



STUDY OF INTERMOLECULAR FORCES AND INTERACTIONS IN BINARY LIQUID MIXTURE CHLOROFORM, ACETONE, M-XYLENE, AND CYCLOHEXANE IN DMSO

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Abstract: Thermodynamic studies like density (ρ), ultrasonic speed (u) and excess molar volume (V_m^E) of binary liquid mixture of Chloroform, Acetone, m- Xylene, Cyclohexane+ DMSO 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: Ultrasonic Speed, Excess Molar Volume, Schaaff's Collision Factor Theory, Chloroform, Acetone, m-Xylene and Cyclohexane and DMSO.

INTRODUCTION:-

Intermolecular forces are the forces that exist between different molecules. These forces have been classified into four categories.

- 1) Gravitational forces
- 2) Electromagnetic forces
- 3) Strong nuclear forces
- 4) Weak nuclear forces

The gravitational force is extremely long range and as the molecular dimensions are of the order of 5×10^{-1} nm, the gravitational potential energy is much less than the intermolecular forces.

The strong nuclear forces on the other hand are responsible for bonding the neutrons and protons inside the nucleus and are significant over distance of 10^{-4} nm. The weak nuclear forces are of similar short range. Intermolecular forces must, therefore have an electromagnetic origin and must be due to the charge particles, electrons and protons, that make up the atom or molecule. The intermolecular forces are mainly of two kinds.

- 1) short range forces,
- 2) long range forces

REVIEW OF LITERATURE

Numbers of studies on the measurements of ultrasonic speeds and isentropic compressibility's 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. Ultrasonic speed 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 ultrasonic speed measurement. It is well recognized that speed of sound, isentropic compressibility, and molar volume of Liquid mixtures provide information on molecular interactions. The high precisions of speed of sound measurements make it possible to calculate reliable values of two Parameters characterizing deviations of the system from ideality, the excess molar Isentropic compressibility which proves to be one of the most reproducible of the excess molar properties and deviation u^D of the speed of sound u , from those in ideal mixtures u^{id} . Molecular association in solution and some important correlation with various parameters e.g. ratio of the heat capacity, molar isentropic and isothermal compressibility $K_{S,m}$ and $K_{T,m}$, free volume V_f , apparent molar compressibility $K_{S,i,\phi}$ * available volume V_a , isentropic compressibility K_s , deviation in isentropic compressibility ΔK_s , mixing function Δu etc. can be very well studied through speed of sound measurement in liquid mixtures. In recent years, there has been an increased interest in the determination of either isothermal or isentropic compressibility's.

MATERIAL AND METHOD :-

The short range repulsive forces arise when molecules approach each other sufficiently close enough together to cause their electron clouds to overlap so that Pauli's principle prohibits some electrons from occupying the overlap region thereby producing a nodal plane in this region. The nuclei are thus incompletely shielded from each other and consequently repel each other. Short range forces are usually repulsive but this is not always the case, even in the case of closed shells. If it were so, chemical combinations would have been impossible. Further, even among "physical interactions" there are two which deserve special mention as being attractive rather than repulsive; one is the hydrogen bond and other is the Mulliken force which contributes the energy for charge transfer complexes. In the language of perturbation theory, the binding energy of a charge transfer complex arises partly from a virtual transition to an excited state in which an electron has been transferred from donor to acceptor. An intense absorption band in the region where neither partner absorbs on its own, indicates the existence of such a charge Transfer complex. The long range attractive components of intermolecular forces are significant when the overlap of the electron clouds of the approaching molecules is small. The various contributions to the long range forces may vary inversely as some power of intermolecular separation and include:

- i) the electrostatic contribution
- ii) The inductive contribution
- iii) The dispersion contribution

The electrostatic contribution to the intermolecular potential energy is attractive in nature and results from the following interactions:

- I) ion-ion interactions
- II) Ion-dipole interactions
- III) Dipole-dipole interactions
- IV) Ion-induced dipole interactions
- V) Dipole-induced dipole interactions
- VI) Quadruple-octupole interactions

Table .1 Different types of interaction Present between binary liquid.

