



Contents lists available at ScienceDirect
Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

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



I. Bahadur^{a,*}, S. Singh^b, N. Deenadayalu^b, P. Naidoo^a, D. Ramjugernath^a

^a Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

^b Department of Chemistry, Durban University of Technology, P.O. Box 1334, Durban, 4000, South Africa

ARTICLE INFO

Article history: Received 7 March 2014 Received in revised form 26 June 2014 Accepted 28 June 2014 Available online 30 June 2014

Keywords: Density Sound velocity Refractive index Carboxylic acid Sound velocity mixing rules Lorentz–Lorenz approximation

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.

© 2014 Published by Elsevier B.V.

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 \geq 0.99 and was supplied by Aldrich. The pentanoic acid (CAS No. 109-52-4) had a

^{*} Corresponding author. Tel.: +27 31 2602858; fax: +27 31 2602858. *E-mail addresses*: bahaduri@ukzn.ac.za, bahadur.indra@gmail.com (I. Bahadur).

purity of mass fraction \geq 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 cm³ 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	<i>T</i> (K)	$ ho (m gcm^{-3})$		$u ({ m ms^{-1}})$	$u (m s^{-1})$		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]	
i ciltunole dela	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]	

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.

<i>x</i> ₁	$ ho~({ m gcm^{-3}})$	$u ({ m ms^{-1}})$	n	$V_{\rm m}^{\rm E}({\rm cm}^3{\rm mol}^{-1})$	$\Delta \kappa_{\rm s}({\rm TPa}^{-1})$	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

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

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

$$\kappa_{\rm s}^{-1/7} V_{\rm m} = \sum_{i=1}^{2} \kappa_{{\rm s},i}^{-1/7} x_i V_i \therefore u = \left(\sum_{i=1}^{2} u_i^{2/7} \rho_i^{1/7} x_i V_i / \left(\rho^{1/7} V_{\rm m}\right)\right)^{7/2}$$
(3)

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

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

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 $0.6 \,\mathrm{m\,s^{-1}}$ 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 nvalues 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):

$$n = \left(\frac{2\left[\left(\frac{n_{1}^{2}-1}{n_{1}^{2}+2}\right)x_{1}\rho\frac{M_{1}}{\rho_{1}}+x_{2}\left(\frac{n_{2}^{2}-1}{n_{2}^{2}+2}\right)\rho\frac{M_{2}}{\rho_{2}}\right] + \left[x_{1}M_{1}+x_{2}M_{2}\right]}{\left[x_{1}M_{1}+x_{2}M_{2}\right] - \left[\left(\frac{n_{1}^{2}-1}{n_{1}^{2}+2}\right)x_{1}\rho\frac{M_{1}}{\rho_{1}}+x_{2}\left(\frac{n_{2}^{2}-1}{n_{2}^{2}+2}\right)\rho\frac{M_{2}}{\rho_{2}}\right]}\right)^{1/2}$$
(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:

$$V_{\rm m}^{\rm E} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{7}$$

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.

Densities, ρ , excess molar volume, $V_{\rm m}^{\rm E}$, sound velocity, u, isentropic compressibility, $\kappa_{\rm s}$, excess isentropic compressibility, $\kappa_{\rm s}^{\rm E}$, 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.

