

STUDY OF INTERNAL PRESSURE OF CHLOROFORM AGAINST MOLE FRACTION OF DMSO

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ABSTRACT

Thermodynamic studies like Internal Pressure and Mole Fraction have been Carried out over the different range of composition at 308.15 K. Thermodynamic Parameters like isentropic compressibility K_s , interaction parameter, χ_{12} , Flory Parameters, coefficients, A_i and standard deviations, $\sigma (Y^E)$ have been Computed from experimental findings. The excess thermodynamic functions have Been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic Speeds have been analyzed in terms of Jacobson Free Length Theory (FLT), Schaaff's Collision Factor Theory (CFT), Nomoto's relation, and Van Dael's ideal Mixture relation. Intermolecular Free Length, L_f , and available volume, V_a , have Been calculated from FLT, CFT and thermo acoustic approach.

Key Words: Internal pressure Ultrasonic Speed, Excess Molar Volume, Schaaff's Collision Factor Theory, chloroform and DMSO

INTRODUCTION

In order to assess the molecular interaction of the chloroform +DMSO binary systems, internal pressure values are calculated from ultrasonic velocity and density values at various concentrations. The plots of internal pressure against mole fraction of DMSO are given in Figure 1. Generally internal pressure increases with increase in molecular attraction. It is seen from the plots that internal pressure increases with addition of any polar liquid to DMSO and during the initial addition the increase in internal pressure is not significant. The internal pressure is not significant. However, the internal pressure values increase steeply when the mole fraction of DMSO is greater than 0.4. In DMSO- Chloroform system, internal pressure increases uniformly with increase in the concentration of DMSO, suggesting that the strength of these types of interaction increases with increase in mole fraction of DMSO. However, in case of other systems, the internal pressure either increases slightly or remains constant when the mole fraction of the polar compound is 0.4-0.8. This suggests that in Di substituted benzenoid component i.e. Chloroform, the dipole-dipole interaction are strong and these interactions

overcome the interactions between DMSO and the molecules of the second component. This is further supported by the variation in cohesive energy values with concentration. The cohesive energy is a measure of intermolecular attraction. In DMSO-chloroform system, there is a steady increase in cohesive energy with increase in the mole fraction of DMSO suggesting that the intermolecular attraction increases uniformly with the increase in DMSO concentration. However, in the other systems, the cohesive energy shoots up when the mole fraction of the second component is 0.3-0.5. These observations support that there is competition between dipole-dipole and dipole-induced dipole interactions in these systems and it becomes significant when the mixtures contains equal - molar amounts of the two components.

Absorption coefficient and relaxation time calculated from ultrasonic velocity, density and viscosity values are given and these values can be used to characterize the intermolecular interactions. It is found that the two parameters do not change significantly at a given temperature. This suggests that similar interactions exist in system.

Table 1 Internal pressure π atm of binary liquid mixtures of Chloroform and DMSO at 308.15 K.

Mole fraction of DMSO	Internal Pressure π atm
0.0000	1694
0.1000	3969
0.2000	5501
0.3000	6038
0.4000	6106
0.6000	5650
0.8000	5263
1.0000	5099

The linear variation in Rao Constant value with concentration suggests that the interactions are concentration dependent. In this systems, the value of Rao constant , decreases with increase in the concentration of polar component. Thus, the dipole- induced dipole attraction increases with increase in the concentration of polar component.

REVIEW OF LITERATURE

In the literature of physical chemistry, the thermodynamic properties of liquids and liquid mixtures constitute an important area of research. The study of liquids and liquid mixtures and internal pressure has been exhaustive since the pioneering work of Vander Waal`s around 1887, who suggested that the shape of the liquid molecules determine the intermolecular interactions. The first few issues of the

“Zeitschrift Fur Physikalische Chemie” 90 years ago, devoted large fractions of their pages to the experimental and theoretical studies on the equilibrium properties of liquid mixtures. Since then, numerous research articles dealing with such studies have been published. This publication covered in textbooks, reviews and monographs. Numbers of studies on the measurements of Internal Pressure of liquid- liquid mixtures have been carried out as it has gained much importance in investigating the physicochemical behavior of liquid mixtures such as molecular association and dissociation. Internal Pressure and related data of liquid mixtures are found to be the most powerful tool in testing theories of liquid stage. In addition, some more useful properties of liquid mixtures which are not easily accessible by other means can be deduced by means of data obtained from Internal Pressure measurement.

