

Direct acoustic impedance measurements of dimethyl sulphoxide with benzene, carbon tetrachloride and methanol liquid mixtures

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Ultrasonic impedance has directly been measured for various binary mixtures using a novel experimental technique. The mixtures are dimethyl sulphoxide with benzene, carbon tetrachloride and methanol at 295 K in different mole fraction ratios. The acoustic impedance of binary mixtures thus obtained was found to be in good agreement with those calculated from experimentally measured ultrasonic velocity and density values. It is shown that the new method can be used to replace the time consuming conventional method of measuring velocity and density separately and then calculating impedance from these two parameters.

Keywords: Ultrasonics, Acoustic impedance, Binary liquid mixtures

1 Introduction

Studies of liquid mixtures are of interest for both understanding of basic chemical processes and in industries. The molecular level interactions in binary and ternary liquid mixtures employing various methods like diffusion measurement technique by Raman spectroscopy¹, studying fluctuations in refractive indices² in liquid mixtures, dielectric relaxation method using microwave technique³ and ultrasonic methods⁴ have already been studied. For the past few decades, liquids have been studied extensively by both theoretical and experimental techniques using ultrasonic velocity measurements⁵⁻¹⁰ as an important measurement parameter. Knowledge of ultrasonic velocity and density of different mole fractions of solvent-solute mixtures can, further, be used to compute important thermodynamic functions like isentropic compressibility, intermolecular free length, molar sound velocity, molar compressibility, excess values of isentropic compressibility, intermolecular free length, and acoustic impedance. These functions have proved to be of immense value in predicting nature and strength of molecular associations in the liquid medium.

Acoustic impedance of a material is the opposition exerted by the medium to displacement of the medium's particles by the sound energy. It is important to measure acoustic impedance because studies have shown that in solvent mixtures when a molecular interaction occurs acoustic impedance exhibits a non-linear variation with increasing mole

fractions of solute. It has been found that the acoustic impedance gives a peak in conjunction with ultrasonic velocity maxima and isentropic compressibility minima. This is used as an essential tool to predict molecular level interactions in binary and ternary liquid mixtures.

The authors have proposed a new experimental technique for investigating molecular associations/interactions in binary and ternary liquid mixtures. The technique involves simultaneous evaluation of both ultrasonic velocity and density by measuring acoustic impedance of liquid mixtures directly at one instance itself. Almost all the analysis of liquids performed by researchers involve measuring ultrasonic velocity and densities separately. Ultrasonic techniques consist of reading ultrasonic velocity using a variable path single crystal interferometer and determining densities of various mole fractions of solute-solvent mixtures which in itself is a cumbersome process. The new technique is more precise, cost effective, and eliminates cumbersome determinations of densities of the test liquid mixtures each time the experiment has to be performed. The details of the new technique are described elsewhere¹¹.

In the present paper, the authors have made an attempt to study the effectiveness of the new experimental set-up by estimating acoustic impedances (Z) of some well documented solvent mixtures at different mole fractions. The values of Z obtained by the new technique were then compared with the experimental values of ultrasonic velocity

and density obtained in the laboratory, impedance values calculated from them. The three binary liquid mixtures chosen for the experiments are DMSO with benzene, DMSO with carbon tetrachloride and DMSO with methanol, the experiments are performed at 295 ± 0.1 K temperature.

2 Theory

The reflection coefficient R of ultrasonic wave is given by the following expression¹²:

$$R = \frac{(Z - Z_0)}{(Z + Z_0)} \quad \dots(1)$$

where Z_0 is the acoustic impedance of incident medium and Z is the acoustic impedance of reflecting medium (Fig. 1). The height of the echo signal H is proportional to the reflection coefficient R . If the echo height is H_a when reflecting medium is air and it is H_1 when reflecting medium is liquid in study, the ratio of two echo heights is given by the following expression.

$$\frac{H_a}{H_1} = \frac{(Z_a - Z_0)(Z_1 + Z_0)}{(Z_a + Z_0)(Z_1 - Z_0)} \quad \dots(2)$$

