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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]

Table 2
Densities, ρ, sound velocity, u, refractive index, n, excess molar volume, V_m^E, deviation in isentropic compressibility, $\Delta\kappa_s$, and deviation in refractive index Δn, for the binary system {diethyl carbonate (x_1) + ethanol (x_2)} at 298.15 K.

x_1	ρ (g cm^{-3})	u (m s^{-1})	n	V_m^E(cm^3 mol^{-1})	$\Delta\kappa_s$(TPa^{-1})	Δn
0.0000	0.78524	1142.8	1.35945	0.000	0.0	0.00000
0.0415	0.80030	1145.2	1.36136	0.011	−12.8	0.00095
0.0943	0.81771	1147.3	1.36347	0.022	−24.4	0.00185
0.1932	0.84585	1150.9	1.36698	0.046	−38.1	0.00308
0.2929	0.86958	1154.0	1.36981	0.071	−44.2	0.00361
0.3938	0.88996	1156.9	1.37241	0.096	−45.0	0.00389
0.4965	0.90782	1159.8	1.37460	0.111	−42.0	0.00371
0.5970	0.92299	1162.8	1.37647	0.125	−36.5	0.00326
0.6924	0.93573	1166.0	1.37805	0.127	−29.9	0.00265
0.7911	0.94758	1169.7	1.37957	0.113	−21.9	0.00189
0.8990	0.95927	1173.7	1.38109	0.074	−11.7	0.00093
0.9413	0.96358	1175.0	1.38167	0.046	−7.0	0.00053
1.0000	0.96932	1176.6	1.38249	0.000	0.0	0.00000

$$\rho = \frac{\left(\frac{n^2-1}{n^2+2}\right)(x_1M_1 + x_2M_2)}{\left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{x_1M_1}{\rho_1} + \left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{x_2M_2}{\rho_2}} \quad (1)$$

The root mean square deviation (rmsd) between the experimental and predicted density are given in Table 5. The root mean square deviation show that the density predicted from the refractive index was good for both binary systems with the lowest rmsd of 0.00001 g cm^{-3} for the (butanoic acid + pentanoic acid) system.

3.1.2. Sound velocity

Sound velocity is also an important property which describes the solvent–solvent, solute–solvent and solute–solute interactions in the mixture [27]. Tables 3 and 4, reveals that the u values decrease with an increase in temperature for both binary systems. The values of u were found to increase with an increasing composition of heptanoic acid for the (heptanoic acid + pentanoic acid) system whereas this decreases with increasing composition of butanoic acid for the (butanoic acid + pentanoic acid) system at all temperatures.

The sound velocity mixing rules were used to calculate the sound velocity of the binary mixture. The sound velocity mixing rules used were that of Rao [28] Eq. (2), Wada [29] Eq. (3), Nomoto [30] Eq. (4) and Berryman [31] Eq. (5).

$$u^{1/3}V_m = \sum_{i=1}^{2} u_i^{1/3}x_iV_i \therefore u = \left(\sum_{i=1}^{2} u_i^{1/3}x_iV_i/V_m\right)^3 \quad (2)$$

$$\kappa_s^{-1/7}V_m = \sum_{i=1}^{2} \kappa_{s,i}^{-1/7}x_iV_i \therefore u = \left(\sum_{i=1}^{2} u_i^{2/7}\rho_i^{1/7}x_iV_i/\left(\rho^{1/7}V_m\right)\right)^{7/2} \quad (3)$$

$$u = \left(\sum_{i=1}^{2}\phi_i u_i^{1/3}\right)^3 \quad (4)$$

$$\kappa_s = \sum_{i=1}^{2}\phi_i\kappa_{s,i} \therefore u = \left(\rho\sum_{i=1}^{2}\phi_i\kappa_{s,i}\right)^{-1/2} \quad (5)$$

where V_i, u_i, x_i, and ρ_i are the molar volume, sound velocity, mole fractions and density of the pure component i, respectively. The rmsd values calculated between the experimental and calculated sound velocity data using different mixing rules are given in Table 6. These results show that the sound velocity calculated from the different mixing rules was quite good. The maximum root mean square deviation of 0.6 m s^{-1} was obtained using the mixing rule of Rao for the (butanoic acid + pentanoic acid) system.

3.1.3. Refractive index

Refractive indices were measured for butanoic acid, pentanoic acid, heptanoic acid and their binary systems (butanoic acid or heptanoic acid + pentanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K, and at p = 0.1. Tables 3 and 4, reveal that the n values increase with an increasing composition of heptanoic acid for the (heptanoic acid + pentanoic acid) system whereas this decreases with an increasing composition of butanoic acid for the (butanoic acid + pentanoic acid) system at all temperatures. The n values decrease with an increase in temperature for both binary systems.

