



THERMODYNAMICAL STUDY OF N-N DIMETHYLFORMAMIDE WITH 2-BUTYLAMINOETHANOL AND 1-BUTANOL

Sangeeta Sagar

Department of Physics, University of Lucknow, Lucknow, U.P, 226007

Manisha Gupta*

Prof. Department of Physics, University of Lucknow, Lucknow, U.P, 226007

*Corresponding Author

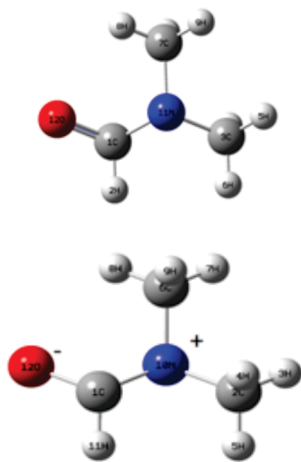
ABSTRACT Thermodynamical parameters are used to understand different kinds of associations like molecular packing, molecular motion, physico-chemical behaviour and various types of intermolecular interactions and their strengths, which are influenced by the sizes in pure components and mixtures. This paper presents the experimental data of ultrasonic velocities and densities of N-N Dimethylformamide (DMF) with 2-Butylaminoethanol (2-BAE) and 1-Butanol (1-BuOH) at five temperatures in the range (293.15 to 313.15)K and entire composition range. The calculated values of pseudo Grüneisen parameter (Γ), relaxation time (τ) and surface tension (σ) at different mole fractions of DMF have been used to explain the intermolecular interactions present in the mixture.

KEYWORDS : Intermolecular interactions, Dimethylformamide, pseudo Grüneisen parameter, surface tension, relaxation time.

1. INTRODUCTION

Liquids and liquid mixtures are extensively used in product formulation in many industrial applications. When two or more liquids are mixed together, then their physical and thermodynamic properties change due to free volume change, change in energy, change in molecular orientations, steric hindrances etc. These changes in transport and thermodynamic properties provide useful information about physical forces acting between the molecules of the liquids and liquid mixtures. Properties like ultrasonic velocity, density and their variation with temperature and composition of the liquid mixtures are valuable in various engineering, chemical and biological industries [1].

DMF (N-N Dimethylformamide) is a versatile solvent and has no hydrogen bonding in pure form. Its linear aliphatic configuration contributes to the volume contraction of the mixture. It has a dipole moment and dielectric constant ($\mu = 3.24$ D and $\epsilon = 36.71$ at 25°C) [2] and can dissolve wide range of both organic and inorganic substances because of its good donor and acceptor properties. The resonance structure of DMF is



In continuation of our earlier work [3], in the present work ultrasonic velocity (u), density (ρ), viscosity (η) have been measured for the binary mixtures DMF with BAE (Butylamino ethanol) and 1-BuOH (1-Butanol). Pseudo Grüneisen parameter (Γ), relaxation time (τ) and surface tension (σ) have been calculated.

2. MATERIALS AND METHOD:

N-N Dimethylformamide (molecular weight $M_n = 73.09$), Butylaminoethanol (BAE) (molecular weight $M_n = 117.19$) and 1-Butanol (1-BuOH) (molecular weight $M_n = 74.12$) have been obtained from Sigma Aldrich Chemicals Pvt. Ltd. and no further purification was done.

Mixtures were prepared by weighing the liquids in specially designed

ground glass stoppered weighing bottles, taking extreme precautions to minimize preferential evaporation. An OHAUS (AR2140, USA) single pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ± 0.0001 .

The ultrasonic velocity of the pure components and their mixtures were measured with a variable path, fixed frequency, interferometer provided by Mittal Enterprises, New Delhi (Model F-81). It consists of a high frequency generator, a measuring cell, and digital display micrometer. The interferometer measures the ultrasonic velocity of liquids by determining the wavelength of ultrasonic pulses over the distance within the sample using a digital display micrometer. Measurements of ultrasonic velocity were made at a fixed frequency of 2MHz. The calibration of the ultrasonic interferometer was done by measuring the velocity in AR grade benzene and CCl_4 with an accuracy of 0.08%. Uncertainty of ultrasonic interferometer is ± 0.5 m/sec.

