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ULTRASONIC BEHAVIOUR OF BINARY LIQUID MIXTURES CONTAINING *n*-OCTANOL AS A COMMON COMPONENT

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Ultrasonic wave propagation in binary liquid mixtures of benzene, tolune, *O*-xylene and ethyl-benzene in *n*-octanol was studied at 313.16 K. The compressibilities, available volumes, freelengths, relative associations, molar sound velocities and molar compressibilities were calculated from the density and velocity measurements. The systems studied show non-ideal behaviour and the deviations from linearity are explained on the basis of molecular dissociation of *n*-octanol in the solvents. The sound velocities in these systems have also been calculated theoretically, based on the Free Length Theory (FLT) due to Jacobson and Collision Factor Theory (CFT) due to Schaaffs.

Introduction

The non-linear variation of ultrasonic velocity and compressibility throws much light on the structural changes occurring in a liquid, as its concentration is varied in a mixture. This method has the ability of characterising the physicochemical behaviour of liquid systems. Molecular association, dissociation in a liquid mixture as well as some important relations with the other parameters such as available volume, free lengths, relative associations, isothermal and adiabatic compressibilities etc, can be studied by ultrasonic measurements. The molar sound velocities (R) [1] and molar compressibilities (W) [2] gives information on the formation of a complex, molecular association and dissociation of the components. The sound velocities in binary mixtures can be calculated theoretically at different concentrations from the JACOBSON'S *Free Length Theory* (*FLT*) [3] and also from *Collision Factor Theory* (*CFT*) [4] due to SCHAAFF'S. Both the theories have been applied successfully by many workers [5–11].

A survey of the literature has shown that, more amount of work has been carried with lower aliphatic alcohols where as a little amount of work is attempt-

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ed with higher alcohols. Hence we report new experimental data for sound velocities and allied parameters of binary mixtures of *n*-octanol with benzene, tolune, *O*-xylene and ethylbenzene. The sound velocities were also calculated theoretically using *FLT* and *CFT* for these mixtures and the results were compared with the experimental data.

Theoretical

From the measured ultrasonic velocity (U) and density (ϱ) measurements, the adiabatic compressibilities can be calculated using the Laplace equation

$$\beta_{ad} = (U^2 \varrho)^{-1}. \tag{1}$$

The free lengths in the liquids can be calculated from the JACOBSON'S equation (2)

$$L_f' = \frac{K}{U \varrho^{1/2}} = K(\beta_{ad})^{1/2}, \tag{2}$$

where K is a temperature dependent constant ($K = 642$ at 313.16 K). In the case of mixtures free lengths can be calculated as

$$L_f^{M'} = \frac{K}{U_{\mathrm{mix}} \varrho_{\mathrm{mix}}^{1/2}}. \tag{3}$$

The free lengths in pure liquids or mixtures can also be calculated without involving velocity data using the relation

$$L_f = \frac{2V_a}{Y} = \frac{2(V_T - V_0)}{Y}, \tag{4}$$

where V_a is the available volume per mole V_T and V_0 are the molar volumes at the temperature T and absolute zero, respectively, Y is the surface area per mole of the liquid and is given by $Y = (36\pi N V_0^2)^{1/3}$, where N is Avogadro's number. From the knowledge of the pure liquids, the ideal free lengths $\supset L_f^M \supset$ in mixtures at different concentrations may be evaluated from the equation

$$L_f^M = \frac{2V_a^M}{X_A V_A + V_B Y_B}, \tag{5}$$

where X_A and X_B are mole fractions, Y_A and Y_B are surface areas per mole of the components A and B, respectively.

The relative association (*R.A.*) of the liquids or liquid mixtures [12] may be evaluted from the relation

$$R.A. = (L_f^{M'} / L_f^M)^3. \tag{6}$$

The molar sound velocities (R) and molar compressibilites (W) of the pure liquids as well as mixtures can be calculated by using the Eqs. (7) and (8) which are as follows:

$$R = (M/\varrho)\,V^{1/3}\,, \tag{7}$$

$$W = (M/\varrho)\,\beta_{ad}^{-1/3}\,, \tag{8}$$

where M is the molecular weight.