Since Z_a is negligible in comparison with Z_0 if the incident medium is metallic alloy, the Eq. (2) modifies to:

$$\frac{H_a}{H_1} = \frac{(Z_1 + Z_0)}{(Z_1 - Z_0)} \quad \dots(3)$$

Eq. (3) can be rewritten in terms of Z_1 as follows:

$$Z_1 = Z_0 \frac{H_a + H_1}{H_a - H_1}$$

Thus, if the acoustic impedance of the incident medium is known, the acoustic impedance of liquid can be calculated from this equation by substituting the values of echo heights of air and liquid.

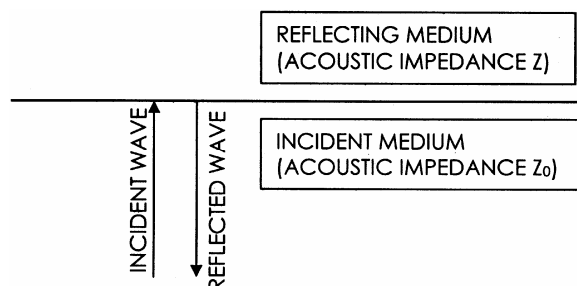


Fig. 1 — Schematic diagram for reflection coefficient

3 Experimental Details

Dimethyl sulphoxide used for the experiments was of S.D. Fine Chemicals make laboratory grade having a purity of 99.5% and was distilled before use. Benzene, carbon tetrachloride and methanol used for the experiments were of BDH make, Analar grade having 99.9% purity. No further purification was done as the purpose of the work is only to study the effectiveness of new method.

The binary mixtures were prepared by carefully weighing each liquid component in an airtight container which is previously washed, and dried; the test solvents were weighed in a Mettler electronic balance having a precision of 0.1 mg.

An Ultrasonic Instrument model Sonatest UFD 300 was used for all the measurements. The receiving output was displayed on Tektronix make digital storage oscilloscope. A 2 MHz frequency transducer was used for the entire experiment¹¹. The temperature was maintained by circulating water in the external jacket from a thermostatically constant temperature bath, the accuracy of which was tested to be $\pm 0.1^\circ\text{C}$.

The new experimental set-up consists of a 2 MHz transducer fixed underneath an aluminium plate. A cylindrical cell is placed over the aluminium plate just above the transducer to hold the test liquid mixture. The pattern of the reflected pulse changes each time the liquid in contact with the plate is changed. This forms the basis of analysis. Echo signals of ultrasonic pulses from the aluminium plate with empty cell was read each time right in the beginning of the experiment to check the reproducibility of the signal voltage which varied from 0.849 to 0.857 mV. The change in the pattern of the reflections is recorded in the form of a sonic echo signals. Measuring the amplitude height of the reflected echo signal in millivolts, is used to compute acoustic impedances of the various liquid mixtures.

The travel time for the arrival of reflected echoes through the liquid and the knowledge of the distance travelled by the pulse are used to calculate the ultrasonic velocity. Densities of the different mixtures are measured using a precise pycnometer.

4 Results and Discussion

The experimental values of densities and ultrasonic velocities of pure solvents used in the binary liquid mixtures are listed in Table 1. The experimental density values, the experimental ultrasonic velocities, the acoustic impedance values calculated from measured densities and ultrasonic velocities and the acoustic impedance values measured from new

Pure solvent component	Temperature °C	Ultrasonic velocity, ms^{-1}	Density kg/m^{-3}	Acoustic impedance $\text{Ns m}^{-3} \times 10^{-3}$
Dimethyl Sulphoxide	25	1487	1092	1624
Benzene	28	1292	879	1136
Carbon Tetrachloride	25	926	1594	1476
Methanol	25	1103	791	872

