



Ultrasonic Study of n-Butanol and N-N-Dimethyl Acetamide Binary Mixtures

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Received 28th January 2014; Revised 23rd February 2014; Accepted 10th June 2014

ABSTRACT

Density and viscosity, ultrasonic study for the binary mixtures of n-butanol and N-N-dimethyl acetamide over the entire concentration range were measured at temperatures 303.15 K. The experimental data then used to calculate the compressibility and acoustic impedance, molecular free length, inverse relaxation time, and excess parameters. The values of excess properties further fitted with Redlich–Kister polynomial equation to estimate the binary coefficients. The resulting excess functions were interpreted in terms of the interactions between the molecules in the binary mixtures.

Key words: Compressibility, Acoustic impedance binary mixtures, Excess parameters.

1. INTRODUCTION

The viscosity (η), density (ρ), and ultrasonic velocity (U) measurements find many applications in characterizing the physico-chemical behavior of liquid mixtures and in the study of molecular interaction. Such studies as a function of concentration are useful in gaining an insight into the structure and bonding of associated molecular complexes and other molecular processes. Further, they play an important role in many chemical reactions due to their ability to undergo self-association with manifold internal structures [1-5].

The ultrasonic velocity study is more important in understanding of behavior of binding forces between atoms and molecules of the liquid. The ultrasonic velocity has been adequately employed in understanding the nature of molecular interaction in pure liquids and their liquid mixture. These data are particularly important in the pharmaceutical, food, and flavor industries.

The process of studying the molecular interaction from the variation of thermodynamic parameters and their properties such as viscosity and excess values with composition of pure liquids and their binary liquid mixture are very useful to understand the thermodynamic and transport properties associated with heat and fluid flow which gives an insight into the molecular process [6]. This characterized behavior of the binary liquid mixtures have attracted the considerable attention due to their importance for both practical and theoretical point of view, since they are used in many application, like high performance liquid chromatography (HPLC), calorimetric, titration, pharmaceuticals etc., [5-10].

1.1. Theory

The specific acoustic impedance is given by,

$$Z = U \cdot \rho$$

Where “ U ” is the ultrasonic velocity (of the mixture) and “ ρ ” is the density of the mixture.

The adiabatic compressibility is given by,

$$\beta = 1/(U^2 \cdot \rho)$$

Where, “ U ” and “ ρ ” are the velocity and density of the liquid mixture.

The general formula for calculating the excess parameters is given below

$$A^E = A_M - (x_1 M_1 + (1-x_1) M_2)$$

Where, A^E is the excess parameter such as excess density x_1 mole fraction.

And the excess parameters are fitted by the Redlich-Kister polynomial equation [8] of third order and this equation is given by

$$A^E = x_1 x_2 \sum_{i=0}^n A_i (1 - 2x_2)^i$$

Where x_1 is the mole fraction of pure component 1 and 2.

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2. EXPERIMENTAL

2.1. Chemicals

In the present system of N-N-dimethyl acetamide (DMA), +n-butanol binary mixture DMA n-butanol and both are of HPLC grade. Both the liquids are used without further purification. The liquid mixtures of different compositions were prepared by measuring appropriate volumes of each composition.

2.2. Density Measurement

The density measurements were carried out by portable digital density meter (DMA-35, Anton Paar) for pure liquids and the binary mixture. This digital density meter uses the vibrating U-tube principle to calculate the density of the sample. The required quantity of sample is approximately 2 ml. (The temperature of the sample is controlled by environmental temp around U-tube/sample cell). The measured values of pure liquids are found to be in good agreement with standard values. Accuracy of the instrument used is $= 0.0001 \text{ g/cm}^3$. The instrument is calibrated by various pure liquids and found to be in good agreement with literature/standard values.

2.3. Viscosity Measurements

Viscosity of the sample in the present study was measured using Brookfield Viscometer (Brookfield Viscometer, Model: LV DV-II+ Pro, cone-plate model with CPE-40 spindle). The required sample is very low in quantity (0.5 ml). The device is calibrated using the doubly distilled water and other pure liquids of known viscosity at 25°C room temperature and found to be in good agreement with a standard value from the literature. The accuracy of the instrument is $= 0.01 \text{ cP}$. The sample cell of the instrument is double-walled, and electronically operated programmable constant temperature water bath is used to circulate water through the double-walled measuring cell made up of steel containing the experimental liquid at the desired temperature.

