

Ultrasonic absorption in binary liquid mixtures

N PRABHAKARA RAO and K C REDDY

Department of Physics, S. V. University, Tirupati 517502

MS received 20 August 1976; in revised form 18 November 1976

Abstract. Ultrasonic absorption in binary liquid mixtures containing benzene, chloroform, cyclohexane and toluene with triethylamine, a rotational isomeric relaxing liquid, as a common component has been studied at a frequency of 7.56 MHz. A pulse technique has been used for the measurement of absorption with an accuracy of $\pm 5\%$. Bauer-Sette formula has been used to calculate the absorption of these liquid mixtures at different concentrations. The theoretical values evaluated on the basis of Bauer-Sette theory appear to have good agreement with experimental values. In view of the discrepancy pointed out by Mallikarjuna Rao and Suryanarayana, the mixtures of benzene and ethylacetate have been studied in this context and found the theoretical values coinciding with experimental values.

Keywords. Ultrasonic absorption; Bauer-Sette theory; triethylamine; benzene; chloroform; cyclohexane; toluene; ethylacetate.

1. Introduction

The study of ultrasonic absorption in binary liquid mixtures of unassociated liquids has been undertaken by several investigators. This study leads to an understanding of the mechanism of absorption in each liquid. Pinkerton (1949) and Bauer (1949) gave a theoretical interpretation of ultrasonic absorption in binary mixtures of unassociated liquids with different absorption coefficients. Sette (1950) eliminating some of the simplifying assumptions made by Bauer, obtained an equation which is equally applicable to liquid components of mixtures whose absorption coefficients are of the same magnitude. The theory of Bauer and Sette (known as Bauer-Sette theory) is applicable in the case of binary liquid systems containing two unassociated, non-interacting and vibrationally relaxing liquid components. However the Bauer-Sette theory has been holding good for the binary mixtures in which one of the components exhibit rotational or ring inversion relaxation (Venkateswarlu and Sivarama Sastry 1970, Sivarama Sastry and Venkateswarlu 1973, Prabhakara Rao and Reddy 1977). Mallikarjuna Rao and Suryanarayana (1976) studied absorption in benzene-ethylacetate mixtures, in which ethylacetate exhibits rotational isomeric relaxation and found large disagreement with experimental and theoretical values. In the present investigation, absorption measurements were carried out in binary liquid mixtures of benzene, chloroform, cyclohexane and toluene with triethylamine (a rotational isomeric relaxing liquid having ultrasonic relaxation frequency 111 MHz at 30°C) as a common component and of benzene with ethylacetate. The results are discussed in the light of the Bauer-Sette theory.

2. Experimental

The ultrasonic absorption measurements were made in the liquid mixtures at a frequency $\nu = 7.56$ MHz by using a conventional pulse technique. The block diagram of the experimental set up is shown in figure 1. X-cut quartz crystals of one inch dia having fundamental frequency 0.5 MHz have been used for transmitting and receiving transducers. These crystals were mounted on two fused quartz rods which act as both delay lines and provide temperature isolation. A double walled glass cell was mounted on the lower quartz rod to which the transmitting crystal was attached. The quartz delay line at the receiving side is of 12 cm long. The accuracy of the precision micrometer for the measurement of path length is 0.0001 cm. The receiving crystal with the quartz rod attached to the micrometer moves along a vertical axis while the stationary crystal was aligned to this direction by proper levelling screws. Water, whose temperature was controlled by a U-10 thermostat was circulated between the walls of the cell. The liquid in the cell was constantly stirred (magnetically) to avoid the temperature gradients. The temperature of the liquid in the cell was measured by using a glass bead thermister and was found constant to within $\pm 0.1^\circ\text{C}$.