The density of each liquid mixture has been measured using a pycnometer. The pycnometer consists of a long tube graduated in 0.01 ml scale, fitted to a specific gravity bottle of capacity 8 ml. A certain mass of the solution is allowed to expand at the desired temperature and the densities were calculated from the fixed mass and the volume at various temperature. Pycnometer was immersed vertically in a doubled walled cylindrical water jacket. The liquid rise in the capillary of pycnometer was measured by travelling microscope (having a least count of 0.001 cm) for accuracy. The precision of the measured densities is of the order of $\pm 1 \times 10^{-4} \text{ g cm}^{-3}$ and with an uncertainty of $\pm 0.0005 \text{ g cm}^{-3}$. An average of four to five measurements was taken for each sample mixtures.

The viscosity data used in the evaluation of various thermodynamic parameters were measured experimentally using Brookfield LVDV- II + Pro programmable viscometer (Brookfield Engineering Laboratories, Inc., USA) with complete control by PC using Brookfield Rheocalc 32 Software. The experimental assembly allows measurement of viscosities in the range of 0.15 cP to 3065 cP (with spindle CPE-40) and 4.6 cP to 92130 cP (with spindle CPE-52) with an accuracy of $\pm 1.0\%$ of full scale range and repeatability of $\pm 0.2\%$. The apparatus requires only 0.5 mL of the mixture for measurement of viscosity. The apparatus measures fluid absolute viscosity directly in cP.

Circulating water bath with programmable temperature controller (TC-502, Brookfield Engineering Laboratories, Inc., USA), having variable pump speeds, has been used for water circulation in water jackets of the apparatuses. The temperature controller covers the temperature measurement range of -20°C to 200°C , with temperature stability of $\pm 0.01^\circ\text{C}$.

The following thermodynamic parameters were calculated

i. The pseudo-Grüneisen parameter (Γ) has been calculated in terms of specific heat ratio as

$$\Gamma = \frac{\gamma - 1}{\alpha T} \quad (1)$$

ii. Relaxation time (τ) is given by

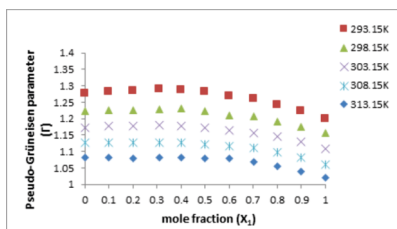
$$\tau = \frac{4\eta}{3u^2\rho} \quad (2)$$

iii. Surface tension (σ) is given as

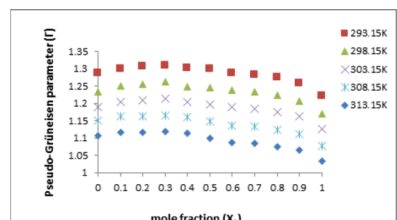
$$\sigma = 6.3 \times 10^{-4} \rho u^{3/2} \quad (3)$$

3. RESULTS AND DISCUSSION:

One of the most important parameter which is used to study the internal structure, clustering phenomenon and thermodynamic properties of solid crystalline lattice is pseudo-Grüneisen parameter (I). It is well established that liquids support a quasi-crystalline model for their structure, the lattice nature being increased at high pressure and low temperature hence the pseudo-Grüneisen parameter can also be used to study liquids. Fig. 1 shows that I decreases with increasing concentration of DMF as well as the rise in temperature. The non linear behavior of this parameter suggests the presence of specific interactions. Similar results are also observed by Yasmin et al. [4].

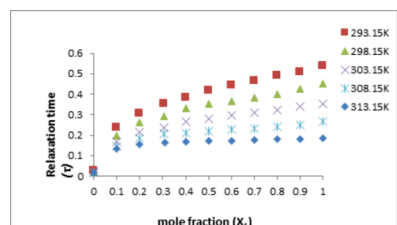


(a)

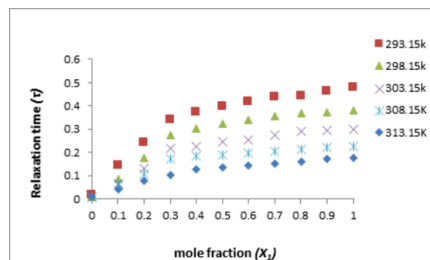


(b)

Fig. 1 Pseudo-Grüneisen parameter (I) versus the mole fraction of DMF (x_1) for binary mixtures: (a) DMF + 2-BAE and (b) DMF + 1-BuOH at 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.



