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Thermodynamic and acoustic properties of binary mixtures of PEGDME 200 with 1-propanol

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ABSTRACT: *The work presented in this paper deals with the study of thermodynamic properties of new working fluids for absorption machines, mainly for characterization of absorbent–refrigerant pairs that could improve the cycle performance. The study of atomic motion in liquids plays an important role in understanding the solid-like behavior of liquids. The accurate measurement of the energy changes due to scattering can be used to study the dynamical behavior of liquids. Measurements of the ultrasonic velocity (u), density (ρ), and viscosity (η) for binary mixtures of polyethylene glycol 200 dimethyl ether with 1-propanolover the entire composition range to investigate the nature of intermolecular interactions between the components of these liquid mixtures. Non-linear variation of derived quantities with the mole fraction supports the molecular interaction occurring between component molecules.*

Keywords: *Glymes, density, ultrasonic, velocity, inter molecular interaction, thermophysical properties*

INTRODUCTION

Thermodynamic properties of binary or ternary mixtures of liquids are of key importance from a theoretical and technological viewpoint. Their immense importance lies in various industrial applications like heat transfer, fluid flow, mass transfer, equipment designing, chemical separation. Generally, the mixing of two or more compounds results in deviations from the ideal behavior. The degree of these deviations can be studied in terms of various calculated excess thermodynamics functions. The calculated excess thermodynamic functions reflect a qualitative way to extract the information regarding the molecular structure and intermolecular interactions present in different solvents and solutes. The measurements of such properties of binary mixtures containing self associated and polar compounds like benzyl alcohol and aliphatic amines exhibit remarkable deviation from ideality. The reason for significant deviations may be a difference in sizes or the presence of intermolecular hydrogen bonding among the different components of a binary mixture. The choice of solvents used in the present study has been done based on their vast industrial applications. Benzyl alcohol is an aromatic alcohol flow toxicity, high polarity, and low vapor pressure. As a solvent, it is the main component of inks, liquor, shellac, paints, and epoxy raisin coatings. In health care practices, benzyl alcohol also acts as a bacteriostatic preservative at low concentrations used to treat intravenous medications. It shows its potential incometic industry, photography as well as in the food industry also. Several studies have been reported on their thermodynamic data due to its distinctive physicochemical properties. Amines (the organic derivatives of ammonia) are in abundance in nature. Amines are also released by certain amino acids and proteins which also constitute the basis of life DNA. Primary and secondary amines are regarded as weak self associated class of compounds possessing low dipole moment and low vapor pressure. Amines are very inserting important industrial chemicals used as an additive in the manufacturing of petrochemicals, initiator form an ufacturingo fazodyesetc. Primary, secondary, and tertiary amine differs strongly by their static environment to ftheirnucle ophiliccentre.To extendour previous study and to reveal the structural influence of a liphaticlinear and branch edamines, the present research work has been focused on the measurement of density and speed of sound of binary mixtures containing benzyl alcohol and amines(propylamine, diisopropylamine, diisopropylamine, and tri-propyl amine) over the entire range of mole fraction with an interval of 6K and at atmospheric pressure = 0.1MPa.Further, the measured data on density and ultrasonic velocity has been used to compute the excess parameters like excess molar volume(Vm E), excessive topic compression (κS E), and excess speed of sound (uE). The nature of interaction in liquid mixtures also influences the physicochemical properties. The Prigogine–Flory–Patterson (PFP) theory has also been examined to estimate the excess molar volume and excess isentropic compression for the studied mixtures and the results were compared.

Thespecificationsofpurecomponents used in the present study.

Components	Source	CAS Number	Purity in Mass Function	Analysis Method
Benzyl alcohol	S.D fine chemicals, India	100-51-6	≥ 0.994	GC
Prophyl amine	S.D fine chemicals, India	107-10-8	≥ 0.995	GC
Disco- Propyl amine	S.D fine chemicals, India	108-18-9	≥ 0.995	GC
Tri-Propyl amine	S.D fine chemicals, India	102-69-2	≥ 0.995	GC

GC= gas chromatography.
Experimental densities (ρ), speeds of sound (u) and calculated specific heat capacity (CP) for pure liquids at pressure P = 0.1 MPa.