MATERIAL AND METHOD

Molecular interaction parameters with respect to velocity calculated is given in Table 1. Negative interaction parameter values in the systems suggest the existence of dipole- dipole attraction between the molecules of the component and dipole-induced dipole attraction between the molecules of the component DMSO-Chloroform binary liquids. These forces are strong in DMSO-Chloroform system as indicated by the large negative values of molecular interaction parameter values at all studied concentrations range.

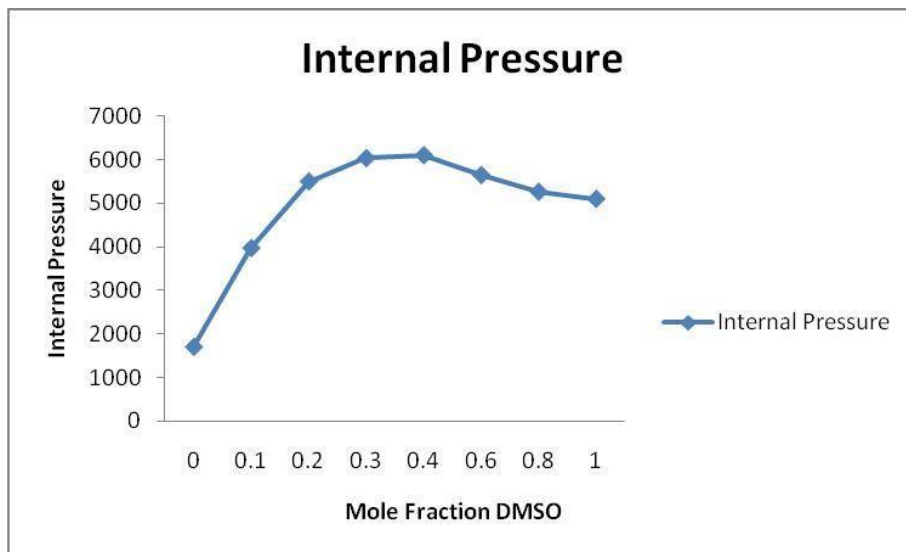


Figure 1 Plot of Internal pressure of Chloroform against mole fraction of DMSO

RESULT

The result is further fortified by the increasing value of relative association, R_A included. All the trends of the above parameters

Indicate that the mixtures are less compressible than their corresponding ideal mixtures. Generally, the deviation parameter is considered to be the reflecting agents of the magnitude of polarity at the site of interaction in the molecules.

The intermolecular free length, L_f , can be related to the space filling ability

Assuming that the molecules are incompressible hard spheres having uniform radius. The intermolecular free length, L_f , for the (DMSO + Chloroform) decreases with the increase in mole fraction of DMSO. The relative association, R_A ,

For the (DMSO + Chloroform) increases with the increase in mole fraction of DMSO. Both these results prove stronger dipole-dipole chemical interaction between unlike polar molecules which results in contraction of volume.

The study of standard deviations, σk_s^E , presented in, reveals that the results of ultrasonic velocity for DMSO with chloroform systems can be satisfactorily explained by Van Deal Ideal Mixture relation (minimum < 0.1). However, the prediction of these results is better for the DMSO with chloroform system by the CFT formulation.

Theoretical values of ultrasonic speed calculated from FLT theory shows large percentage error in DMSO with chloroform binary liquid mixtures at 308.15 K. Internal pressure π atm of binary liquid mixtures of chloroform and DMSO at 308.15 K. Theoretical values of ultrasonic speed calculated from Nomoto's and Van Dael and Vangeel's ideal mixing relations are almost identical. These relations show minimum percentage error in theoretical ultrasonic speed.

CONCLUSION=

Order of internal Pressure is :

Internal pressure increase when mole fraction of DMSO Increase .maximum peak comes at 0.4 value of mole fraction of DMSO.

m-xylene + DMSO > Chloroform+DMSO>Acetone+ DMSO > Cyclohexane + DMSO.

Internal pressure between binary liquid mixtures of Chloroform +DMSO was studied at 303.15 and 308.15K Temperatures.

Thermodynamic properties like internal pressure were calculated for the above said binary liquid systems at different compositions and at two different temperatures.

From these thermodynamic properties, properties like internal pressure were calculated for chloroform + DMSO binary liquid mixtures at all the composition range.

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