Arenberg PG-650-C pulsed R.F. oscillator was used to excite the transmitting crystal. The R.F. pulses used were about $10\ \mu\text{sec}$. long and had repetition frequency 60 cycles per sec. Output from the receiving crystal, after preamplification, was passed through a wide band amplifier and then fed to a Tektronix oscilloscope. The comparison signal was taken from the potential divider at the output of the pulsed oscillator and passed through a precision attenuator. The

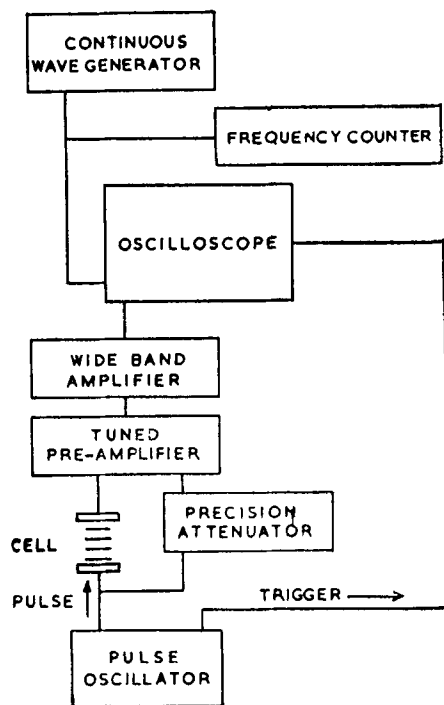


Figure 1. Block diagram of the pulse technique.

output from the attenuator followed the same path as that of the acoustic pulse from the receiving crystal. The frequency of the pulsed signal was measured by beating it with a signal from CW generator. The uncertainty in the absorption measurements is estimated to be of the order of $\pm 5\%$.

3. Theoretical

It has been fairly established that in a pure liquid, the absorption coefficient depends on the efficiency of deexcitation of the excited molecules when they collide with the unexcited molecules of the liquid. In a mixture of molecules of two liquids A and B , there will be collisions of the type (A^*A) (B^*B) (A^*B) and (B^*A) (where A^* and B^* represent excited molecules of A and B respectively). If liquid A has a large absorption coefficient than liquid B collisions (B^*B) are more efficient in deexcitation than (A^*A) collisions; because the mean dispersion frequency of A molecules ν_m^A is smaller than that of B molecules ν_m^B . When an excited molecule (A^* or B^*) strike against a molecule of a different kind (B or A respectively) the collision has a higher deexcitation efficiency than the collision between two molecules of the same kind (A^*A) or (B^*B) . Bauer made the assumption that (B^*A) and (A^*B) type collisions are as efficient as (B^*B) type, in the mixtures of the type referred to above. He obtained an equation for the absorption coefficient α of binary liquid mixtures at a given concentration a as

$$(\alpha/\alpha_B)_a = (1 - fa) \left[(1 - a) + \frac{az}{z - a(z - 1)} \frac{C_A}{C_B} \right]. \quad (1)$$

Here α_B = the absorption coefficient of liquid B ; f = a constant; $z = \nu_m^B/\nu_m^A$; C_A and C_B are the molar vibrational specific heats.

But in a mixture where the absorption values of the two components are of the same order, the assumption made by Bauer no longer holds good. Sette has, therefore, modified the above equation taking into account that all the four types of collisions are distinctly different with regard to their efficiencies. He obtained an equation (popularly known as Bauer-Sette equation) for the absorption coefficient of the mixture at a particular concentration as

$$(\alpha/\alpha_B)_a = (1 - fa) \left[\frac{az C_A/C_B}{a + t(1 - a)} + \frac{1 - a}{1 + a(u - 1)} \right]. \quad (2)$$

The two additional parameters t and u stand for the ratios of vibrational relaxation times τ_{AA}/τ_{AB} and τ_{BB}/τ_{BA} respectively. The constant f can be evaluated by putting $\alpha = \alpha_A$ at $a = 1$. The parameters t and u can be calculated from the experimental values of absorption in two mixtures that are very rich in liquids A and B .

4. Results and discussion

The values of ultrasonic absorption α/v^2 at different concentrations in the binary liquid mixtures of benzene, chloroform, cyclohexane and toluene with triethylamine as a common component are given in tables 1, 2, 3, and 4 respectively.

