TEMPERATURE DEPENDENT ACOUSTICAL STUDY OF THERMOPHYSICAL PROPERTIES OF BINARY MIXTURES OF DIETHYL CARBONATE + 2-METHOXYETHANOL

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ABSTRACT

The aim of present study is to determine the internal pressure (π_i), enthalpy (H), entropy (T_s), excess internal pressure (π_i^E), excess enthalpy (H^E) and excess entropy (T_s^E) at temperatures 303.15, 308.15, 313.15 and 318.15 K over the entire mole fraction range. The measured values of densities (ρ) and ultrasonic velocities (u) of (Diethyl carbonate (DEC) + 2-Methoxyethanol (2-ME)) binary mixtures have been used. The excess values are fitted to the Redlich−Kister smoothing polynomial equation to estimate the binary coefficients and standard deviation between the experimental and calculated values. The results have been discussed in terms of molecular interactions due to physical, chemical and structural effects between the unlike molecules.

Keywords: Thermodynamic properties, internal pressure, enthalpy, DEC, 2-ME

1. INTRODUCTION

Ultrasonic technology finds many applications in the fields of Physics, Chemistry, Biology and Medicine. Ultrasonic measurements are very useful in chemical, food processing, material testing, under water ranging and cleaning. The information about the physical properties of pure liquids and liquid mixtures containing aromatic and aliphatic compounds and their dependence with composition and temperature is very important basic data. The study on the possible change of thermodynamic properties of mixtures and their degree of deviation from ideality has been formed to be an excellent qualitative and quantitative way to obtain information about the molecular structure and intermolecular forces in liquid mixtures.The Knowledge of thermodynamic properties of multicomponent systems is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow and so forth. Sound velocity measurements are very useful in the technology of polymers to understand polymer solvent and polymer interactions, and structure of polymers. Liquid mixtures are used in studies of polymer miscibility, polymer phase diagrams and preferential interaction of polymers and mixed solvents. They may help in the study of chemical and biological processes in the liquid mixtures[1].Experimental densities are important for design of production in industrial plants. Properties of liquid-liquid mixtures are thermodynamically very important as part of studies of thermodynamic, acoustic and transport aspects. The intermolecular forces of liquids in a mixture show a considerable effect on the physical and chemical properties.[2-6]

Diethyl Carbonate(DEC) is a solvent of both extraction and reaction used in many industries, pharmaceuticals, agrochemicals, hydrocarbon refinery, paint and coatings and fragrances. It is used as a methylation and carbonylation agent in organic synthesis. It can be used as afuel and lube additive[7]. 2-Methoxyethanol (2-ME) is a colorless liquid with ether-like odor. It is used as a solvent for cellulose acetate, natural and synthetic resins, somealcohol-soluble dyes; in nail polishes, quick-drying varnishes and enamels, and wood stains. It is also used as a as a jet fuel de-icer[8].

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1.Materials:

DEC, 2-Methoxyethanol (sigma Aldrich, India, GC mass fraction purity 0.99),were used as such.Prior to experimental measurements, all chemicals were dried and then fractionally distilled under reduced pressure. The chemicals were stored in tightly sealed amber coloured glass vials with screw caps having PFE septa, and securely sealed with parafilm to keep the atmospheric moisture absorption to minimum. Further, the chemicals were vacuumed degassed, and the moisture content was reduced

with the help of molecular sieves, and was then stirred for > 30 minutes to ensure total dissolution of the mixtures. The samples were taken from the vials with a syringe through the PFE septum.

2.2.Apparatus and procedure:

The density and speed of sound of the pure liquids and their binary mixtures have been measured by digital oscillating Density and sound Analyzer (DSA 5000M, Anton Parr, Austria) with reproducibility of $\pm 1 \times 10^{-3}$ kg.m^{-3} for density and $\pm 1 \times 10^{-2}$ m.s^{-1} for speed of sound. The densimeter automatically performs the viscosity corrections for density during measurements up to 700mpa. The speed of sound is measured using a propagation time technique and measures the speed of sound at frequency of 3MHz. The densimeter was calibrated randomly with dry air[9] at atmospheric pressure and triply-distilled, freshly degassed and deionized water (ρ=997.075kg.m^{-3} at 298.15K)supplied by Anton-Paar as described elsewhere[10].After each measurement, the distilled water and anhydrous ethanol were used to clean the vibrating tube. The standard and uncertainties associated with the measurements for temperature, density and speed of sound are estimated to be within +0.01K, +0.5Kg.m^{-3} and +0.6m.s^{-2}, respectively. All the solutions used in the measurements were made a fresh on Sartorius CPA 225D balance having precision of ± 0.01mg. Uncertainties in the solution concentration are estimated at $\pm 1 \times 10^{-4}$ in calculations. All molar quantities expressed in this paper are based on the IUPAC, relative atomic mass table[11].A more detailed description and experimental procedure of these pieces of equipment can be found in our previous literature reports[12,13].

