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Volumetric properties of piperidine + 1-alkanol binary liquid mixtures experimental results and application of Prigogine–Flory–Patterson theory

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ABSTRACT

Densities of binary liquid mixtures of piperidine with methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and1-octanol have been measured at 293.15, 298.15, 308.15 and 313.15 K and at atmospheric pressure, over the entire range of composition, with a vibrating u-tube densimeter. Density data were used to calculate the excess molar volumes V^E. All the mixtures exhibit large and negative V^E value over the whole mole fraction range indicating strong interactions between unlike molecules. These interactions increase with increasing alkanol chain length and are far stronger for piperidine + methanol system. Temperature effect on V^E is insignificant. Experimental V^E values were fitted with the Redlich–Kister equation. Partial molar volumes at infinite dilution were also determined. Finally, the applicability of the Prigogine–Flory–Patterson theory was tested and discussed.

1. Introduction

Knowledge of physical properties of liquids and excess thermodynamic functions for mixing process is essential for good design of industrial chemical process and for testing theories on liquid mixtures. Among these excess functions, the volume change on mixing is one of the most interesting changes because it is a good thermodynamic tool to explore the behaviour of liquid systems and, also, a sensitive indicator to accuracy of liquid mixture theories.

Amines and alcohols are two classes of technically important compounds. Alcohols, the most well-known polar self-associated solvents, are frequently used in pharmaceutical and cosmetic processes and also such as gasoline additives. Piperidine, a self-associated heterocyclic secondary amine soluble in water, in alcohol and ether, is often used as a solvent for its mild basic properties. It is a structural element of many pharmaceutical drugs. Due to the biological and potential therapeutics of piperidine derivatives, much attention has been paid toward the developments of an efficient synthesis and to the employment of these compounds in drug-like molecules with medicinal uses [1]. A literature survey reveals many recent and less recent experimental and theoretical investigations on thermodynamic properties of mixtures of amines with alcohols [2–21]. In our best knowledge, no excess molar volume data were reported in the open literature, for piperidine + 1-alkanols (from ethanol to 1-octanol) binary systems, whereas there are two reports for piperidine + methanol [6,7].

Continuing our systematic study on thermodynamic properties of mixtures containing piperidine [22–26], we are presently focused on piperidine + methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol and 1-octanol binary liquid systems, with three major aims. The first is to provide, for these mixtures, some quantitative insight concerning their experimental volumetric behaviour. The second is to examine the alcohol length chain and temperature effects on their excess molar volume and to analyse, in terms of molecular interactions, the sign and the magnitude of this excess property. The third aim is to test the applicability of the Prigogine–Flory–Patterson (PFP) theory [27–35]. In this paper, we report experimental densities, excess molar volumes and other derived volumetric properties, for the seven investigated liquid binary mixtures of piperidine with 1-alkanol. Finally, the results of the theoretical V^E calculations along with the discussion on the prediction ability of the PFP model, for these mixtures, are also reported.

2. Experimental section

2.1. Materials

Methanol (99.8 mass %) was purchased from Prolabo. Ethanol (99.8 mass %), 1-propanol (99.5 mass %) and 1-butanol (99.5 mass %) are Riedel De Haën products. 1-Pentanol (99 mass %) and 1-hexanol (99 mass %) were purchased from Fluka. 1-Octanol (99.5 mass %) and piperidine (99 mass %) are Riedel De Haën products. All the chemicals were used without any further purification. Experimental densities of the pure liquids are well compared, in Table 1, with corresponding literature values [36–39].

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Table 1
Experimental densities, ρ, of pure liquids with corresponding literature data.

Chemical	CAS number	T/(K)	ρ /(g·cm^{-3})	
			This work	Lit.
Piperidine	110-89-4	293.15	0.86182	0.86164[a]
		298.15	0.85718	0.85700[a]
		308.15	0.84782	0.84763[a]
		313.15	0.84311	0.84292[a]
Methanol	67-56-1	298.15	0.78680	0.78694[b]
Ethanol	64-17-5	298.15	0.78531	0.78525[b]
1-Propanol	71-23-8	298.15	0.79995	0.79955[b]
1-Butanol	71-36-3	293.15	0.81005	0.809644[c]
		298.15	0.80608	0.805842[c]
1-Pentanol	71-41-0	293.15	0.81469	0.814738[c]
		298.15	0.81103	0.811067[c]
1-Hexanol	111-27-3	293.15	0.81880	0.818962[c]
		298.15	0.81524	0.815387[c]
1-Octanol	111-87-5	298.15	0.82171	0.82161[d]

[a] Ref [36].
[b] Ref [37].
[c] Ref [38].
[d] Ref [39].

2.2. Apparatus and procedure

The densities were measured at 293.15, 298.15, 303.15 and 313.15 K and atmospheric pressure, with an Anton Paar DMA 5000 vibrating u-tube densimeter. The apparatus, certified precise to within 10^{-5} g cm^{-3}, whose temperature is controlled to within 0.01 K by a built-in Peltier device, was calibrated with dry air and bidistilled water. After calibration, the accuracy in the determination of the density, ρ, is estimated to be less than 2 10^{-5} g cm^{-3}. Mixtures were prepared by weighing, using a Metler balance with a precision of $\pm 10^{-3}$ g. Uncertainties in mole fraction and excess molar volume are estimated to be less than $\pm 10^{-4}$ and ± 2 10^{-3} cm^3 mol^{-1}, respectively.