For the theoretical evaluation of velocities in pure liquids or binary mixtures, in addition to JACOBSON'S *Free Length Formula*, SCHAAFF'S *Collision Factory Theory* [4] may also be used. Schaaff presented the following formula for velocities in pure liquids

$$U = U_\infty s r_f = U_\infty SB/V\,, \tag{9}$$

where $U_\infty = 1600$ m/s, S is the collision factor and B is the actual volume of the mole given by

$$B = (4/3)\,\pi r^3 N\,. \tag{10}$$

The molecular radius r may be calculated from the formula due to SCHAAFF'S [4] and also GOPALA RAO and VENKATASESHAIAH [12] NUTACH-KUHNKIES [9] extended the theory to binary mixtures as

$$U_{\text{mix}} = U_\infty (X_A S_A + X_B S_B)\,(X_A B_A + X_B B_B)/V_{\text{mix}}\,, \tag{11}$$

where S_A and S_B are collision factors and B_A and B_B are the actual volumes of the pure components A and B respectively.

Experimental

Ultrasonic velocities were determined using a single crystal interferometer working at a fixed frequency of 2 MHz with an accuracy of $0.01^0/_0$. Densities were measured using a double stem pyknowmeter having capillaries of narrow bore and the open ends which were fitted with "Teflon Caps" in order to prevent evaporation. The accuracy in density determination is 1 in 10^5 parts. All the measurements were made at a constant temperature 313.16 K, maintained to an accuracy of ±0.01 K.

Results and Discussion

From the measured ultrasonic velocites and densities the available volumes, adiabatic compressibilities, free lengths relative associations, molar sound velocities and molar compressibilities were calculated for the binary mixtures of *n*-octanol with benzene, tolune *O*-xylene, and ethylbenzene and the results are given in Table 1. The ultrasonic velocities, free lengths and adiabatic compressibilities of the mixtures studied are polted against mole fraction of the alcohol component $B(X_B)$ in Fig. 1. From the free lengths and surface areas of the pure components, the free lengths and sound velocities of mixtures were evaluated. From *CFT*, the collision factors for the pure liquids were calculated and are used in evaluating sound velocities in mixtures. Molecular radii were calculated from both the formulas due to SCHAAFF'S [4] and GOPALA RAO and VENKATASESHAIAH [12] and the mean is employed in the evalution of actual volume. The mean values of molecular radii and collision factors of; pure liquids are presented in Table 2. The sound velocities calculated theoretically are presented in Fig. 1 along with the experimental data.

The ultrasonic velocity, free length and compressibility curves of all the systems studied show a non-linear variation with mole fractions of *n*-octanol H_B. The curves have not exhibited any maximum in velocity or any dip in compressibility thereby indicating the absence of complex formation [13]–[15]. This will also be further evidenced by the following points of discussion.

The deviations from linearity in the binary mixtures are attributed mainly due to *a* the formation of complexes and *b* the molecular assotiation by weak bonds, if the deviations in free lengths are negative. If the deviations are negative in velocity curves and positive in free length curves, they are attributed to the molecular dissociation of an associated species caused by the addition of an inert solvent or an active solvent producing considerable, dissociation. In addition to these effects, non-lineartics can also be attributed to size difference of molecules and the difference of the boiling points of solute solvent. In the present systems absence of sudden variation in the curves of velocity and comperessibility indicates absence of complex formation.

