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Influence of alkyl group and temperature on thermophysical properties of carboxylic acid and their binary mixtures

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ABSTRACT

In this work, volumetric, acoustic and refractive index methods have been used to study the interactions between carboxylic acids mixtures as a function of temperature and concentration. The density (ρ), sound velocity (u), refractive index (n) of butanoic acid, pentanoic acid and heptanoic acid and their binary systems (butanoic or heptanoic acid + pentanoic acid) have been measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K and at $p = 0.1$ MPa. The Lorentz–Lorenz approximation and sound velocity mixing rules were used to test the accuracy of the experimental data. The derived properties such as excess molar volumes, V_m^E, isentropic compressibilities, κ_s, excess isentropic compressibilities, κ_s^E, and deviation in refractive indices, Δn, were also calculated. The Redlich–Kister polynomial equation was used to fit the excess/deviation properties. These results are useful for describing the intermolecular interactions that exist between the components in mixtures. This work also tests various sound velocity mixing rules to calculate the sound velocity of the binary mixture from pure component data, as well as examine the use of the Lorentz–Lorenz approximation to predict density from refractive index and vice versa.

1. Introduction

Carboxylic acids are important chemicals used in a variety of industrial applications such as separation processes, manufacture of pharmaceutical products, cleaning agents, food and beverages as an acidulant, the manufacture of polyester resins, pharmaceutical and chemical industries [1–3]. Carboxylic acids are also used as buffers, food preservatives, flavouring agents, fungicides, insecticides and catalysts [1–5]. A large number of natural products are either derivatives of carboxylic acids or are derived from this group of compounds. The carboxylic acid consists of two functional groups; a carbonyl group and a hydroxyl group. The hydroxyl group is bonded to a carbonyl (>C═O) group in the carboxyl group.

To better understand the nature of the butanoic acid, pentanoic acid and heptanoic acid and to expand on its usefulness, a detailed knowledge of the thermodynamic behaviour of these acids is essential [6,7]. In particular, for its use as a solvent, it is important to understand the thermo physical properties: density, sound velocity, refractive index, viscosity; thermodynamic properties: heat capacity, Gibbs free energy, excess molar volume, excess molar enthalpy of the carboxylic acid and its mixtures. These properties also provide information about the intermolecular interactions [8–11] and allows for the development of new correlations and/or thermodynamic predictive models. To this end, a database of the thermodynamics properties for butanoic acid, pentanoic acid and heptanoic acid can be quite useful [12], and this is the rationale for this study.

Although carboxylic acids have been widely studied, there is no data available in the literature on the properties such as density, sound velocity and refractive index for the binary systems of butanoic or heptanoic acid with pentanoic acid. This investigation is a continuation of the studies on carboxylic acid mixtures [2,13–20].

2. Experimental

2.1. Chemicals

The butanoic acid (CAS No. 107-92-6) and heptanoic (CAS No. 111-14-8) acids had a purity of mass fraction ≥0.99 and was supplied by Aldrich. The pentanoic acid (CAS No. 109-52-4) had a

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purity of mass fraction ≥0.98 and was supplied by Merck. All the chemicals were stored over 0.4 nm molecular sieves to remove moisture. The mass percent water content was determined using a Metrohm 702 SM Titrino Metter and was found to be 0.39% in butyric acid, 0.20% in pentanoic acid, 0.26% in heptanoic acid, 0.50% in diethyl carbonate and 0.36% in ethanol. Furthermore, the purities of the chemicals were checked by comparing the experimental density, sound velocity and refractive index values for the pure chemicals at various temperatures with those reported in literature [15,21–24]. These results are given in Table 1. No further purification of these chemicals were necessary.

2.2. Apparatus and procedure

Binary mixtures were prepared by mass, using an OHAUS analytical balance with a precision of ±0.0001 g. The estimated error in the mole fraction was 0.0005. The details of the experimental procedure can be found elsewhere [15]. A binary test system (diethyl carbonate + ethanol) [24] was done at 298.15 K to validate the experimental technique. The calculated excess molar volumes, isentropic compressibilities, excess isentropic compressibilities and deviation in refractive index was compared to the literature values. The results for the test system are given in Table 2. The difference between the experimental and literature excess molar volumes, isentropic compressibilities, excess isentropic compressibilities and deviation in refractive index for the test system was within the experimental error.

