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Research Article

THERMODYNAMIC STUDY OF BINARY LIQUID MIXTURE OF CYCLOHEXANE AND DMSOAT T = 308.15K

Dheeraj Kumar and Devi Parshad

Research Scholar, Department of Chemistry,
Singhania University, Rajasthan, Jaipur, India.

ABSTRACT

Density (ρ), ultrasonic speed (u) and excess molar volume (V_m^E) of binary liquid mixture of 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, σ (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 FreeLength, L_f , and available volume, V_a , have been calculated from FLT, CFT and thermo acoustic approach.

Keywords: Ultrasonic Speed, Excess Molar Volume, Schaaff's Collision Factor Theory, cyclohexane.

INTRODUCTION

The thermodynamic and acoustic properties are very essential for understanding the physicochemical behavior of the binary and multi-component liquid mixtures. Excess properties of liquid systems, such as molar volumes, are required for testing the theories of solutions, development of separation techniques and equipment, and for other industrial applications. DMSO is an important polar solvent. It is less toxic than other members of this class such as dimethylformamide, dimethylacetamide, *N*-methyl-2-pyrrolidone, and hexa methyl phosphoramide. Because of its excellent solvating power, DMSO is frequently used as a solvent for chemical reactions involving salts. Thus, a study of physical properties data on the binary mixture containing DMSO has attracted considerable interest in the literature. Thus, Cyclohexane in DMSO mixed solvent would enable us to have a large number of solvents with appropriate physico-chemical properties, which can be used for a particular chemical process. Moreover, literature survey indicates that no ultrasonic study on this binary system has been reported at 308.15 K. Therefore, present study was undertaken in order to have deeper understanding of the intermolecular interaction between the components of the above binary liquid mixture. Thus, a study of thermodynamic properties data on the binary mixture of cyclohexane in DMSO has attracted considerable interest in our present study.

Research workers in the past have shown that NMR, IR and Raman spectra, have been used to study molecular interactions. The velocity measurement of the propagation of ultrasonic waves and their absorption has already been found to be useful in the study of molecular interactions for inorganic, organic and organo-metallic binary systems. Likewise, researchers have also employed ultrasonic measurements to look into the important consequences of ion-solvent interactions for the structure of electrolytic solutions. References related to the field of medicine, whereas references based on studies on emulsions micro emulsions, polymer surfactants interactions and ultrasonic destruction of surfactants are only a few cases to suggest versatility of the technique.

REVIER OF LITERATURE

In the literature of physicalchemistry, the thermodynamic properties of liquids and liquid mixtures constitute an important area of research. The study of liquids and liquid mixtures 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 PhysikalischeChemie" 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.

MATERIAL AND METHOD

Table 1: Values of Parameters A_j of the Redlich-Kister polynomial equation and corresponding standard deviations, $\sigma(k_s^E)$for the binary liquid mixture at 308.15 K

A_0	A_1	A_2	A_3	$\sigma(\kappa\sigma E)(T\,\Pi\alpha^{-1})$
DMSO + Cyclohexane				
74.3	-37.20	8.30	-12.05	0.11

DMSO was procured from Fischer Scientific Ltd. and was further purified by the methods given in Vogel text book of practical organic chemistry. Prior to the experimental measurements, both the organic 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 thermodynamic 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 theBinary liquid mixtures (with an uncertainty of ± 0.3%) at a constant temperature of 308.15 K by using a digital constant temperature water bath. The temperature stability is maintained within ± 0.001 K by circulating thermo stated 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 $d=n\lambda/2$ 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 doublelimbed glass dilatometer fitted with a micro capillary (± 0.01 cm) in the centre. The density of solutions was measured by a double arm pyknometer of 10 ml bulb capacity and a Capillary of an internal diameter of about 1.0 mm. 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 308.15 K, respectively and cyclohexane with buoyancy corrected. The accuracy of the density results was ± 0.0001 (g cm^{-3}). Before each series of measurements, the instrument was calibrated with triple distilled freshly degassed water. The accuracy of the density results was ± 0.00001 (g/cm^3). 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 thepure liquids were in good agreement with the values found in the literature and are presented in Table 1.