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>x</i> ₁	$ ho ({ m gcm^{-3}})$	$V_{\rm m}^{\rm E}({\rm cm}^3{\rm mol}^{-1})$	$u(m s^{-1})$	$\kappa_{\rm s}~({\rm TPa}^{-1})$	$\kappa_{\rm s}^{\rm E}({\rm TPa}^{-1})$	n	Δn
0.0000 0.0472 0.23941 0.04641 0.0000 0.0472 0.24640 0.04641 0.00000 0.00021 0.0487 0.4464 0.0005 1232.6 702 5.1 1.4677.0 0.00021 0.0488 0.4464 0.0005 1232.6 702 5.1 1.4677.0 0.00021 0.4344 0.94448 0.0005 1222.5 711 -133 1.46481 0.00023 0.4322 0.94758 0.015 1213.8 714 -133 1.44078 0.00018 0.4322 0.94758 0.011 1213.8 714 -133 1.44078 0.00018 0.6229 0.93788 0.000 1203.8 724 -42 1.46660 0.00028 0.0001 0.93848 0.0001 1216.0 725 -52 1.46671 0.00002 0.93778 0.0002 1205.2 723 -13 1.44074 0.00025 0.23840 0.012 1205.2 723 -13 1.44074 0.00025 0.23841	T=29315K							
0.0672 0.04065 0.0607 123.3 700 -2.8 1.48871 0.00077 0.0538 0.04665 0.0005 1226.9 715 -9.3 1.40676 0.00019 0.3524 0.44608 0.012 1223.3 708 -11.3 1.40676 0.00019 0.3521 0.44608 0.012 123.3 714 -1.3.3 1.40481 0.00019 0.3538 0.44608 0.013 121.9 714 -1.3.3 1.40481 0.00019 0.3538 0.44645 0.010 1208.0 720 -1.10 1.40174 0.00018 0.3583 0.35778 0.020 1.3882 727 -4.7 1.38448 0.00016 0.3660 0.35778 0.020 1.4382 0.20001 0.38285 0.0001 1.3828 0.00014 0.00025 0.0014 0.00225 0.3485 0.00014 0.00225 0.34865 0.0007 0.0014 0.00225 0.44666 0.0001 0.00225 0.44666 <t< td=""><td>0.0000</td><td>0 93941</td><td>0.000</td><td>1234.0</td><td>699</td><td>0.0</td><td>1 40840</td><td>0 00000</td></t<>	0.0000	0 93941	0.000	1234.0	699	0.0	1 40840	0 00000
0.058 0.5444 0.0009 1.2365 702 31 1.40770 0.00021 0.2524 0.54446 0.012 1.223.3 708 -11.9 1.40581 0.00035 0.3544 0.01452 1.223.3 708 -11.9 1.40481 0.00035 0.3545 0.0145 1.119 1.77 -1.27 1.40273 0.00035 0.5334 0.94462 0.010 1.0208 7.24 -3.2 1.404614 0.00005 0.7373 0.53548 0.000 1.2058 7.24 -3.2 1.40600 0.00028 0.8850 0.03552 0.003 1.214.0 7.23 0.0 1.40641 0.00016 0.6472 0.93455 0.000 1.212.6 7.25 -3.3 1.40674 0.00017 0.6472 0.93455 0.0012 1.212.6 7.25 -3.3 1.40674 0.00021 0.4384 0.93457 0.013 1.212.6 7.35 -1.3 1.40475 0.00022 </td <td>0.0000</td> <td>0.00014</td> <td>0.002</td> <td>1234.0</td> <td>700</td> <td>2.8</td> <td>1,40040</td> <td>0.00000</td>	0.0000	0.00014	0.002	1234.0	700	2.8	1,40040	0.00000
01944 09446 0009 12283 095 33 146678 000980 03986 0.94468 0.012 12233 705 -113 140581 0.00019 04982 0.94756 0.013 12138 711 -133 140383 0.00018 0.4922 0.94756 0.013 12138 714 -133 140383 0.00018 0.4922 0.94756 0.015 12018 717 -127 140771 0.00118 0.7571 0.95748 0.0000 1955 730 0.0 139526 0.00016 0.0000 0.95778 0.000 1216.0 72 -2.4 140697 0.0014 0.0972 0.93555 0.003 1214.3 725 -2.4 140697 0.0017 0.444 0.93562 0.003 1208.9 710 -33 140374 0.0017 0.4566 0.012 126.5 740 -113 14077 0.0012 0	0.0472	0.04096	0.002	1220.6	700	-2.0	1.40815	0.00017
D233 D3448 D012 L223 778 -13 L40881 D00019 0.3466 0.4452 0.94562 0.015 1215.8 714 -13.5 1.40881 0.00019 0.4522 0.94756 0.015 1215.8 714 -13.5 1.40881 0.00018 0.6839 0.93945 0.000 1208.0 727 -4.7 1.40604 0.00028 0.000 0.95778 0.000 1195.5 730 0.0 138820 0.00000 7-283.15K 0.000 1195.5 730 0.0 138820 0.00000 0.0472 0.93545 0.003 124.6 728 -3.3 1.40673 0.0001 0.0444 0.03772 0.033 124.6 735 -1.3 1.40774 0.00024 0.3544 0.012 126.2 733 -1.3 1.40774 0.00024 0.3544 0.015 1197.6 740 -1.3 1.40774 0.00024 0.3544 </td <td>0.0938</td> <td>0.94080</td> <td>0.005</td> <td>1230.0</td> <td>702</td> <td>-3.1</td> <td>1.40770</td> <td>0.00021</td>	0.0938	0.94080	0.005	1230.0	702	-3.1	1.40770	0.00021
Lossing Lossing <thlossing< th=""> <thlossing< th=""> <thl< td=""><td>0.1944</td><td>0.94240</td><td>0.009</td><td>1220.9</td><td>705</td><td>-9.5</td><td>1.40070</td><td>0.00030</td></thl<></thlossing<></thlossing<>	0.1944	0.94240	0.009	1220.9	705	-9.5	1.40070	0.00030
Losso Losso Lisso Lisso <th< td=""><td>0.2928</td><td>0.94408</td><td>0.012</td><td>1223.3</td><td>708</td><td>-11.9</td><td>1.40581</td><td>0.00035</td></th<>	0.2928	0.94408	0.012	1223.3	708	-11.9	1.40581	0.00035
LB422 LB432 LB432 LB433 LB433 LB433 LB433 LB4333 LB43333 LB433333 LB433333 LB433333 LB433333 <thlb433333< th=""> <thlb433333< <="" td=""><td>0.3946</td><td>0.94582</td><td>0.014</td><td>1219.5</td><td>/11</td><td>-13.3</td><td>1.40481</td><td>0.00039</td></thlb433333<></thlb433333<>	0.3946	0.94582	0.014	1219.5	/11	-13.3	1.40481	0.00039
L338 U3943 U113 L119 7/7 -L27 L442/8 U0108 103873 0.0313 0.003 12109 7/7 -L2 140/20 0.0003 03873 0.0313 0.003 1199.9 727 -L2 1.39249 0.00016 0.04 1.38250 0.00016 1.39349 0.00016 0.00016 0.0400 0.39453 0.000 1.212.0 7.23 -L2 1.40641 0.00001 0.0400 0.39454 0.0001 1.212.3 7.72 -L2 1.40649 0.00001 0.2528 0.03940 0.012 1.205.2 7.33 -119 1.40774 0.00023 0.2528 0.93140 0.015 1.201.4 7.75 -1.33 1.40649 0.00023 0.34545 0.0113 1193.6 7.43 42.8 1.40775 0.00023 0.49422 0.94840 0.013 1183.4 7.74 4.7 1.39744 0.00023 0.049320 <td>0.4922</td> <td>0.94/56</td> <td>0.015</td> <td>1215.8</td> <td>/14</td> <td>-13.5</td> <td>1.40383</td> <td>0.00040</td>	0.4922	0.94/56	0.015	1215.8	/14	-13.5	1.40383	0.00040
0.023 0.3148 0.010 1208.0 720 -1.0 1.407.4 0.00022 0.1000 0.05348 0.000 1195.5 730 -0.2 1.400.0 0.00022 0.1000 0.95778 0.000 1195.5 730 0.0 1.39826 0.00000 0.0000 0.93485 0.000 1216.0 723 -2.3 1.40631 0.00017 0.0472 0.93525 0.003 1214.3 725 -2.2 1.40631 0.00017 0.1338 0.93485 0.005 1212.5 728 -2.5 1.40631 0.00017 0.1338 0.9346 0.015 1007.4 740 -1.33 1.40724 0.00022 0.3246 0.010 1197.6 740 -1.3 1.4073 0.00022 0.5231 0.94664 0.013 1193.6 743 -1.28 1.40070 0.00022 0.5232 0.94664 0.013 1185.4 754 -4.1 1.39560 0.00020	0.5938	0.94945	0.013	1211.9	/1/	-12.7	1.40278	0.00038
0.7371 0.83848 0.006 1203.8 724 -4.2 1.40080 0.00016 0.0000 0.95577 0.000 1185.5 730 0.0 1.58558 0.00016 0.0000 0.95578 0.0001 1185.5 730 0.0 1.40541 0.000014 0.0472 0.93555 0.003 1214.3 725 -2.8 1.40563 0.00014 0.0384 0.93782 0.005 1212.6 733 -1.13 1.40469 0.00025 0.2284 0.93940 0.012 1205.2 733 -1.13 1.40724 0.00025 0.3345 0.94468 0.013 1193.6 746 -1.11 1.39965 0.00025 0.7773 0.94860 0.000 11759 758 0.0 1.39744 0.000025 0.0000 0.95281 0.000 11759 758 0.0 1.39744 0.00002 0.0316 0.001 1165.2 773 -3.4 1.400760 0.00000 <td>0.6929</td> <td>0.95138</td> <td>0.010</td> <td>1208.0</td> <td>720</td> <td>-11.0</td> <td>1.40174</td> <td>0.00035</td>	0.6929	0.95138	0.010	1208.0	720	-11.0	1.40174	0.00035
0.8850 0.03552 0.003 1199.9 727 -4.7 1.399.40 0.0000 17-38.15 K 0.000 0.93778 0.000 12160 773 0.0 139826 0.0000 0.0472 0.33555 0.003 12143 725 -2.8 1.40607 0.0001 0.0472 0.33555 0.009 12166 726 -5.2 1.40633 0.0007 0.1344 0.93782 0.009 1208.9 730 -3.3 1.40464 0.00025 0.2228 0.3346 0.011 1035 11276 740 -1.13 1.40274 0.00029 0.4522 0.94281 0.015 11276 740 -1.13 1.40274 0.00029 0.4522 0.94281 0.015 11276 740 -1.13 1.40274 0.00029 0.4522 0.94281 0.013 1193.6 743 -1.13 1.40075 0.00029 0.4522 0.94281 0.013 1193.6 743 -1.13 1.40070 0.00029 0.4523 0.94564 0.013 1193.6 743 -1.13 1.39865 0.00029 0.4523 0.94564 0.013 1193.6 743 -1.13 1.39865 0.00029 0.05580 0.050 11814 754 -4.7 1.39344 0.00009 0.05580 0.050 11814 754 -4.7 1.39345 0.00000 17-33.15.K 0.0000 0.95781 0.000 1176.9 758 0.0 1.396530 0.00009 0.0472 0.93966 0.003 11842 753 -3.3 1.40255 0.00009 0.0472 0.93986 0.000 1176.9 758 0.0 1.396530 0.00009 0.0338 0.93165 0.005 1194.5 752 -3.3 1.40255 0.00002 0.0383 0.93165 0.005 1194.5 752 -3.3 1.40255 0.00002 0.0383 0.93165 0.005 1194.5 752 -3.3 1.40255 0.00002 0.0383 0.93165 0.005 1194.5 752 -3.3 1.40259 0.00002 0.0384 0.9318 0.014 11871 739 -1.0 1.40144 0.00024 0.0328 0.93987 0.013 11752 770 -1.2 1.39574 0.00027 0.2328 0.93473 0.013 11752 770 -1.2 1.39575 0.00027 0.2350 0.94573 0.006 1166.9 778 -3.3 1.39539 0.0000 0.738 0.93987 0.013 11752 770 -1.2 1.39575 0.00002 0.0355 0.03474 0.000 1176.9 778 -3.3 1.39539 0.00007 7-308.15 K 0.0000 0.94774 0.000 1176.9 778 -3.3 1.39539 0.00007 7-308.15 K 0.0000 0.94774 0.005 1175.5 779 -3.2 1.40146 0.00007 7-308.15 K 0.0000 0.94774 0.005 1175.2 770 -1.2 1.39573 0.00002 1.0000 0.94774 0.005 1175.2 778 -3.3 1.39539 0.00001 0.777 0.94373 0.006 1162.9 788 -3.3 1.39541 0.00000 0.742 0.93185 0.005 1175.5 779 -3.2 1.40146 0.00007 7-308.15 0.005 1175.2 779 -1.2 1.39553 0.00001 0.0422 0.93367 0.011 1152.9 803 -1.12 1.39544 0.00000 0.472 0.92178 0.000 1162.1 864 0.0 1.4020 1.39421 0.00000 0.472 0.92178 0.0003 1164.9 806 -2.8 1.39383 0.00001 0.0444 0.92839	0.7973	0.95348	0.006	1203.8	724	-8.2	1.40060	0.00028
1.0000 0.3578 0.000 115.5 730 0.0 1.388,56 0.0000 7-303.15 K 0.03355 0.000 1216.0 723 0.0 1.406,61 0.00014 0.0472 0.335,65 0.005 1212.6 723 -2.8 1.406,67 0.00014 0.0483 0.335,65 0.005 1212.6 723 -1.3 1.404,69 0.00025 0.2328 0.3394 0.012 1205.2 733 -1.13 1.40274 0.000225 0.3464 0.0411 0.015 1201.4 736 -1.23 1.40070 0.00023 0.4822 0.34466 0.013 1137,6 740 -1.3 1.39744 0.00023 0.737 0.34860 0.006 1185.4 756 -4.7 1.39744 0.00023 0.0000 0.35281 0.000 1175.9 758 0.0 1.39540 0.00003 0.0000 0.35281 0.000 1197,9 749 0.0 1.40438 </td <td>0.8950</td> <td>0.95552</td> <td>0.003</td> <td>1199.9</td> <td>727</td> <td>-4.7</td> <td>1.39949</td> <td>0.00016</td>	0.8950	0.95552	0.003	1199.9	727	-4.7	1.39949	0.00016