3. RESULTS AND DISCUSSION

The internal pressure was calculated using the following relation,

$$\pi_i = \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\alpha_P}{k_T}\right) - P \qquad \ldots (1)$$

whereα_P is the isobaric expansivity and k_T is the isothermal compressibility of the mixture. For most of the liquids, the thermal pressure coefficient multiplied by absolute temperature, i.e., $T(\alpha_P/k_T)$ is very high so that the external pressure (P) becomes negligible in comparison[14], therefore it may be neglected in Eq. (1) in the present calculations. Thus, the internal pressure can be shown to be equal to the following relationship[15,16]

$$\pi_{i=\frac{\alpha_P}{k_T}}T \qquad \ldots (2)$$

The free volume, V_f of the mixtures are calculated from the relation[17,18]

$$V_f = \frac{RT}{(P+\pi_i)} \qquad \ldots (3)$$

since P is very small as compared to π_i, it has been neglected in the Eq. (3) in the present calculations. k_T is calculated using the well-known thermodynamic relationship[19,20]

$$k_T = k_s + \frac{TV\alpha_P^2}{C_P} \qquad \ldots (4)$$

where$k_s[=1/(\rho u^2)]$ is isentropic compressibility, V is the molar volume and C_p is the heat capacity of the mixture. The α_p values for the mixtures were evaluated from temperature dependence of density data[8]. The C_p values of pure liquids have been taken from the literature[21-23] and the C_p values for the mixtures have been calculated by using the following relationship.

$$C_p = x_1 C_{p,1} + x_2 C_{p,2} \qquad \ldots (5)$$

The values of various parameters, C_p, α_p, k_s and k_T of pure liquids used in the calculations are taken from our earlier paper[8]. The π_i^E and V_f^E of binary mixtures have been calculated using the relationship,

$$Y^E = Y - (x_1 Y_1 + x_2 Y_2) \qquad \ldots (6)$$

where Y is π_i or V_f and subscripts 1 and 2 refers to pure 1,4-butanediol and picolines, respectively. The excess enthalpies (H^E) and excess entropies (T$_s^E$) are calculated from π_i and V_f by using the following relations based on regular solution theory.

$$H^E = \pi_i V - [x_1\pi_{i,1}V_1 + x_2\pi_{i,2}V_2] \qquad \ldots (7)$$

$$T_S^E = R [x_1\ln V_{f,1} + x_2\ln V_{f,2} - \ln V_f] \qquad \ldots (8)$$

The values of π_i^E, H^E, and T_S^E were fitted to a Redlich-Kister[24]type polynomial equation

$$Y^E = x_1(1-x_1)\sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \qquad \ldots (9)$$

where Y^E is π_i^E or H^E or T_S^E. The values of coefficients, A_i in Eq. (9) were evaluated by using least-square method with all points weighted equally. The standard deviations, σ of fit have been calculated by using the relation.

$$\sigma (Y^E) = [\sum(Y_{obs}^E - Y_{cal}^E)^2/(m - n)]^{1/2} \qquad \ldots (10)$$

where, m is the total number of experimental points and n is the number of coefficients.

The values of π_i, H, and Ts for the binary mixtures of Diethyl carbonate (DEC) + 2-Methoxyethanol (2-ME) as function of mole fraction, x_1 of DEC at various temperatures are listed in Table 1. The values of coefficients, $A_i$of Eq. (9) for the excess functions and the corresponding standard deviations, σ are listed in Table 2. The variation of π_i^E, H^E and T_S^E with composition and temperature of the mixtures are presented graphically in Figs 1 - 3, respectively.