Table 1. Variation of ultrasonic absorption coefficient with concentration in benzene-triethylamine mixture

Frequency = 7.56 MHz		Temperature = 32° C	
Mole fraction of benzene (a)	Absorption (α/v^2) $\times 10^{17}$ sec ² cm ⁻¹	Ratio of (α/a_B) experimental	Ratio of (α/a_B) calculated
0	380	1.000	1.000
0.112	327	0.860	0.909
0.191*	322	0.847	0.847
0.300	302	0.795	0.765
0.452	267	0.702	0.661
0.605	257	0.676	0.582
0.712	271	0.713	0.558
0.799	294	0.774	0.585
0.903	333	0.876	0.791
0.952*	449	1.132	1.132
0.981	661	1.739	1.641
1.000	914	2.405	2.405

* Concentrations at which the absorption values are taken to evaluate the parameters t and u .

Table 2. Variation of ultrasonic absorption coefficient with concentration in chloroform-triethylamine mixture

Frequency = 7.56 MHz		Temperature = 32° C	
Mole fraction of chloroform (a)	Absorption (α/v^2) $\times 10^{17}$ sec ² cm ⁻¹	Ratio of (α/a_B) experimental	Ratio of (α/a_B) calculated
0	380	1.000	1.000
0.092	319	0.839	0.857
0.201*	270	0.711	0.711
0.300	238	0.627	0.602
0.416	202	0.530	0.498
0.589	142	0.373	0.396
0.701	129	0.339	0.372
0.796	149	0.392	0.395
0.902*	196	0.516	0.516
0.959	260	0.684	0.697
1.000	370	0.974	0.974

* Concentrations at which the absorption values are taken to evaluate the parameters t and u .

The parameters needed to fit the theoretical curves based on eq. (2) to the experimentally observed data of the binary system are evaluated as follows.

The vibrational specific heat for benzene and triethylamine has been calculated using the Plank-Einstein relation

Table 3. Variation of ultrasonic absorption coefficient with concentration in cyclohexane-triethylamine mixture

Frequency = 7.56 MHz		Temperature = 32°C	
Mole fraction of cyclohexane (a)	Absorption (α/ν^2) $\times 10^{17}$ sec ² cm ⁻¹	Ratio of (α/α_B) experimental	Ratio of (α/α_B) calculated
0	380	1.000	1.000
0.104	352	0.926	0.912
0.198*	318	0.837	0.837
0.307	275	0.724	0.753
0.462	236	0.621	0.645
0.590	210	0.553	0.569
0.699	192	0.505	0.518
0.810	180	0.474	0.485
0.900*	183	0.482	0.482
0.952	194	0.511	0.498
1.000	205	0.539	0.539

* Concentrations at which the absorption values are taken to evaluate the parameters t and u .

Table 4. Variation of ultrasonic absorption coefficient with concentration in triethylamine-toluene mixture

Frequency = 7.56 MHz		Temperature = 32°C		
Mole fraction of triethylamine (a)	Absorption (α/ν^2) $\times 10^{17}$ sec ² cm ⁻¹	Ratio of (α/α_B) experimental	Ratio of (α/α_B) calculated from Equation (1)	Equation (2)
0	91	1.000	1.000	1.000
0.090*	167	1.176	1.235	1.176
0.179	144	1.582	1.467	1.427
0.275	166	1.824	1.720	1.727
0.342	187	2.055	1.900	1.945
0.437	212	2.330	2.163	2.260
0.563	249	2.736	2.533	2.684
0.699	284	8.121	2.973	3.146
0.799	325	3.571	3.332	3.487
0.907*	351	3.857	3.762	3.857
1.000	380	4.176	4.176	4.176

* Concentrations at which the absorption values are taken to evaluate the parameters t and u

$$C_{vib} = \sum R \left(\frac{h\nu_i}{kT} \right)^2 \frac{\exp(-h\nu_i/kT)}{[1 + \exp(+h\nu_i/kT)]^2} \quad (3)$$

where ν_i is a vibrational frequency of the molecule for a given mode. The values of ν_i for benzene are taken from Herzberg (1945) and for triethylamine from literature (Choudhuri 1937, Pace 1961). The vibrational specific heat for cyclohexane is obtained by subtracting the contribution of translational and rotational degree of freedom, namely $3R$, from the values of C_v , the specific heat at constant volume. Bauer's (1949) values of vibrational specific heat for chloroform and toluene have been used in the present calculation.