The observed non-lineartics in velocity, free length and compressibility curves can be explained as follows. There is considerable evidence to show that

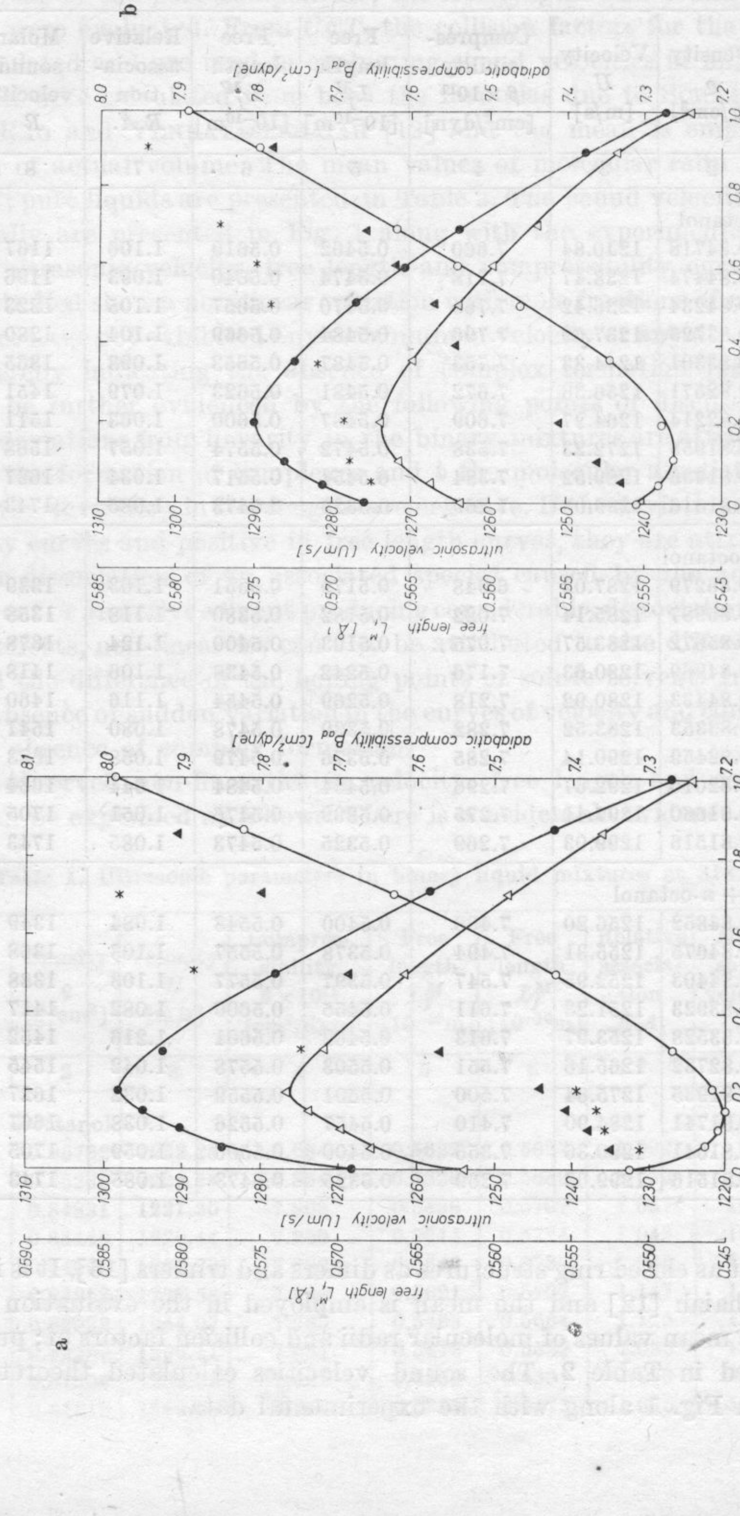
Table 1. Ultrasonic parameters in binary liquid mixtures at 313.16 K

