Volumetric, Acoustic and Refractive Index for the Binary System (Butyric acid + Hexanoic acid) at Different Temperatures

I. Bahadur · N. Deenadayalu · P. Naidoo · D. Ramjugernath

Abstract In this paper density, sound velocity, and refractive index for the binary system (butyric acid + hexanoic acid) were measured over the entire composition range and at 5 K intervals in the temperature range 293.15–313.15 K. The excess molar volumes, isentropic compressibilities, excess isentropic compressibilities, deviation in refractive indices, molar refractions, and deviation in molar refractions were calculated by using the experimental densities, sound velocities, and refractive indices, respectively. The Redlich–Kister equation was used to fit the excess molar volume, excess isentropic compressibility, deviation in refractive index and deviation in molar refraction data. The Lorentz–Lorenz approximation was used to correlate the excess molar volume from the deviation in refractive index and also to predict the density from refractive index or the refractive index from density of the binary mixtures. Four sound velocity mixing rules were tested and the best model for the systems studied in this work was the Berryman mixing rule. The thermodynamic properties are discussed in terms of intermolecular interactions between the components of the mixtures.

1 Introduction

Carboxylic acids are important chemicals used in a variety of industrial applications such as separation processes, manufacture of pharmaceutical products, and cleaning agents [1, 2]. Carboxylic acids are attractive raw material for the production of biodegradable

I. Bahadur · N. Deenadayalu (✉)
Department of Chemistry, Durban University of Technology, P. O. Box 1334, Durban 4000, South Africa
e-mail: Nirmalad@dut.ac.za

P. Naidoo · D. Ramjugernath
Thermodynamics Research Unit, School of Chemical Engineering, University of Kwazulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa

plastics, and are also used as buffers, food preservatives, flavoring agents, fungicides, insecticides, and catalysts [1–3]. Carboxylic acids are being used as catalysts in the synthesis of biodiesel [4]. Biodiesels are being produced as replacements for fuels from petroleum sources because of the rising costs of crude oil. Therefore the large scale production of carboxylic acids by fermentation is receiving greater attention [1].

For developing reliable correlations and/or predictive models and to test solution theories, there is a need for thermodynamic properties such as: excess molar volume, excess isentropic compressibility and deviation in refractive index [5]. Excess properties of carboxylic acid mixtures assist in understanding the nature of the intermolecular interactions such as van der Waal's interactions and hydrogen bonding occurring in binary carboxylic acid mixtures [6–8].

It is also necessary to know thermophysical or thermodynamic properties, for example. densities, sound velocities, refractive indices, viscosities, heat capacities, Gibbs energies, excess molar volumes, excess molar enthalpies [9] also including phase equilibria data: solid–liquid equilibria (SLE) [10, 11], vapor–liquid equilibria (VLE) [12], and liquid–liquid equilibria (LLE) [13–15] in order to design industrial processes using carboxylic acids.

Carboxylic acids have been widely studied but there are no data available on the density, sound velocity and refractive index at several temperatures of carboxylic acid binary mixtures. There is a paucity of data published on the density, sound velocity and refractive index data of carboxylic acids with other solvents [16–27] but there is no sound velocity data for carboxylic acid binary mixtures.

The densities, sound velocities and refractive indices for the binary system (butyric acid + hexanoic acid) was measured over the entire composition range and at 5 K intervals in the temperatures range 293.15–313.15 K. These results were used to calculate excess molar volumes, isentropic compressibilities, excess isentropic compressibilities, deviation in refractive indices, molar refractions, and deviation in molar refractions over the entire composition range and at each temperature. The Redlich–Kister equation was used to fit the excess molar volume, excess isentropic compressibility, deviation in refractive index and deviation in molar refraction data. The Lorentz–Lorenz approximation was used to correlate the excess molar volume from the deviation in refractive index and also to predict the density from refractive index or the refractive index from density of the binary mixtures. Four sound velocity mixing rules were tested. The thermodynamic properties were discussed in terms of intermolecular interactions between the components of the mixtures. This work is a continuation of our research group's studies on thermodynamic properties of carboxylic acid mixtures [2, 11–13, 28–30].