Table 2: Theoretical values of ultrasonic speed calculated from FLT, CFT, Nomoto's and Van Dael and Vangeel's idealmixing relation and percentage error in calculated values for Cyclohexane + DMSO

x_1	*u*(m/s)				% error			
DMSO	FLT	CFT	NOM	VD	FLT	CFT	NOM	VD
0.0000	1478.5	1481.5	1480.5	1482.5	0.00	0.00	0.00	0.00
0.1342	1481.6	1483.9	1483.3	1486.2	0.46	0.41	0.27	0.78
0.2356	1487.6	1488.7	1487.2	1484.8	1.16	1.32	1.56	0.81
0.3467	1495.8	1494.4	1493.6	1491.5	2.12	2.45	2.01	2.18
0.4631	1499.6	1498.4	1497.5	1499.2	3.05	3.20	2.45	2.55
0.5579	1504.8	1505.3	1503.8	1508.3	5.93	4.14	7.06	3.11
0.6632	1487.3	1492.4	1491.3	1485.4	6.62	5.49	8.26	5.98
0.7587	1474.8	1486.7	1480.7	1474.8	5.03	5.08	6.38	4.96
0.8145	1470.1	1475.8	1474.7	1470.6	3.75	3.84	4.22	2.54
0.9385	1468.3	1471.4	1472.3	1480.4	2.09	1.39	2.98	2.08
1.0000	1486.3	1485.3	1484.3	1487.3	0.00	0.00	0.00	0.00

CONCULSION AND RESULT

Density (ρ), ultrasonic speed (u) and molar excess volume (V_m^E) of binary liquid mixture of cyclohexane+ DMSO have beenobserved over the entire range of composition and at 308.15 K. From these experimental results, parameters such asdeviation in isentropic compressibility, ΔK_s, interaction parameter, χ_{12} , Flory parameters, Coefficients A_i , standarddeviations σ (Y^E) and molar sound velocity, R_m , have been estimated. The excess functions have been fitted to the Redlich-Kister polynomial equation. The experimental ultrasonic velocities have been analyzed in terms of Nomoto's relation, Van Dael's ideal mixture relation, Jacobson Free Length theory and Schaaff's Collision Factortheory. IntermolecularFree Length, L_f , and availablevolume,V_a , have been calculated from Jacobson Free Length theory, Schaaff`s Collision Factor theory, and Thermo acoustic Approach for binary liquid system of cyclohexane+ DMSO at 308.15 K. The observed negative values of ΔK_s and excess molar volume V_m^E and positive values of Δu for these mixtures imply that the specific chemical dipole-dipole interactions between unlike molecules dominate over the physical dispersive interaction and dipole-dipole interaction between like molecules.

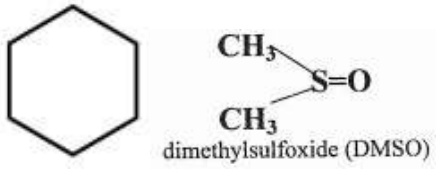

Fig. 1: Molecular structure of cyclohexane and DMSO

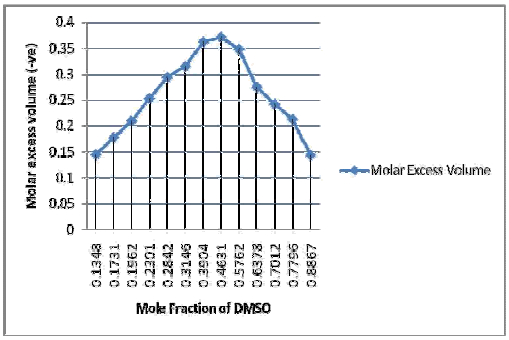

Fig. 2: Molar excess volume of binary liquid mixture of cyclohexane in DMSO

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