Components	T/K	ρ × 10−3/kg m−3 u/ms−1 CP/(J·K−1·mol−1) Expt. Lit				u/ms−1 t. Expt. Lit.	CP/(J·K−1·mol−1) Expt. Lit
Benzyl alcohol	303.15	1.03721.0376 [29] 1.0365 [5]				1513.01514.0 [29] 1510.8 [5] 1511.0 [31]	222.94 [32]
	308.15	1.0333 1.0333 [29]				1498.01496.3 [5]	224.5 [32]
	313.15	1.0295 10291 [29] 1029.2 [5]				1482.01483.6 [5] 1485.0 [29]	227.6 [32]
Propyl amine	303.15	0.70750.7075 [33] 0.7092 [34] 0.7090 [36] 0.7093 [40]				1191.91193.96 [34] 1189.5 [36] 1193.1 [40]	229.1[32] 161 [33]
	308.15	0.70180.7026 [33] 0.7012 [35] 0.7039 [34] 0.7036 [36] 0.7031 [40]				1169.01169.9 [34] 1164.9 [36] 1170.6 [40]	162 [33]
	313.15	0.69770.6977 [33] 0.6982 [36] 0.6960 [39] 0.6982 [36] 0.6960 [40]				1148.61149.0 [33] 1140.4 [36] 1140.4 [36] 1150.6 [40]	164 [33]
	318.15	0.6926				1122.6	165.9[31]

Di-propylamine	303.15	0.72860.7282 [37] 0.7312 [33] 0.7313 [34] 0.7291 [41] 0.7290 [42]	1169.21170.4[34] 1174.0 [33] 1167.4 [41] 1167.1 [42] 1167.6 [43]	253[33]
	308.15	0.72390.7236 [37] 0.7248 [35] 0.7267 [33] 0.7267 [34]	1149.81149.0 [34] 1151.0 [33]	254 [33]
	313.15	0.72170.7222 [33] 0.7216 [39]	1127.51127.0 [33]	256 [33]
Diisopropyl amine	318.15	0.71770.7177 [33]	1103.01103.0 [33]	257 [33]
	303.15	0.70660.7066 [38] 0.7099[33] 0.7102 [44]	1069.31069.3 1071.0 [33]	268 [33]
	308.15	0.70170.7017 [38] 0.7051 [33]	1047.01047.0 [38] 1046.0 [33]	270 [33]

	313.15	0.69680.7003 [33]	1023.81019.0 [33]	272 [33]
Tri-propyl amine	318.15	0.69550.6955 [33]	993.0 993.0 [33]	274 [33]
	303.15	0.74920.7498 [33] 0.7491 [45]	1168.2 1171 [33]	305 [33]
	308.15	0.74570.7458 [33]	1153.71150 [33]	307 [33]
	313.15	0.74150.7417 [33] 0.7404 [45] 0.7404 [39]	1132.61128 [33]	309 [33]
	318.15	0.73770.7377 [33]	1107.0 1107.0 [33]	311 [33]

Standarduncertaintiesuareu(T)=±0.02K,u(p)=±0.04MPaandthecombinedexpandeduncertaintyUcinmolefraction,densityandsoundvelocitywereUc(x)=±0.005,Uc (ρ) = ±0.0008 × 10−3/kgm−3 and Uc(u) = ± 0.8 m·s−1 respectively,(0.95level ofconfidence.

Experimental

Materials and methods :

The specification of chemicals used in the present study has been summarized in Table 1. These liquids are dried over a molecular sieve of 4 Å. The purities of the experimental liquids declared by the manufacturer were ascertained by comparing the densities and speeds of sound with those reported in the literature [29–45] and are listed in Table 2. There is good consistency in measured and literature data. The preparations of the mixtures have been without further purification of chemicals by using airtight stoppered bottles to avoid evaporation of the liquids.

Apparatus and procedures

Density and speed of sound of pure liquids and the binary mixtures have been measured using a calibrated single stem capillary pycnometer (capacity ≈14 ml) and an ultrasonic interferometer (Mittal Enterprises, New Delhi, Model: M-82) operating at 2 MHz respectively. During the experiment, all the measurements and temperatures were controlled by circulating the water through an ultra-thermostat JULABOF-25(made in Germany) keeping temperature accuracy within ±0.02K. The details of the experimental setup, calibration, and measuring procedure have been described elsewhere [46]. All the mass measurements were performed on an electronic balance (MettlerAE240, Switzerland) with precision upto±0.05mg. Freshly prepared samples have been analyzed. The uncertainty in densities and speeds of sound measurements was within±0.1kg·m−3and±1m·s−1. For better interpretation of result the I.R.spectra of the pure components and their equimolar mixtures were also recorded by using a Fourier Transform Infrared Spectro meter based on double be am performance having a resolution of 2 cm−1 provided with a sample space 150 mm2. The spectrum was recorded at a temperature of 303.15 K using quartz crystal in the region 4000cm−1 to 400 cm−1.