T - 2813 K U 0.0000 0.93485 0.000 1216.0 723 0.0 146641 0.00001 0.0472 0.93555 0.003 1212.6 726 5.2 140563 0.00017 0.1444 0.93782 0.009 1208.9 730 -9.3 140449 0.00025 0.2384 0.93440 0.015 1201.4 736 -13.3 140074 0.00022 0.4522 0.94481 0.015 1177.6 740 -13.3 140070 0.00023 0.4522 0.94481 0.015 1187.6 740 -13.3 13074 0.00023 0.7373 0.95500 0.030 1185.4 776 -13 13835 0.0000 0.0472 0.93969 0.003 1186.2 773 -2.8 140395 0.0000 0.0472 0.93969 0.003 1196.2 751 -2.8 140395 0.0000 0.0472 0.93969 0.005 1194.5 7	1.0000	0.95778	0.000	1195.5	730	0.0	1.39826	0.00000
0.0000 0.33485 0.000 1216.0 723 0.0 1.40641 0.00000 0.0472 0.33555 0.005 1212.4 725 -2.8 1.40667 0.00014 0.0393 0.33782 0.005 1212.5 733 -11.9 1.40498 0.00022 0.2324 0.33946 0.012 1205.2 733 -11.9 1.40774 0.00023 0.4222 0.34461 0.013 1133.6 746 -12.8 1.40074 0.00023 0.43940 0.016 1189.4 766 -11.3 1.30890 0.00026 0.4393 0.3466 0.016 1189.4 764 -12.8 1.40074 0.00026 0.4393 0.3466 0.016 1189.4 776 -4.7 1.3374 0.00000 0.4472 0.33965 0.003 1196.2 751 -2.8 1.40399 0.00001 0.4441 0.3318 0.009 1197.7 776 -9.4 1.402280 0.00021 <td>T=298.15 K</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	T=298.15 K							
0.0472 0.033555 0.003 1214.3 725 -2.8 1.40607 0.00014 0.0434 0.03762 0.009 1208.9 730 -9.3 1.40469 0.00025 0.2328 0.03946 0.111 0.015 1201.4 736 -1.13 1.40374 0.00032 0.4922 0.94281 0.015 1197.6 740 -1.16 1.40175 0.00022 0.5338 0.94466 0.013 1193.6 743 -1.28 1.40070 0.00022 0.5321 0.006 1185.4 750 -8.3 1.38933 0.00012 0.773 0.94860 0.006 1185.4 754 -4.7 1.3974 0.00012 0.0370 0.35060 0.003 1195.5 751 -2.8 1.40335 0.00001 0.4042 0.33802 0.000 1195.2 751 -2.8 1.40335 0.00012 0.3444 0.3316 0.005 1194.5 752 -5.3 1.40335	0.0000	0.93485	0.000	1216.0	723	0.0	1.40641	0.00000
0.038 0.039262 0.005 1212.6 726 -5.2 1.40453 0.00077 0.1344 0.03782 0.009 1208.9 730 -9.3 1.40459 0.00029 0.23243 0.33940 0.012 1205.2 733 -1.19 1.40274 0.00029 0.4222 0.42421 0.015 1197.6 740 -1.3.6 1.40175 0.00032 0.6529 0.94465 0.010 1189.7 746 -1.11 1.398965 0.00025 0.7873 0.94466 0.013 118.4 754 -47 1.39744 0.00001 0.7873 0.39466 0.003 118.4 754 -47 1.39744 0.00000 0.4072 0.39065 0.003 1195.2 751 -2.8 1.40398 0.00000 0.40438 0.03165 1.005 1194.5 752 -5.3 1.40250 0.00021 0.40438 0.33465 0.03347 0.013 1175.7 770 -12.2	0.0472	0.93555	0.003	1214.3	725	-2.8	1.40607	0.00014
0.1544 0.93782 0.009 1208.9 720 3.3 1.40469 0.00025 0.23946 0.93940 0.012 1205.2 733 -11.9 1.40374 0.00025 0.3946 0.94111 0.015 1201.4 736 -13.3 1.40274 0.00032 0.5939 0.94465 0.010 1183.7 746 -11.1 1.39656 0.00025 0.5829 0.94654 0.010 1183.4 750 -8.3 1.39850 0.00000 0.58290 0.030 1181.4 754 -0.7 1.39744 0.00000 0.0900 0.59560 0.003 1181.4 754 -4.7 1.39744 0.00000 0.0000 0.59580 0.003 1165.2 751 -0.4 1.40438 0.00000 0.0000 0.59596 0.003 1165.2 752 -5.3 1.40450 0.00020 0.0173 0.39165 0.004 1183.1 759 -1.2.0 1.40454 0.00	0.0938	0.93626	0.005	1212.6	726	-5.2	1 40563	0.00017
0.2928 0.93940 0.012 1205.2 733 −119 ⊥40374 0.00032 0.3926 0.94121 0.015 1197,6 740 −13.6 1.40175 0.00032 0.5398 0.94466 0.013 1193,6 743 −12.8 1.40070 0.00029 0.5398 0.94466 0.010 1189,7 746 −11.1 1.39965 0.00029 0.5395 0.95060 0.003 1181,4 754 −4.7 1.39740 0.00000 0.5395 0.95060 0.003 1176.9 749 0.0 1.40438 0.00000 0.0472 0.39306 0.0003 1196.2 751 −2.8 1.40399 0.00009 0.0393 0.39165 0.005 1194.5 752 −5.3 1.40555 0.0012 0.1228 0.39473 0.012 1187.0 739 −12.0 1.40164 0.00024 0.23248 0.39457 0.0015 1179.3 777 −13.7 1.3989	0 1944	0.93782	0.009	1208.9	730	_93	1 40469	0.00025
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 2928	0 93940	0.012	1205.2	733	-11.9	1 40374	0.00029
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 3946	0.94111	0.015	1200.2	736	-13.3	1 40274	0.00032
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4922	0.94281	0.015	11976	740	-13.6	1.40175	0.00032
0.6829 0.04654 0.010 11897 746 -111 119965 0.00025 0.7973 0.94560 0.000 11775 758 0.0 139734 0.0000 0.0000 0.95281 0.000 11775 758 0.0 139630 0.0000 1.30315K 0.000 117759 749 0.0 1.40339 0.0000 0.0472 0.33060 0.003 11962 751 -2.8 1.40399 0.00000 0.0373 0.33165 0.005 11945 752 -5.3 1.40356 0.0002 0.0394 0.33165 0.005 11970 759 -12.0 1.40164 0.00026 0.3346 0.33935 0.015 1179.3 767 -13.7 1.39964 0.00026 0.4322 0.33805 0.015 1179.3 767 -13.7 1.39964 0.00026 0.4393 0.33867 0.003 1172.2 774 -11.2 1.39753 0.0001	0.5938	0.94466	0.013	1193.6	743	_12.8	1.40070	0.00032
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.5550	0.04654	0.010	1190.7	745	11 1	1,40070	0.00025
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0323	0.04860	0.006	1105.7	740	- 11.1	1,33303	0.00025
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.7975	0.94800	0.000	1103.4	750	-8.3	1.39830	0.00013
$\begin{array}{c ccccc} T-303.15 K \\ 0.0000 \\ 0.0000 \\ 0.0000 \\ 0.0000 \\ 0.00$	1,0000	0.95000	0.003	1176.0	758	-4.7	1.39744	0.00008
T-303.15 K 0.000 0.93096 0.000 1197.9 749 0.0 1.40438 0.0000 0.472 0.93096 0.005 1196.2 751 -2.8 1.40359 0.00012 0.9344 0.93318 0.009 1190.7 756 -9.4 1.40260 0.00020 0.2428 0.93473 0.012 1187.0 759 -12.0 1.40164 0.00026 0.3246 0.93805 0.013 1175.2 770 -12.9 1.39964 0.00027 0.5938 0.93877 0.013 1175.2 776 -13.7 1.39964 0.00021 0.5939 0.94171 0.010 1171.2 774 -11.2 1.33751 0.00012 0.5939 0.94473 0.006 1166.9 778 -8.3 1.39639 0.00012 0.7973 0.94373 0.000 1172.7 78 -2.8 1.4016 0.00007 0.9345 0.02704 0.005 1176.5 778 -2.2 <td>1.0000</td> <td>0.99281</td> <td>0.000</td> <td>1170.5</td> <td>750</td> <td>0.0</td> <td>1.55050</td> <td>0.00000</td>	1.0000	0.99281	0.000	1170.5	750	0.0	1.55050	0.00000
0.0000 0.93029 0.000 11979 749 0.0 1.40438 0.00000 0.0972 0.93065 0.003 1196.2 751 -2.8 1.40339 0.00009 0.0938 0.93165 0.005 1194.5 752 -5.3 1.40355 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 1.40064 0.00026 0.5938 0.93897 0.013 1175.2 770 -12.9 1.39857 0.00023 0.6929 0.94171 0.010 1171.2 774 -11.2 1.39751 0.00012 0.8950 0.94568 0.003 1152.2 786 0.0 1.39421 0.00005 0.0000 0.92573 0.000 1178.2 778 -2.8 1.40190 0.00007 0.49244 0.025 0.012 1168.5 777 -5.2 1.40146	<i>T</i> = 303.15 K							
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 0.00025 0.4922 0.93805 0.015 1179.3 767 -13.7 1.3964 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 0.39350 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 0.4072 0.92573 0.003 1178.2 778 -2.8 1.40190 0.00004 0.0378 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 0.00001 0.3936 0.92704 0.005 1176.5 779 -5.2 1.40146 0.00015 0.2928 0.93005 0.012 1168.9 787 -12.0 1.39955 0.00012 0.3936 0.014 1164.9 791 -13.4 1.39853 0.00020 0.4922 0.93300 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.93300 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.9330 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.93330 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.93330 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.93330 0.015 1161.0 795 -13.7 1.39753 0.00020 0.4922 0.9338 0.93766 0.011 1152.9 803 -11.2 1.39541 0.00012 0.7973 0.93885 0.006 1148.3 802 -8.3 1.39431 0.00008 0.4924 0.003 1144.3 812 -4.7 1.39326 0.00002 0.0000 0.94292 0.000 1139.7 817 0.0 1.39217 0.00000 0.4924 0.005 11548 808 -5.2 1.39937 0.00000 0.4924 0.005 11548 808 -5.2 1.39937 0.00000 0.4924 0.005 11548 812 -9.3 1.39441 0.00009 0.9384 0.9244 0.005 11548 812 -9.3 1.39441 0.00009 0.9394 0.92285 0.016 1148.0 824 -13.7 1.39542 0.00014 0.4942 0.92855 0.016 1148.0 824 -13.7 1.39542 0.00014 0.4942 0.92855 0.016 1143.0 824 -13.7 1.39542 0.00014 0.4942 0.92855 0.016 1143.0 824 -13.7 1.39542 0.00014 0.4942 0.92855 0.016 1143.0 824 -13.7 1.39542 0.00014 0	0.0000	0.93029	0.000	1197.9	749	0.0	1.40438	0.00000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0472	0.93096	0.003	1196.2	751	-2.8	1.40399	0.00009
0.1944 0.93318 0.009 1190.7 756 -9.4 1.40260 0.00020 0.2928 0.93473 0.012 1187.0 759 -1.2.0 1.40164 0.00026 0.4922 0.3365 0.015 1179.3 767 -13.7 1.39954 0.00023 0.5938 0.93987 0.013 1175.2 770 -12.9 1.39653 0.00018 0.7973 0.94373 0.006 1166.9 778 -8.3 1.39659 0.00018 0.7973 0.94373 0.000 1158.2 786 0.0 1.39421 0.0000 0.94568 0.003 1178.2 778 -2.8 1.40190 0.0000 0.472 0.92573 0.003 1178.2 778 -2.8 1.40190 0.0004 0.4472 0.92637 0.003 1178.2 778 -2.8 1.40146 0.00015 0.2928 0.93005 0.012 166.9 787 -1.2 1.39955 0.00015 0.2928 0.93005 0.012 166.9 787 -12.9	0.0938	0.93165	0.005	1194.5	752	-5.3	1.40355	0.00012
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1944	0.93318	0.009	1190.7	756	-9.4	1.40260	0.00020
0.3366 0.33639 0.014 1183.1 763 -13.4 1.40063 0.00025 0.4922 0.33805 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 0.00012 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 1.40234 0.00000 0.472 0.92637 0.003 1178.5 779 -5.2 1.40190 0.00007 0.4922 0.93005 0.012 1168.9 787 -12.0 1.39853 0.00001 0.4922 0.93005 0.012 1168.9 787 -12.0 1.39855 0.00019 0.4922 0.93308 0.013 1156.9 799 -12.9 1.39845	0.2928	0.93473	0.012	1187.0	759	-12.0	1.40164	0.00024
