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Synergistic behaviour in binary mixtures of DEHPA and MIBK - an acoustic study

B DALAI[1], S K PRADHAN[2], S K DASH[3*], S K SINGH[4] and B B SWAIN[5]

[1]Dept. of Physics, GIET University, Gunupur, Rayagada, Odisha – 765022
[2]Dept. of Physics, Nayagarh Autonomous College, Nayagarh, Odisha - 752069
[3]Dept. of Physics, R. I. E. (NCERT), Bhubaneswar, Odisha– 751022
[4]Institute of Minerals and Materials Technology (CSIR), Bhubaneswar, Odisha – 751013
[5]Plot No. 15, Chintamaniswar Area, Bhubaneswar, Odisha - 751006
E-mail: skdash59@yahoo.com

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Abstract. Density (ρ), viscosity (η) and ultrasonic velocity (U) of binary mixture of methyl isobutyl ketone (MIBK) and di-(2-ethyl hexyl) phosphoric acid (DEHPA) including those of pure liquids were measured over the entire composition range of DEHPA at 303.15K and 0.1Mpa. The deviations of isentropic compressibility, $\Delta\beta_s$, intermolecular free length, ΔL_f, viscosity, $\Delta\eta$, ultrasonic velocity, ΔU, acoustic impedance, ΔZ, excess molar volume, V^E and excess Gibb's energy of activation of viscous flow, ΔG^E have been calculated using experimentally measured values of ρ, η and U. The results have been discussed in terms of molecular interactions between unlike molecules of the studied binary mixture.

Keywords: Density, viscosity, ultrasonic velocity, binary mixture, deviation function, molecular interaction

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1. Introduction

In solvent extraction process, synergistic liquid mixtures rather than single component liquid system are used in processing and product formulation [1-3]. To enhance the efficiency in extraction of metals from ores, it is feasible to use synergistic mixtures of two or more extractants. The common extractants such as di(2-ethyhexyl) phosphoric acid (DEHPA), methyl isobutyl ketone (MIBK),

di-butyl butyl phosphate (DBBP), di-octyl phenyl phosphoric acid (DOPPA), di-nonyl phenyl phosphoric acid (DNPPA), tri-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO) etc. are used for the extraction of beryllium, vanadium, chromium, cobalt, nickel, copper, zinc, actinide elements (e.g. thorium, uranium, plutonium) and rare earth elements (e.g. scandium, yttrium, cerium, europium) [4-7]. MIBK can also be used to extract gold, silver and other precious metals from cyanide solutions, such as those found at gold mines, to determine the levels of those dissolved metals. The study on acoustic properties of binary organic liquid mixtures is of considerable importance in several industrial, engineering and technological processes [8-10]. Acoustic properties are applied in understanding physico-chemical behaviour and molecular interaction in liquid mixtures. In continuation to our earlier work [11-14], the present work is a part of our program to provide data for the characterization of the molecular interactions in binary mixture of MIBK and DEHPA. The ultrasonic velocity (at 2 MHz), density and viscosity of the binary mixture have been determined at temperature 303.15K and atmospheric pressure 0.1MPa. The experimental data are used to evaluate excess / deviation in acoustic properties of liquid mixtures such as deviations of isentropic compressibility, $\Delta\beta_s$, intermolecular free length, ΔL_f, viscosity, $\Delta\eta$, ultrasonic velocity, ΔU, acoustic impedance, ΔZ, excess molar volume, V^E and excess Gibb's energy of activation of viscous flow, ΔG^E. These properties are of considerable interest in understanding the specific and non-specific molecular interactions between components of a liquid binary mixture.

2. Experimental

The chemicals used in this present investigation were of analytical reagent (AR) grade and obtained from E-Merck chemicals Ltd India. The procedures of measurement of density, viscosity and ultrasonic velocity are same as reported in our earlier works [13, 14]. The purity of all samples has been verified by comparing with the literature values [15]. All samples were kept in air tight bottles and adequate precautions were taken to avoid evaporation and contamination. Temperature of all samples was maintained to an accuracy of ± 0.1K in an electronically controlled thermostatic water bath.

3. Results and discussion

The excess molar volume, V^E, excess Gibb's energy of activation of viscous flow, ΔG^E and deviation of isentropic compressibility, $\Delta\beta_s$, intermolecular free

length, ΔL_f, viscosity, $\Delta\eta$, ultrasonic velocity, ΔU, acoustic impedance, ΔZ of DEHPA and MIBK mixtures over the entire mole fraction range of DEHPA are obtained from the experimental values of density, ρ, viscosity, η, ultrasonic velocity, U by following standard relations [16-18] and presented in Table 1.

$$\text{Excess molar volume, } V^E = \sum_{i=1}^{2} X_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \tag{1}$$

where ρ, M_i, X_i and ρ_i are the mixture density, molecular weight, mole fraction, density of i^{th} component in the mixture, respectively.