The inverse predictive expression for n can be obtained from Eq. (1) within the framework of the Lorentz–Lorenz approximation [26] and was used to predict the refractive index from the density data using Eq. (6):

$$n = \left(\frac{2\left[\left(\frac{n_1^2-1}{n_1^2+2}\right)x_1\rho\frac{M_1}{\rho_1}+x_2\left(\frac{n_2^2-1}{n_2^2+2}\right)\rho\frac{M_2}{\rho_2}\right] + [x_1M_1 + x_2M_2]}{[x_1M_1 + x_2M_2] - \left[\left(\frac{n_1^2-1}{n_1^2+2}\right)x_1\rho\frac{M_1}{\rho_1}+x_2\left(\frac{n_2^2-1}{n_2^2+2}\right)\rho\frac{M_2}{\rho_2}\right]}\right)^{1/2} \quad (6)$$

The root mean square deviation (rmsd) between the measured refractive index and predicted refractive index are given in Table 5. The maximum rmsd value was 0.00026 for the (heptanoic acid + pentanoic acid) system. The rmsd results show that the refractive index predicted from the density data gave good results for both systems. These results confirm that the Lorentz–Lorenz approximation is suitable for the prediction of density from the refractive index or vice versa.

3.2. Derived properties

3.2.1. Excess molar volume

The excess molar volumes, V_m^E, for the binary systems were calculated using Eq. (7) with the density data of the mixture and the pure components:

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (7)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 denote molar masses; ρ_1 and ρ_2 are the densities; where 1 refers to butanoic or heptanoic acid and 2 refers to pentanoic acid, and ρ is the density of the binary mixtures.

Table 3
Densities, ρ, excess molar volume, V_m^E, sound velocity, u, isentropic compressibility, κ_s, excess isentropic compressibility, κ_s^E, refractive index, n, and deviation in refractive index, Δn, for the binary system {butanoic acid (x_1) + pentanoic acid (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