0.4922 0.39305 0.015 1179.3 767 -13.7 1.39964 0.00027 0.5938 0.39387 0.010 1171.2 770 -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 0.00015 0.0000 0.94794 0.000 1158.2 786 0.0 1.39421 0.0000 0.0000 0.92573 0.000 1178.2 778 2.8 1.40190 0.00004 0.0472 0.92637 0.003 1178.2 778 2.8 1.40190 0.00004 0.9383 0.92704 0.005 1176.5 779 5.2 1.40146 0.00015 0.1944 0.2823 0.0012 1168.9 787 -12.0 1.39955 0.0019 0.2928 0.93050 0.012 1168.9 791 -13.4 1.3985	0.3946	0.93639	0.014	1183.1	763	-13.4	1.40063	0.00026
0.5938 0.93987 0.013 11752 770 -12.9 1.39857 0.0002 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 1.396.39 0.00012 0.8950 0.94568 0.003 1152.2 786 0.0 1.39421 0.00000 0.773 0.94573 0.000 1179.9 776 0.0 1.40234 0.00000 0.0472 0.92637 0.003 1175.5 779 -5.2 1.40146 0.00007 0.1944 0.92853 0.009 1172.7 783 -9.3 1.40051 0.00012 0.4922 0.93005 0.012 1168.9 787 -12.0 1.39853 0.0002 0.4922 0.9330 0.015 1161.0 795 -13.7 1.39753 0.0002 0.5938 0.93508 0.013 1155.9 799 -12.9 1.39646	0.4922	0.93805	0.015	1179.3	767	-13.7	1.39964	0.00027
0.6929 0.94171 0.010 1171.2 774 -11.2 1.39751 0.00012 0.7973 0.94373 0.006 1166.9 778 -8.3 1.39639 0.00012 0.8950 0.94568 0.003 1158.2 782 -4.7 1.39533 0.00005 1.0000 0.94754 0.000 1178.2 778 -2.8 1.40190 0.00000 0.0472 0.92637 0.003 1176.5 779 -5.2 1.40146 0.00001 0.9474 0.005 1176.5 779 -5.2 1.40146 0.00001 0.9346 0.93168 0.012 1168.9 787 -12.0 1.39855 0.00020 0.3946 0.91368 0.013 1164.9 791 -13.4 1.39853 0.00020 0.4922 0.93330 0.015 1161.0 795 -13.7 1.39753 0.00020 0.5928 0.93066 0.148.5 808 -8.3 1.39431 0.00020 <tr< td=""><td>0.5938</td><td>0.93987</td><td>0.013</td><td>1175.2</td><td>770</td><td>-12.9</td><td>1.39857</td><td>0.00023</td></tr<>	0.5938	0.93987	0.013	1175.2	770	-12.9	1.39857	0.00023
0.7973 0.94373 0.006 1166.9 778 -8.3 1.39639 0.0012 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 7-308.15 K 0.00 1.40234 0.00000 0.0472 0.92637 0.003 1178.2 778 -2.8 1.40190 0.00004 0.9336 0.92704 0.005 1176.5 779 -5.2 1.40146 0.000015 0.2928 0.93005 0.012 1188.9 787 -12.0 1.39853 0.0020 0.3946 0.93168 0.014 1164.9 791 -13.4 1.39853 0.0020 0.5938 0.93508 0.013 1155.9 799 -12.9 1.39646 0.00012 0.5938 0.9367 0.011 1152.9 803 -11.2 1.39541 0.00	0.6929	0.94171	0.010	1171.2	774	-11.2	1.39751	0.00018
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 0.0000 7=308.15 K	0.7973	0.94373	0.006	1166.9	778	-8.3	1.39639	0.00012
1.0000 0.94794 0.000 1158.2 786 0.0 1.39421 0.00000 7=308.15 K	0.8950	0.94568	0.003	1162.8	782	-4.7	1.39533	0.00005
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1.0000	0.94794	0.000	1158.2	786	0.0	1.39421	0.00000
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	T - 308 15 K							
0.0400 0.52637 0.003 117.5.3 776 -0.3 1.402-4 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 0.00020 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 0.00022 0.7973 0.93885 0.006 1148.5 808 -8.3 1.39431 0.00002 1.0000 0.94076 0.003 1144.3 812 -4.7 1.39326 0.00002 1.0000 0.92178 0.003 1160.4 806 -2.8 1.39983	0 0000	0 02573	0.000	1170.0	776	0.0	1/023/	0,0000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0000	0.02627	0.000	1179.0	770	0.0	1.402.54	0.00000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0472	0.92037	0.005	1176.2	770	-2.0	1.40190	0.00004
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0958	0.92704	0.005	1170.5	775	-3.2	1.40140	0.00007
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.1344	0.92833	0.009	11/2.7	785	-9.5	1.40051	0.00013
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.2320	0.33003	0.012	1164.0	707	- 12.0	1,39933	0.00019
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.3340	0.02220	0.014	1104.9	791	- 13.4	1,25023	0.00020
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.4922	0.93330	0.013	1101.0	790	-13./	1.39/33	0.00020
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.5938	0.93508	0.011	1156.9	/99	- 12.9	1.39646	0.00016
0.7975 0.93885 0.000 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 7=313.15 K	0.6929	0.93687	0.000	1152.9	809	-11.2	1.39541	0.00012
0.850 0.9407b 0.003 1144.3 812 -4.7 1.39326 0.0002 1.0000 0.94292 0.000 1139.7 817 0.0 1.39217 0.0000 7=313.15 K 7 0.0 1.4030 0.0000 0.0000 0.0472 0.92116 0.003 1162.1 804 0.0 1.40030 0.0000 0.0472 0.92178 0.003 1160.4 806 -2.8 1.39983 0.0001 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 1.3941 0.00099 0.2928 0.92537 0.012 1151.0 816 -12.0 1.39745 0.0014 0.4922 0.92855 0.016 1143.0 824 -13.7 1.39642 0.0014 0.4922 0.92855 0.016 1143.0 824 -13.7 1.39437 0.00013 0.5938	0.7973	0.93885	0.006	1148.5	808	-8.3	1.39431	0.00008
1.0000 0.94292 0.000 1139.7 817 0.0 1.39217 0.00000 T=313.15 K	0.8950	0.94076	0.003	1144.3	812	-4.7	1.39326	0.00002
T = 313.15 K 0.0000 0.92116 0.000 1162.1 804 0.0 1.40030 0.0000 0.0472 0.92178 0.003 1160.4 806 -2.8 1.39983 0.0001 0.0938 0.92244 0.005 1158.6 808 -5.2 1.39937 0.0003 0.1944 0.92389 0.009 1154.8 812 -9.3 1.39745 0.0001 0.2928 0.92537 0.012 1151.0 816 -12.0 1.39745 0.0014 0.3946 0.92697 0.014 1146.9 820 -13.4 1.39642 0.0014 0.4922 0.92855 0.016 1143.0 824 -13.7 1.39542 0.0014 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 1.39212 0.00005 0.8950 0.93584 0.003<	1.0000	0.94292	0.000	1139.7	817	0.0	1.39217	0.00000
0.00000.921160.0001162.18040.01.400300.00000.04720.921780.0031160.4806-2.81.399830.00010.09380.922440.0051158.6808-5.21.399870.00030.19440.923890.0091154.8812-9.31.397450.00010.29280.925370.0121151.0816-12.01.397450.00140.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393320.00090.79730.933980.0061130.2838-8.31.392120.000150.89500.935840.0031126.0843-4.81.391180.000111.00000.938050.0001121.38480.01.390100.00000	T=313.15 K							
0.04720.921780.0031160.4806-2.81.399830.00010.09380.922440.0051158.6808-5.21.399370.00030.19440.923890.0091154.8812-9.31.398410.00090.29280.925370.0121151.0816-12.01.39450.00140.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393320.00090.79730.933980.0061130.2838-8.31.392220.00050.89500.935840.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.0000	0.92116	0.000	1162.1	804	0.0	1.40030	0.00000
0.09380.922440.0051158.6808-5.21.399370.00030.19440.923890.0091154.8812-9.31.398410.00090.29280.925370.0121151.0816-12.01.397450.00140.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.000130.69290.932040.0111134.7833-11.21.393230.00090.79730.933980.0061130.2838-8.31.392220.00050.89500.938540.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.0472	0.92178	0.003	1160.4	806	-2.8	1.39983	0.00001
0.19440.923890.0091154.8812-9.31.398410.00090.29280.925370.0121151.0816-12.01.397450.00140.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393320.00090.79730.933980.0061130.2838-8.31.392120.00050.89500.938540.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.0938	0.92244	0.005	1158.6	808	-5.2	1.39937	0.00003
0.29280.925370.0121151.0816-12.01.397450.00140.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.90290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393220.00090.79730.933980.0061130.2838-8.31.391220.000150.89500.938540.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.1944	0.92389	0.009	1154.8	812	-9.3	1.39841	0.00009
0.39460.926970.0141146.9820-13.41.396420.00140.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393220.00090.79730.933980.0061130.2838-8.31.391220.000010.89500.938640.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.2928	0.92537	0.012	1151.0	816	-12.0	1.39745	0.00014
0.49220.928550.0161143.0824-13.71.395420.00140.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393320.000990.79730.933980.0061130.2838-8.31.392220.000050.89500.935840.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.00000	0.3946	0.92697	0.014	1146.9	820	-13.4	1.39642	0.00014
0.59380.930290.0131138.9829-12.91.394370.00130.69290.932040.0111134.7833-11.21.393320.00090.79730.933980.0061130.2838-8.31.392220.00050.89500.935840.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.4922	0.92855	0.016	1143.0	824	-13.7	1.39542	0.00014
0.69290.932040.0111134.7833-11.21.393320.00090.79730.933980.0061130.2838-8.31.392220.00050.89500.935840.0031126.0843-4.81.391180.00011.00000.938050.0001121.38480.01.390100.0000	0.5938	0.93029	0.013	1138.9	829	-12.9	1.39437	0.00013
0.7973 0.93398 0.006 1130.2 838 -8.3 1.39222 0.0005 0.8950 0.93584 0.003 1126.0 843 -4.8 1.39118 0.0001 1.0000 0.93805 0.000 1121.3 848 0.0 1.39010 0.0000	0.6929	0.93204	0.011	1134.7	833	-11.2	1.39332	0.00009
0.8950 0.93584 0.003 1126.0 843 -4.8 1.39118 0.0001 1.0000 0.93805 0.000 1121.3 848 0.0 1.39010 0.00000	0.7973	0.93398	0.006	1130.2	838	-8.3	1.39222	0.00005
1.0000 0.93805 0.000 1121.3 848 0.0 1.39010 0.00000	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