The mean dispersion frequency for benzene, chloroform and toluene were taken from Bauer (1949) and were assumed to be independent of temperature. For triethylamine and cyclohexane the mean dispersion frequencies were calculated by the method followed by Bauer (1949). The values of ν_m , C_A , C_B , f , Z , t and u used in the present investigation are given in table 5. The calculated and experimental values of the ratio of absorption (a/a_B) for these mixtures are presented in figures 2 to 6.

For the first three mixtures benzene, chloroform and cyclohexane are treated as liquid *A* and triethylamine as liquid *B*. In the case of benzene-triethylamine mixtures, benzene is more absorbing than triethylamine. Since a/a_B is less than one at some intermediate concentrations the Bauer-Sette formula has been used for the present calculations. In this mixture there is a maximum deviation of about 20% (at high concentration region of benzene), between the experimental and theoretical values. In the case of chloroform and cyclohexane though the absorption is smaller, the mean dispersion frequencies are also smaller than that of triethylamine. In general, it is considered that if *A* is more absorbing than *B*, then *AA** collisions are less efficient in deexcitation than *BB** collisions. But it is not the case in the mixtures of chloroform-triethylamine and cyclohexane-triethylamine. In Bauer-Sette theory the four types of collisions are treated distinctly different with regards to their efficiencies. Hence for these systems though the absorption of chloroform (almost equal) and cyclohexane are less, they are treated as liquid *A* and triethylamine as liquid *B*. In the case of benzene-triethylamine and cyclohexane-triethylamine mixtures the value of u obtained is less than unity. However the theory is holding good in both the mixtures.

Table 5. The parameter used in the calculation of ultrasonic absorption coefficient in binary liquid mixtures,

Liquid	Vib. Sp. ht C_A Cal/mole/°C	ν_m MHz	z	f	t	u
Benzene	12.9	1200	4.8	0.57	26.8	0.46
Chloroform	7.8	2230	2.6	0.47	11.3	1.35
Cyclohexane	25.6	1600	3.6	0.94	17.5	0.39
Toluene	13.6	7500	1.3	-2.77	0.22	0.68
Triethylamine (liquid <i>B</i>)	11.1	5806

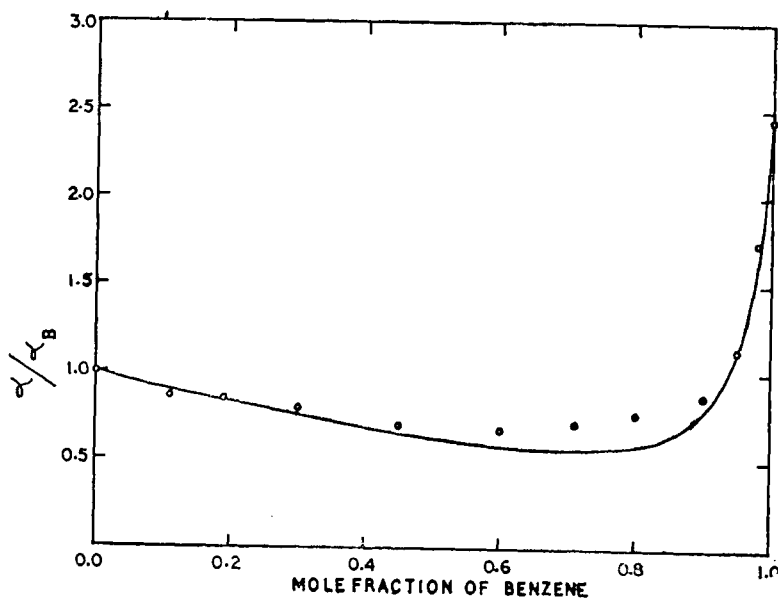


Figure 2. Ratio of the absorption coefficient of a mixture of benzene-triethylamine. Points represent experimental results and solid line represents theoretical curve.