x_1	ρ (g cm^{-3})	V_m^E(cm^3 mol^{-1})	u(m s^{-1})	κ_s (TPa^{-1})	κ_s^E(TPa^{-1})	n	Δn
T = 293.15 K							
0.0000	0.93941	0.000	1234.0	699	0.0	1.40840	0.00000
0.0472	0.94014	0.002	1232.3	700	−2.8	1.40813	0.00017
0.0938	0.94086	0.005	1230.6	702	−5.1	1.40770	0.00021
0.1944	0.94246	0.009	1226.9	705	−9.3	1.40676	0.00030
0.2928	0.94408	0.012	1223.3	708	−11.9	1.40581	0.00035
0.3946	0.94582	0.014	1219.5	711	−13.3	1.40481	0.00039
0.4922	0.94756	0.015	1215.8	714	−13.5	1.40383	0.00040
0.5938	0.94945	0.013	1211.9	717	−12.7	1.40278	0.00038
0.6929	0.95138	0.010	1208.0	720	−11.0	1.40174	0.00035
0.7973	0.95348	0.006	1203.8	724	−8.2	1.40060	0.00028
0.8950	0.95552	0.003	1199.9	727	−4.7	1.39949	0.00016
1.0000	0.95778	0.000	1195.5	730	0.0	1.39826	0.00000
T = 298.15 K							
0.0000	0.93485	0.000	1216.0	723	0.0	1.40641	0.00000
0.0472	0.93555	0.003	1214.3	725	−2.8	1.40607	0.00014
0.0938	0.93626	0.005	1212.6	726	−5.2	1.40563	0.00017
0.1944	0.93782	0.009	1208.9	730	−9.3	1.40469	0.00025
0.2928	0.93940	0.012	1205.2	733	−11.9	1.40374	0.00029
0.3946	0.94111	0.015	1201.4	736	−13.3	1.40274	0.00032
0.4922	0.94281	0.015	1197.6	740	−13.6	1.40175	0.00032
0.5938	0.94466	0.013	1193.6	743	−12.8	1.40070	0.00029
0.6929	0.94654	0.010	1189.7	746	−11.1	1.39965	0.00025
0.7973	0.94860	0.006	1185.4	750	−8.3	1.39850	0.00015
0.8950	0.95060	0.003	1181.4	754	−4.7	1.39744	0.00008
1.0000	0.95281	0.000	1176.9	758	0.0	1.39630	0.00000
T = 303.15 K							
0.0000	0.93029	0.000	1197.9	749	0.0	1.40438	0.00000
0.0472	0.93096	0.003	1196.2	751	−2.8	1.40399	0.00009
0.0938	0.93165	0.005	1194.5	752	−5.3	1.40355	0.00012
0.1944	0.93318	0.009	1190.7	756	−9.4	1.40260	0.00020
0.2928	0.93473	0.012	1187.0	759	−12.0	1.40164	0.00024
0.3946	0.93639	0.014	1183.1	763	−13.4	1.40063	0.00026
0.4922	0.93805	0.015	1179.3	767	−13.7	1.39964	0.00027
0.5938	0.93987	0.013	1175.2	770	−12.9	1.39857	0.00023
0.6929	0.94171	0.010	1171.2	774	−11.2	1.39751	0.00018
0.7973	0.94373	0.006	1166.9	778	−8.3	1.39639	0.00012
0.8950	0.94568	0.003	1162.8	782	−4.7	1.39533	0.00005
1.0000	0.94794	0.000	1158.2	786	0.0	1.39421	0.00000
T = 308.15 K							
0.0000	0.92573	0.000	1179.9	776	0.0	1.40234	0.00000
0.0472	0.92637	0.003	1178.2	778	−2.8	1.40190	0.00004
0.0938	0.92704	0.005	1176.5	779	−5.2	1.40146	0.00007
0.1944	0.92853	0.009	1172.7	783	−9.3	1.40051	0.00015
0.2928	0.93005	0.012	1168.9	787	−12.0	1.39955	0.00019
0.3946	0.93168	0.014	1164.9	791	−13.4	1.39853	0.00020
0.4922	0.93330	0.015	1161.0	795	−13.7	1.39753	0.00020
0.5938	0.93508	0.013	1156.9	799	−12.9	1.39646	0.00016
0.6929	0.93687	0.011	1152.9	803	−11.2	1.39541	0.00012
0.7973	0.93885	0.006	1148.5	808	−8.3	1.39431	0.00008
0.8950	0.94076	0.003	1144.3	812	−4.7	1.39326	0.00002
1.0000	0.94292	0.000	1139.7	817	0.0	1.39217	0.00000
T = 313.15 K							
0.0000	0.92116	0.000	1162.1	804	0.0	1.40030	0.00000
0.0472	0.92178	0.003	1160.4	806	−2.8	1.39983	0.00001
0.0938	0.92244	0.005	1158.6	808	−5.2	1.39937	0.00003
0.1944	0.92389	0.009	1154.8	812	−9.3	1.39841	0.00009
0.2928	0.92537	0.012	1151.0	816	−12.0	1.39745	0.00014
0.3946	0.92697	0.014	1146.9	820	−13.4	1.39642	0.00014
0.4922	0.92855	0.016	1143.0	824	−13.7	1.39542	0.00014
0.5938	0.93029	0.013	1138.9	829	−12.9	1.39437	0.00013
0.6929	0.93204	0.011	1134.7	833	−11.2	1.39332	0.00009
0.7973	0.93398	0.006	1130.2	838	−8.3	1.39222	0.00005
0.8950	0.93584	0.003	1126.0	843	−4.8	1.39118	0.00001
1.0000	0.93805	0.000	1121.3	848	0.0	1.39010	0.00000

Table 4
Densities, ρ, excess molar volume, V_m^E, sound velocity, u, isentropic compressibility, κ_s, excess isentropic compressibility, κ_s^E, refractive index, n, and deviation in refractive index, Δn, for the binary system {heptanoic acid (x_1) + pentanoic acid (x_2)} at 293.15, 298.15, 303.15, 308.15 and 313.15 K.