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.

<i>x</i> ₁	$\rho (\mathrm{g}\mathrm{cm}^{-3})$	$V_{\rm m}^{\rm E}({\rm cm}^3{\rm mol}^{-1})$	$u (m s^{-1})$	$\kappa_{\rm s}~({\rm TPa}^{-1})$	$\kappa_{\rm s}^{\rm E}({\rm TPa}^{-1})$	n	Δn
T - 203 15 K							
1 - 293.13 K	0.020/1	0.000	1224.0	600	0.0	1 409 40	0.00000
0.0000	0.93941	0.005	1234.0	605	0.0	1,40040	0.00000
0.0041	0.93739	0.003	1230.0	695	-0.1	1.40990	0.00034
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
10000	0.91765	0.000	1295.4	649	0.0	1 42336	0,00000
10000	0101700	01000	120011	0.10	010	112000	0.00000
T = 298.15 K							
0.0000	0 93485	0.000	1216.0	723	0.0	1 40641	0 00000
0.06/1	0.03306	0.005	1220.8	710	0.0	1.100 11	0.00051
0.1207	0.02151	0.005	1220.0	715	-0.1	1,40004	0.00051
0.1207	0.93131	0.017	1223.0	715	-0.2	1.40504	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	/02	-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	0.013/7	0.000	1273.0	671	0.0	1 /2138	0.00000
1.0000	0.31347	0.000	1277.7	0/1	0.0	1.42150	0.00000
T = 202.15 V							
I = 505.15 K	0.02020	0.000	1107.0	740	0.0	1 40 420	0.00000
0.0000	0.93029	0.000	1197.9	749	0.0	1.40438	0.00000
0.0641	0.92852	0.006	1202.7	/45	-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
0.0233	0.01058	0.010	1255.5	607	0.1	1 /18/2	0.00033
0.0620	0.01000	0.006	1255.7	605	-0.1	1,41042	0.00051
1.0000	0.90987	0.000	1257.9	695	0.0	1.41090	0.00018
1.0000	0.90929	0.000	1259.9	693	0.0	1.41935	0.00000
T-2001EV							
I = 508.15 K	0.02572	0.000	1170.0	776	0.0	1 40224	0.00000
0.0000	0.92573	0.000	11/9.9	776	0.0	1.40234	0.00000
0.0641	0.92398	0.007	1184.8	//1	-0.1	1.40383	0.00049
0.1207	0.92248	0.014	1189.0	/6/	-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	-01	1,41643	0.00034
0.9620	0.90568	0.006	1240.3	718	0.0	1 /1605	0.000001
1,0000	0.90511	0.000	1240.5	716	0.0	1.41033	0.00013
1.0000	0.50511	0.000	12-12.2	/10	0.0	1.41755	0.00000
T = 313 15 K							
0.0000	0 02116	0.000	1162.1	804	0.0	1 /0020	0.00000
0.0000	0.02110	0.000	1102.1	700	0.0	1.40050	0.00000
0.0041	0.91944	0.006	1107.0	/99	-0.2	1.401/0	0.00049
0.1207	0.91/9/	0.015	11/1.2	/94	-0.3	1.40283	0.00072
0.2317	0.91529	0.021	11/9.1	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
10000	0 90094	0.000	1224 7	740	0.0	1 41530	0.00000
	0.00001	0.000	1.7	. 10	0.0		0.00000