2.4. Ultrasonic Velocity Measurements

The ultrasonic velocity measurements are studied using Ultrasonic Interferometer (Model F-05, mittal enterprises, New Delhi). It is a single crystal interferometer operating at 2 MHz fixed frequency. The sample cell of the instrument is made up of steel and is double-walled; the required amount of the sample is approximately 10 cc. The sample cell is double-walled to maintain the temperature of the sample by circulating water through the walls. The programmable constant temperature water bath is used to maintain the temperature. The calibration of the instrument is performed using the double distilled water and some pure liquids of known values of ultrasonic velocity, and found to be in good agreement with standard values. The temperature of the sample is measured using a

digital thermometer (Fisher scientific) of the range -50°C - 150°C .

3. RESULTS AND DISCUSSION

Figure 1 gives excess molar volume of DMA+n-butanol. As concentration of n-butanol increases, excess molar volume becomes negative. Negative values indicate that volume contraction takes place upon mixing due to cross association between dissimilar molecules. Negative values also attributed to strong interaction between unlike molecules through hydrogen bonding.

Figure 2 gives an excess viscosity of DMA+n-butanol. Positive values of η^E for the mixture can be explained on the basis of complex formation between unlike molecules through hydrogen bonding. Charge transfer, hydrogen bonding forces leading to the formation of complex species between unlike molecules results in positive deviation. Positive deviation of η^E also indicates that the interaction between binary mixtures is strong.

As shown in Figure 3, excess velocity becomes positive, as concentration of n-butanol increases. Positive deviation and non-linear dependence suggest the presence of strong interaction between the components of the mixture positive excess

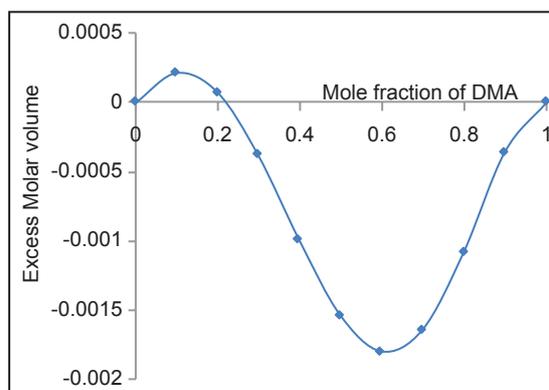


Figure 1: Excess molar volume of N-N-dimethyl acetamide+n-butanol.

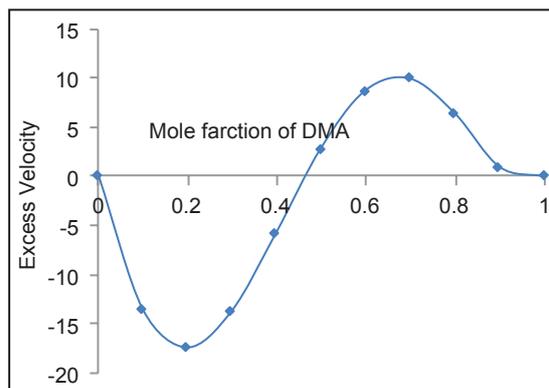


Figure 2: Excess viscosity of N-N-dimethyl acetamide+n-butanol.

velocity can be concluded as the formation of the structure. Strong interaction arises among the components of the mixture leading to the formation of molecular aggregates and more compact structure than sound will travel faster through the mixture by means of longitudinal waves and hence speed of sound with respect to linear behavior will be positive.

Figure 4 indicates excess compressibility of DMA+n-butanol. Negative excess compressibility of values is due to closed packed molecules, which accounts for the existence of strong molecular interaction between unlike molecules sign of compressibility plays vital role in assessing the compactness due to molecular interaction in liquid mixture through hydrogen bonding, charge transfer, dipole-dipole interactions and dipole induced-dipole interaction, interstitial accommodation, and orientational ordering, leading to more compact structure making negative excess compressibility.

Positive values of acoustic impedance as shown in Figure 5 hint to the possibility of the presence of strong

attractive forces between the reacting components of the mixture.

Negative values exhibit strong interaction. Decrease in values of free length with concentration can be concluded as there is significant interaction between two liquids (Figure 6).

4. CONCLUSION

In this study, the measurement of density, viscosity, ultrasonic velocity, and other acoustical parameters of DMA in n-butanol solution was studied in different concentrations at 303 K (Table 1). The experimental ultrasonic velocity data and other acoustical parameters contain valuable information regarding the solute-solvent interactions in the measurements, it can be concluded that the concentration of the n-butanol affects and gives rise to strong hydrogen bonding interaction. Increase in concentration of n-butanol plays an important role in forming hydrogen bonding interactions in the solutions. All the parameters support each other and confirm that with an increase in concentration of DMA, the strength of hydrogen bonding in the system increases.

