

STUDY OF MOLECULAR INTERACTIONS IN BINARY MIXTURES USING EXCESS PARAMETERS

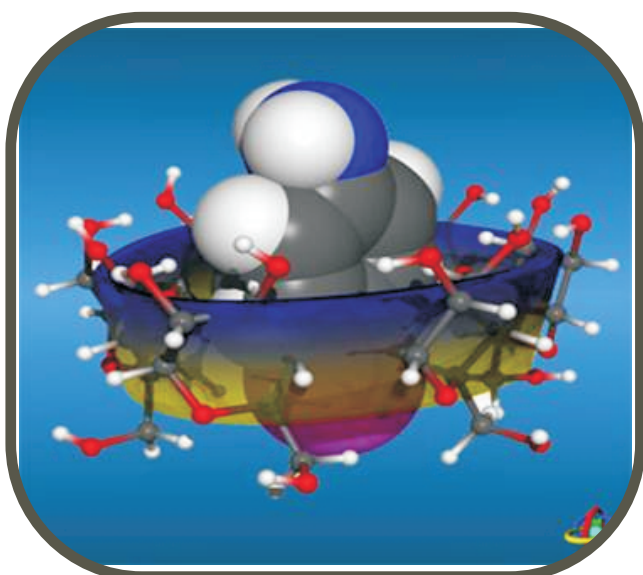


Abstract:-

Speeds of sound, densities and viscosities of the binary mixture of anisaldehyde with nonanol were measured over the entire mole fraction at (303.15, 308.15, 313.15 and 318.15) K and normal atmospheric pressure. Excess molar volume, V_m^E , Excess internal pressure, π^E , excess enthalpy, H^E , excess Gibbs's free energy of activation for viscous flow, G^*E , and excess viscosity, η^E have been calculated using experimental data. The V_m^E values are positive whereas π^E , H^E , G^*E , and η^E are negative and positive with no definite trend.

Keywords:

Speeds of sound, viscosity, excess parameters, anisaldehyde.



Narendra Kolla

Department of Physics, V.R. Siddhartha
Engineering College (Autonomous), Vijayawada ,
Andhra Pradesh, INDIA.

INTRODUCTION

The study of molecular interactions has been a subject of extensive investigations by dielectrics¹, NMR², IR³, Raman⁴ and ultrasonic absorption^{5,6}. The ultrasonic studies require less amount of sample when compared to other and gives more accurate results. The study of thermodynamic and acoustic properties of pure liquids, liquid mixtures and solutions have wide applications in chemical, leather, textile, pharmaceutical and many others⁷. In predicting the physico-chemical properties of liquid mixtures it is important to measure the speeds of sound, density and viscosity. Ultrasonics has wide range of applications in the field of physics, chemistry, biology and medicine.

Anisaldehyde is widely used in the fragrance and flavor industry. It is used as an intermediate in the synthesis of other compounds important in pharmaceuticals and perfumery. It is also a useful stain in thin layer chromatography. Nonanol is a colourless to slightly yellow liquid with a citrus odor. It occurs naturally in the oil of orange. It is used in the manufacture of artificial lemon oil. Various esters of nonanol are used in perfumery and flavors.

Estimation of molecular interactions of binary mixtures and information needed to test existing theories of solutions may be related to the magnitude of excess thermo acoustic properties such as excess molar volume, V_m^E , Excess internal pressure, π^E , excess enthalpy, H^E , excess Gibbs free energy of activation for viscous flow, $G^{\ddagger E}$, and excess viscosity, η^E . This paper aims to determine above properties with the purpose of obtaining some insight into interactions between molecules and studying the influence of higher order alcohols on above parameters.

No data on excess molar volume, Excess internal pressure, excess enthalpy, excess Gibbs free energy of activation for viscous flow and excess viscosity have been found in the literature for the anisaldehyde + nonanol mixture studied in this paper.

EXPERIMENTAL DETAILS

The analytical grade chemicals obtained from Merck were used. They were purified by standard procedure⁸. The purity of samples was checked by density and viscosity measurements⁹. To prepare the mixtures in the required proportions, Job's method of continuous variation was used. The mixtures were preserved in well-stoppered conical flasks. After mixing the liquids thoroughly, the flasks were left undisturbed to allow them to attain thermal equilibrium.

Single crystal ultrasonic pulse echo interferometer (Mittal enterprises, India) was used for measuring ultrasonic velocities. It consists of a high frequency generator and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 3MHz. The calibration of the equipment was done by measuring the velocity in benzene and carbon tetrachloride. The ultrasonic velocity has an accuracy of $\pm 0.1 \text{ m.s}^{-1}$. The temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath (accuracy $\pm 0.01 \text{ K}$).