Mole fraction X_B	Density ϱ [g/cm^3]	Velocity U [m/s]	Compressibility $\beta \times 10^{11}$ [cm^2/dyn]	Free length L_f^M [10^{-10}m]	Free length $L_f^{M'}$ [10^{-10}m]	Relative association *R.A.*	Molar sound velocity R	Molar compressibility W
1	2	3	4	5	6	7	8	9
benzene + *n*-octanol								
0.0000	0.85762	1232.25	7.684	0.5622	0.5627	1.002	977	2538
0.0532	0.85230	1222.25	7.854	0.5629	0.5689	1.032	1014	2635
0.1004	0.84831	1221.30	7.903	0.5638	0.5707	1.037	1050	2725
0.1501	0.84448	1220.44	7.950	0.5644	0.5724	1.043	1087	2820
0.2005	0.84098	1221.60	7.982	0.5646	0.5735	1.048	1125	2917
0.2991	0.83952	1227.58	7.904	0.5621	0.5707	1.147	1195	3096
0.4976	0.82992	1244.07	7.785	0.5463	0.5664	1.115	1348	3485
0.6935	0.82289	1266.11	7.581	0.5418	0.5589	1.098	1502	3875
0.8458	0.81906	1282.56	7.422	0.5359	0.5331	1.099	1620	4176
1.0000	0.81516	1299.03	7.269	0.5325	0.5473	1.085	1743	4486

Table 1 — cont.

Mole fraction X_B	Density ϱ [g/cm^3]	Velocity U [m/s]	Compressibility $\beta \times 10^{11}$ [cm^2/dyn]	Free length L_f^M [10^{-10}m]	Free length $L_f^{M'}$ [10^{-10}m]	Relative association *R.A.*	Molar sound velocity R	Molar compressibility W
1	2	3	4	5	6	7	8	9
tolune + *n*-octanol								
0.0000	0.84718	1240.84	7.660	0.5462	0.5619	1.106	1167	3028
0.0513	0.84474	1238.47	7.718	0.5474	0.5640	1.093	1196	3100
0.1017	0.84234	1236.42	7.765	0.5470	0.5657	1.105	1223	3170
0.2023	0.83725	1237.69	7.796	0.5484	0.5669	1.104	1280	3315
0.3613	0.83301	1244.33	7.753	0.5487	0.5653	1.093	1365	3537
0.4973	0.82571	1256.38	7.672	0.5481	0.5623	1.079	1451	3748
0.5985	0.82214	1264.27	7.609	0.5487	0.5600	1.063	1511	3899
0.6947	0.81955	1272.23	7.538	0.5472	0.5574	1.057	1568	4042
0.8960	0.81436	1289.52	7.384	0.5454	0.5517	1.034	1687	4344
1.0000	0.81516	1299.03	7.269	0.5325	0.5473	1.085	1743	4486
O-xylene + *n*-octanol								
0.0000	0.86279	1287.02	6.948	0.5179	0.5351	1.103	1339	3477
0.0506	0.85987	1285.14	7.022	0.5182	0.5380	1.118	1358	3524
0.1029	0.85672	1283.57	7.075	0.5193	0.5400	1.124	1378	3574
0.2016	0.84969	1280.63	7.176	0.5242	0.5438	1.106	1418	3675
0.3052	0.84433	1280.92	7.218	0.5269	0.5454	1.116	1460	3779
0.5014	0.83353	1283.52	7.282	0.5339	0.5478	1.080	1541	3982
0.6972	0.82459	1290.14	7.285	0.5376	0.5479	1.058	1623	4185
0.7952	0.82016	1292.67	7.296	0.5404	0.5484	1.044	1664	4287
0.8994	0.81660	1297.41	7.275	0.5399	0.5476	1.051	1705	4390
1.0000	0.81516	1299.03	7.269	0.5325	0.5473	1.085	1743	4486
ethylbenzene + *n*-octanol								
0.0000	0.84852	1256.20	7.468	0.5400	0.5548	1.084	1349	3499
0.0538	0.84675	1255.31	7.494	0.5378	0.5557	1.103	1368	3547
0.1046	0.84403	1252.95	7.547	0.5397	0.5577	1.103	1388	3595
0.2018	0.83923	1251.23	7.611	0.5455	0.5600	1.082	1417	3668
0.2640	0.83528	1253.97	7.613	0.5462	0.5601	1.216	1452	3757
0.5005	0.82732	1265.16	7.551	0.5503	0.5578	1.042	1545	3990
0.6968	0.81935	1275.64	7.500	0.5501	0.5559	1.032	1627	4193
0.7985	0.81741	1284.90	7.410	0.5457	0.5526	1.038	1667	4294
0.8906	0.81641	1290.36	7.356	0.5400	0.5506	1.059	1705	4390
1.0000	0.81516	1299.03	7.269	0.5325	0.5473	1.085	1743	4486