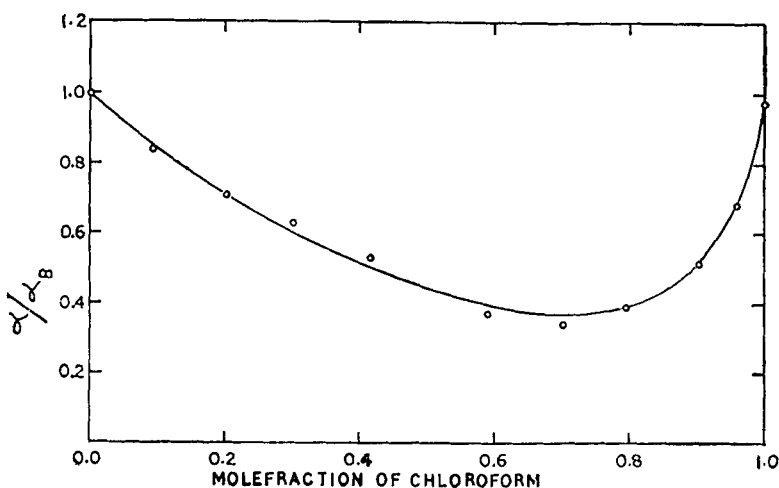


Figure 3. Ratio of the absorption coefficient of a mixture of chloroform-triethylamine. Points represent experimental results and solid line represents theoretical curve.

In triethylamine and toluene mixtures the experimental values of α/α_B are decreasing linearly with increase of concentration of toluene. For theoretical evaluation, triethylamine with high absorption and a rotational isomer is considered as liquid *A* and toluene with low absorption is considered as liquid *B*. In this case u cannot be calculated from the mixture that is rich in liquid *B* directly because at mole fraction, $a = 0.09$ the contribution to α/α_B from the quantity containing the term t is about 35%. This leads to a large error in the evaluation of the parameter u . Hence in the present calculations two α/α_B values, one at $a = 0.09$ and the other at $a = 0.907$, are taken and t and u are calculated by

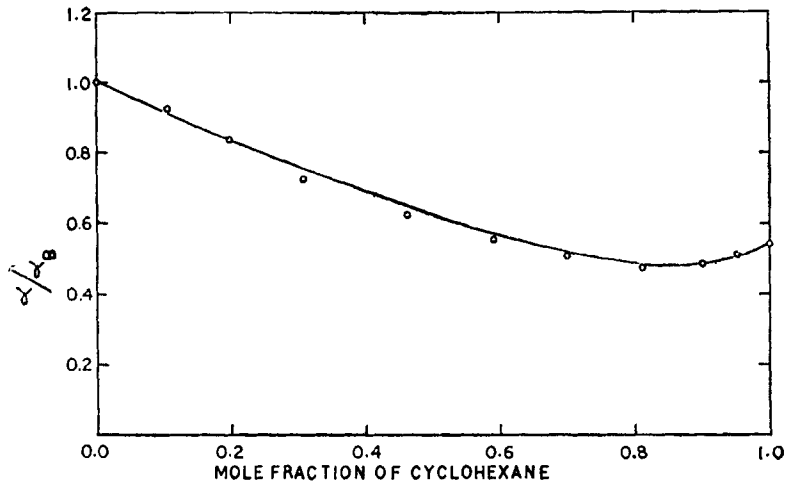


Figure 4. Ratio of the absorption coefficient of a mixture of cyclohexane-triethyl amine. Points represent experimental results and solid line represents theoretical curve.

