where  $\gamma$ ,  $\beta_T$  and  $\rho$  are the ratio of  $C_p$  to  $C_v$ , isothermal compressibility and density respectively. All these quantities in SST are evaluated in terms of the partition function,  $f$ , using the relations,

$$C_p = C_v + \frac{\alpha^2 TV}{\beta_T}, \quad (2)$$

$\alpha$  being the thermal expansion coefficient.

$$C_v = \left[ \frac{\partial}{\partial T} \left\{ kT^2 \left( \frac{\ln f}{T} \right)_v \right\} \right] \quad (3)$$

$$\beta_T = \left[ V kT \left( \frac{\partial^2 \ln f}{\partial V^2} \right)_T \right]^{-1} \quad (4)$$

$$\alpha = \frac{[\partial^2(-kT \ln f)/\partial V \cdot \partial T]_{T,V}}{V kT (\partial^2 \ln f / \partial V^2)_T} \quad (5)$$

However, it should be noted that the partition function,  $f$ , in the present case is the partition function of the mixture and can be expressed in terms of the partition functions,  $f_1$  and  $f_2$ , of the pure components 1 and 2 respectively,

$$f = \left[ \frac{(N_1 + N_2)!}{N_1! N_2!} \right] f_1 f_2 \times [1 + n(X - 1) \exp - (\xi N (V_s/V))] \exp[N(E_s/RT)(V_s/V)] \quad (6)$$

where

$$f_1 = (f_{1s})^{N_1(V_s/V)} (f_{1g})^{N_1(V-V_s)/V},$$

and

$$f_2 = (f_{2s})^{N_2(V_s/V)} (f_{2g})^{N_2(V-V_s)/V}.$$

Here,  $F_s$ ,  $f_g$ ,  $N_1$ ,  $N_2$ ,  $V_s$ , and  $V$  are respectively the solid like partition function, gas like partition function, number of molecules of types 1 and 2, the molar volume of the solid at the melting point and the molar volume of the liquid.  $X$  and  $\xi$  are given by  $V/V_s$  and  $a \cdot E_s/[RT(X - 1)]$ ,  $a$  being a proportionality factor,  $E_s$  is the energy of sublimation at the melting point and  $n$  is the coordination number of the lattice. The detailed expressions for  $f_{1s}$ ,  $f_{2s}$ ,  $f_{1g}$ , and  $f_{2g}$  for the various liquids under the present study viz. benzene, cyclohexane, and carbontetrachloride have been derived by Eyring and coworkers [10–11]. These expressions in conjunction with eqs (1) and (6) have

been used to deduce the value of the ultrasonic velocity in binary liquid mixtures from SST.

Sound velocity can also be deduced on the basis of FPT [13–16]. The method of deduction has also been extended to binary mixtures during recent years [16, 19–20]. The resulting expressions for the velocity of sound according to this theory has the following forms [23]:

$$u = 5.663 \left( \frac{k^2 P^{*4} T^{*2} L^2}{\rho^2 M} \right)^{1/6} \left[ M \tilde{V}^{-5/3} - \left( \frac{V^{1/3} - 1}{V^2} \right) \ln \left( \frac{\tilde{V}^{1/3} - 0.5}{\tilde{V}^{1/3} - 1} \right) \right]^{2/3} \quad \text{(FPT-Altenberg Relation)} \quad (7)$$

and

$$u = \left( \frac{k P^{*2} T^*}{6.3 \times 10^{-4} \rho} \right)^{2/9} \left[ M \tilde{V}^{-5/3} - \left( \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^2} \right) \ln \left( \frac{V^{1/3} - 0.5}{V^{1/3} - 1.0} \right) \right]^{2/3} \quad \text{(FPT-Auerbach Relation)} \quad (8)$$

where,  $P^*$ ,  $T^*$ , and  $\tilde{V}$  are respectively the characteristic pressure, characteristic temperature and reduced volume of the binary liquid mixtures,  $k$  is the Boltzmann constant,  $L$ , the Laschmidt number, and  $M$  is a constant having value less than 1. Its significance has been discussed earlier [15, 16]. Evaluation procedure for  $P^*$ ;  $T^*$  and  $V$  are detailed out in previous papers [13–19]. The other symbols have their usual notations.