x_1	ρ (g cm^{-3})	V_m^E(cm^3 mol^{-1})	u (m s^{-1})	κ_s (TPa^{-1})	κ_s^E(TPa^{-1})	n	Δn
T = 293.15 K							
0.0000	0.93941	0.000	1234.0	699	0.0	1.40840	0.00000
0.0641	0.93759	0.005	1238.8	695	−0.1	1.40990	0.00054
0.1207	0.93602	0.010	1242.9	692	−0.2	1.41110	0.00089
0.2317	0.93314	0.016	1250.6	685	−0.2	1.41293	0.00107
0.3413	0.93046	0.022	1257.9	679	−0.3	1.41469	0.00118
0.4383	0.92825	0.023	1264.1	674	−0.3	1.41617	0.00121
0.5402	0.92608	0.022	1270.3	669	−0.2	1.41760	0.00112
0.6442	0.92397	0.021	1276.3	664	−0.2	1.41903	0.00099
0.7342	0.92225	0.018	1281.4	660	−0.2	1.42021	0.00082
0.8259	0.92058	0.014	1286.4	656	−0.1	1.42135	0.00060
0.9173	0.91900	0.008	1291.2	653	0.0	1.42244	0.00032
0.9620	0.91826	0.004	1293.4	651	0.0	1.42297	0.00018
1.0000	0.91765	0.000	1295.4	649	0.0	1.42336	0.00000
T = 298.15 K							
0.0000	0.93485	0.000	1216.0	723	0.0	1.40641	0.00000
0.0641	0.93306	0.005	1220.8	719	−0.1	1.40789	0.00051
0.1207	0.93151	0.011	1225.0	715	−0.2	1.40904	0.00082
0.2317	0.92868	0.017	1232.8	709	−0.3	1.41092	0.00105
0.3413	0.92605	0.023	1240.1	702	−0.4	1.41267	0.00115
0.4383	0.92388	0.024	1246.3	697	−0.4	1.41413	0.00116
0.5402	0.92174	0.024	1252.5	692	−0.3	1.41562	0.00112
0.6442	0.91968	0.022	1258.6	686	−0.3	1.41705	0.00099
0.7342	0.91798	0.019	1263.7	682	−0.2	1.41820	0.00080
0.8259	0.91635	0.015	1268.7	678	−0.1	1.41936	0.00058
0.9173	0.91479	0.010	1273.5	674	0.0	1.42048	0.00033
0.9620	0.91407	0.005	1275.8	672	0.0	1.42099	0.00017
1.0000	0.91347	0.000	1277.7	671	0.0	1.42138	0.00000
T = 303.15 K							
0.0000	0.93029	0.000	1197.9	749	0.0	1.40438	0.00000
0.0641	0.92852	0.006	1202.7	745	−0.1	1.40585	0.00051
0.1207	0.92699	0.013	1206.9	741	−0.3	1.40698	0.00079
0.2317	0.92422	0.019	1214.7	733	−0.3	1.40886	0.00101
0.3413	0.92164	0.024	1222.1	726	−0.4	1.41062	0.00113
0.4383	0.91951	0.025	1228.3	721	−0.4	1.41208	0.00114
0.5402	0.91740	0.025	1234.6	715	−0.4	1.41356	0.00109
0.6442	0.91538	0.023	1240.7	710	−0.3	1.41498	0.00096
0.7342	0.91371	0.020	1245.8	705	−0.3	1.41620	0.00083
0.8259	0.91211	0.016	1250.8	701	−0.2	1.41733	0.00059
0.9173	0.91058	0.010	1255.7	697	−0.1	1.41842	0.00031
0.9620	0.90987	0.006	1257.9	695	0.0	1.41896	0.00018
1.0000	0.90929	0.000	1259.9	693	0.0	1.41935	0.00000
T = 308.15 K							
0.0000	0.92573	0.000	1179.9	776	0.0	1.40234	0.00000
0.0641	0.92398	0.007	1184.8	771	−0.1	1.40383	0.00049
0.1207	0.92248	0.014	1189.0	767	−0.3	1.40496	0.00077
0.2317	0.91975	0.020	1196.9	759	−0.4	1.40684	0.00099
0.3413	0.91723	0.024	1204.2	752	−0.5	1.40857	0.00109
0.4383	0.91514	0.026	1210.5	746	−0.5	1.41004	0.00111
0.5402	0.91307	0.026	1216.8	740	−0.4	1.41151	0.00105
0.6442	0.91108	0.024	1223.0	734	−0.4	1.41294	0.00094
0.7342	0.90945	0.021	1228.1	729	−0.3	1.41413	0.00077
0.8259	0.90787	0.017	1233.1	724	−0.2	1.41531	0.00058
0.9173	0.90638	0.011	1238.0	720	−0.1	1.41643	0.00034
0.9620	0.90568	0.006	1240.3	718	0.0	1.41695	0.00019
1.0000	0.90511	0.000	1242.2	716	0.0	1.41733	0.00000
T = 313.15 K							
0.0000	0.92116	0.000	1162.1	804	0.0	1.40030	0.00000
0.0641	0.91944	0.008	1167.0	799	−0.2	1.40175	0.00049
0.1207	0.91797	0.015	1171.2	794	−0.3	1.40283	0.00072
0.2317	0.91529	0.021	1179.1	786	−0.5	1.40471	0.00094
0.3413	0.91282	0.025	1186.6	778	−0.6	1.40649	0.00107
0.4383	0.91077	0.026	1192.9	772	−0.6	1.40796	0.00109
0.5402	0.90874	0.026	1199.2	765	−0.5	1.40944	0.00103
0.6442	0.90679	0.025	1205.4	759	−0.4	1.41086	0.00090
0.7342	0.90519	0.022	1210.5	754	−0.3	1.41209	0.00077
0.8259	0.90364	0.017	1215.6	749	−0.2	1.41324	0.00056
0.9173	0.90217	0.011	1220.4	744	−0.1	1.41437	0.00031
0.9620	0.90149	0.007	1222.7	742	0.0	1.41490	0.00017
1.0000	0.90094	0.000	1224.7	740	0.0	1.41530	0.00000

Table 5
Root mean square deviation, rmsd, between the experimental and the predicted density, ρ, or refractive index, n, of the binary systems at different temperatures.