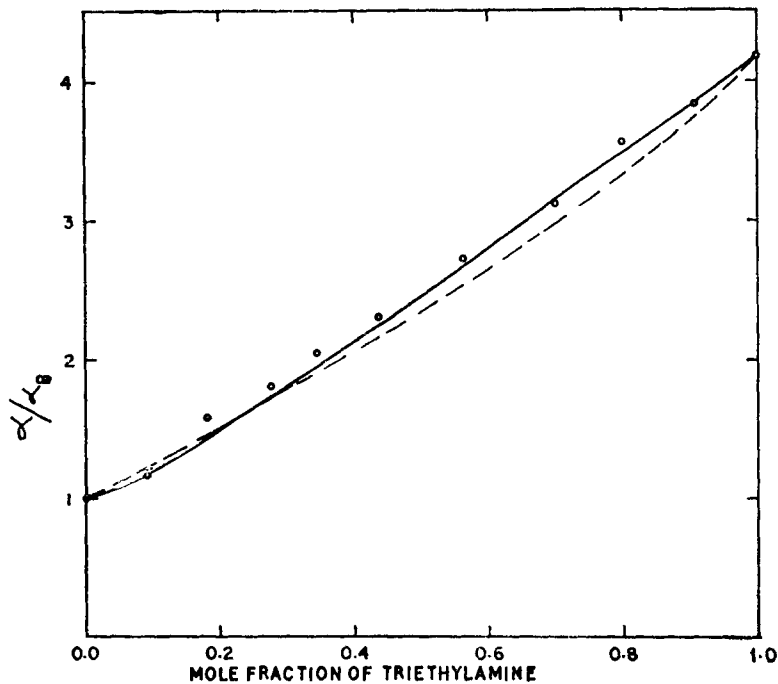


Figure 5. Ratio of absorption coefficient of a mixture of triethylamine-toluene. Points represent experimental results, broken line represents theoretical curve from eq. (1) and solid line represents theoretical curve from eq. (2).

solving two simultaneous equations obtained from the formula (2). The α/α_B values for this mixture are also calculated using eq. (1) and are presented in table 4 and figure 5. It is noticed that close agreement has been found between the experimental values and calculated values from eq. (2). Here the t value is less than unity which means that AA collisions are more efficient than AB collisions.

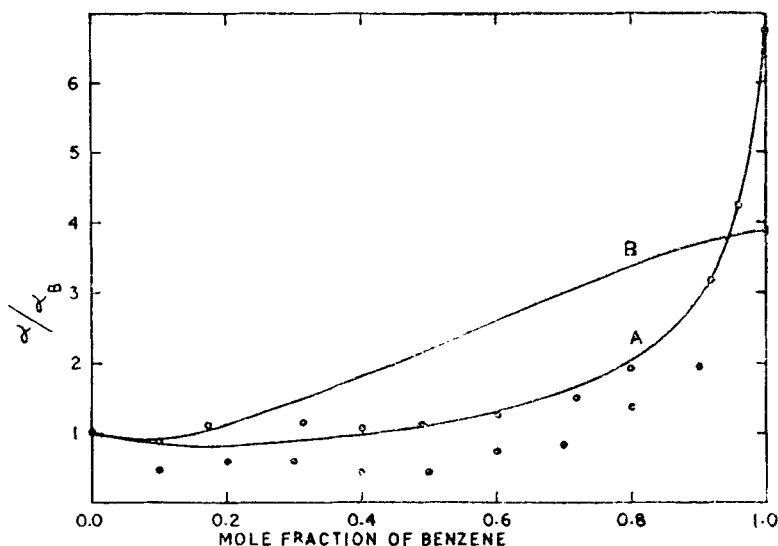


Figure 6. Ratio of absorption coefficient of a mixture of benzene-ethylacetate. Open circles and solid line *A* represent experimental points and theoretical curve. Closed circles and solid line *B* represent experimental points and theoretical curve of Mallikarjuna Rao and Suryanarayana (1976) at 1.2 MHz.

It is interesting to see that the Bauer-Sette theory is holding good for mixtures in which triethylamine is one of the components exhibiting rotational isomeric relaxation. Similarly good agreement has also been found between theory and experiment in the case of cyclohexanol mixtures (Prabhakara Rao and Reddy 1977). Sivarama Sastry and Venkateswarlu (1970, 1973) have studied the binary systems of 1,2-dichloropropane and 1,2-dichloroethane and verified the validity of Bauer-Sette theory. In their calculations, they have used the rotational isomeric relaxation frequency for the mean dispersion frequency, under the assumption that the deexcitation in a binary collision takes place through the lowest mode. In contrast Mallikarjuna Rao and Suryanarayana (1976) studied the benzene ethylacetate system and found a large disagreement between the experimental and theoretical values.