156

Table C

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 ($ ho$ an	rmsd (ρ and n)					
T (K)	293.15	298.15	303.15	308.15	313.15		
{Butanoic aci ρ (g cm ⁻³)	d (x ₁)+penta 0.00005	noic acid (x ₂) 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_m^E , 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_m^E 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_m^E value for the system (heptanoic acid + pentanoic acid) > (butanoic acid + pentanoic acid) = (butanoic acid + pentanoic acid) = (butanoic acid + pentanoic acid) system which is possibly due to the additional CH₂ group on the heptanoic acid. The V_m^E , 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 $V_{m, max}^E$ 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:

$$\kappa_{\rm s} = \frac{1}{\rho u^2} \tag{8}$$

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):

$$\Delta \kappa_{\mathrm{s}(\phi)} = \kappa_{\mathrm{s}} - \sum_{i}^{2} \phi_{i} \kappa_{\mathrm{s},i} \tag{9}$$

where $\kappa_{s,i}$ and ϕ_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):

Table 0
Root mean square deviation, rmsd, in sound velocity, <i>u</i> , at different temperatures for
the studied mixing rules.

Equation	rmsd (u)							
<i>T</i> (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 ac	{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			



Fig. 1. Excess molar volumes, $V_{\rm m}^{\rm E}$, 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 (\blacklozenge), 298.15 K (\blacksquare), 303.15 K (\diamondsuit), 308.15 K (\blacklozenge) and 313.15 K (\diamondsuit). The solid lines were generated using Redlich–Kister curve-fitting.

$$\kappa_{\rm s}^{\rm E} = \Delta \kappa_{\rm s}(\phi) - T \left[\sum_{\rm i} \phi_{\rm i} \frac{(\alpha_{\rm p,i}^{*})^2}{\sigma_{\rm p,i}^{*}} - \frac{(\Sigma_{\rm i} \phi_{\rm i} \alpha_{\rm p,i}^{*})^2}{\Sigma_{\rm i} \phi_{\rm i} \sigma_{\rm p,i}^{*}} \right]$$
(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^F , 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 7 Heat capacity, C_{p_r} [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	$\textbf{1.82}\times 10^5$	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	$\textbf{1.23}\times \textbf{10}^{5}$
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, $\kappa_{\rm S}^{\rm E}$, 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 (\blacklozenge), 298.15 K (\blacksquare), 303.15 K (\bigstar), 308.15 K (\blacklozenge) and 313.15 K (\diamondsuit). 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):

$$\Delta n = n - x_1 n_1 - x_2 n_2 \tag{11}$$

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 Δn_{max} values occurrs at x_1 =0.4922 and 0.4383, respectively, at each



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 (\blacklozenge), 298.15 K (\blacksquare), 303.15 K (\bigstar), 308.15 K (\diamondsuit) and 313.15 K (\diamondsuit). The solid lines were generated using Redlich–Kister curve-fitting.

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:

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

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

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.