Properties	rmsd (ρ and n)				
T (K)	293.15	298.15	303.15	308.15	313.15
{Butanoic acid (x_1) + pentanoic acid (x_2)}					
ρ (g cm^{-3})	0.00005	0.00002	0.00001	0.00002	0.00002
n	0.00002	0.00001	0.00001	0.00001	0.00001
{Heptanoic acid (x_1) + pentanoic acid (x_2)}					
ρ (g cm^{-3})	0.00051	0.00047	0.00045	0.00042	0.00037
n	0.00026	0.00024	0.00023	0.00021	0.00019

The results of excess molar volume, V^E_m, for the (butanoic or heptanoic acid + pentanoic acid) systems are given in Tables 3 and 4, and are also plotted in Fig. 1(a and b), respectively. The V^E_m values for both binary systems are positive. The positive contributions arise due to the dipole–dipole interaction between the heptanoic or butanoic or pentanoic acid monomers [32]. The V^E_m value for the system (heptanoic acid + pentanoic acid) > (butanoic acid + pentanoic acid) system which is possibly due to the additional CH_2 group on the heptanoic acid. The $V^E_{m,\,max}$ values occurrs at x_1 = 0.4922 and 0.4383 for the (butyric or heptanoic acid + pentanoic acid) systems, respectively, and at all temperatures. In general, the $V^E_{m,\,max}$ values increase with an increase in temperature for both systems.

3.2.2. Isentropic compressibilities, deviation in isentropic compressibilities and excess isentropic compressibilities

The isentropic compressibilities, κ_s, were calculated using the Newton–Laplace equation given below:

$$\kappa_s = \frac{1}{\rho u^2} \quad (8)$$

where ρ is the density and u is the sound velocity of the binary mixtures.

The deviations in isentropic compressibility, $\Delta\kappa s$ (ϕ), were calculated using Eq. (9):

$$\Delta\kappa_{s(\phi)} = \kappa_s - \sum_i^2 \phi_i \kappa_{s,i} \quad (9)$$

where $\kappa_{s,i}$ and $\boldsymbol{\phi}_i$ are the isentropic compressibility and volume fractions of the pure component i, respectively. The volume fractions were calculated using an ideal mixture.

The excess isentropic compressibility [33] for the binary system was calculated using Eq. (10):

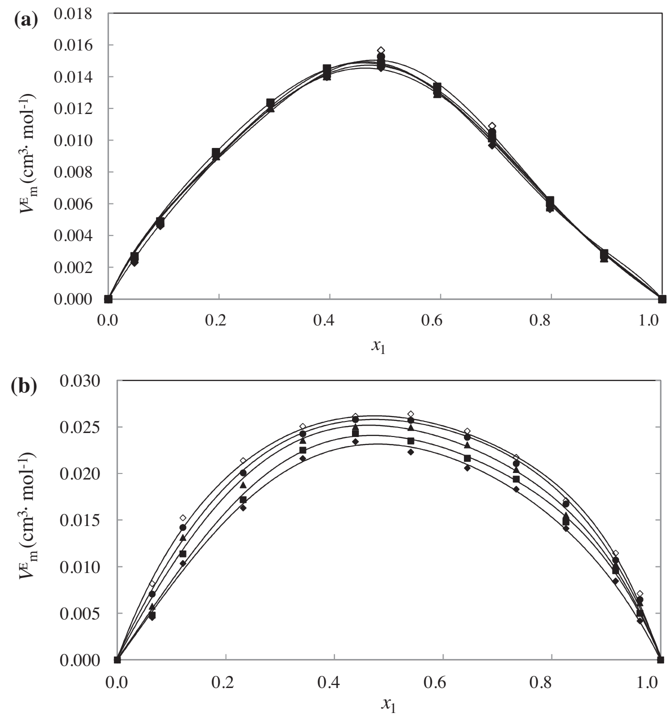

Fig. 1. Excess molar volumes, V^E_m, of binary mixtures of (a) {butanoic acid (x_1) + pentanoic acid (x_2)}, (b) {heptanoic acid (x_1) + pentanoic acid (x_2)} against mole fraction of heptanoic acid at 293.15 K (◆), 298.15 K (■), 303.15 K (▲), 308.15 K (●) and 313.15 K (◇). The solid lines were generated using Redlich–Kister curve-fitting.