2 Experimental

2.1 Chemicals

Butyric acid (Aldrich, South Africa, CAS No. 79-09-4, purity ≥ 99.5 %), hexanoic acid (Aldrich, South Africa, CAS No. 142-62-1, purity ≥ 99.5 %), diethyl carbonate (Aldrich, South Africa, CAS No. 105-58-8, purity ≥ 99 %) and ethanol (Aldrich, South Africa, CAS No. 64-17-5, purity ≥ 99.8 %) were purchased and used in the experiments. All the solvents were stored over 0.4 nm molecular sieves to prevent adsorption of water. The mass percent water content was determined using a Metrohm 702 SM Titrino Metter and found to be 0.39 % in butyric acid and 0.40 % in hexanoic acid. The comparison of the

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	
		Expt.	Lit.	Expt.	Expt.	Lit.
Butyric acid	293.15	0.95778	0.9576 [27]	1195.5	1.39826	1.39826 [30]
						1.3980 [34]
	298.15	0.95282	0.9528 [27]	1176.9	1.39615	1.39615 [30]
						1.3963 [34]
	303.15	0.94784	0.9479 [27]	1,158.2	1.39398	1.39398 [30]
						1.3950 [34]
	308.15	0.94288	0.9429 [27]	1,139.7	1.39183	1.39183 [30]
						1.3938 [34]
	313.15	0.93791	0.9379 [27]	1,121.3	1.38969	1.38969 [30]
						1.3921 [34]
Hexanoic acid	293.15	0.92729	0.9254 [27]	1,269.7	1.41687	1.4170 [34]
			0.9272 [31]			1.4171 [35]
	298.15	0.92295	0.9212 [27]	1,251.7	1.41483	1.4156 [34]
			0.9230 [31]			1.4152 [35]
	303.15	0.91859	0.9170 [27]	1,233.7	1.41278	1.4133 [34]
			0.91832 [31]			1.4134 [35]
	308.15	0.91424	0.9126 [27]	1,215.8	1.41073	1.4118 [34]
			0.912602 [32]			1.4117 [35]
	313.15	0.90989	0.9083 [27]	1,198.2	1.40866	1.4100 [34]
			0.9101 [33]			1.4099 [35]

experimental density, sound velocity and refractive index values of the pure solvents, at various temperatures, show good agreement with those reported in the literature [27, 30–35] and are given in Table 1. The refractive index values are lower than the literature values for all acids except butyric acid at 293.15 K, where it slightly higher than the literature values and increasing with temperature. The maximum difference between the literature and the experimental density and the refractive index for hexanoic acid is 0.0016 g·cm^{-3} at 308.15 K and 0.0012 at 313.15 K, respectively. No further purification of these chemicals was carried out.

2.2 Apparatus and Procedure

Measurements were carried out on a binary test system (diethyl carbonate + ethanol) [36] at 298.15 K to validate the experimental technique by the determination of the excess molar volumes, isentropic compressibilities, excess isentropic compressibilities, deviation in refractive index, molar refraction, and deviation in molar refraction and comparing them with literature values. The difference between the experimental and literature values for the above thermodynamic properties was within the experimental error. This test system was chosen because all three parameters to be measured in this work namely: density, sound velocity and refractive index, are reported in the literature and the comparison with the literature data was used to validate the experimental technique. The results obtained for the

Table 2 Densities, ρ, sound velocity, u, refractive index, n, excess molar volume, V_m^E, deviation in isentropic compressibility, $\Delta \kappa_s^\varphi$, and deviation in refractive index Δn, for the binary system (diethyl carbonate + ethanol) 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	1,142.8	1.35945	0.000	0.0	0.00000
0.0415	0.80030	1,145.2	1.36136	0.011	−12.8	0.00095
0.0943	0.81771	1,147.3	1.36347	0.022	−24.4	0.00185
0.1932	0.84585	1,150.9	1.36698	0.046	−38.1	0.00308
0.2929	0.86958	1,154.0	1.36981	0.071	−44.2	0.00361
0.3938	0.88996	1,156.9	1.37241	0.096	−45.0	0.00389
0.4965	0.90782	1,159.8	1.37460	0.111	−42.0	0.00371
0.5970	0.92299	1,162.8	1.37647	0.125	−36.5	0.00326
0.6924	0.93573	1,166.0	1.37805	0.127	−29.9	0.00265
0.7911	0.94758	1,169.7	1.37957	0.113	−21.9	0.00189
0.8990	0.95927	1,173.7	1.38109	0.074	−11.7	0.00093
0.9413	0.96358	1,175.0	1.38167	0.046	−7.0	0.00053
1.0000	0.96932	1,176.6	1.38249	0.000	0.0	0.00000