Excess Gibbs free energy of activation,

$$\Delta G^E = RT\left[\ln \eta V - \sum_{i=1}^{2} X_i \ln \eta_i V_i\right] \tag{2}$$

where R is universal gas constant. η_i and V_i are the viscosity and molar volume of i^{th} components, respectively.

The deviation functions *viz.* $\Delta\beta_s$, ΔL_f, $\Delta\eta$, ΔU, ΔZ were calculated using the expression:

$$\Delta Y = Y_{\exp} - Y_{ideal} = Y_{\exp} - \left[\left(1 - X_2\right) Y_1 + X_2 Y_2\right] \tag{3}$$

where Y represents the parameters β_s, L_f, η, U, Z and X_2 is the mole fraction of DEHPA. Subscript 1 and 2 refer to MIBK and DEHPA, respectively.

From Table 1, the negative values of V^E, $\Delta\beta_s$ and ΔL_f and positive values of ΔZ, ΔU, ΔG^E indicate strong specific interactions [15-17] between component molecules, leads to compact structure in mixing. This discloses closeness of unlike molecules in the binary mixture and the dominant nature of hydrogen bonding among molecules of MIBK and DEHPA. This also suggests that the unlike molecules acquire closely packed in the mixture than in the pure stage [14, 18]. Both MIBK and DEPHA are having dipole moments 2.8D and 2.74D respectively. The molecular interaction between unlike molecules may be due to hydrogen bonding through lone pair $O^{\delta-}$ of phosphoryl group of DEHPA and $H^{\delta+}$ of methyl group of MIBK. The variation of $\Delta\eta$ has been observed negative over entire mole fraction range of DEHPA. According to Fort and Moore [19], the negative $\Delta\eta$ values in mixtures of components having unequal size may be due to dispersion forces between the unlike molecules. It implies that

the interstitial accommodation due to size effect of unlike molecules in the binary mixtures along with the van der Waals dispersion force, may not be ignored in the computation of resultant effect [13, 19].

Table 1. Variation of density, viscosity, ultrasonic velocity, excess molar volume and deviation of adiabatic compressibility, inter molecular free length, viscosity, acoustic impedance in binary mixtures of MIBK + DEHPA over entire mole fraction of DEHPA at 303.15K and 0.1 MPa.

Mole fraction (X_2)	U (m s^{-1})	ρ (kg m^{-3})	η (cP)	$V^E \times 10^6$ (m^3 mol^{-1})	$\Delta\beta_s$ $\times 10^{10}$ (m^2 N^{-1})	$\Delta L_f \times 10^{11}$ (m)	$\Delta G^E \times 10^{-2}$ (J.mol^{-1})	ΔU $\times 10^{-2}$ (m s^{-1})	$\Delta\eta$ (cP)	$\Delta Z \times 10^{-5}$ (kg m^{-2} s^{-1})
0	1164.0	792.0	0.5	0	0	0	0	0	0	0
0.08	1183.5	825.0	0.8	-0.221	-0.417	-0.137	3.464	0.092	-1.204	0.288
0.13	1195.0	841.0	1.0	-0.538	-0.590	-0.196	4.300	0.142	-1.944	0.414
0.25	1218.0	875.0	1.6	-0.727	-0.841	-0.285	6.589	0.218	-3.600	0.637
0.32	1229.0	889.7	2.2	-0.806	-0.887	-0.304	8.830	0.237	-4.316	0.689
0.41	1241.0	905.4	3.2	-0.855	-0.878	-0.303	10.938	0.241	-5.008	0.702
0.49	1250.5	917.5	4.1	-0.976	-0.832	-0.289	9.665	0.233	-5.612	0.682
0.58	1260.0	929.6	5.5	-1.228	-0.747	-0.263	8.749	0.212	-5.904	0.633
0.65	1267.0	938.0	6.9	-1.474	-0.665	-0.235	7.804	0.192	-5.820	0.580
0.71	1273.0	943.0	8.3	-1.251	-0.576	-0.205	6.870	0.174	-5.548	0.508
0.79	1279.0	949.0	10.7	-0.959	-0.431	-0.154	5.527	0.131	-4.652	0.384
0.82	1281.0	951.0	11.7	-0.827	-0.371	-0.132	4.652	0.112	-4.216	0.333
0.88	1286.0	954.6	13.6	-0.513	-0.259	-0.094	2.910	0.085	-3.444	0.234
0.94	1289.5	958.0	16.2	-0.228	-0.130	-0.047	1.511	0.042	-1.972	0.119
1.00	1293.0	961.3	19.3	0	0	0	0	0	0	0

4. Conclusion

The trend of variation of density, viscosity, ultrasonic velocity and the excess/ deviation in acoustic and thermodynamic properties of liquid mixtures over entire composition of DEHPA indicate the presence of molecular interaction in the binary mixture of MIBK and DEHPA. The macroscopic results of the acoustic investigations indicate the presence of H-bonded dipole-dipole molecular interaction between MIBK and DEHPA molecules. The present synergistic study of the two extractants can be utilized for improving the extraction efficacy of the actinide and lanthanide elements in the extraction process.

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