Mole fraction of DMSO	Density kg m^{-3} (experimental)	Ultrasonic velocity, ms^{-1} (experimental)	Acoustic impedance $\text{Nsm}^{-3} \times 10^{-3}$ (calculated)	Acoustic impedance $\text{Nsm}^{-3} \times 10^{-3}$ (experimental)
DMSO + benzene system				
0.1448	902	1298	1171	1007
0.3393	928	1330	1234	1047
0.6392	1008	1372	1383	1174
0.7321	1030	1385	1427	1215
DMSO + CCl_4 system				
0.2713	1415	1025	1450	1238
0.5273	1274	1293	1647	1398
0.6336	1239	1382	1712	1415
0.7567	1290	1397	1662	1450
DMSO + methanol system				
0.1177	986	1361	1342	1136
0.3035	990	1364	1350	1142
0.5202	1013	1421	1438	1228
0.6176	1028	1432	1473	1247

method are presented in Table 2 for DMSO-benzene system, DMSO-carbon tetrachloride system and DMSO-methanol system. The graphs of calculated acoustic impedance values and experimentally measured acoustic impedance values found by the new method as a function of concentration are shown in Figs 2-4.

It is significant to measure acoustic impedance as it directly indicates the pressure-velocity changes at a particular point in the nodal plane of the liquid mixtures. Acoustic impedance is read as one of the parameters to ascertain the formation of a heterogeneous molecular complex in liquid mixtures. Acoustic impedance is dependent on both material and its geometry and is complicated by the fact that the velocity and pressure are not necessarily in phase but exhibits efficient transfer of sound energy from point to point and therefore, serves further to describe solvent behaviour in altogether different perspective.

It is seen from Figs 2 to 4 that the acoustic impedance (Z) increases with increasing concentration in all the three systems at temperature 295 K,

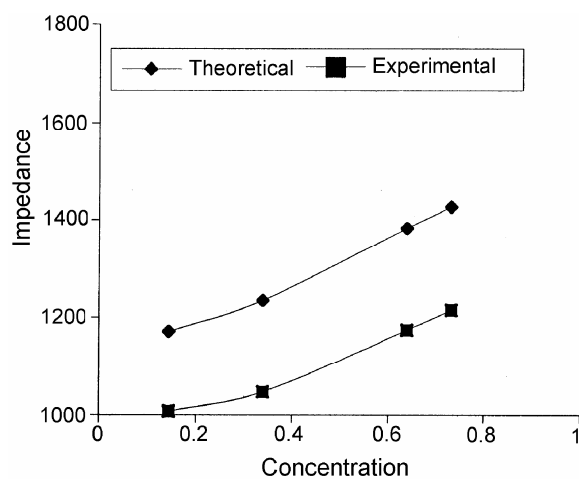


Fig. 2 — DMSO + benzene system

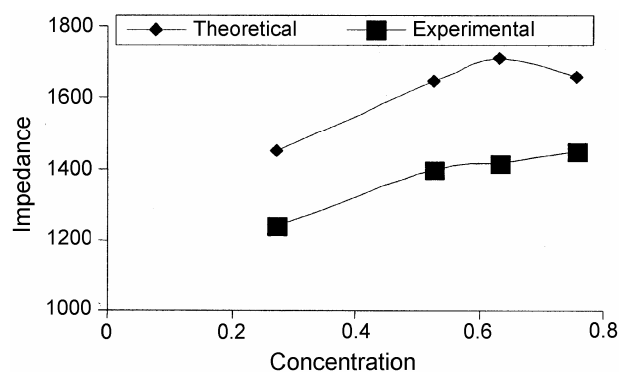
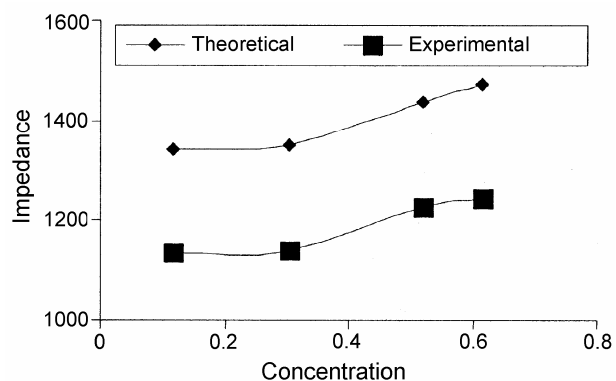
Fig. 3 — DMSO + CCl_4 system