test system are reported in Table 2. The estimated error in density and sound velocity is less than $\pm 1 \times 10^{-5}$ g·cm^{-3} and ± 0.5 m·s^{-1}, respectively. The estimated errors in excess molar volume, isentropic compressibility, excess isentropic compressibility, deviation in refractive index, molar refraction and deviation in molar refraction are ± 0.002 cm^3·mol^{-1}, ± 1 TPa^{-1}, ± 0.7 TPa^{-1}, ± 0.00009, ± 0.03 cm^3·mol^{-1}, and ± 0.04 cm^3·mol^{-11}, respectively.

Densities and sound velocities of the 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 repeatability and accuracy in experimental measurements have been found to be ($\pm 2 \times 10^{-6}$ and $\pm 5 \times 10^{-6}$) g·cm^{-3} for density and (± 0.1 and ± 0.5) m·s^{-1} for the sound velocity. The calibration for the DSA 5000 M was done with Anton Paar ultrapure water and dry air at 298.15 K. Measurement of the refractive index of 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 is less than $\pm 2 \times 10^{-5}$. The repeatability and accuracy in experimental measurements is $\pm 4 \times 10^{-6}$ and $\pm 2 \times 10^{-5}$ for refractive index. The calibration of the RXA 156 was done by measuring the refractive index of Anton Paar ultrapure water at 298.15 K and checked every week. The binary mixtures were prepared gravimetrically by injecting known masses of pure components into bottles that were stoppered to reduce evaporation losses. The binary mixtures were placed into an automatic sampler (Xsample 452) which was connected to the DSA 5000 M. The sample changer automatically filled the samples from the stoppered bottles into the measuring cell to minimize evaporation losses or the formation of bubbles. The instrument detects gas bubbles in the measuring cell by an advanced analysis of its oscillation patterns and generates a warning message on an external PC. After each measurement, the measuring cell was automatically rinsed and cleaned with two rinsing liquids: ethanol and acetone, and subsequently dried. The mass of each component of the mixture was obtained using an OHAUS mass balance with an accuracy of 0.0001 g. The estimated error in the mole fraction is 0.0006.

3 Results and Discussion

3.1 Density and Excess Molar Volume

The density, ρ, of the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K was measured over the entire composition range. The excess molar volume, V_m^E, for the binary system was calculated from the experimental density of the mixture and the pure components using Eq. 1:

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

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 butyric acid and 2 refers to hexanoic acid, and ρ is the density of the binary mixture.

Table 3 lists the ρ and V_m^E for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K and shows that the ρ values decrease with an increase in temperature and increase with an increase in concentration of butyric acid.

Tables 3, shows that the V_m^E values for the system (butyric acid + hexanoic acid) are positive for all temperatures and depend more strongly on concentration than temperature. The $V_{m,max}^E$ values occur at $x_1 = 0.5053$ for the system (butyric acid + hexanoic acid) at all temperatures. A plot of V_m^E versus composition of butyric acid for the binary system (butyric acid + hexanoic acid) at 313.15 K is presented in Fig. 1.

3.2 Sound Velocity, Isentropic Compressibility and Excess Isentropic Compressibility

The isentropic compressibilities, κ_s, were calculated using the Newton–Laplace Eq. 2:

$$\kappa_s = \frac{1}{\rho u^2} \tag{2}$$

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

The deviation in isentropic compressibility, $\Delta\kappa_{s(\phi)}$, were calculated using Eq. 3:

$$\Delta\kappa_{s(\phi)} = \kappa_s - \sum_i^N \phi_i \kappa_{s,i} \tag{3}$$

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 assuming ideal mixing.