A specific gravity bottle was used for the measurement of densities of pure liquids and liquid mixtures. Weights were measured with an electronic balance (Shimadzu AUY220, Japan) capable of measuring up to 0.1mg. An average of 4-5 measurements were taken for each sample. Ostwald's viscometer was used for measuring viscosities at the desired temperature, which was calibrated using water and benzene. After the mixture had attained bath temperature, flow time has been measured. The flow measurements were made with an electronic stopwatch with a precision of 0.01 s. The viscosity is determined using the relation

$$\eta = kt \quad (1)$$

where k , η and t are viscometric constant, density of liquid and time of efflux for a constant volume of liquid, respectively.

RESULTS AND DISCUSSION

The excess functions were calculated from our measurements using the following equations.

$$V_m^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2 \quad (2)$$

where x_1 and x_2 are mole fractions, M_1 and M_2 are the molar masses, and ρ_1 and ρ_2 are the densities of pure components 1 and 2 respectively.

$$G^E = RT (\ln \eta V - x_1 \ln V_1 - x_2 \ln \eta_2 V_2) \quad (3)$$

where V is the molar volume of the mixture and RT is the usual energy term.

$$\pi^E = \pi - x_1 \pi_1 - x_2 \pi_2 \quad (4)$$

where π is the internal pressure of the mixture

$$H^E = H - x_1 H_1 + x_2 H_2 \quad (5)$$

where H is the enthalpy of the mixture

$$\eta^E = \eta - x_1 \eta_1 + x_2 \eta_2 \quad (6)$$

where η is the viscosity of the mixture

The variation of excess molar volume, excess internal pressure, excess enthalpy, excess Gibb's free energy and excess viscosity with mole fraction of anisaldehyde at different temperatures are shown in Figures 1 to 5.

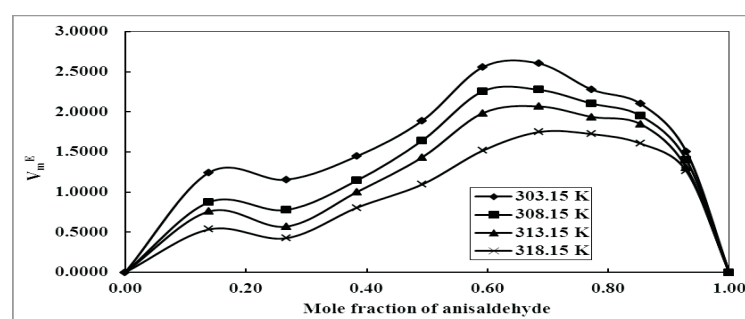


Figure 1: Variation of Excess molar volume (V_m^E) with mole fraction of anisaldehyde at different temperatures

From Figure 1 it can be observed that the V_m^E values are positive over the entire composition range and decrease with increase in temperature. Based on literature¹⁰ we can say that the excess volumes depend on three parameters. 1. Physical: including non-polar interactions for nonpolar liquid mixtures, dipole-dipole interactions for polar liquid mixtures, dipole-induced dipole for polar nonpolar liquid mixtures, these leads negative V_m^E . 2. Chemical: due to hydrogen bonding and electron donor-acceptor interactions, breaking of structures giving positive V_m^E . 3. Structural characteristics: Changes in interstitial accommodation owing to the difference in shape and size of the components of free volume.

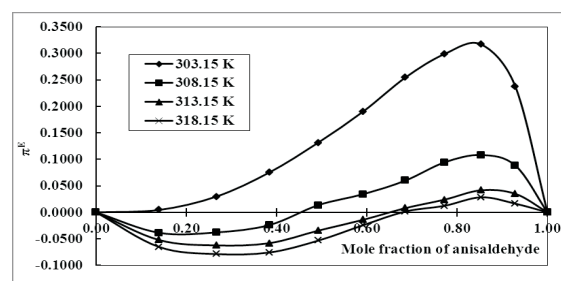


Figure 2: Variation of Excess internal pressure (π^E) with mole fraction of anisaldehyde at different temperatures

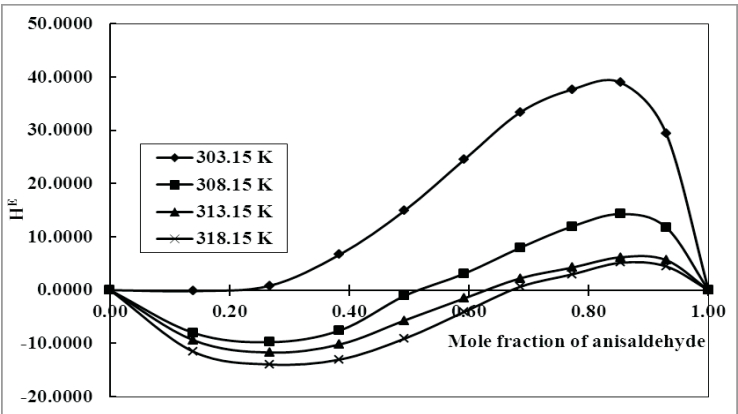


Figure 3: Variation of Excess enthalpy (H^E) with mole fraction of anisaldehyde at different temperatures