$$\kappa_s^E = \Delta\kappa_s(\phi) - T\left[\sum_i \phi_i \frac{(\alpha^*_{p,i})^2}{\sigma^*_{p,i}} - \frac{(\Sigma_i \phi_i \alpha^*_{p,i})^2}{\Sigma_i \phi_i \sigma^*_{p,i}}\right] \quad (10)$$

where $\sigma^*_{p,i} = C_p/V_m$ is the heat capacitance or heat capacity per unit volume of the mixture. Since heat capacities were not measured in this work, these values were obtained from literature or calculated from literature values at the experimental temperature [34] and are given in Table 7. The thermal expansion coefficients defined as $\alpha^*_{p,i} = 1/V_m(\delta V_m/\delta T)_p = -1/\rho(\delta\rho/\delta T)_p$ have been calculated at each temperature from the experimental density [33]. The results for isentropic compressibility, κ_s, and excess isentropic compressibility, κ_s^E, for the binary systems (butanoic or heptanoic acid + pentanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are given in Tables 3 and 4.

The isentropic compressibility, κ_s, values increases with an increase in temperature at a fixed composition for both binary systems due to an increase in thermal agitation, making the solution more compressible [35]. The κ_s values increase with an

Table 6
Root mean square deviation, rmsd, in sound velocity, u, at different temperatures for the studied mixing rules.

Equation	rmsd (u)				
T (K)	293.15	298.15	303.15	308.15	313.15
{Butanoic acid (x_1) + pentanoic acid (x_2)}					
Rao	0.6	0.5	0.4	0.4	0.4
Wada	0.5	0.5	0.4	0.4	0.4
Nomoto	0.5	0.5	0.4	0.4	0.4
Berryman	0.4	0.3	0.3	0.3	0.2
{Heptanoic acid (x_1)+ pentanoic acid (x_2)}					
Rao	0.1	0.1	0.2	0.2	0.2
Wada	0.1	0.2	0.2	0.2	0.3
Nomoto	0.5	0.4	0.4	0.4	0.4
Berryman	0.1	0.1	0.1	0.1	0.1

Table 7
Heat capacity, C_p, [34] values of pure component at several temperatures used in this work.

T/K	293.15	298.15	303.15	308.15	313.15
Butanoic acid					
C_p (JK^{-1} kmol^{-1})	1.76×10^5	1.78×10^5	1.80×10^5	1.82×10^5	1.84×10^5
Pentanoic acid					
C_p (JK^{-1} kmol^{-1})	1.15×10^5	1.17×10^5	1.19×10^5	1.21×10^5	1.23×10^5
Heptanoic acid					
C_p (JK^{-1} kmol^{-1})	1.59×10^5	1.62×10^5	1.64×10^5	1.67×10^5	1.69×10^5

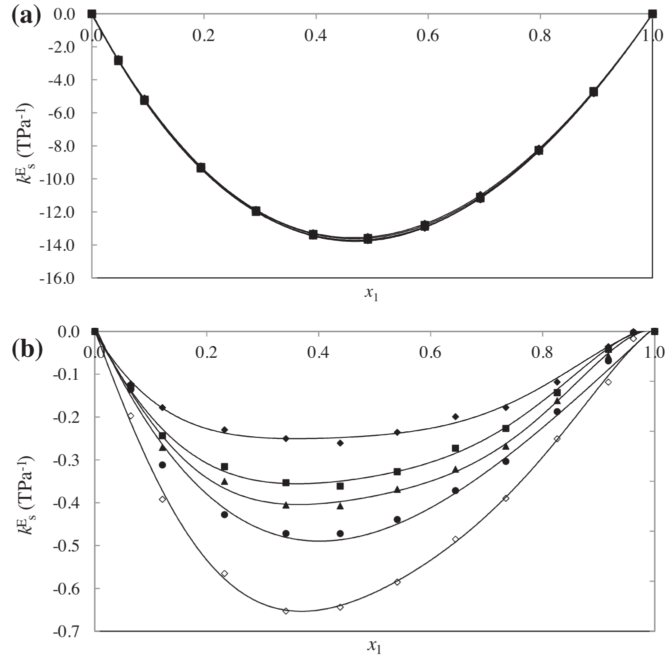

Fig. 2. Excess isentropic compressibility, κ_s^E, of binary mixtures of (a) {butanoic acid (x_1) + pentanoic acid (x_2)}, (b) {heptanoic acid (x_1) + pentanoic acid (x_2)} against mole fraction of heptanoic acid at 293.15 K (◆), 298.15 K (■), 303.15 K (▲), 308.15 K (●) and 313.15 K (◇). The solid lines were generated using Redlich–Kister curve-fitting.