The excess isentropic compressibility [37] for the binary system was calculated using Eq. 4:

$$\kappa_s^E = \Delta\kappa_{s(\phi)} - T\left[\sum_i \phi_i \frac{(\alpha_{p,i}^*)^2}{\sigma_{p,i}^*} - \frac{(\sum_i \phi_i \alpha_{p,i}^*)^2}{\sum_i \phi_i \sigma_{p,i}^*}\right] \tag{4}$$

where $\sigma_{p,i}^* = C_{p,m}/V_m$ is the heat capacitance or heat capacity per unit volume of the mixture; since heat capacities were not measured in this work, heat capacity values from the literature were used or calculated from literature values at the experimental temperatures [38, 39]. The thermal expansion coefficients defined as $\alpha_{p,i}^* = 1/V_m(\delta V_m/\delta T)_p = -1/\rho(\delta\rho/\delta T)_p$ was calculated at each temperature from the experimental density [37]. The

Table 3 Densities, ρ, excess molar volume, V_m^E, sound velocity, u, isentropic compressibility, κ_s, and excess isentropic compressibility, κ_s^E, for the binary system (butyric acid + hexanoic acid) 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})
$T = 293.15$ K					
0.0000	0.92729	0.000	1269.7	669	0.0
0.0537	0.92848	0.005	1,266.5	671	−8.8
0.1058	0.92966	0.010	1,263.1	674	−15.6
0.2060	0.93204	0.018	1,256.6	679	−25.8
0.3065	0.93456	0.026	1,250.0	685	−32.2
0.4058	0.93723	0.030	1,243.2	690	−35.5
0.5053	0.94010	0.031	1,236.1	696	−35.7
0.6039	0.94316	0.027	1,228.7	702	−33.3
0.7045	0.94652	0.020	1,220.8	709	−28.4
0.8080	0.95021	0.012	1,212.4	716	−20.9
0.9067	0.95398	0.005	1,204.0	723	−11.3
1.0000	0.95778	0.000	1,195.5	730	0.0
$T = 298.15$ K					
0.0000	0.92295	0.000	1,251.7	692	0.0
0.0537	0.92411	0.004	1,248.6	694	−8.9
0.1058	0.92526	0.010	1,245.0	697	−15.6
0.2060	0.92759	0.018	1,238.7	703	−26.1
0.3065	0.93006	0.026	1,232.0	708	−32.6
0.4058	0.93268	0.030	1,225.3	714	−36.0
0.5053	0.93549	0.030	1,217.9	721	−36.1
0.6039	0.93849	0.027	1,210.4	727	−33.7
0.7045	0.94178	0.019	1,202.5	734	−28.7
0.8080	0.94540	0.012	1,194.0	742	−21.1
0.9067	0.94910	0.005	1,185.6	750	−11.6
1.0000	0.95282	0.000	1,176.9	758	0.0
$T = 303.15$ K					
0.0000	0.91859	0.000	1,233.7	715	0.0
0.0537	0.91973	0.004	1,230.6	718	−9.0
0.1058	0.92086	0.010	1,227.0	721	−15.8
0.2060	0.92314	0.017	1,220.6	727	−26.3
0.3065	0.92557	0.025	1,213.8	733	−32.9
0.4058	0.92813	0.029	1,207.0	740	−36.4
0.5053	0.93088	0.030	1,199.6	746	−36.4
0.6039	0.93382	0.027	1,192.1	754	−34.0
0.7045	0.93704	0.019	1,184.1	761	−29.0
0.8080	0.94059	0.012	1,175.5	769	−21.4
0.9067	0.94421	0.004	1,167.0	778	−11.8
1.0000	0.94784	0.000	1,158.2	786	0.0
$T = 308.15$ K					
0.0000	0.91424	0.000	1,215.8	740	0.0
0.0537	0.91536	0.004	1,212.7	743	−9.1

Table 3 continued

| 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})
0.1058	0.91646	0.010	1,209.0	746	−15.9
0.2060	0.91870	0.017	1,202.6	753	−26.5
0.3065	0.92107	0.025	1,195.8	759	−33.2
0.4058	0.92358	0.029	1,188.9	766	−36.7
0.5053	0.92627	0.030	1,181.5	773	−36.8
0.6039	0.92915	0.027	1,173.9	781	−34.4
0.7045	0.93231	0.019	1,165.8	789	−29.3
0.8080	0.93578	0.012	1,157.1	798	−21.6
0.9067	0.93932	0.004	1,148.5	807	−11.9
1.0000	0.94288	0.000	1,139.7	817	0.0
$T = 313.15$ K					
0.0000	0.90989	0.000	1,198.2	766	0.0
0.0537	0.91098	0.004	1,195.0	769	−9.2
0.1058	0.91206	0.009	1191.3	773	−16.0
0.2060	0.91425	0.017	1,184.8	779	−26.7
0.3065	0.91657	0.025	1,177.9	786	−33.5
0.4058	0.91903	0.029	1,171.0	793	−37.0
0.5053	0.92167	0.030	1,163.5	801	−37.2
0.6039	0.92448	0.026	1,155.8	810	−34.7
0.7045	0.92757	0.019	1,147.7	819	−29.6
0.8080	0.93097	0.011	1,138.9	828	−21.9
0.9067	0.93444	0.003	1,130.3	838	−12.1
1.0000	0.93791	0.000	1,121.3	848	0.0