Fig. 4 — DMSO + methanol system

which is in conjunction with the increase in values of ultrasonic velocity and densities of the above liquid mixtures reported earlier by Nikam *et al.*¹³ and Tiwari *et al.*¹⁴. The variation in acoustic impedance with concentration shows the same trend in both the cases i.e. in calculated Z values and the experimental Z values. It has been observed as shown in Figs 2 to 4 that the values of Z obtained by new method showed a

maximum of about 15% variation from the values of acoustic impedance calculated by ultrasonic velocity and density values.

The cause of 15% variation in calculated and available values could be attributed to the fact that the new method calculates the acoustic impedance using the simple expression for reflectivity $(Z_2 - Z_1)/(Z_2 + Z_1)$. This is best estimated only when the wave incident on interface is a plane wave. In the experimental set-up used in this paper, the wave incident until just one reflection can only be said as plane wave. This is because the near field extends only up to 33 mm for a 19 mm/2 MHz transducer in aluminium alloy. The thickness of aluminium base plate used in this experiment is 15 mm, which means that one round trip after a reflection is 30 mm. After that, divergence starts and the wave incident is not a plane wave. This seems to be a possible reason of getting lower value of impedance in all the cases. The situation can be improved by selecting high frequency transducer of larger diameter. This will, however, result in larger liquid cell. This will also give shorter echo heights, thus reducing the sensitivity. If one is interested only in trends in variation of ultrasonic velocity with temperature or concentration, it is better to use higher sensitivity as has been done in the present paper.

Here in the present context, it is significant to note that in no form the exact numerical values of velocities and densities of mixtures are important, these values in fact basically indicate the increasing or decreasing trends rather the trends exhibited by the various thermodynamic parameters are of concern. A deviation of ~15% is, therefore, not of much concern in this reference as it in itself may help to predict the molecular behaviour in liquid mixtures. It is suggested that this variation of ~15% may be employed as a correction factor in liquid mixture studies

Most of the liquid mixture studies, reported in literature, measure density using a pycnometer which is calibrated using low conductivity water of known density at a particular temperature. The pycnometer maintained at a set temperature condition is filled with the test liquid mixtures and the position of liquid levels is read using a travelling microscope. The density values are reported to show reproducibility of 0.1 kg/m^3 . It is of concern to mention here that in case of actual practical measurements, one may invariably encounter some deviance in density measurements.

Various physical parameters calculated from the measured ultrasonic velocity and density like isentropic compressibility, intermolecular free length,

molar sound velocity, molar association compressibility, available volume, excess properties of all these functions are used to know the molecular environments in liquid mixtures. It has been established¹⁵ that the non-linear variation of ultrasonic velocity with concentration shows occurrence of complex formation between unlike molecules. The molecular association becomes maximum where a velocity peak is obtained at a particular weight fraction. The derived parameters also show a consecutive non-linear behaviour with the concentration. These findings are employed to suggest the possible nature of associations like the presence of hydrogen bonding between the unlike components, molecular reactions due to dipole-dipole interactions, dipole-induced dipole reactions, charge-transfer reactions etc within the components.

The new technique presented altogether eliminates this cumbersome process of density measurements of various concentrations of liquid mixtures each time a velocity measurement is undertaken.

Further work is in progress to obtain more near results for acoustic impedance values so as to minimize the observed ~15% variance of Z values obtained from the new technique.

5 Conclusions

The purpose of this work is the need to further simplify the existing methods of studying molecular conditions in liquid mixtures. The simplicity of the new method, combined with the fact that the acoustic impedance is measured at one instance itself implies that the method has great potential in process industry. It could provide a quick online alternative for characterization of process liquids without physically taking the liquids to the laboratory, once a pocket size device is available based on the new technique.

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