STUDY OF MOLAR EXCESS VOLUME OF BINARY LIQUID MIXTURE CHLOROFORM+DMSO

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ABSTRACT

De-ionized water was taken and a little $KMnO_4$ and 2 or 3 pallets of NaOH were added to it. The solution was double distilled in an all glass distillation apparatus and the first fraction was rejected. The chloroform, is AR grade and further purified by distillation before use.

The purity of the compound like Chloroform, and DMSO were checked by measuring their densities at 303.15 K and these agreed well within $5X10^{-5}g/cm^3$ with the values reported in the literature. Molar excess volumes for the various binary mixtures of non-electrolytes were measured in a two limbed specially designed dilatometer

INTRODUCTION

The dilatometer used in the present work consists of two limbs having vacuum tested B-7 standard joints at their ends. The limbs are interconnected through small bent tubing. A thin uniform bored capillary having a reference mark, R is fused to the side of compartment A, as shown in Figure 1. An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquid with a high degree of accuracy. With the help of an ultrasonic interferometer we can determine various thermodynamic parameters like ultrasonic velocity, Adiabatic Compressibility (β_{ad}), Isentropic Compressibility(β), Isothermal Compressibility (β_T), Effective Debye Temperature (Q_D), Grunesian Parameters (T), Intermolecular Free Path length (L_f), Internal Pressure (π_i), free volume (V_f), Rao`s constant (R ) , Surface Tension ($S_t$), Mean Square Thermodynamic Fluctuation, Vander Waal`s Constant (b), Wada Constant (W), Space Filling Factor (r) and Relative Association (R_a). With the help of these thermodynamic properties calculated with the help of ultrasonic interferometer, we can study phenomenon like azeotropism, intermolecular interactions, miscibility and compatibility of binary liquid mixture, phase transition between various phases, various thermodynamic properties ofbinary and ternary liquid mixture, transport related phenomenon and various properties related with transport phenomenon etc.

MATERIAL AND METHOD

A column of mercury was placed in the dilatometer and weighed. One of the degassed liquids say (i) was added in the bulb B with the help of a hypodermic syringes. The bulb was then closed with stopper in such a way so that no air bubbles were entrapped in it. The dilatometer was weighed again. The second degassed liquid (j) was then added to the bulb A and the stopper was replaced keeping the liquid level in the capillary at a suitable position. The dilatometer was then placed in a water thermostat (controlled to $\pm0.01K$ or better by a mercury in toluene regulator). The reference mark and the liquid level in the capillary were noted.
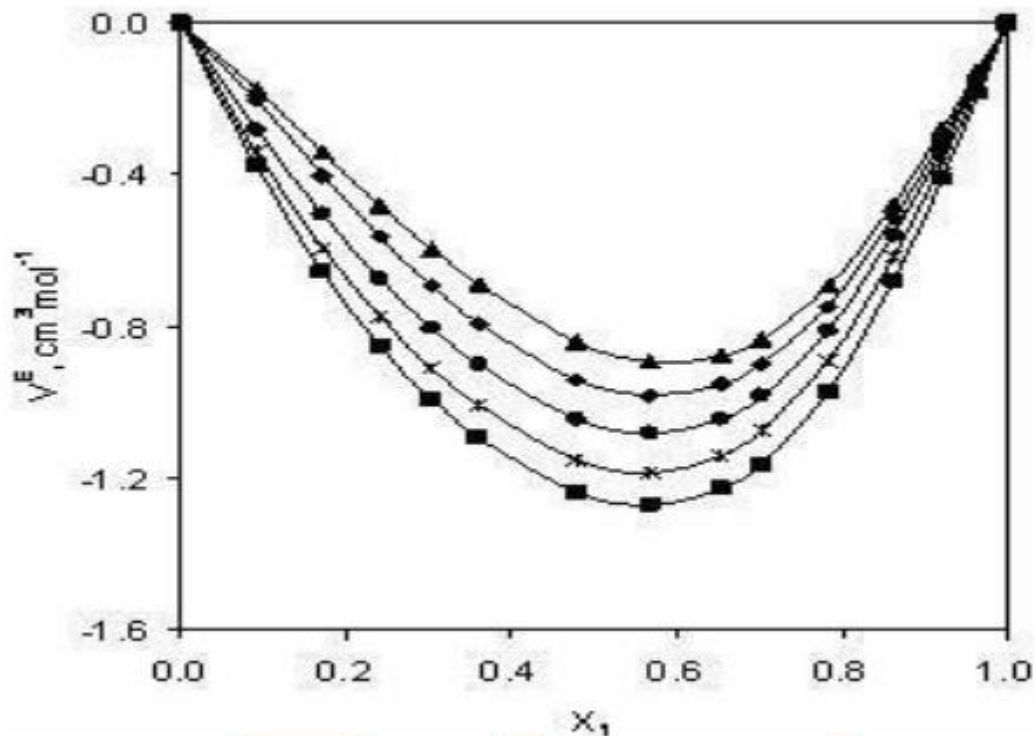
Figure 1 Excess molar volume vs. mole fraction for binary systems of CHCl₃

+ DMSO at 293.15 K (▲), 298.15 K (♦), 303.15 K (•), 308.15 K(2, 313.15 K (■).