results for sound velocity, u, isentropic compressibility, κ_s, and excess isentropic compressibility, κ_s^E, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 3. The sound velocity data provides information about interactions in a mixture [40]. The sound velocity decreases with increases in temperature and concentration.

The isentropic compressibility values κ_s increase with an increase in temperature at a fixed composition, due to an increase in thermal agitation making the solution more compressible [41]. For the binary system (butyric acid + hexanoic acid), the κ_s values increase with an increase in concentration of the butyric acid at a fixed temperature.

The values of κ_s^E are negative. In general the κ_s^E values decrease with an increase in temperature at a fixed composition. The $\kappa_{s,min}^E$ values occur at $x_1 = 0.5053$, at all temperatures.

3.3 Refractive Index, Deviation in Refractive Index, Molar Refraction and Deviation in Molar Refraction

The deviation in refractive index, $\Delta n(\phi)$, was calculated using Eq. 5:
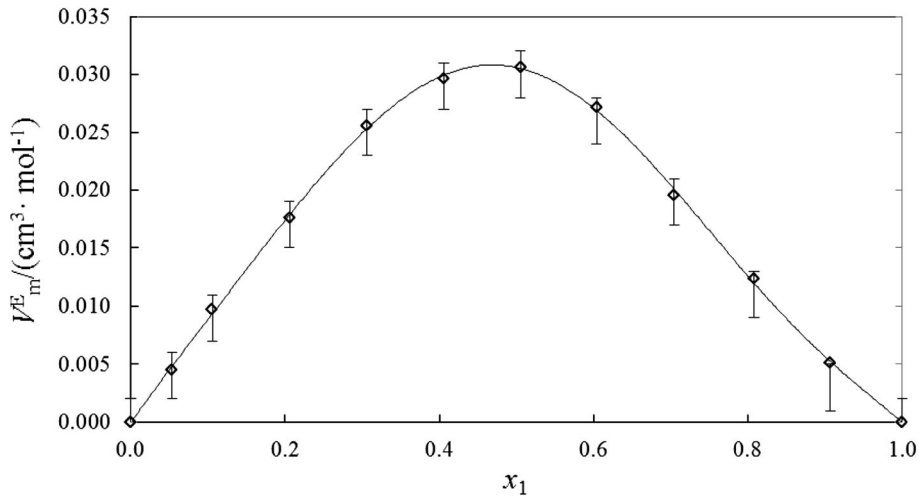
Fig. 1 Excess molar volumes, V_m^E, for the binary system (butyric acid + hexanoic acid) against mole fraction of butyric acid at 313.15 K (*open diamond*). The *solid lines* were generated using Redlich–Kister curve-fitting

$$\Delta n(\phi) = n - n^{id}(\phi) \tag{5}$$

where n is the measured refractive index of the mixtures.

The $n^{id}(\phi)$ was calculated from volume fractions [42] using Eq. 6:

$$n^{id}(\phi) = \phi_1\, n_1 + \phi_2\, n_2 \,. \tag{6}$$

Therefore,

$$\Delta n(\phi) = n - \phi_1 n_1 - \phi_2 n_2 \tag{7}$$

where n_1 and n_2 are the refractive indices, and where 1 refers to butyric acid and 2 refers to hexanoic acid. The results for refractive index, n, and deviation in refractive index, $\Delta n(\phi)$, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 4 and plotted in Fig. 2. Table 4 shows that the n values decrease with an increase in the temperature and concentration. The $\Delta n(\phi)$ values are negative at all temperatures. In general the $\Delta n(\phi)$ values increase very slowly with an increase in temperature. The $\Delta n(\phi)_{min}$ values occur at $x_1 = 0.5053$ for (butyric acid + hexanoic acid) at all temperatures.