Table. 1.Values of π_i, H, and Ts for the binary mixtures of DEC + 2-ME as function of mole fraction, x_1 of DEC at various temperatures

x_1	π_i $(10^8$ N m$^{-2})$	H (kJ mol^{-1})	Ts $(10^{-2}$J mol$^{-1})$	π_i $(10^8$ N m$^{-2})$	H (kJ mol^{-1})	Ts $(10^{-2}$J mol$^{-1})$
	T = 303.15 K			T = 308.15 K		
0.0000	4.086	32.53	99.736	4.051	32.41	99.528
0.0645	4.004	33.01	99.567	3.966	32.86	99.352
0.1406	3.922	33.64	99.396	3.882	33.46	99.174
0.2248	3.846	34.39	99.232	3.804	34.19	99.004
0.3025	3.786	35.13	99.101	3.742	34.92	98.869
0.3928	3.726	36.04	98.969	3.682	35.81	98.734
0.4994	3.669	37.18	98.841	3.624	36.93	98.603
0.6007	3.626	38.32	98.743	3.581	38.05	98.502
0.7212	3.586	39.75	98.651	3.540	39.45	98.406
0.8496	3.557	41.36	98.582	3.509	41.04	98.333
1.0000	3.534	43.33	98.529	3.485	42.99	98.278
	T = 313.15 K			T = 318.15 K		
0.0000	4.015	32.28	99.319	3.976	32.13	99.107
0.0645	3.927	32.70	99.135	3.886	32.52	98.916
0.1406	3.840	33.28	98.950	3.797	33.07	98.724
0.2248	3.761	33.99	98.776	3.716	33.76	98.544
0.3025	3.698	34.69	98.637	3.653	34.46	98.402
0.3928	3.638	35.57	98.500	3.591	35.32	98.261
0.4994	3.580	36.68	98.366	3.533	36.40	98.124
0.6007	3.535	37.79	98.262	3.488	37.50	98.017
0.7212	3.494	39.17	98.164	3.445	38.86	97.916
0.8496	3.462	40.73	98.088	3.413	40.39	97.837
1.0000	3.438	42.66	98.031	3.388	42.29	97.777

Table.2. Coefficients (A_i) of Eq. (9) for π_i^E, H^E and T_s^E with standard deviations (σ) for DEC + 2-ME binary mixtures at different temperatures.

Property	T(K)	A_1	A_2	A_3	A_4	A_5	σ
$\pi_i^E(10^8)$(Nm^{-2})	303.15	-0.1663	0.0051	0.0144	0.0166	-0.0234	1.0000
	308.15	-0.1633	0.0116	0.0037	0.0111	-0.0256	1.0000

	313.15	-0.1611	0.0175	-0.0140	0.0124	-0.0136	1.0000
	318.15	-0.1579	0.0204	-0.0187	0.0144	-0.0193	0.9999
H^E (kJ mol^{-1})	303.15	2.9962	-0.3239	0.0471	-0.2724	0.2284	0.9999
	308.15	3.0630	-0.4469	0.1747	-0.1924	0.2399	1.0000
	313.15	3.1319	-0.5504	0.3530	-0.2144	0.1285	1.0000
	318.15	3.1932	-0.6490	0.4081	-0.2202	0.1857	1.0000
T_S^E (10^{-2}) (J mol^{-1})	303.15	0.3544	-0.0756	0.0131	-0.0195	0.0185	1.0000
	308.15	0.3715	-0.0867	0.0213	-0.0155	0.0229	1.0000
	313.15	0.3884	-0.0962	0.0370	-0.0195	0.0118	1.0000
	318.15	0.4061	-0.1058	0.0436	-0.0206	0.0163	0.9999

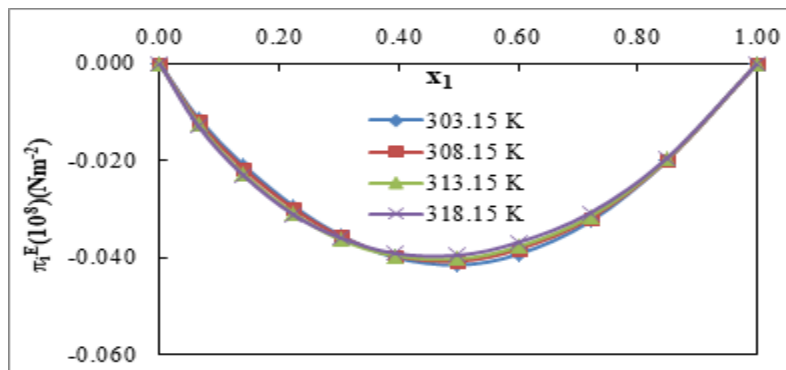**Fig.1.** Variation of excess internal pressure, π_i^E with mole fraction of DEC for the binary mixture DEC + 2-ME at temperatures: 303.15K($\blacklozenge$), 308.15K($\blacksquare$), 313.15K ($\blacktriangle$) and 318.15K(x).
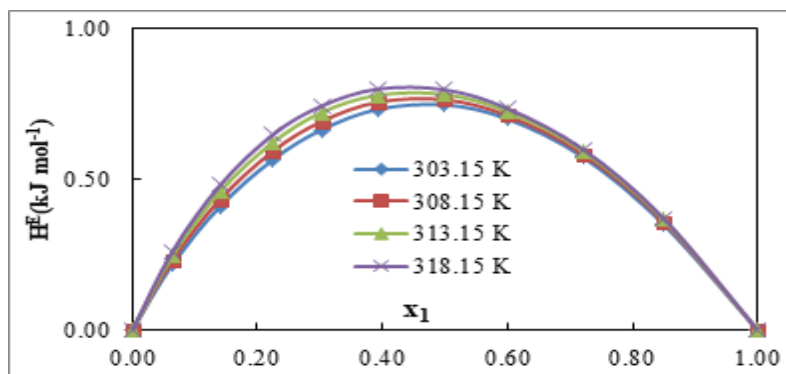