(a)

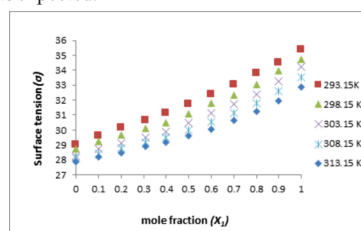


(b)

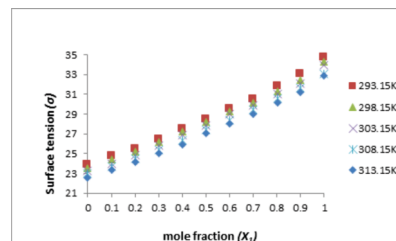
Fig. 2 Relaxation time (τ) versus the mole fraction of DMF (x_1) for binary mixtures: (a) DMF + 2-BAE and (b) DMF + 1-BuOH at 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.

Surface tension (σ) is one of the most accessible parameter that describes thermodynamic state and contains atleast implicit information on the internal structure of a liquid interface and plays a vital role in industries [5-6] such as paints, detergents, agrochemicals and petroleum. From Fig. 3 surface tension of both the mixtures increases with increase in concentration. Substances which involve hydrogen bonding exist as associated molecules and have high surface tension, in contrast to those substances which involve intramolecular

H-bonds exist as discrete and hence have low surface tension. The surface tension values decrease with increase in temperature for both the systems as expected.



(a)



(b)

Fig. 3 Surface tension (σ) versus the mole fraction of DMF (x_1) for binary mixtures: (a) DMF + 2-BAE and (b) DMF + 1-BuOH at 293.15K, 298.15K, 303.15K, 308.15K and 313.15K.

4. CONCLUSIONS

The density and ultrasonic velocity of binary mixtures DMF with BAE and 1-BuOH were measured at different temperatures. From the experimental data, various parameters pseudo Grüneisen parameter (I), relaxation time (τ) and surface tension (σ) were calculated. It may be concluded that observed values of these parameters shows the presence of dispersive forces.

5. Acknowledgement

One of the authors (SS) is thankful to UGC for financial support through Rajiv Gandhi National Fellowship.

REFERENCES

1. Parveen S., Singh S., Shukla D., Yasmine M., Gupta M. and Shukla J. P., Study of Molecular interactions in binary mixtures of aniline with carboxylic acids at 293.15K, 303.15K, 313.15K, Journal of Solution Chemistry, 41 (2012) 156-172.
2. J. A. Riddick, W. B. Bunger and T. K. Sakano, Organic Solvents, 4th ed., Wiley-Interscience, New York, (1986).
3. S. Sagar, L. Kumari and M. Gupta, Thermoacoustical analysis of binary mixtures of N-N dimethylformamide (DMF) with BAE and 1-BuOH, Journal of Pure Appl. Ultrason., 39 (2017) 71-78.
4. M. Yasmine, K. P. Singh, S. Parveen, M. Gupta and J. P. Shukla, Thermoacoustical Excess Properties of binary liquid mixtures- A Comparative Experimental and Theoretical Study, Acta Physica Polonica A, 115 (2009) 890-900.
5. L. C. Wang, H. S. Xu, J. H. Zhao, C. Y. Song and C. Y. Wang, Density and viscosity of (3-picilone+water)binary mixtures from T= (193.15 to 343.15)K, Journal of Chem. Thermodyn., 37 (2005) 477-483.
6. A. Mchaweh, A. Alsaygh, Kh. Nabvifar and M. A. Moshfeghian, A simplified method for calculating saturated liquid densities, Fluid Phase Equilibria, 224 (2004) 157-167.