The molar refraction, R, was calculated using the Lorentz–Lorenz equation [43] given below:

$$R = \left(\frac{n^2 - 1}{n^2 + 2} \right) V_m \tag{8}$$

where V_m is the molar volume of the mixture. The results for the molar refraction, R, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 4. This shows that the polarizability of the butyric acid + hexanoic acid system decreases with an increase in concentration of butyric acid. The molar refraction only depends on concentration and is only slightly affected by temperature [44].

Table 4 Refractive index, n, deviation of refractive index, $\Delta n(\phi)$, molar refraction, R, and deviation in molar refraction $\Delta R(\phi)$, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K

x_1	n	$\Delta n(\phi)$	R (cm$^3 \cdot$mol^{-1})	$\Delta R(\phi)$ (cm$^3 \cdot$mol^{-1})
$T = 293.15$ K				
0.0000	1.41687	0.00000	31.49	0.00
0.0537	1.41609	−0.00003	30.99	−0.13
0.1058	1.41532	−0.00007	30.51	−0.24
0.2060	1.41379	−0.00010	29.58	−0.43
0.3065	1.41217	−0.00014	28.65	−0.57
0.4058	1.41050	−0.00016	27.73	−0.67
0.5053	1.40873	−0.00016	26.81	−0.71
0.6039	1.40689	−0.00015	25.89	−0.70
0.7045	1.40490	−0.00013	24.96	−0.63
0.8080	1.40273	−0.00008	24.00	−0.49
0.9067	1.40052	−0.00003	23.08	−0.27
1.0,000	1.39826	0.00000	22.22	0.00
$T = 298.15$ K				
0.0000	1.41483	0.00000	31.51	0.00
0.0537	1.41406	−0.00002	31.01	−0.13
0.1058	1.41328	−0.00006	30.52	−0.24
0.2060	1.41175	−0.00009	29.59	−0.43
0.3065	1.41012	−0.00013	28.66	−0.57
0.4058	1.40844	−0.00015	27.74	−0.66
0.5053	1.40667	−0.00015	26.82	−0.71
0.6039	1.40481	−0.00015	25.90	−0.70
0.7045	1.40282	−0.00012	24.97	−0.63
0.8080	1.40064	−0.00007	24.01	−0.49
0.9067	1.39841	−0.00003	23.09	−0.27
1.0000	1.39615	0.00000	22.23	0.00
$T = 303.15$ K				
0.0000	1.41278	0.00000	31.52	0.00
0.0537	1.41200	−0.00002	31.02	−0.13
0.1058	1.41123	−0.00005	30.54	−0.24
0.2060	1.40968	−0.00009	29.60	−0.43
0.3065	1.40804	−0.00013	28.67	−0.57
0.4058	1.40635	−0.00014	27.75	−0.66
0.5053	1.40457	−0.00014	26.83	−0.71
0.6039	1.40271	−0.00014	25.91	−0.70
0.7045	1.40070	−0.00011	24.98	−0.63
0.8080	1.39850	−0.00007	24.02	−0.48
0.9067	1.39626	−0.00003	23.10	−0.27
1.0000	1.39398	0.00000	22.23	0.00
$T = 308.15$ K				
0.0000	1.41073	0.00000	31.53	0.00
0.0537	1.40995	−0.00002	31.03	−0.13

Table 4 continued

x_1	n	$\Delta n(\phi)$	R (cm^3·mol^{-1})	$\Delta R(\phi)$ (cm^3·mol^{-1})
0.1058	1.40917	−0.00004	30.55	−0.24
0.2060	1.40762	−0.00008	29.62	−0.42
0.3065	1.40598	−0.00012	28.68	−0.57
0.4058	1.40428	−0.00014	27.76	−0.66
0.5053	1.40249	−0.00014	26.84	−0.71
0.6039	1.40061	−0.00013	25.92	−0.70
0.7045	1.39859	−0.00011	24.99	−0.63
0.8,080	1.39639	−0.00006	24.03	−0.48
0.9067	1.39413	−0.00002	23.11	−0.27
1.0000	1.39183	0.00000	22.24	0.00
$T = 313.15$ K				
0.0000	1.40867	0.00000	31.54	0.00
0.0537	1.40789	−0.00002	31.04	−0.13
0.1058	1.40711	−0.00004	30.56	−0.24
0.2060	1.40554	−0.00008	29.63	−0.42
0.3065	1.40389	−0.00012	28.69	−0.57
0.4058	1.40219	−0.00013	27.77	−0.66
0.5053	1.40039	−0.00013	26.85	−0.71
0.6039	1.39851	−0.00013	25.93	−0.70
0.7045	1.39647	−0.00011	25.00	−0.63
0.8080	1.39426	−0.00006	24.04	−0.48
0.9067	1.39200	−0.00002	23.12	−0.27
1.0000	1.38969	0.00000	22.25	0.00