Fig.2. Variation of excess enthalpy, H^E with mole fraction of DEC for the binary mixture DEC + 2-ME at temperatures: 303.15K($\blacklozenge$), 308.15K($\blacksquare$), 313.15K ($\blacktriangle$) and 318.15K(x).

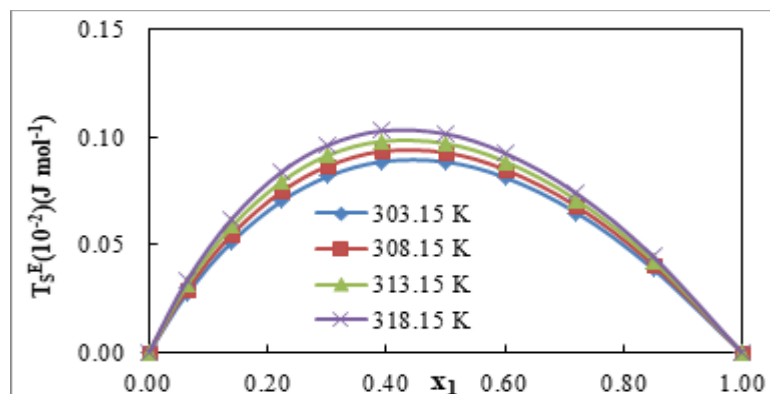**Fig.3.** Variation of excess entropy, T_s^E with mole fraction of DEC for the binary mixture DEC + 2-ME at temperatures: 303.15K($\blacklozenge$), 308.15K($\blacksquare$), 313.15K ($\blacktriangle$) and 318.15K(x).

From Fig.1 the π_i^E values are observed to be negative for the binary mixtures over the entire composition range and at all investigated temperatures. With increase in temperature the decrease in π_i^E values can also be observed. It has been established that the sign and magnitude of excess functions give good estimate of the strength of the unlike interactions in a binary mixture. Chemical contributions include breaking up of associates present in pure liquids resulting in negative π_i^E and specific interactions, like formation of strong hydrogen bonds, charge-transfer complexes and other complex forming interactions including strong dipole–dipole interactions between component molecules. From Fig. 2 the H^E values are observed to be positive for the binary mixtures at all the temperatures studied. It can also be observed from the same figure that with the increase in temperature, the H^E values are increased. In general, H^E values of mixing depend upon the relative enthalpies of endothermic and exothermic effects that arise on mixing of the components[25].It can be observed that the positive value of H^E indicate endothermic process[26] in the mixing of the DEC with 2-ME systems. The positive H^E values may be attributed to ion-dipole interactions between the solvent molecules and DEC and are dominant over the ion-ion or dipole-dipole interaction between unlike molecules. From Fig 3 the T_s^E values are observed to be positive for the binary mixtures at all the temperatures studied. The positive T_s^E values of the mixtures further support the conclusions drawn from the π_i^E and H^E values, that the hydrogen bonding in 2-ME are broken, and dipole-dipole interactions between DEC with 2-ME are formed and leads to increase in volume. This leads to an increase in the entropy of the mixture resulting in positive T_s^E values.

4. CONCLUSIONS

Using the experimental values of density and speed of sound, the internal pressure (π_i), enthalpy (H), entropy (T_s), excess internal pressure (π_i^E), excess enthalpy (H^E) and excess entropy (T_s^E) at temperatures 303.15, 308.15, 313.15 and 318.15 K over the entire mole fraction range have been calculated. The excess internal pressure values are observed to be negative whereas excess enthalpy and excess entropy are observed to be positive. Our previous results of excess molar volume, excess isentropic compressibility support these results.

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