3. Results and discussion

3.1. Experimental results

The experimental densities, ρ, and excess molar volumes, V^E, are reported in Table 2 (see supplementary file).

The excess molar volumes were calculated from the density data, according to:

$$V^E = \left[\frac{x_1M_1 + x_2M_2}{\rho}\right] - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2}\mathbb{S} \quad (1)$$

where, x_1 and x_2, M_1 and M_2, and ρ_1 and ρ_2 represent the mole fractions, molar masses and densities of piperidine (1) and 1-alkanol (2), respectively. ρ stands for the mixture density.

The V^E values were correlated by Redlich–Kister type polynomial equation [40]

$$V^E = x_1x_2\sum_{k=0}^{k=3} A_k(x_1 - x_2)^k. \quad (2)$$

The coefficients A_k of Eq. (2) and corresponding standard deviations σ obtained from a least squares fit with equal weights assigned to each point are given in Table 3.

Fig. 1 shows the dependence of the excess molar volume V^E on composition, for the seven investigated mixtures, at 298.15 K. It can be seen that all these mixtures exhibit large and negative V^E value over the entire composition range indicating the existence of a strong cross association between the alkanol and piperidine molecules, through the hydrogen bond of O – H···N. The interactions between unlike molecules increase with increasing alkanol chain length and are far stronger for the mixture of piperidine with methanol. One can be seen also that our V^E data, for piperidine + methanol system, well agree with literature V^E data [6], which are obtained from densities measured with a pycnometer. It should be pointed out, also, that our V^E results, at 303.15 K, for this system, strongly disagree with literature V^E data [7], which are determined from densities measured with a standardized specific gravity bottle. Table 2 (See supplementary file) reveals, for all the mixtures, an insignificant temperature effect on V^E.

Knowledge of partial molar properties at infinite dilution provides useful information about solute–solvent interaction since, at the infinite dilution, solute–solute interactions disappear. This information is of particular interest because it is independent of the composition of the mixture. In this work, we are focused on partial molar volume of piperidine at infinite dilution ($x_1 = 0$) in an alkanol and vice versa. These limiting values of partial molar volumes were calculated as follows.

Partial molar volumes, V_1 and V_2, of piperidine (1) and alkanol (2), respectively, are given by:

$$V_1 = V^E + V_1^0 + (1-x_1)\left(\partial V^E/\partial x_1\right)_{P,T} \quad (3)$$

$$V_2 = V^E + V_2^0 - x_1\left(\partial V^E/\partial x_1\right)_{P,T} \quad (4)$$

where V_1^0 and V_2^0 are the molar volumes of the pure liquids 1 and 2, respectively.

Table 3
Parameters A_k of Eq. (2) and standard deviations, σ, at different temperatures.

T K	A_0	A_1	A_2	A_3	σ (cm^3·mol^{-1})
Piperidine (1) + methanol (2)					
293.15	−5.0234	1.2567	0.3778	−0.5015	0.004
298.15	−5.1172	1.2724	0.3521	−0.5035	0.004
303.15	−5.2798	1.2936	0.3639	−0.5902	0.004
313.15	−5.3841	1.3187	0.2884	−0.5200	0.004
Piperidine (1) + ethanol (2)					
293.15	−4.3375	1.2494	0.4291	−0.7487	0.004
298.15	−4.3918	1.2586	0.3989	−0.7442	0.004
303.15	−4.4917	1.2661	0.3271	−0.7425	0.004
313.15	−4.5380	1.2645	0.2894	−0.7150	0.004
Piperidine (1) + 1-propanol (2)					
293.15	−4.4035	1.0473	0.4176	−0.2792	0.005
298.15	−4.4423	1.0480	0.3889	−0.2675	0.005
303.15	−4.4896	1.0186	0.3746	−0.3373	0.004
313.15	−4.5518	1.0330	0.2890	−0.2337	0.005
Piperidine (1) + 1-butanol (2)					
293.15	−4.1418	0.9123	0.4002	−0.4759	0.003
298.15	−4.2051	0.9357	0.3040	−0.3702	0.004
303.15	−4.2376	0.8972	0.3091	−0.4542	0.003
313.15	−4.3045	0.9115	0.1982	−0.3242	0.004
Piperidine (1) + 1-pentanol (2)					
293.15	−3.7830	0.8837	0.4014	−0.5174	0.005
298.15	−3.8160	0.8687	0.3761	−0.4922	0.005
303.15	−3.8938	0.8413	0.3138	−0.4576	0.005
313.15	−3.9318	0.8352	0.2759	−0.4543	0.005
Piperidine (1) + 1-hexanol (2)					
293.15	−3.5794	0.9407	0.5090	−0.4606	0.004
298.15	−3.6140	0.9305	0.4953	−0.4520	0.004
303.15	−3.6874	0.9014	0.4163	−0.4263	0.004
313.15	−3.7313	0.8839	0.3866	−0.3952	0.004
Piperidine (1) + 1-octanol (2)					
293.15	−2.9851	1.0946	0.4876	−0.6372	0.004
298.15	−3.0315	1.0813	0.4659	−0.6210	0.004
303.15	−3.1329	1.0576	0.3962	−0.6084	0.004
313.15	−3.1920	1.0436	0.3607	−0.5804	0.004