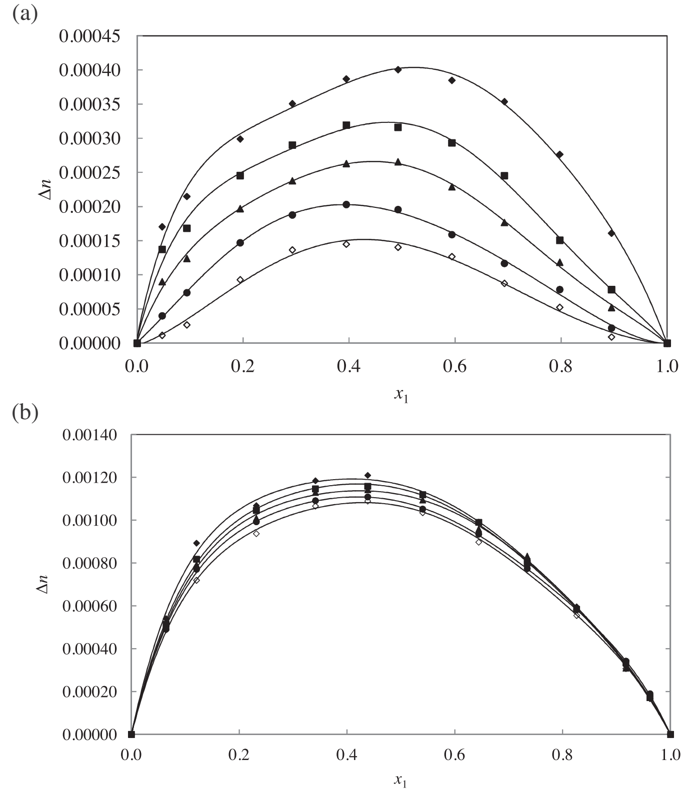

Fig. 3. Deviation in refractive index, Δn, of binary mixtures of (a) {butanoic acid (x_1) + pentanoic acid (x_2)}, (b) {heptanoic acid (x_1) + pentanoic acid (x_2)} against mole fraction of heptanoic acid at 293.15 K (◆), 298.15 K (■), 303.15 K (▲), 308.15 K (●) and 313.15 K (◇). The solid lines were generated using Redlich–Kister curve-fitting.

increase in composition of butanoic acid at a fixed temperature for the (butanoic acid + pentanoic acid) system whereas decreases with an increase in composition of heptanoic acid at a fixed temperature for the (heptanoic acid + pentanoic acid) system. At a particular temperature, the (butanoic acid + pentanoic acid) solution is more compressible than the (heptanoic acid + pentanoic acid) solution.

The excess isentropic compressibility κ_s^E over the entire composition range of butanoic acid or heptanoic acid for both systems is plotted in Fig. 2(a and b). It can be seen from these figures that the values of κ_s^E are negative for both systems. In general, the κ_s^E values decrease with an increase in temperature for both systems at a fixed composition of butanoic or heptanoic acid as shown in Tables 3 and 4. The κ_s^E values show that the (heptanoic acid + pentanoic acid) system is more compressible than the (butanoic acid + pentanoic acid) solution. The $\kappa_{s,\min}^E$ values occurrs at $x_1 = 0.4922$ and 0.4383, respectively for each system at all temperatures.

3.2.3. Deviation in refractive index

The deviation in refractive index, Δn, was calculated using Eq. (11):

$$\Delta n = n - x_1 n_1 - x_2 n_2 \qquad (11)$$

where n_1 and n_2 are the refractive index of the pure components (1 and 2) and n is the refractive index of the mixture. The results for the deviations in the refractive index, Δn, for the binary systems (butanoic or heptanoic acid + pentanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are given in Tables 3 and 4, and are also plotted in Fig. 3(a and b), respectively. The Δn values are positive for both systems at each temperature. The $\Delta n_{\max}$ values occurs at $x_1 = 0.4922$ and 0.4383, respectively, at each temperature and in general decrease with an increase in temperature for both systems.

3.3. Correlation of derived properties

Experimental excess/deviation properties of the (butanoic or heptanoic acid + pentanoic acid) systems are given in Tables 3 and 4. These properties such as V_m^E, κ_s^E, and Δn were correlated by smoothing the Redlich–Kister equation [36] given below:

$$X = x_1 x_2 \sum_{i=1}^{k} A_i (1 - 2x_1)^{i-1} \qquad (12)$$

where X is excess molar volumes, V_m^E, excess isentropic compressibility, κ_s^E, and deviation in refractive index, Δn. The values of the parameters A_i have been determined using a least-square method. These results are summarized in Table 8, together with the corresponding standard deviations, σ, for the correlation as determined using Eq. (13):

$$\sigma(X) = \sum_{i=1}^{N} \left[\frac{(X_{expt} - X_{calc})^2}{(N - k)} \right]^{1/2} \qquad (13)$$

where N is the number of experimental points and k is the number of coefficients used in the Redlich–Kister equation. The values of V_m^E, κ_s^E, and Δn, as well as the plots of the Redlich–Kister model are displayed in Figs. 1–3 as a mole fraction dependence. The standard deviations between the experimental data and the calculated data from the Redlich–Kister equation are also presented in Table 8 and indicate very low standard deviations.