Nature of Interaction	R = 5Å	R = 10Å
Ion-ion (coulomb's law)	2.88eV	1.44eV
Ion-dipole	0.180eV	0.045eV
Ion-induced dipole	0.0346eV	0.0022eV
Dipole-dipole	0.0225eV	0.0028eV
Dipole-induced dipole	5.4×10^{-4} eV	8.4×10^{-6} eV

RESULTS-

- i) **Ion-ion interactions:** The force of attraction between the charges e_1 and e_2 at a distance R from one another, is given by
 $f = \frac{e_1 \times e_2}{R^2} \dots (1)$

This type of interaction is important in solution of electrolytes and lattice energies of electrolytes



Figure 1. Force of attraction between the charges e_1 and e_2 at a distance R

2) ION-dipole interactions: These are the interactions of the ion and a polar molecule. At long range the field of ion will be essentially that of a point charge, whereas the field of the polar molecule will be essentially that of an ideal dipole; two point charges $+q$ and $-q$ a distance δ apart, such that $\mu=q\cdot\delta$

The vectors q and δ both point from $-q$ toward $+q$. If the center of the dipole lies a distance R from the ion of charge Q , in a direction that form an angle θ with μ (fig.2) and if $R \gg \delta$ than the distance from Q to $\pm q$ can be taken simply $R \pm \frac{1}{2}\delta \cos \theta$ The coulomb force on the dipole then has the z component given by

$$F_Z = F_+ + F_- = \left[\frac{q \cdot Q}{4\pi\epsilon_0 \left(R + \frac{1}{2}\delta \cos \theta\right)^2} \right] - \left[\frac{q \cdot Q}{4\pi\epsilon_0 \left(R - \frac{1}{2}\delta \cos \theta\right)^2} \right] \dots (2)$$

Using Binomial expression and solving, equation (2) yields

$$F_Z = \mu \frac{\partial E}{\partial R} \dots (3)$$

Where, μ is the dipole moment of molecule and E is the electric field of the ion of magnitude

$$E = \frac{Q}{4\pi\epsilon_0 R^2} \dots (4)$$

For a molecule with permanent dipole, this force corresponds to an interaction energy given by

$$V(R, \theta) = -\mu \cdot E = -\frac{\mu \cdot Q \cos \theta}{4\pi\epsilon_0 R^2} \dots (5)$$

Since $F_Z = -\frac{\partial V}{\partial R}$

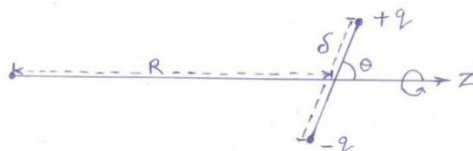


Figure 2.The vectors q and δ both point from $-q$ toward $+q$.

iii) Ion-induced dipole Interaction:

In this case the ions field will induce a dipole moment in a molecule. If μ is the induced moment, in a uniform field E and α is the polarizability (which is assumed to be constant) then,

$$\mu = \alpha \cdot E \dots (6)$$

The instantaneous force on the induced dipole for R, δ would then be given by

$$F_Z = \mu \frac{\partial E}{\partial R} = -\frac{\alpha Q^2}{8\pi^2 \epsilon_0^2 R^5} \dots (7)$$

The interaction energy at a given R , is then given by

$$V_{\text{ind}}(R) = - \int_{\infty}^R F \cdot dS = - \int_{\infty}^R Fz \cdot dR = \frac{\alpha Q^2}{8\pi\epsilon^2} \int_{\infty}^R dR/R^5$$

$$= - \frac{\alpha Q^2}{32\pi^2\epsilon^2 R^4} \dots \dots \dots (8)$$

As the induced dipole is taken to be the field, so no angle θ appears in the expression. An induction effect of this kind is also present when the molecule has a permanent dipole moment, but at long range is much smaller than the direct interaction given by equation (5).

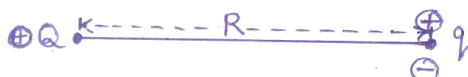


Figure 3 Molecule showing permanent dipole moment

iv) Dipole-Dipole Interactions: This type of interaction is illustrated in Fig.4. For two permanent dipoles A and B, each oriented at angles θ and ϕ , relative to the A-B axis, the long range interaction energy is given by

$$V(R, \theta_A, \theta_B, \phi_A, \phi_B) = U_A U_B / 4\pi\epsilon^2 R^3$$

$$[- 2 \cos \theta_A \cos \theta_B + \sin \theta_A \sin \theta_B \cos(\phi_B - \phi_A) \dots \dots \dots (9)]$$

These forces play an important role in intermolecular attraction between polar molecules

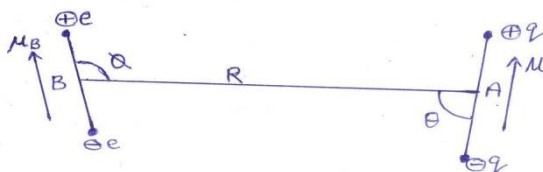


Figure 4 Two permanent dipoles A and B, each oriented at angles θ and ϕ , relative to the A-B axis.