#### 4. Results and discussion

The sound velocity,  $u$ , in three binary liquid mixtures, namely, benzene + cyclohexane (I), carbon tetrachloride + cyclohexane (II), and benzene + carbontetrachloride (III), at 298.15 K are computed theoretically from SST using eqs (1) to (6). Theoretical sound velocities for these three systems have also been evaluated on the basis of FPT, employed earlier [23] for such purpose, using two different approaches, vide eqs (7) and (8). The values of pure components parameters needed for these computations were taken from literature [10–11, 21–23]. Theoretically computed values of sound velocity in systems (I), (II), and (III) on the basis of SST and FPT are compared with those experimentally determined. The standard deviations (per cent) of theoretical values deduced from these theories with observed ones are:

	I	II	III
SST	0.76	3.53	2.97
FPT (Auerbach)	1.65	5.35	3.11
FPT (Altenberg)	5.66	3.96	6.98

Thus, both the statistical theories (SST and FPT) yield fairly reasonable agreement (within 7.0 per cent) for all the three systems under the present investigation.

The composition dependence of sound velocity in all the three binary liquid mixtures has been investigated both theoretically and experimentally. The results obtained from SST [vide eqs (1) to (6)] and FPT [vide eqs (7) and (8)] are shown graphically in figures 1–3 corresponding to systems (I), (II), and (III) respectively. In these figures the experimental sound velocity-composition curves have also been plotted. For the system benzene + cyclohexane (I), the theoretical and observed sound velocity values are plotted against the mole fraction of benzene. By increasing the benzene content in the mixture the velocity first decreases and then increases continuously. Such a trend is also observed in the case of theoretical sound velocity values deduced both from SST and FPT. The unusual trend in the velocity-composition curve observed here, both experimentally and theoretically at 298.15 K in the case of this system, has also been verified earlier by Reddy *et al* [24] at 27.5°C and by Moore *et al* [25] at 25°C.

Benzene is diatomic i.e. it can sustain induced ring current due to the presence of  $6\pi$  electrons in the form of a closed loop, while cyclohexane is a flat ring without any such characteristics.

It is well known that benzene rings stack together side by side, with the  $\pi$ -electrons interacting to form weak bonds shown below by dotted lines while maintaining a minimum fixed distance. When cyclohexane is mixed the molecules of the two orient themselves in a way that there is disruption in the intermolecular  $\pi$ - $\pi$  bonding of benzene ring currents, the two being identical in molecular shape and size. This explains the initial drop in ultrasonic velocity. On increasing the concentration of



Stacking of benzene ring

either, there is no such disruption of orientation (stacking), resulting in continuous increase in the velocity.

By increasing the mole fraction of cyclohexane in system (II) and benzene in system (III), the sound velocity is found to increase continuously, as evident from figures 2 and 3. The same trend is also predicted by FPT and SST. Moreover, the experimental curve is very much closer to the theoretical curves obtained from both the theories. Such behaviour is in agreement with the earlier findings [24, 25]. Thus, it may be concluded that both the statistical mechanical theories (FPT and SST) predict the same trend of composition dependence of sound velocity as observed experimentally in case of all the three systems under the present investigation.

It appears from the magnitude of standard deviations that SST has an edge over the FPT in all the three systems. The validity of SST in case of binary liquid mixtures depends on two factors. Firstly, this theory does not contain any adjustable parameters, although a criticism is generally raised against this theory. This is regarding the number of adjustable parameters  $E_s$ ,  $\theta$ ,  $V_s$ ,  $a$ , and  $\mu$  in the evaluation of partition functions. In these calculations the values of  $E_s$ ,  $\theta$ , and  $V_s$  are obtained from the solid state data, and  $\mu$  and  $a$  obtained through the relations:

$$\mu = ZV_s/V$$

and

$$a = [(n - 1)/2Z(V_m - V_s)^2]/V_m V_s.$$

Sound velocity in binary liquid mixtures

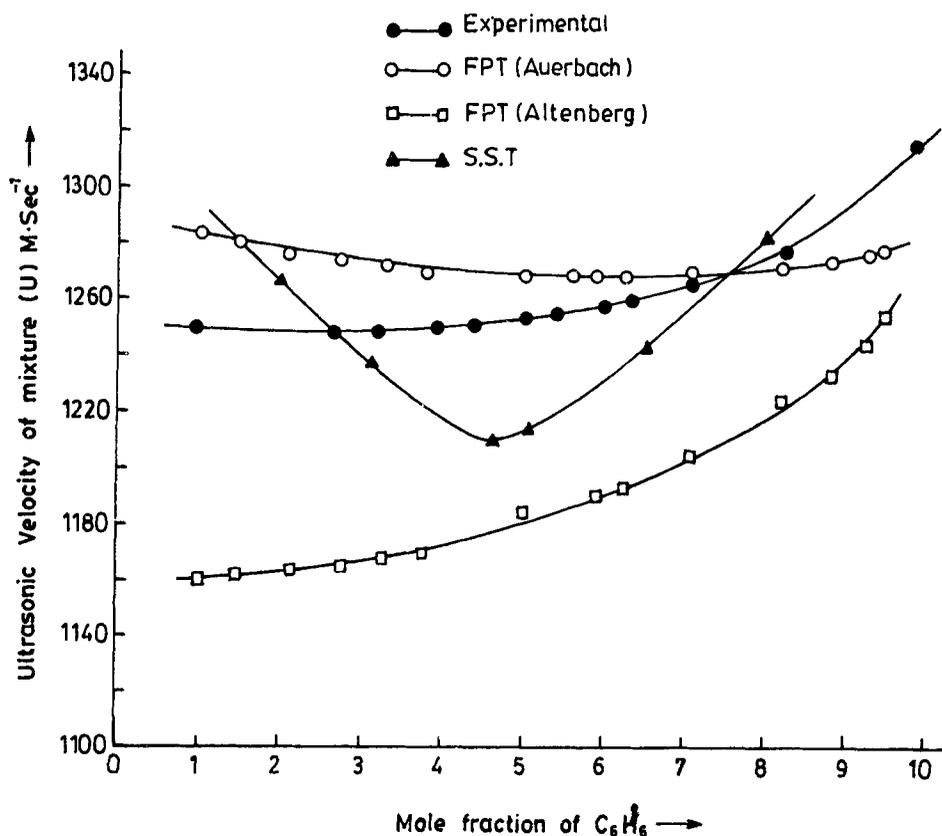


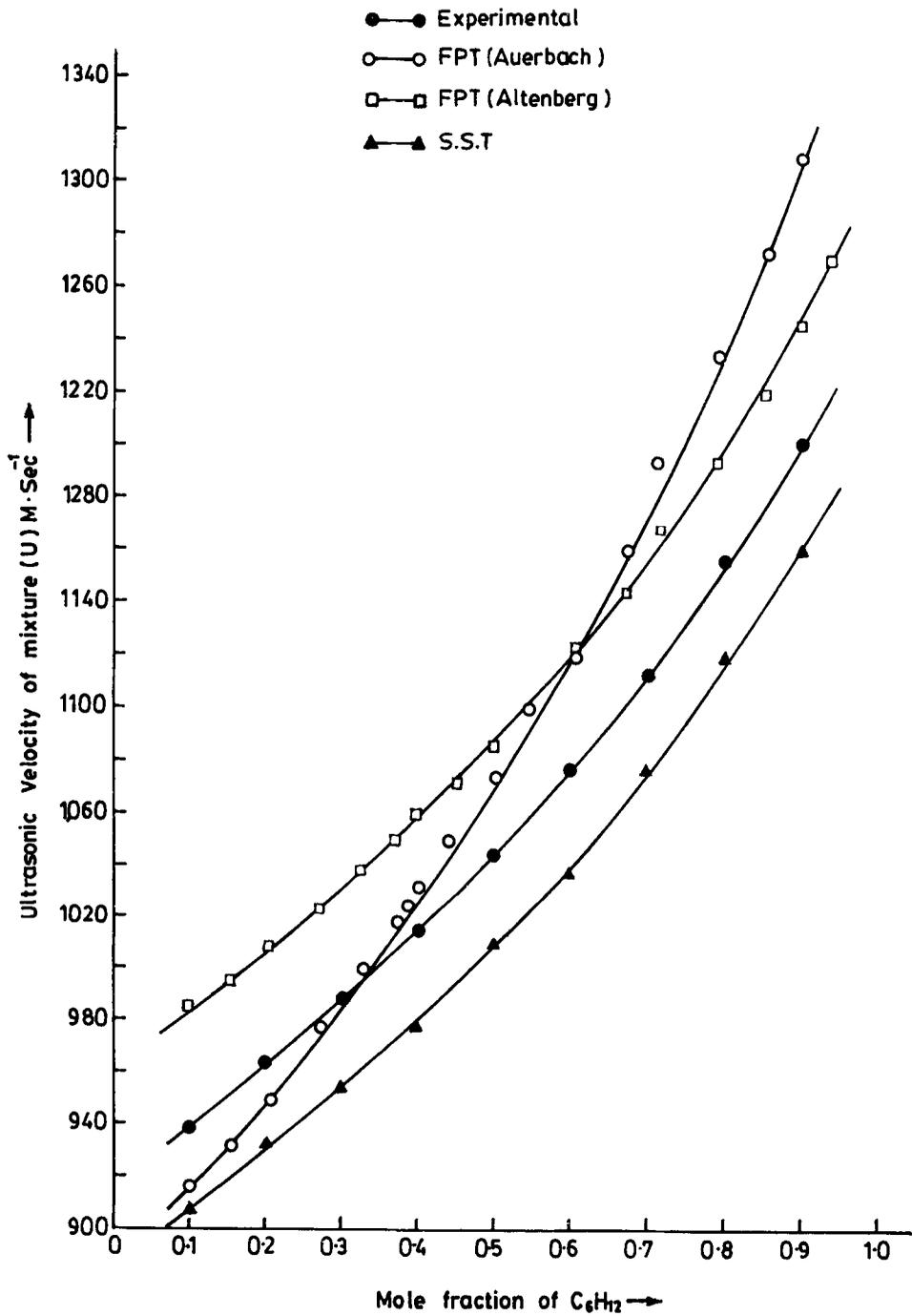
Figure 1. Variation of ultrasonic velocity of mixture  $C_6H_6 + C_6H_{12}$  as function of mole fraction of benzene.

Thus, the introduction of adjustable parameters is avoided. Secondly, in formulating the partition functions, both solid like and gas like freedom have been considered, which gives an ideal representation of all the possible states. On the other hand, FPT contains one adjustable parameter i.e. the fraction of nearest neighbours which a molecule loses on moving from the bulk of the liquid to the surface,  $M$ . In the present case the value of  $M$  has been taken to be 0.28. However, it can vary from 0.26 to 0.31 [15, 17]. Another reason of discrepancy in FPT may be due to the use of empirical relations of Auerbach and Altenberg in transforming surface tension to sound velocity [23]. Although these relations have been well verified for liquid mixtures [16, 23]. Despite these facts FPT gives reasonable agreement with observed sound velocity values and its composition dependence for all the three systems (I), (II) and (III).

For most of the liquid mixtures the temperature dependence of ultrasonic velocity is given by,

$$u = \left( \frac{\Delta u}{\Delta t} \right) t + u_0. \quad (9)$$

Here,  $\Delta u/\Delta t$  is the temperature coefficient of ultrasonic velocity and  $u_0$  is the sound velocity at  $0^\circ C$ . It has been shown quite early by Rao [26] and verified by several workers that the following expression holds approximately true for many liquid



**Figure 2.** Variation of ultrasonic velocity of mixture C<sub>6</sub>H<sub>12</sub> + CCl<sub>4</sub> as a function of mole fraction of cyclohexane.