After the thermal equilibrium had been attained, contents of the dilatometer were mixed by tilting it gently sideways several times. In order to ensure that the liquid in the capillary had the same composition as that of the bulk solution on mixing, the dilatometer was placed in a cold bath so that minimum liquid was there in the capillary. The dilatometer was again placed in the thermostat and this procedure was repeated three or four times. The reference mark and the level of liquid in the capillary were again noted after thermal equilibrium. The dilatometer was then taken out of the thermostat, dried completely and weighed again to determine the weight of the second liquid (j).

Molar excess volume, V_{IJ}^E for binary (i+j) mixtures were calculated from the expression:

$$V_{IJ}^E = \pi r^2 \, \Delta h / n_i + nj \quad\text{...} (1)$$

Where, πr^2 is the area of the capillary and Δh is the change in the liquid level in the capillary after mixing r is the radius of the capillary and $\Box$ ni $\Box$ nj $\Box$ are the total number of moles of (i) mixture. The dilatometer's capillary was calibrated from the weight of a length of mercury column in it. The length of the mercury column in the capillary at various positions was read by a traveling microscope that could read to ± 0.01 cm. The density of mercury was taken from literature at the room temperature of that day. From the weight of the mercury column of length l, the area, πr^2 of the capillary was evaluated from

$$\pi r^2 = W_{Hg} / \rho_{hg} \cdot l_{Hg} \quad\text{...} (2)$$

Where, W_{Hg} is the mass of an average length, l_{Hg} of the mercury and ρ_{Hg} is the density of mercury.

RESULT
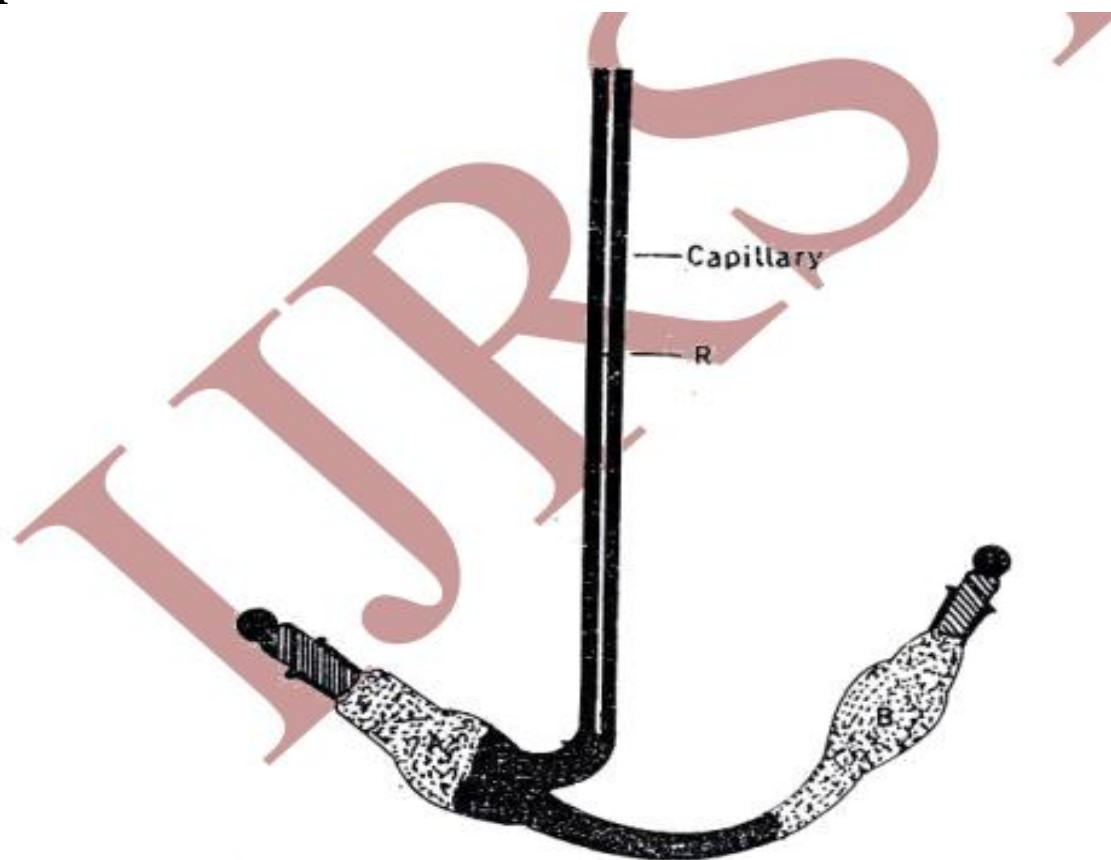
Figure 2 An Image of Dilatometer for measuring molar excess volume.