Density and sound velocity for pure components and binary mixtures were measured using a digital vibrating-tube densimeter and sound velocity analyzer (Anton Paar DSA 5000 M) with an accuracy of ±0.02 K in temperature. The estimated errors in density and sound velocity were less than $\pm 1 \times 10^{-5}$ g cm^{-3} and ±0.5 m s^{-1}, respectively. The instrument can measure simultaneously density in the range of (0–3) g cm^{-3} and sound velocity from (1000 to 2000) m s^{-1} at temperature range of (273.15–343.15) K with pressure variation from (0 to 0.3) MPa. The sound velocity is measured using a propagation time technique [25]. The sample is sandwiched between two piezoelectric ultrasound transducer. One transducer emits sound waves through the sample-filled cavity (frequency around 3 MHz) and the second transducer receives those waves. Thus, the sound velocity is obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound waves [25]. The details regarding sound velocity measurement using the Anton Paar DSA 5000 M are described in literature [25]. Measurement of the refractive index for pure components and binary mixtures were obtained by a digital automatic refractometer (Anton Paar RXA 156) with an accuracy of ±0.03 K in temperature. The estimated error in refractive index was less than $\pm 2 \times 10^{-5}$. The estimated error in excess molar volume, isentropic compressibility, excess isentropic compressibility and deviation in refractive index was ±0.003 cm^3 mol^{-1}, ±1 TPa^{-1}, ±0.6 TPa^{-1} and ±0.00008, respectively.

3. Results and discussion

3.1. Thermophysical properties

3.1.1. Density

The thermophysical properties such as ρ, u and n were measured at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1 MPa for the binary systems (butanoic or heptanoic acid + pentanoic acid) and are given in Tables 3 and 4. It can be seen from these results that the ρ values decrease with an increase in temperature for both binary systems. The ρ values increase with composition for the (butanoic acid + pentanoic acid) system whereas decease for the (heptanoic acid + pentanoic acid) system.

The Lorentz–Lorenz approximation was used to predict density from the measured refractive indices. The predictive expression for ρ can be obtained from the Lorentz–Lorenz approximation [26]:

Table 1
Comparison of experimental density, ρ, sound velocity, u, and refractive index, n, of the pure component with the corresponding literature values at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

Component	T (K)	ρ (g cm^{-3})		u (m s^{-1})		n	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Butanoic acid	293.15	0.95778	0.9576 [21]	1195.5	1195.5 [15]	1.39826	1.3980 [22]
	298.15	0.95281	0.9528 [21]	1179.9	1176.9 [15]	1.39630	1.3963 [22]
	303.15	0.94794	0.9479 [21]	1158.2	1158.2 [15]	1.39421	1.3950 [22]
	308.15	0.94292	0.9429 [21]	1139.7	1139.6 [15]	1.39217	1.3938 [22]
							1.39183 [15]
	313.15	0.93805	0.9379 [21]	1121.3	1121.3 [15]	1.39010	1.3921 [22]
							1.38969 [15]
Pentanoic acid	293.15	0.93941	0.9392 [22]	1234.0		1.40840	1.4080 [22]
	298.15	0.93485	0.9340 [22]	1216.0		1.40641	1.4062 [22]
	303.15	0.93029	0.9303 [22]	1197.9		1.40438	1.4048 [22]
	308.15	0.92573	0.9263 [22]	1179.9		1.40234	1.4030 [22]
	313.15	0.92116	0.921113 [23]	1162.1		1.40030	1.4009 [22]
Heptanoic acid	293.15	0.91765	0.9176 [22]	1295.4		1.42336	1.4230 [22]
	298.15	0.91347	0.9143 [22]	1277.7		1.42138	1.4212 [22]
	303.15	0.90929	0.910259 [23]	1259.9		1.41935	1.4192 [22]
	308.15	0.90511	0.906036 [23]	1242.2		1.41733	1.4174 [22]
	313.15	0.90094	0.901988 [23]	1224.7		1.41530	1.4152 [22]
Diethyl carbonate	298.15	0.96932	0.9691 [24]	1176.6	1176 [24]	1.38249	1.38240 [24]
Ethanol	298.15	0.78524	0.7850 [24]	1142.8	1142 [24]	1.35945	1.35941 [24]