alcohols exist as closed ring structures as dimers and trimers [16]. It is important to notice eshaiah [12] and the mean is employed in the evaluation of actual volume. The mean values of molecular radii and collision factors of; pure liquids are presented in Table 2. The sound velocities calculated theoretically are presented in Fig. 1 along with the experimental data.


b
adiabatic compressibility β_{ad} [cm²/dyne]
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
free length L_f [Å]
0.585
0.580
0.575
0.570
0.565
0.560
0.555
0.550
0.545
ultrasonic velocity [U m/s]
1310
1300
1290
1280
1270
1260
1250
1240
1230
0
0.2
0.4
0.6
0.8
1.0
mole fraction X_B
a
adiabatic compressibility β_{ad} [cm²/dyne]
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
free length L_f [Å]
0.590
0.585
0.580
0.575
0.570
0.565
0.560
0.555
0.550
0.545
ultrasonic velocity [U m/s]
1310
1300
1290
1280
1270
1260
1250
1240
1230
1220
0
0.2
0.4
0.6
0.8
1.0
mole fraction X_B

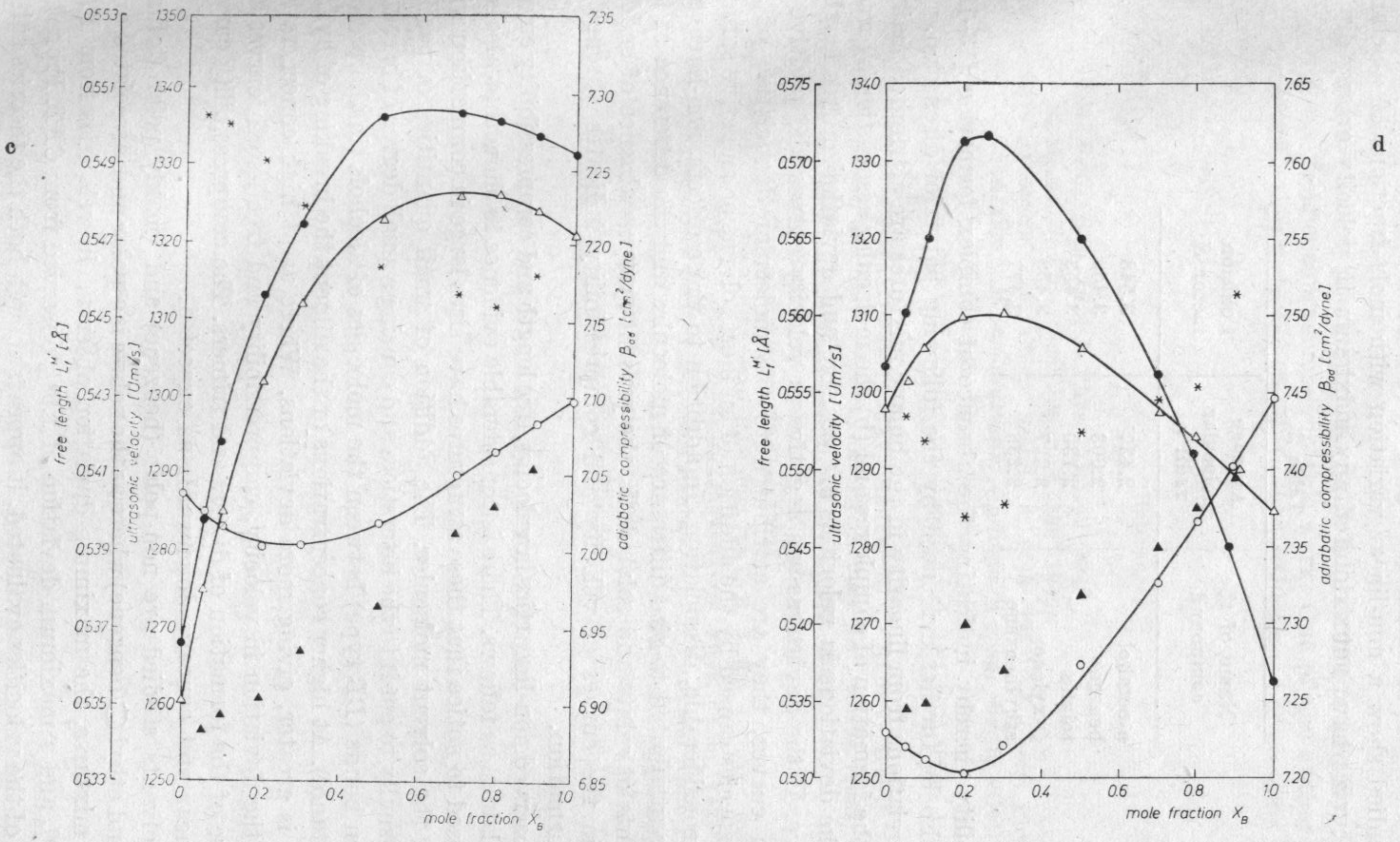


Fig. 1. Variation of ultrasonic velocity U (○○○), adiabatic compressibility (●●●), free-length $L_f^{M'}$ (▲▲▲), ultrasonic velocity calculated from *CFT* (△△△) and from *FLT* (∗∗∗) as a function of mole fraction (X_B) of alcohol in the systems: (a) benzene + *n*-octanol, (b) tolune + *n*-octanol, (c) *O*-xylene + *n*-octanol, (d) ethylbenzene + *n*-octanol

The ultrasonic velocity, free length and compressibility curves of all the systems studied show a non-linear variation with mole fractions of *n*-octanol (X_B). The curves have not exhibited any maximum in velocity or any dip in compressibility thereby indicating the absence of complex formation [13–15]. This will also be further evidenced by the following points of discussion.

Table 2

Name of the compound	Average molecular radii *r*	Collision factor *S*
n-octanol	2.437	3.548
benzene	2.003	3.459
tolune	2.130	3.453
O-xylene	2.227	3.458
ethylbenzene	2.238	3.471