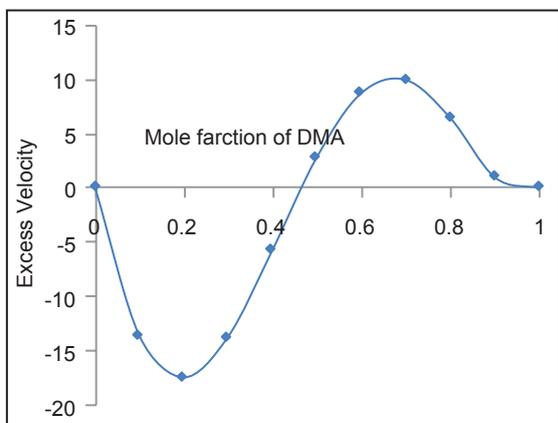


Figure 3: Excess velocity of N-N-dimethyl acetamide+n-butanol.

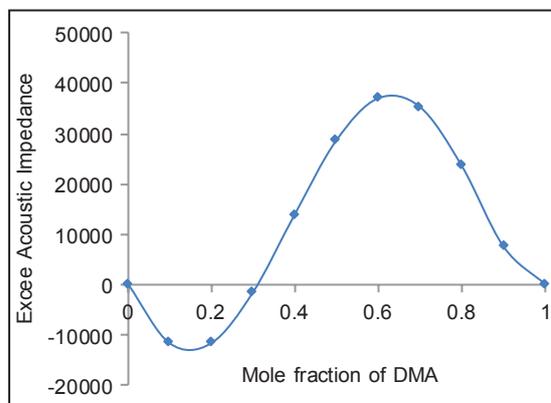


Figure 5: Excess acoustic impedance of N-N-dimethyl acetamide+n-butanol.

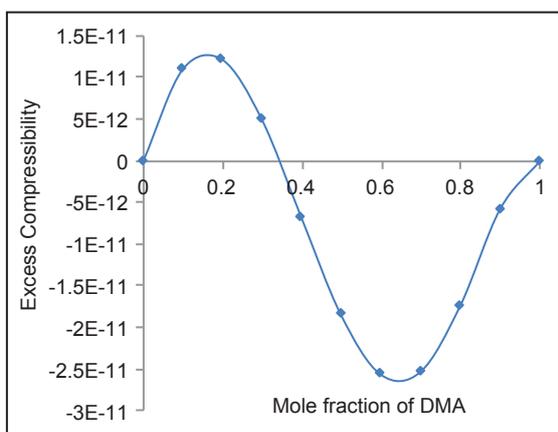


Figure 4: Excess compressibility of N-N-dimethyl acetamide+n-butanol.

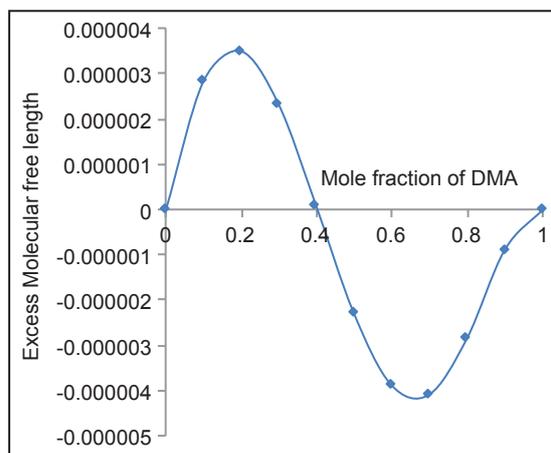


Figure 6: Excess molecular free length of N-N-dimethyl acetamide+n-butanol.

Table 1: Density, viscosity, ultrasonic velocity of DMA+n-butanol.

Volume fraction of	Density (g/cm ³)	Viscosity (cP)	Ultrasonic velocity (m/s)
0	0.8095	2.46	1447.2
0.1	0.8212	1.91	1416.4
0.2	0.833	1.7	1394.8
0.3	0.8447	1.53	1383.2
0.4	0.8665	1.44	1372
0.5	0.8882	1.31	1361.6
0.6	0.8965	1.28	1354.4
0.7	0.9058	1.17	1336.4
0.8	0.9139	1.12	1313.2
0.9	0.921	1.13	1293.2
1	0.927	0.99	1273.6

DMA=N-N-dimethyl acetamide

5. REFERENCES

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