In view of the above-mentioned discrepancy, in the present investigation, benzene and ethylacetate mixtures at 30°C have been studied at a frequency of 7.56 MHz. For ethylacetate values of vibrational specific heat (11.6 cal mol⁻¹ °C⁻¹) and mean dispersion frequency (85800 MHz) calculated by Mallikarjuna Rao and Suryanarayana (1976) have been used in the present theoretical evaluation of α/α_B . In this case at a concentration $a = 0.101$, the contribution to α/α_B from the quantity containing the term t is about 25%. Hence t and u are evaluated by similar method followed in the case of triethylamine-toluene mixture. The parameters f , t and u obtained are 0.81, 20.6 and 3.11 respectively. The theoretical values of α/α_B calculated using these parameters are in good agreement with the experimental values (table 6). In this case experimental frequency 7.56 MHz is close to the relaxation frequency of ethylacetate 13.7 MHz, even then the experimental values of absorption coincide with Bauer-Sette theory which is based on the assumption of purely vibrational deexcitation of the concerned excited

Table 6. Variation of ultrasonic absorption coefficient with concentration in benzene-ethylacetate mixture

Frequency = 7.56 MHz		Temperature = 30°C	
Mole fraction of benzene (<i>a</i>)	Absorption (a/v^2) $\times 10^{17}$ sec ² cm ⁻¹	Ratio of experimental (a/a_B)	Ratio of calculated (a/a_B)
0	138	1.000	1.000
0.101*	118	0.855	0.854
0.173	152	1.100	0.823
0.310	158	1.145	0.871
0.401	146	1.058	0.962
0.489	156	1.130	1.090
0.602	173	1.253	1.317
0.717	206	1.493	1.658
0.797	265	1.920	2.022
0.917	440	3.188	3.181
0.960*	586	4.246	4.246
1.000	933	6.761	6.761

* Concentrations at which the absorption values are taken to evaluate the parameters *t* and *u*.

molecules. The theoretical curve and experimental points along with the values of Mallikarjuna Rao and Suryanarayana (at 1.2 MHz) have been presented in figure 6 for comparison.

Hence a thorough investigation has to be made in a number of liquid mixtures, in which one of the components exhibits a rotational isomeric relaxation, in order to prove the validity of Bauer-Sette theory. In fact the Bauer-Sette theory is valid for binary liquid mixtures containing two unassociated, noninteracting and vibrationally relaxing liquid components. A complete study of the application of Bauer-Sette theory to liquid mixtures, in which one of the components is a rotational isomeric relaxing molecule may throw some light on the mechanism of absorption in these mixtures.

Acknowledgement

One of us (NPR) is thankful to CSIR (India) for the award of a Fellowship.

References

- Bauer E 1949 *Proc. Phys. Soc. (London)* **A62** 141
 Choudhuri B K 1937 *Indian J. Phys.* **11** 203
 Herzberg G 1945 *Infra-red and Raman Spectra of Polyatomic Molecules* (Van Nostrand: New York) Chap. 3
 Mallikarjuna Rao S P and Suryanarayana M 1976 *Acustica* **35** 63
 Pace R J, Williams J W and Williams R L 1961 *J. Chem. Soc.* **83**, 2196
 Pinkerton J M M 1949 *Proc. Phys. Soc. (London)* **A62** 129
 Prabhakara Rao N and Reddy K C 1977 *Acustica* **37** (to be published)
 Sette D 1950 *Nuovo Cimento* **7** 318
 Sette D 1950 *J. Chem. Phys.* **18** 1592
 Sivarama Sastry G and Venkateswarlu M 1973 *J. Acoust. Soc. India* **1** 75
 Venkateswarlu M and Sivarama Sastry G 1970 *Acustica* **23** 261