The deviations from linearity in the binary mixtures are attributed mainly due to (a) the formation of complexes and (b) the molecular association by weak bonds, if the deviations in velocities are positive and deviation in free lenghts are negative. If the deviations are negative in velocity curves and positive in free length curves, they are attributed to the molecular dissociation of an associated species caused by the addition of an inert solvent or an active solvent producing considerable, dissociation. In addition to these effects, non-lineartics can also be attributed to size difference of molecules and the difference of the boiling points of solute and solvent. In the present systems absence of sudden variation in the curves of velocity and compressibility indicates absence of complex formation.

The observed non-lineartics in velocity, free length and compressibility curves can be explained as follows. There is considerable evidence to show that alcohols exist as closed to notice that these structures have sizes large in comparison with the size of the solvent molecules. The addition of small quantities of passive diluent is usually to get into the interstices and causing a small degree of breaking of hydrogen bonds (*BB* type) between the molecules of alcohols (in the present study *n*-octanol). At higher concentrations of the diluent the breaking of hydrogen bonds is greater, giving more deviations. Where as at high concentration of alcohol the deviation in velocity, compressibility and free length curves are less because of the formation of dimers and trimers. The compressibility curves are non-linear and concave downwards as expected.

The solvents studied are non-polar (benzene) and weakly polar (tolune, *O*-xylene and ethyl ⊂ benzene) where as the solute is a polar and associated one. In all the mixtures, the maximum deviation observed in velocities from *FLT* is about 3⁰/₀ and a maximum deviation of 1.9⁰/₀ observed from *CFT*. From the deviations of the velocities evaluated, it appears though both the theories suited well, however, *CFT*, has an edge over *FLT*.

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