Table 8
Coefficients A_i, and standard deviations, σ, obtained for the {butanoic or heptanoic acid (x_1) + pentanoic acid (x_2)} at different temperatures for the Redlich–Kister equation.

	T (K)	A_0	A_1	A_2	A_3	A_4	σ
{Butanoic acid (x_1) + pentanoic acid (x_2)}							
V_m^E (cm3 mol -1)	293.15	0.058	0.015	−0.026	0.003	–	0.0003
	298.15	0.058	0.016	−0.026	0.004	–	0.0004
	303.15	0.057	0.013	−0.024	0.011	–	0.0004
	308.15	0.058	0.008	−0.024	0.018	–	0.0004
	313.15	0.059	0.008	−0.028	0.019	–	0.0006
κ_s^E (TPa -1)	293.15	−53.9	−7.4	−3.9	1.2	2.8	0.1
	298.15	−54.2	−6.4	−3.7	−0.9	2.4	0.1
	303.15	−54.6	−6.4	−3.9	−1.9	3.0	0.1
	308.15	−54.7	−6.4	−3.0	−1.0	2.5	0.1
	313.15	−54.7	−6.7	−2.3	0.4	0.4	0.1
Δn	293.15	−0.00036	−0.00004	0.00001	−0.00007	–	0.00000
	298.15	−0.00035	−0.00011	0.00007	−0.00006	–	0.00000
	303.15	−0.00031	−0.00008	0.00002	−0.00004	–	0.00000
	308.15	−0.00029	−0.00009	0.00003	−0.00004	–	0.00000
	313.15	−0.00028	−0.00008	0.00009	−0.00008	–	0.00000
{Heptanoic acid (x_1) + pentanoic acid (x_2)}							
V_m^E (cm3 mol -1)	293.15	0.092	0.010	0.009	−0.030	−0.004	0.000
	298.15	0.098	0.012	−0.003	−0.045	0.032	0.001
	303.15	0.101	0.013	0.012	−0.036	0.030	0.001
	308.15	0.105	0.008	0.012	−0.023	0.047	0.001
	313.15	0.106	0.007	0.026	−0.014	0.044	0.001
κ_s^E (TPa -1)	293.15	−1.0	−0.4	−0.7	−0.7	1.2	0.1
	298.15	−1.4	−0.8	−0.1	−0.2	1.3	0.1
	303.15	−1.6	−0.3	−0.6	−0.6	0.5	0.1
	308.15	−1.8	−0.9	−1.2	0.2	2.1	0.1
	313.15	−2.2	−1.5	0.0	0.5	0.3	0.1
Δn	293.15	0.00466	0.00126	0.00085	0.00212	0.00292	0.00002
	298.15	0.00458	0.00117	0.00071	0.00183	0.00258	0.00001
	303.15	0.00448	0.00098	0.00105	0.00190	0.00205	0.00001
	308.15	0.00435	0.00115	0.00067	0.00128	0.00292	0.00001
	313.15	0.00426	0.00102	0.00041	0.00142	0.00277	0.00001

4. Conclusions

In this work, new physico-chemical properties, which include density, sound velocity and refractive index as a function of temperature and composition, for butanoic acid, pentanoic acid and heptanoic acid and their binary mixtures, were measured. The Lorentz–Lorenz approximation predicted the refractive index from density quite accurately. Four sound velocity mixing rules were applied and these results agreed favourably; however, the most satisfactory result was obtained using the mixing rule of Berryman. Furthermore, the excess/deviation properties were calculated from density, sound velocity and refractive index data. The Redlich–Kister polynomial equation was fitted to the excess molar volume, excess isentropic compressibility and the deviation in refractive index and provides an excellent description for all systems studied.

Positive deviations were observed for excess molar volumes and deviation in refractive index whereas negative deviations were obtained for excess isentropic compressibility for both binary systems at all temperatures. These results are useful for the interpretation of the nature of intermolecular interactions that exist between these components of interest in mixtures. This work also provides an evaluation of the various sound velocity mixing rules which were used to calculate the sound velocity of the binary mixture from pure component data. It was established that the Lorentz–Lorenz approximation does predict the density from refractive index or refractive index from density data favourably well.

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