Results and discussion

The measured values of density (ρ) and speed of sound (u) for the binary mixtures of benzyl alcohol with propylamine, di-propyl amine, diisopropylamine, and tri-propyl amine at different compositions and temperatures has been tabulated in Table3 and graphically represented in Figs.S1 and S2 respectively. Both density values and speed of sound values decrease with an increase of temperature and increase with increasing concentration of benzyl alcohol for all the studied systems. The measured values of densities, ρ and ultrasonic velocity, u were fitted to a polynomial expression given by equation

Fx ðÞ¼X k i¼1 Aixi−1 1 ð1Þ.The values of coefficients Ai and standard deviations σ for both ρ and u are summarized in Table S1.

Excess properties

The excess molar volumes, excess isentropic compression, and excess speed of sound for all the measuring systems have been listed in Table S2.

The excess molar volume Viscosity deviations for

[Et_3S][TFSI] + 1-propanol, [Amim][TFSI] + 1-propanol, and [$(OH)_2$Im][TFSI] + 1-propanol are negative over the entire temperature range. The speed of sound deviations are positive and negative for the binary mixtures of 1-propanol with [Et_3S][TFSI] and [Amim][TFSI], whereas those for the mixture with [$(OH)_2$Im][TFSI] are negative.

whereρandρ∗are the densities of the mixtures and pure components,j respectively; Xj and Mj represent the mole fraction and molar mass of component j in the mixture, respectively.

Theisentropic compression has been calculated by using equation given by Newton and Laplace κS ¼1 ρu2 ð3Þ.
The comparable excessive tropic compressions (κS E) have been calculated from the subsequent equation:
Viscosity deviations for $[Et_3S][TFSI]$ + 1-propanol, [Amim][TFSI] + 1-propanol, and $[(OH)_2Im][TFSI]$ + 1-propanol are negative over the entire temperature range. The speed of sound deviations are positive and negative for the binary mixtures of 1-propanol with $[Et_3S][TFSI]$ and [Amim][TFSI], whereas those for the mixture with $[(OH)_2Im][TFSI]$ are negative**.** The value of CP, i and the thermal expansion coefficient αi have been evaluated from literature [24,49,50] .

FTIR studies :
Infra-red spectroscopy is a leading tool in determining interactions arising due to hydrogen bonding residing in different mixtures. So, the FTIR studies of the pure solvents and their mixtures at equimolar concentration have been performed. The resultant shifts in stretching frequencies and the recorded spectra (Table 8; Figs. S4 –S7) have been provided in supporting information. A view of FTIR data assists the presence of intermolecular hydrogen bonding in the studied systems (except for tributylamine). From the data tabulated in Table 8, a change in stretching vibration frequencies of N\\H bond and O\\H bond in 1:1 mixtures can be spotted. So, hydrogen of primary amine can easily escape towards oxygen atom of benzyl alcohol through the formation of hydrogen bond leading to absorption at a lower frequency. A more negative shift (Δν) has been observed in the case of propylamine which points out the presence of intermolecular hydrogen bonding between the alcoholic group of benzyl alcohol and amino group (O—H—N—H) of propylamine. The negative shift (Δν) has been reduced for dipropyl amine due to the availability of less hydrogen and a large positive shift values incase of diisopropylamine due to an increase in steric hindrance has been observed as compared to propylamine. The shift fortributylamine is not available due to the absence of hydrogen. Also, the hydrogen from –OH group has a lesser tendency to interact with the nitrogen of the amine group of tributylamine due to its bulky size and more electron negativity of the oxygen atom. The shifts authenticate the presence of a cross association between the two components of studied mixtures and support the results obtained from other measured physiological and thermodynamic properties.

Conclusions

The binary mixtures containing benzyl alcohol and aliphatic amines have been studied to measure densities and speed of sound at different temperatures and compositions. This raw data of measured data on density and speed of sound has been utilized to execute excess molar volume and excess molar isentropic compression. These calculated properties have also beenfitted to Redlich Kistertypepolynomial equation and are well demonstrated in the text. TheFTIR studies have also been performed to establish a liaison between the thermodynamic properties and structure elucidation. From the interpretation of excess molar volume data and excess molar isentropic compression, the existence of specific interactions and the interactions due to the formation of hydrogen bonding between the unlike molecule has been revealed. Further, theoretical studies have been done for results obtained for excess molar volume and speed of sound. Excess molar volume was correlated by applying Prigogine–Flory–Patterson theory, which unveils the suppression of P∗contribution by the dominance of interaction and free volume contribution. Intermolecular free length theory and collision frequency theory were used on the speed of sound results. For equimolar compositions, FTIR studies have also been performed, which confirmed the interactional forces present between the studied systems.

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