V) Dipole-Induced-dipole Interactions:

A dipolar molecule can also induce a dipole moment in another molecule, whether or not the latter has dipole moment. The magnitude of this interaction should again be proportional to the product of the two dipoles divided by R^3 but the induced dipole as usual is given by $\alpha \cdot E$, where the field is that of first dipole varying as μ/R^3 . Thus the induced dipole has a magnitude proportional to $\alpha \cdot \mu/R^3$ and the interaction energy between the permanent and induced dipole must vary as $\alpha \cdot \mu^2/R^6$. Detailed calculation gives

$$V_{\text{ind}}(R, \theta_A) = - \frac{\alpha_B \mu_A^2 (3\cos^2 \theta_A + 1)}{2(4\pi\epsilon)^2 R^6} \dots \dots \dots (10)$$

In the interaction of two permanent dipoles there are two such induction terms to be added to equation (9) as each dipole will induce a dipole moment in the other

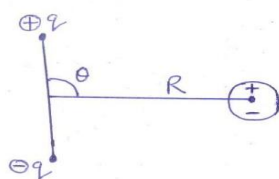


Figure 5 A dipolar molecules inducing a dipole moment in another molecule.

vi) Interactions involving quadrupoles and octupoles: These types of interactions are important only when more accurate values of overall potential energies are required. Their magnitudes can be calculated from the simple laws of electrostatics.

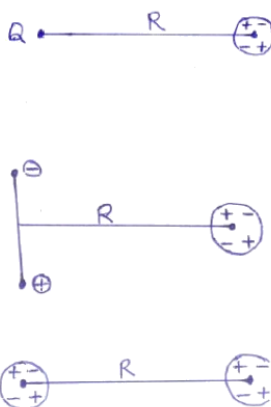


Figure 6 Interactions involving quadrupoles and octupoles

Thus, if we take $Q = \pm e$ (a singly charged ion), $\mu = 1.5D$ (about that of NH_3), $\alpha/4\pi\epsilon_0 = 3\text{\AA}^0$ (typical for small molecules) and set all the θ s Equal to zero (dipoles aligned along the A-B axis), then the magnitudes of the above interaction are

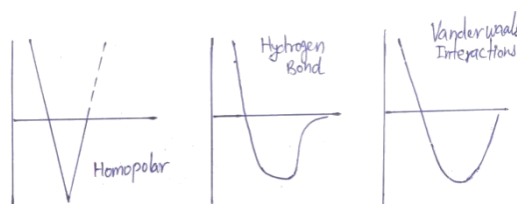


Figure 7 Potential energy distance profile of different type of interactions

CONCLUSIONS =

These types of interactions have been explained by Orgel and Mulliken. The contact charge-transfer absorption can occur whenever the donor and acceptor molecules are in contact. According to Mulliken the absorption bands corresponds to intermolecular charge transfer transition should occur when donor acceptor complex is formed and applied equally well to pairs of molecules when in contact or when sufficiently close to

each other. It does not depend upon the ability of charge-transfer forces to overcome exchange between the components, but on repulsion, the existence of none zero overlap integral between donor and acceptor orbital. The various types of intermolecular forces with the range and energy of interaction are given in Table 1.

Table 1 various types of intermolecular forces with the range and energy of interaction.

Name	Mechanism	Order of Magnitude of interaction energy	Range of action (Å)
Homopolar	Electron sharing	60	1-2
Hydrogen bond	Action of incompletely surrendered hydrogen atom attached to an atom Or other polarisable atom.	06	2.4-3.2
Ionic	Columbic attraction between ions or charged atoms of different sign	10-20	2-3
Vander Waal's	Mutual induction of moments from electrically polar molecules	1-2	3-5

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