Sound velocity in binary liquid mixtures

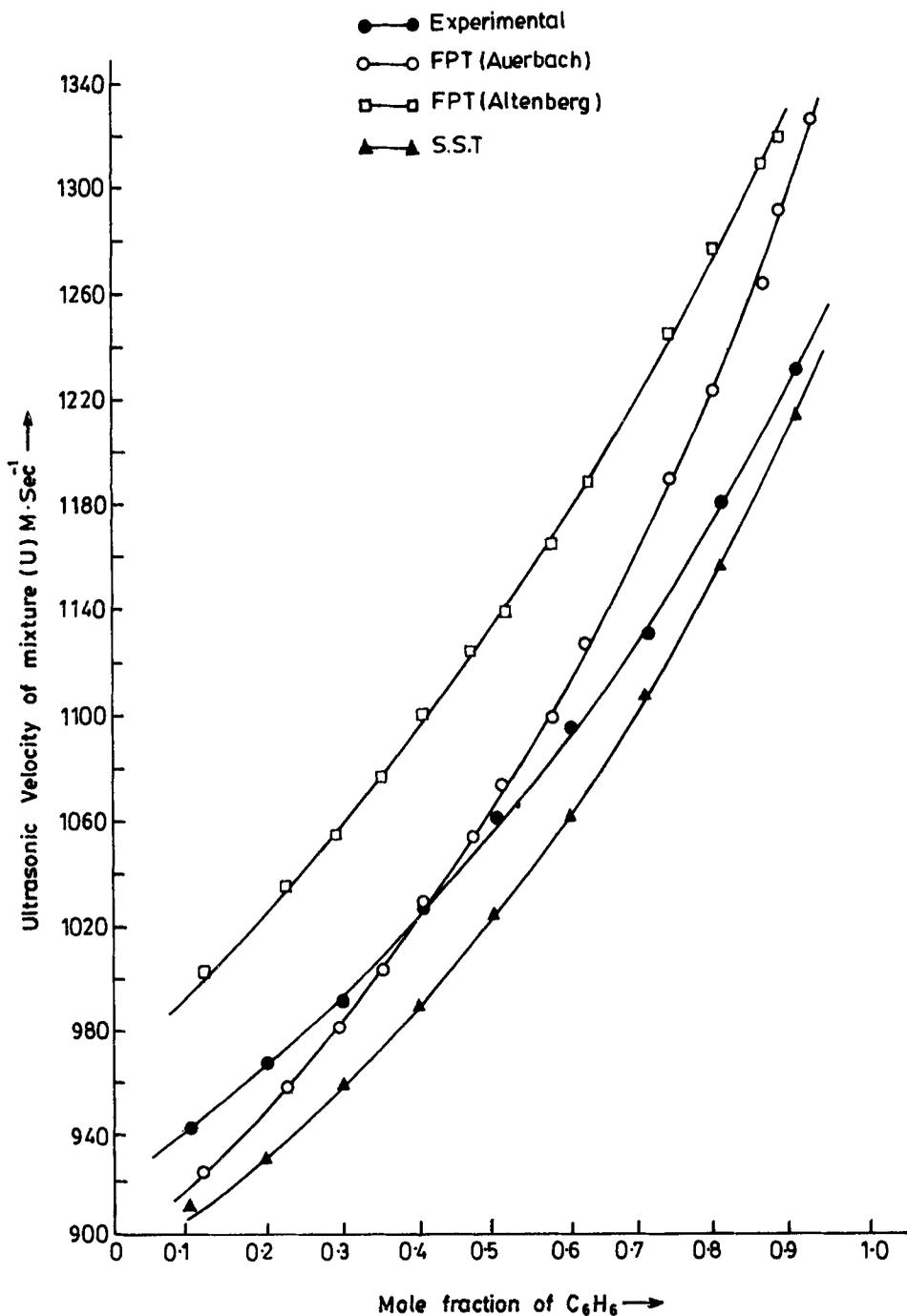


Figure 3. Variation of ultrasonic velocity of mixture C<sub>6</sub>H<sub>6</sub> + CCl<sub>4</sub> as a function of mole fraction of benzene.

systems:

$$\frac{1}{u} \frac{\partial u}{\partial t} \approx 3 \left( \frac{1}{\rho} \right) \left( \frac{d\rho}{dt} \right). \quad (10)$$

Since the density of liquid mixture decreases by increasing the temperature, the ultrasonic velocity will decrease by increasing the temperature. The temperature coefficient of ultrasonic velocity ( $\Delta u/\Delta t$ ) in (9) is always negative for mixtures except aqueous mixtures where the situation is complicated. In the case of pure water the temperature corresponding to minimum in sound velocity shifts by the addition of other component. This is related with structural changes [27–28].

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