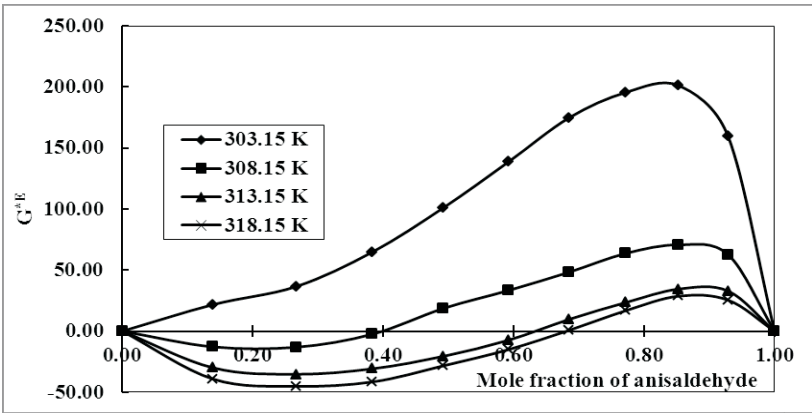


Figure 4: Variation of Excess Gibbs's free energy of activation for viscous flow (G^{*E}) with mole fraction of anisaldehyde at different temperatures

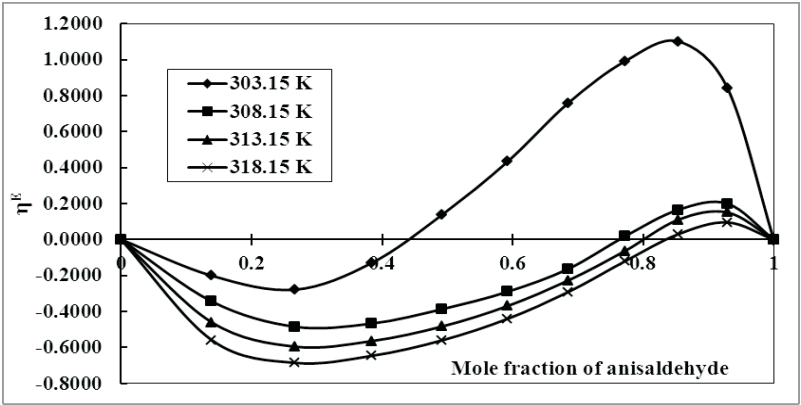


Figure 5: Variation of Excess viscosity (η^E) with mole fraction of anisaldehyde at different temperatures

From Figures 2 to 5, the π^E , H^E , G^{*E} and η^E values are observed to be positive and negative i.e., they are not varying regularly. At lower mole fractions they are negative and at higher mole fractions they are positive. The negative values of these excess functions may be due to the dominant of dispersive forces, particularly for the systems having different molecular sizes¹¹. For all the above parameters the same trends of observed for all the temperatures studied.

CONCLUSION:

The experimental data of speeds of sound, densities and viscosities were measured over the entire composition range at different temperatures. These data have been used to calculate the excess properties of the systems. The results shows that the excess molar volume values were positive and remaining excess parameters are observed to be positive and negative. It is also observed that the values of excess properties are dependent on temperature.

REFERENCES

- 1.Sharma A., Sharma D.R., Chauhan M.S, Indian J Pure & Appl. Phys. 31 (1993) 841.
- 2.Lin W., Tsay S.J, J.Phy.Chem. 74(1970)1037.
- 3.Grunwald E., Coburn W.C, J Americian Chem Soc, 80(1958) 1322.
- 4.Pimental G.C., Macellen A.L, The hydrogen bond (Freeman W.H., San Francisco), 1960, p67.
- 5.Shukla R.K., Atul Kumar, Kirti Srivastava., Shilpi Yadav, Indian J Pure & Appl Phys. 45 (2007) 726.
- 6.Narendra K., Srinivasu Ch., Fakruddin Sk., Narayanamurthy P, J Chem. Thermodyn. 43 (2011) 1604-1611.
- 7.Mehta S.K., Ram G., Mani C., Bhasin K.K, J.Chem.Thermodyn. 38 (2006) 836-848.
- 8.Pandey J.D, Rai R.D, Shukla R.K, Shukhla A.K, Mishra N, Indian J Pure Appl Phys. 1993;31:54.
- 9.Perrin D.D, Armarego W.L.F, Purification of laboratory chemistry. Oxford: Pregamon press; 1988.
- 10.Dal A, Bhardwaj R.K, J.Chem. Eng. Data 47 (2002) 1128-1134.
- 11.McAllister R.A, AIChE J. 6 (1960) 427-431.