Study of volumetric and thermodynamic properties of binary mixtures 1,4-butanediol with methylpyridine isomers at different temperatures ☆

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ABSTRACT

Densities, ρ and speeds of sound, u of {1,4-butanediol (1,4BD) + methylpyridine isomers (α-, or β-picoline)} binary mixtures have been measured over the entire composition range at a temperature of (303.15, 308.15, 313.15 and 318.15) K, and at atmospheric pressure (0.1 MPa). The measured densities and speeds of sound data have been utilized to determine excess molar volumes, V_m^E, excess isentropic compressibilities, κ_s^E, excess molar isentropic compressibilities, $\kappa_{s,m}^E$, excess speed of sound, u^E and excess isobaric coefficient of thermal expansion α_p^E of the investigated mixtures. Excess parameters were correlated by the Redlich–Kister polynomials. Excess partial molar volumes ($\overline{V}_{m,1}^E$ and $\overline{V}_{m,2}^E$) and their limiting values at infinite dilution ($\overline{V}_{m,1}^{0E}$ and $\overline{V}_{m,2}^{0E}$) have been calculated from the experimental density measurements and were analytically obtained using Redlich–Kister and Legendre polynomials. The deviation in V_m^E were investigated by employing Prigogine–Flory–Patterson theory.

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1. Introduction

The thermophysical, thermodynamic, and bulk properties of binary mixtures are studied for many reasons, specifically in light of the fact of their ability to provide information about the nature and extent of molecular interactions in the liquid state. Alkanediols are chemically very similar to alcohols and the hydration properties have been observed for these compounds by several authors [1–4]. Butanediols are four carbon diols that have many industrial and biological applications [5,6]. Due to the presence of two-OH groups in the molecule, and certain molecular flexibility, the solution chemistry of these compounds can be strongly influenced by the intermolecular and intra-molecular hydrogen bond formation.

1,4-BD is a clear viscous liquid, which is miscible with water and most polar organic solvents. The presence of two hydroxyl groups in vicinal positions (at the positions 1 and 4) of this diol makes it suitable as a useful chemical intermediate in the manufacture of many chemical products.

Picoline refers to three different methylpyridine isomers, all are colorless liquids at room temperature and pressure and are miscible with water and most organic solvents. α-Picoline is used as an adhesive for

textile tire cord and also a precursor to the agrochemical, nitrapyrin, which prevents loss of ammonia from fertilizers. β-Picoline is a useful precursor to agrochemicals, such as chlorpyrifos and used to make antidotes for poisoning by organophosphate acetylcholinesterase inhibitors.

It is observed that mixing of different compounds offers improvement in properties such as volume, enthalpy and entropy of mixing, thereby reflecting the degree of the deviations from non-ideality. The excess properties are necessary for the design and calculation of the chemical engineering process involving substance separation, heat transfer, mass transfer and fluid flow [7]. The information about the excess properties of liquid mixtures containing 1,4-BD and picolines, and their dependence on composition and temperature constitute are very important fundamental data owing to their applications in different fields. To date, numerous studies have been centered on binary or ternary systems consisted of H-bond containing chemicals such as alcohols with non-polar or polar solvents [8–13]. With these studies, some important factors responsible for the positive or negative deviations for binary polar–polar or non-polar–polar systems have been discussed. However, a survey of the literature [14–21] reveals that very few reports have been made on the excess quantities for binary solutions of 1,4-BD. To the best of our knowledge, literature survey reveals that no studies have been reported till now pertaining to thermodynamic properties of 1,4-BD with methylpyridine isomers. These mixtures are very interesting from the experimental as well as theoretical point of view

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because 1,4-BD and methylpyridine isomers are polar as indicated by their dipole moments and their dielectric constants($\mu_{1,4-BD} = 2.58$ D, $\varepsilon_{1,4-BD} = 30.2$ and $\mu_{picoline} = 1.96$ D, $\varepsilon_{picoline} = 13.5$) [22,23].

1,4-BD is excellent H-bond donors/acceptors, and, therefore, is strongly associated through intermolecular H-bonding [24]. Diols have three-dimensional networks of hydrogen bonds [25]. Picolines are aprotic co solvents. Therefore, interesting theoretical developments and rationalizations may be anticipated from the experimental measurements that reflect the molecular interactions between the unlike molecules in these binary mixtures. Hence, the present study will be useful in understanding the competitive role of hydrogen bonding (both intra- and intermolecular) and the nonspecific interactions and structural effects. These considerations prompted us to measure densities, speeds of sound and excess molar properties of {1,4-BD + α-, β-picoline} mixtures.

2. Experimental

1,4-BD and methylpyridine isomers (Sigma-Aldrich, USA, mass fraction purity 0.99) used in this study were purified by standard methods [26,27]. Before use, all chemicals were stored over 0.4 nm molecular sieves for 72 h to remove the water content, if any, and were degassed at low pressure. Moreover, name of the chemical, source, CAS number, purification method and purity in mass fraction of the component liquids are given in Table 1. The mixtures were prepared by mass and were kept in special airtight stoppered glass bottles to avoid evaporation. All samples were prepared immediately prior to measurements using an electronic balance (CPA-225D, Sartorius, Germany) precisely within $\pm 1 \times 10^{-5}$ g. The uncertainty in the mole fraction was estimated to be within $\pm 1 \times 10^{-4}$.