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	<i>T</i> (K)		A ₀	<i>A</i> ₁	<i>A</i> ₂	<i>A</i> ₃	A ₄	σ
$ V_{m}^{L} (cm3 mol -1) 293,15 0.058 0.015 -0.026 0.003 -0.0004 -0.00004 0.00007 0.00007 0.000007 0.000006 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000007 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000002 0.000004 0.000000 0.000000 0.000002 0.000004 0.000000 0.000000 0.000000 0.000000 0.000000$	{Butanoic acid (x_1) + pentano	Dic acid (x_2)						
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$V_{\rm m}^{\rm c}$ (cm3 mol -1)	293.15	0.058	0.015	-0.026	0.003	-	0.0003
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$								
$ \left(\begin{array}{cccccccccccccccccccccccccccccccccccc$		298.15	0.058	0.016	-0.026	0.004	-	0.0004
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		303.15	0.057	0.013	-0.024	0.011	-	0.0004
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		308.15	0.058	0.008	-0.024	0.018	-	0.0004
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		313.15	0.059	0.008	-0.028	0.019	-	0.0006
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	κ_{c}^{E} (TPa -1)	202.15	F2 0	74	2.0	10	2.0	0.1
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3 ()	295.15	-55.9	-7.4	-3.9	1.2	2.0	0.1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		298 15	_54.2	-64	_37	_0.9	24	01
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		303 15	-54.6	-64	_39	-19	3.0	01
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		30815	-547	-64	-30	-10	2.5	01
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		313 15	-547	-67	-2.3	0.4	0.4	0.1
$ \begin{split} \Delta n & \begin{array}{c} 293.15 & -0.00036 & -0.0004 & 0.0001 & -0.0007 & - & 0.00006 \\ 288.15 & -0.00035 & -0.00011 & 0.00007 & -0.00064 & - & 0.00000 \\ 303.15 & -0.00029 & -0.0008 & 0.00002 & -0.00004 & - & 0.00000 \\ 308.15 & -0.0028 & -0.0008 & 0.00009 & -0.0004 & - & 0.00000 \\ 313.15 & -0.0028 & -0.0008 & 0.0009 & -0.0004 & - & 0.00000 \\ \end{array} $		515.15	51.7	0.7	2.5	0.1	0.1	0.1
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Δn	293.15	-0.00036	-0.00004	0.00001	-0.00007	-	0.00000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		298.15	-0.00035	-0.00011	0.00007	-0.00006	-	0.00000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		303.15	-0.00031	-0.00008	0.00002	-0.00004	-	0.00000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		308.15	-0.00029	-0.00009	0.00003	-0.00004	-	0.00000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		313.15	-0.00028	-0.00008	0.00009	-0.00008	-	0.00000
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $								
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	{Heptanoic acid (x_1) + pentai	noic acid (x_2)						
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	v _m (cm5mor-r)	293.15	0.092	0.010	0.009	-0.030	-0.004	0.000
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		200.15	0.009	0.012	0.002	0.045	0.022	0.001
$\Delta n = \begin{bmatrix} 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 \\ 0.044 & 0.001 & 0.014 & 0.044 & 0.001 \\ 0.011 & 0.014 & -0.7 & -0.7 & 1.2 & 0.1 \\ 0.011 & 0.014 & -0.8 & -0.1 & -0.2 & 1.3 & 0.1 \\ 0.011 & 0.015 & -1.6 & -0.3 & -0.6 & -0.6 & 0.5 & 0.1 \\ 0.011 & 0.015 & -1.8 & -0.9 & -1.2 & 0.2 & 2.1 & 0.1 \\ 0.011 & 0.015 & -2.2 & -1.5 & 0.0 & 0.5 & 0.3 & 0.1 \\ 0.011 & 0.012 & 0.0025 & 0.0002 \\ 0.0001 & 0.0017 & 0.00071 & 0.00183 & 0.00258 & 0.0001 \\ 0.0012 & 0.0025 & 0.0001 \\ 0.0013 & 0.00258 & 0.0001 \\ 0.0015 & 0.00126 & 0.00105 & 0.00190 & 0.0025 & 0.0001 \\ 0.0025 & 0.0001 \\ 0.0015 & 0.00426 & 0.0015 & 0.00128 & 0.00292 & 0.0001 \\ 0.00277 & 0.0001 \\ 0.0001 & $		298.15	0.098	0.012	-0.003	-0.045	0.032	0.001
$\Delta n = \begin{bmatrix} 308.15 & 0.105 & 0.008 & 0.012 & -0.023 & 0.047 & 0.001 \\ 313.15 & 0.106 & 0.007 & 0.026 & -0.014 & 0.044 & 0.001 \\ 0.044 & 0.001 \\ 0.044 & 0.001 \\ 0.044 & 0.001 \\ 0.044 & 0.001 \\ 0.014 & 0.001 \\ 0.014 & 0.001 \\ 0.014 & 0.001 \\ 0.014 & 0.001 \\ 0.0014 & 0.0014 & 0.0014 \\ 0.0014 & 0.0014 & 0.0014 \\ 0.0014 & 0.0014 & 0.0001 \\ 0.0025 & 0.0001 \\ 0.0001 & 0.0015 & 0.00126 & 0.00025 \\ 0.00010 & 0.0015 & 0.00126 & 0.00025 \\ 0.0002 & 0.00001 \\ 0.0015 & 0.00126 & 0.00015 & 0.00128 & 0.0001 \\ 0.0025 & 0.00001 \\ 0.0025 & 0.0001 \\ 0.0015 & 0.00126 & 0.00015 & 0.00128 & 0.00012 \\ 0.0025 & 0.0001 \\ 0.0025 & 0.0001 \\ 0.0015 & 0.00126 & 0.0002 & 0.0001 \\ 0.00128 & 0.00292 & 0.0001 \\ 0.00277 & 0.0001 \\ 0.0001 & 0.00142 & 0.00277 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.00142 & 0.00277 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.0001 & 0.0001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.00001 \\ 0.00001 & 0.000001 \\ 0.00001 & 0.000001 \\ 0.00001 & 0.000001 \\ 0.000001 & 0.000001 \\ 0.000001 & 0.000001 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000001 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000000 \\ 0.000001 & 0.000000 \\ 0.000000000000000000000 \\ 0.00000000$		303.15	0.101	0.013	0.012	-0.036	0.030	0.001
$\Delta n = \begin{bmatrix} 293.15 & 0.106 & 0.007 & 0.026 & -0.014 & 0.044 & 0.001 \\ 0.026 & -0.014 & 0.044 & 0.001 \\ 0.026 & -0.014 & 0.044 & 0.001 \\ 0.026 & -0.014 & 0.044 & 0.001 \\ 0.044 & 0.001 & 0.014 \\ 0.044 & 0.001 \\ 0.044 & 0.001 \\ 0.1 & 0.1 & 0.1 \\ 0.01 & -0.2 & 1.3 & 0.1 \\ 0.01 & -0.2 & 0.0 & 0.5 & 0.1 \\ 0.01 & -0.2 & 0.0 & 0.5 & 0.1 \\ 0.01 & -0.2 & 0.0 & 0.5 & 0.0 \\ 0.01 & -0.2 & 0.0 & 0.5 & 0.0 \\ 0.00 & 0.5 & 0.0 & 0.5 & 0.0 \\ 0.00 & 0.5 & 0.0 & 0.0 & 0.5 & 0.0 \\ 0.00 & 0.5 & 0.0 & 0.0 & 0.0 \\ 0.00 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & $		308.15	0.105	0.008	0.012	-0.023	0.04/	0.001
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		313.15	0.106	0.007	0.026	-0.014	0.044	0.001
$\Delta n = \begin{bmatrix} 298.15 & -1.4 & -0.8 & -0.1 & -0.2 & 1.3 & 0.1 \\ 303.15 & -1.6 & -0.3 & -0.6 & -0.6 & 0.5 & 0.1 \\ 308.15 & -1.8 & -0.9 & -1.2 & 0.2 & 2.1 & 0.1 \\ 313.15 & -2.2 & -1.5 & 0.0 & 0.5 & 0.3 & 0.1 \end{bmatrix}$	$\kappa_{\rm s}^{\rm E}$ (TPa -1)	293.15	-1.0	-0.4	-0.7	-0.7	1.2	0.1
$\Delta n = \begin{bmatrix} 298.15 & -1.4 & -0.8 & -0.1 & -0.2 & 1.3 & 0.1 \\ 303.15 & -1.6 & -0.3 & -0.6 & -0.6 & 0.5 & 0.1 \\ 308.15 & -1.8 & -0.9 & -1.2 & 0.2 & 2.1 & 0.1 \\ 313.15 & -2.2 & -1.5 & 0.0 & 0.5 & 0.3 & 0.1 \end{bmatrix}$								
$\Delta n = \begin{bmatrix} 303.15 & -1.6 & -0.3 & -0.6 & -0.6 & 0.5 & 0.1 \\ 308.15 & -1.8 & -0.9 & -1.2 & 0.2 & 2.1 & 0.1 \\ 313.15 & -2.2 & -1.5 & 0.0 & 0.5 & 0.3 & 0.1 \end{bmatrix}$		298.15	-1.4	-0.8	-0.1	-0.2	1.3	0.1
$\Delta n = \begin{bmatrix} 308.15 \\ 313.15 \\ -2.2 \\ 298.15 \\ 30.00466 \\ 298.15 \\ 30.00458 \\ 30.0017 \\ 30.0071 \\ 30.0071 \\ 30.0071 \\ 30.00183 \\ 0.00258 \\ 0.00105 \\ 0.00190 \\ 0.00205 \\ 0.00001 \\ 30.00205 \\ 0.00001 \\ 30.0001 \\ 30.0025 \\ 0.00010 \\ 30.0001 \\ 30.0048 \\ 0.00426 \\ 0.00102 \\ 0.00041 \\ 0.00142 \\ 0.00142 \\ 0.00277 \\ 0.00001 \\ 0.00000 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00001 \\ 0.00000 \\ 0.0000 \\ 0.00000 \\ 0.00000 \\ 0.00000 \\ 0.00000 \\ $		303.15	-1.6	-0.3	-0.6	-0.6	0.5	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 0.00026 298.15 0.00458 0.00117 0.00173 0.00183 0.00258 0.00001 303.15 0.00448 0.00098 0.00105 0.00128 0.00292 0.00011 308.15 0.00435 0.00126 0.00067 0.00128 0.00292 0.00011 313.15 0.00426 0.00102 0.00041 0.00142 0.00277 0.00011		308.15	-1.8	-0.9	-1.2	0.2	2.1	0.1
$ \Delta n \qquad \begin{array}{ccccccccccccccccccccccccccccccccccc$		313.15	-2.2	-1.5	0.0	0.5	0.3	0.1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$								
298.150.004580.001170.000710.001830.002580.00001303.150.004480.000980.001050.001900.002050.00001308.150.004350.001150.000670.001280.002920.00001313.150.004260.001020.000410.001420.002770.00001	Δn	293.15	0.00466	0.00126	0.00085	0.00212	0.00292	0.00002
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		298.15	0.00458	0.00117	0.00071	0.00183	0.00258	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		303.15	0.00448	0.00098	0.00105	0.00190	0.00205	0.00001
313.15 0.00426 0.00102 0.00041 0.00142 0.00277 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.