The principle used in the measurement of velocity is based on accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency are produced by a quartz plate fixed at the bottom of the cell. The waves are reflected by a movable metallic plate kept parallel to the quartz plate. If the separation between these plates is exactly a whole multiple of the sound wavelength, standing waves are formed in the medium. The acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelength or multiple of it, anode current again becomes maximum. From the knowledge of wavelength, the velocity can be obtained by the relation

Velocity = wavelength $\times$ frequency

$V = \lambda \times \nu$

The determination of adiabatic and isothermal compressibility's may be done by the following formula;

$v = \sqrt{1/\rho \beta}_{\text{adaib}} = \sqrt{\gamma/}_{\text{isotherm}}$

Where, γ is the ratio of specific heats, ρ is the density of liquid, β_{adaib} is adiabatic compressibility`s and $\beta_{isotharm}$ is the isothermal compressibility`s. The ultrasonic velocities of the above liquids and their mixtures were measured using multi frequency ultrasonic interferometer at a frequency of 2.0 MHz (Mittal Enterprises Model F-81). The accuracy in the measurement of ultrasonic velocity was with in ± 0.01 m/sec. The densities of these solutions were measured using 10 ml specific gravity bottles in an electronic balance precisely within ± 0.01 mg accuracy. Ostwald`s viscometer was used to measure the viscosities of the solutions. The temperature was maintained constants at 303.15 K using proportional temperature controller during the measurement of Ultrasonic velocity, Density and Viscosity values. Acoustical parameters such as

Adiabatic compressibility`s β_{adaib}, Free volume (Vf), Internal pressure πi,

Intermolecular free length (Lf), Absorption coefficient $\dfrac{\alpha}{f^2}$, Relaxation time r, Rao constant (R), Cohesive Energy (CE) and molecular interaction parameters with respect to velocities were calculated using standard equations .

DISCUSSION

Acetone was procured from Fluka-Aldrich, m-xylene and DMSO from Fischer Scientific Ltd. and were further purified by the methods given in Vogel text book of practical organic chemistry. Prior to the experimental measurements, all liquids were stored in dark bottles over 0.4 nm molecular sieves to reduce water content and were partially degassed with a vacuum pump under nitrogen atmosphere. The purities of all the samples determined by chromatographic analysis were better than 0.996 on a molar basis. Binary mixtures are prepared by mixing appropriate volumes of the liquid component in the specially designed glass bottles with air tight Teflon coated caps. The required properties are measured on the same day immediately after preparing each composition. The uncertainty in mole fraction is ± 0.0001. A multi frequency digital micrometer reading ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) operating at 1, 2, 3 and 4 MHz was used to measure the ultrasonic velocity of the binary liquid mixtures (with an uncertainty of ± 0.3 %) at a constant temperature of 303.15 K by using a digital constant temperature water bath. The temperature stability is maintained within ± 0.001 K by circulating thermostated water around the cell with a circulating pump. In order to minimize the uncertainty of the measurement, several maxima are allowed to pass and their number (fifty) is counted. All maxima are recorded with the highest swing of the needle on the micrometer scale. The total distance, d (cm) moved by the reflector is given by $d = \dfrac{n\lambda}{2}$, where λ is the wavelength. The frequency v, of the crystal being accurately known (2.0 MHz), the speed of sound, u in ms^{-1} is calculated by using the relation $u = \lambda v$. Excess molar volume, $V_m{}^E$ was calculated by specially designed double limbed glass dilatometer fitted with a microcapillary (± 0.001 cm) in the centre. The density of solutions was measured by a double arm pyknometer of bulb capacity 10 ml and a capillary of an internal diameter of about 1mm.

The mark of the stem was calibrated by double distilled water. (conductivity less than 1×10^{-6} ohm^{-1} cm^{-1}) with 0.9970 and 0.9940 g cm^{-3} as its density at 298.15 K and 303.15 K respectively and acetone with buoyancy corrected. The accuracy of the density results was $\pm$ 0.0001 (g cm^{-3}). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. Weight measurement were performed on a Mettler Toledo AB 135-S/FACT, single pan analytical balance, with a precision of 0.01 mg. The densities, and ultrasonic velocities, *u* of the pure liquids were in good agreement with the values found in the literature.

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