The densities of the pure liquids and their binary mixtures were measured by using a single-capillary pycnometer (made of Borosil glass) having a bulb capacity of ≈ 10 mL. The capillary, with graduated marks, had a uniform bore and could be closed by a well-fitting glass cap. The marks on the capillary were calibrated by using triply distilled water. The densities of pure water at the required temperature were taken from the literature [28]. The reproducibility of the density measurements was within $\pm 2 \times 10^{-5}$ g·cm^{-3}. The temperature of the test liquids during the measurements was maintained to an accuracy of ± 0.02 K in an electronically controlled thermostatic water bath (Julabo). The speeds of sound in pure liquids and in their binary mixtures were measured using a single-crystal variable-path multifrequency ultrasonic interferometer (Mittal Enterprises, India, model F-81) operating at 2 MHz. The speeds of sound data were reproducible within ± 0.2 m s^{-1}.The reliability of experimental measurements of density and speed of sound was ascertained by comparing the experimental data of the pure liquids with the corresponding literature values [29–34] at the studied temperatures. This comparison is given in Table 2 and the experimental and literature values compare well in general.

3. Theory

The values of the experimental density (ρ), speed of sound (u), excess molar volume (V_m^E), excess isentropic compressibility (κ_s^E), excess molar isentropic compressibility ($\kappa_{s,m}^E$), excess speed of sound (u^E) and excess isobaric coefficient of thermal expansion (α_p^E) for the binary

mixtures of 1,4-BD with methylpyridine isomers over the temperature range from (303.15 to 318.15) K are given in Table 3. The excess molar volume data were obtained from the densities of the pure liquids and their mixtures using the following equation:

$$V_m^E = V_m - V_m^{id} = \frac{x_1 M_1 + (1-x_2)M_2}{\rho} - \left(\frac{x_1 M_1}{\rho_1} + \frac{(1-x_2)M_2}{\rho_2} \right) \tag{1}$$

where x_1 and x_2 are the mole fractions, M_1 and M_2 are molar masses, and ρ_1 and ρ_2 are the densities of the pure liquid components 1 and 2, respectively.

The isentropic compressibility is defined as change in volume with pressure, relative to volume at constant entropy. κ_s gives the compressibility per unit volume. The isentropic compressibility coefficients, κ_s, derived directly from the speed of sound and density measurements using the Newton–Laplace equation:

$$\kappa_s = -V_m^{-1}(\partial V_m / \partial P)_s = (\rho u^2)^{-1}. \tag{2}$$

The molar compressibility, is the compressibility of the volume (V) occupied by one mole of constituents of mixture. Molar isentropic compressibility has been calculated by the relation:

$$\kappa_{s,m} = -(\partial V / \partial P)_S = \kappa_s V. \tag{3}$$

The values of α_p are calculated from the temperature dependence of the density data of pure liquids by using the relation,

$$\alpha_p = \frac{1}{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p = -\left(\frac{\partial \ln \rho}{\partial T}\right)_p. \tag{4}$$

Douheret et al. [35,36] have focused on excess isentropic compressibility and excess molar isentropic compressibility using the relations:

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \tag{5}$$

Table 2
Comparison of densities, ρ, speeds of sound, u, and heat capacities, Cp of pure liquids with their literature values at T = 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure 0.1 Mpa.

Compounds	T(K)	ρ/kg·m^{-3}		u/m·s^{-1}		Cp/JK^{-1} mol^{-1}
		(Expt.)	(Lit.)	(Expt.)	(Lit.)	(Lit.)
1,4 Butanediol	303.15	1.0094	1.00967[29]	1590.4	1590.19[30]	205.82[31]
	308.15	1.0068	1.00670[29]	1580.5	1578.49[30]	208.65[31]
	313.15	1.0038	1.00373[29]	1569.2	1566.90[30]	211.57[31]
	318.15	1.0004	1.00076[29]	1555.2	1555.41[30]	214.55[31]
α-Picoline	303.15	0.9352	0.9351[32]	1360.2	1361.08[32]	160.8[33]
	308.15	0.9303	0.9304[32]	1340.4	1339.9[32]	162.6[33]
	313.15	0.9257	0.9271[34]	1320.3		
	318.15	0.9209		1300.4		
β-Picoline	303.15	0.9474	0.9474[32]	1402.2	1404.1[32]	161.2[33]
	308.15	0.9427	0.9428[32]	1385.0	1384.0[32]	163.5[33]
	313.15	0.9381		1365.2		
	318.15	0.9345		1345.3		

Standard uncertainties, u, are u (T) = ± 0.02 K; u (ρ) = ± 0.6 kg·m^{-3}; u (u) = ± 0.67 m·s^{-1}.
Expt. — Experimental, Lit. — Literature.

Table 1
Details of studied compounds, CAS number, source, purification method, purity and analysis method.

Chemical name	CAS number	Source	Purification method	Mass fraction purity	Analysis method
1,4 Butanediol	110-63-4	Sigma Aldrich	Vacuum distillation	≥0.99	GC
α-Picoline	109-06-8	Sigma Aldrich	Vacuum distillation	≥0.99	GC
β-Picoline	108-99-6	Sigma Aldrich	Vacuum distillation	≥0.99	GC

GC = gas chromatography.