Acknowledgements

The authors acknowledge funding from the Department of Science and Technology (SA) and the National Research Foundation (SA) for the purchase of the DSA 5000 M and University of KwaZulu Natal for a postdoctoral scholarship for Dr I. Bahadur. This work is based upon research supported by the South African Research Chairs Initiative of the Department of Science and Technology and the National Research Foundation.

References

 C.J. King, Amine-based systems for carboxylic acid recovery: tertiary amines and the proper choice of diluent allow extraction and recovery from water, Chemtech 5 (1992) 285–291.

- [2] S.L. Clifford, D. Ramjugernath, J.D. Raal, Subatmospheric vapor pressure curves for propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, hexanoic acid and heptanoic acid, J. Chem. Eng. Data 49 (2004) 1189–1192.
- [3] S. Kumar, B.V. Babu, http://discovery.bits-pilani.ac.in/-bvbabu/Susheel_Babu_JFET_Carboxylic%20acids_Review.pdf.
- [4] Y.K. Hong, W.H. Hong, D.H. Han, Application of reactive extraction to recovery of carboxylic acids, Biotechnol. Bioprocess Eng. 6 (2001) 386–394.
- [5] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin, Synthesis of biodiesel via acid catalysis, Ind. Eng. Chem. Res. 44 (2005) 5353– 5363.
- [6] N. Calvar, E. Gómez, B. González, Á. Domínguez, Experimental determination, correlation, and prediction of physical properties of the ternary mixtures ethanoló+ówater with 1-octyl-3-methylimidazolium chloride and 1-ethyl-3methylimidazolium ethylsulfate, J. Chem. Eng. Data 52 (2007) 2529–2535.
- [7] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, Green Chem. 3 (2001) 156–164.
- [8] P. Abrman, I. Malijevská, Solid-liquid equilibria in the acetic acid-propanoic acid and propanoic acid-trifluoroacetic acid systems, Fluid Phase Equilibria 166 (1999) 47–52.
- [9] Z. Zhou, Y. Shi, X. Zhou, Theoretical studies on the hydrogen bonding interaction of complexes of formic acid with water, J. Phys. Chem. A 108 (2004) 813–822.
- [10] D. Wei, J.-F. Truchon, S. Sirois, D. Salahub, Solvation of formic acid and proton transfer in hydrated clusters, J. Chem. Phys. 116 (2002) 6028–6038.
- [11] G.F. Velardez, J.C. Ferrero, J.A. Beswick, J.P. Daudey, Ab initio study of the structures and $\pi^* n$ electronic transition in formic acid (water) n (n=3, 4, and 5) hydrogen bonded complexes, J. Phys. Chem. A 105 (2001) 8769–8774.
- [12] P.N. Sibiya, N. Deenadayalu, Excess molar volumes and partial molar volumes of binary systems (ionic liquid+methanol or ethanol or 1-propanol) at T = (298, 15, 303, 15 and 313, 15) K, S. Afr. J. Chem. 62 (2009) 20–25.
- [13] R. Sewnarain, J.D. Raal, D. Ramjugernath, Isobaric vapor liquid equilibria for the systems propionic acid + butyric acid, isobutyric acid + butyric acid, butyric acid + isovaleric acid, and butyric acid + hexanoic acid at 14 kPa, J. Chem. Eng. Data 47 (2002) 603–607.
- [14] S.C. Clifford, K. Bolton, D. Ramjugernath, Monte Carlo simulation of carboxylic acid phase equilibria, J. Phys. Chem. B 110 (2006) 21938–21943.
- [15] I. Bahadur, N. Deenadayalu, P. Naidoo, D. Ramjugernath, Density, speed of sound and refractive Index measurements for the binary systems (butanoic acid + propanoic acid or 2-methyl-propanoic acid) at *T* = (293.15–313.15) K, J. Chem. Thermodyn. 57 (2013) 203–211.
- [16] I. Bahadur, N. Deenadayalu, P. Naidoo, D. Ramjugernath, Volumetric, acoustic and refractive index for the binary system (butyric acid+hexanoic acid) at different temperatures, J. Solution Chem. 43 (2014) 487–803.
- [17] M. Tadie, I. Bahadur, P. Reddy, P. Naidoo, N. Deenadayalu, D. Ramjugernath, P. Ngema, Solid–liquid equilibria of (butyric acid+propionic or pentanoic acid) and (heptanoic acid+propionic or butyric or pentanoic or hexanoic acid) binary systems, J. Chem. Thermodyn. 57 (2013) 485–492.

- [18] S.L. Clifford, D. Ramjugernath, J.D. Raal, Vapour–liquid equilibrium of carboxylic acid systems: propionic acid+valeric acid and isobutyric acid+ valeric acid, Fluid Phase Equilibria 237 (2005) 89–99.
- [19] C. Narasigadu, J.D. Raal, P. Naidoo, D. Ramjugernath, Ternary liquid liquid equilibria of acetonitrile and water with heptanoic acid and nonanol at 323.15 K and 1 atm, J. Chem. Eng. Data 54 (2009) 735–738.
- [20] I. Bahadur, P. Naidoo, S. Singh, D. Ramjugernath, N. Deenadayalu, Density, effect of temperature on density, sound velocity, refractive index and their derived properties for the binary systems (heptanoic acid+propanoic or butanoic acids), J. Chem. Thermodyn. (2014) Accepted.
- [21] W.-T. Vong, F.-N. Tsai, Densities, molar volumes, thermal expansion coefficients, and isothermal compressibilities of organic acids from 293.15 K to 323.15 K and at pressures up to 25 MPa, J. Chem. Eng. Data 42 (1997) 1116–1120.
- [22] B.-G. Gabrlela, E. Mercedes, R. Albertina, Densities and refractive indices of pure organic acids as a function of temperature, J. Chem. Eng. Data 35 (1990) 202–204.
- [23] Aspen Plus Version, V7.3, Aspen Technology Inc. 2013.
- [24] A. Rodríguez, J. Canosa, J. Tojo, Density, refractive index, and speed of sound of binary mixtures (diethyl carbonate+alcohols) at several temperatures, J. Chem. Eng. Data 46 (2001) 1506–1515.
- [25] T.J. Fortin, A. Laesecke, M. Freund, S. Outcalt, Advanced calibration, adjustment and operation of a density and sound speed analyser, J. Chem. Thermodyn. 57 (2013) 276–285.
- [26] M.A. Iglesias-Otero, J. Troncoso, E. Carballo, L. Romani, Density and refractive index in mixtures of ionic liquids and organic solvents: correlations and predictions, J. Chem. Thermodyn. 40 (2008) 949–956.
- [27] M.N. Roy, D. Ekka, R. Dewan, Physico-chemical studies of some bioactive solutes in pure ethanoic acid, Acta Chim. Slov. 58 (2011) 792–796.
- [28] M.R. Rao, Velocity of sound in liquids and chemical constitution, J. Chem. Phys. 9 (1941) 682–686.
- [29] Y. Wada, On the relation between compressibility and molal volume of organic liquids, J. Phys. Soc. Jpn. 4 (1949) 280–283.
- [30] O. Nomoto, Empirical formula for sound velocity in liquid mixtures, J. Phys. Soc. Jpn. 13 (1958) 1528–1532.
- [31] J.G. Berryman, Analysis of ultrasonic velocities in hydrocarbon mixtures, J. Acoust. Soc. Am. 93 (1993) 2666–2668.
- [32] R. Ahluwalia, R.K. Wanchoo, S.K. Sharma, J.L. Vashisht, Density, viscosity, and surface tension of binary liquid systems: ethanoic acid, propanoic acid, and butanoic acid with nitrobenzene, J. Solution Chem. 25 (1996) 905–917.
- [33] G. Douhéret, M.I. Davis, J.C.R. Reis, Excess isentropic compressibilities and excess ultrasound speeds in binary and ternary liquid mixtures, Fluid Phase Equilibria 231 (2005) 246–249.
- [34] Aspen Plus Version, V7.3, Aspen Technology Inc. 2011.
- [35] M.T. Zafarani-Moattar, H. Shekaari, Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at *T* = (298.15–318.15) K, J. Chem. Thermodyn. 37 (2005) 1029–1035.
- [36] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, Ind. Eng. Chem. 40 (1948) 345–348.