The deviation in molar refraction, $\Delta R(\phi)$, was calculated using Eq. 9:

$$\Delta R(\phi) = R - R^{\mathrm{id}}(\phi) \tag{9}$$

The $R^{\mathrm{id}}(\phi)$ was calculated from volume fractions [42] using Eq. 10:

$$R^{\mathrm{id}}(\phi) = \phi_1 R_1 + \phi_2 R_2 \tag{10}$$

Therefore,

$$\Delta R(\phi) = R - \phi_1 R_1 - \phi_2 R_2 \tag{11}$$

where R_1 and R_2 are the molar refraction, where 1 refers to butyric acid and 2 refers to hexanoic acid. The results for deviation in molar refraction, $\Delta R(\phi)$, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 4. This, shows that the values of $\Delta R(\phi)$ are negative. The $\Delta R(\phi)$ values also show characteristic nonlinear behavior.

4 Correlation of Derived Properties

The Redlich–Kister equation [45] was fitted to the $V_{\mathrm{m}}^{\mathrm{E}}$, κ_s^{E}, $\Delta n(\phi)$ and $\Delta R(\phi)$ data and is given below:
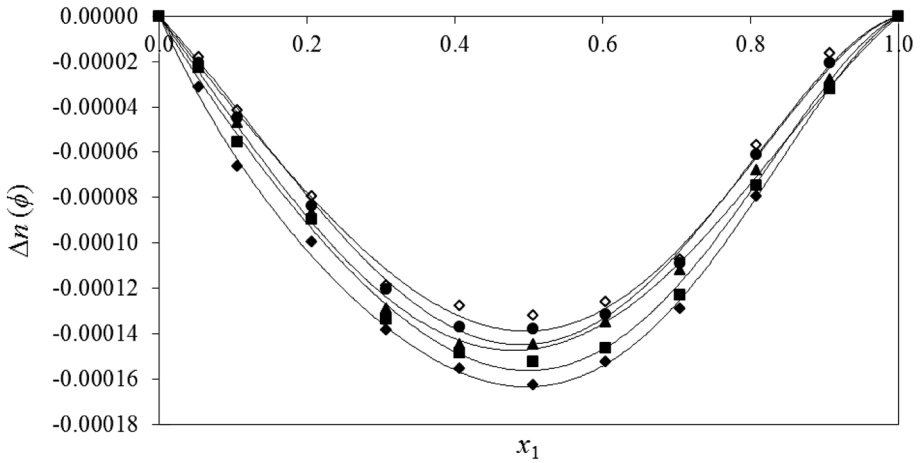
Fig. 2 Deviation in refractive index, $\Delta n(\phi)$, for the binary system (butyric acid + hexanoic acid) against mole fraction of butyric acid at 293.15 K (*black diamond*), 298.15 K (*black square*), 303.15 K (*black up-pointing triangle*), 308.15 K (*black circle*) and 313.15 K (*open diamond*). The *solid lines* were generated using Redlich–Kister curve-fitting

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

where X is the excess molar volume, V_m^E, or excess isentropic compressibility, κ_s^E, or deviation in refractive index, $\Delta n(\phi)$ or deviation in molar refraction, $\Delta R(\phi)$. The coefficients of A_i are the parameters that were obtained by fitting the equation to the experimental data with a least-squares method using the commercial software (MathCAD).

The standard deviation σ is defined as:

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

where N is the number of experimental points and k is the number of coefficients used in the Redlich–Kister equation. Redlich–Kister parameters, A_i, determined by fitting Eq. 12 to the experimental data together with the standard deviation, σ, for the binary system (butyric acid + hexanoic acid) at 293.15, 298.15, 303.15, 308.15 and 313.15 K are presented in Table 5. The excess molar volume, V_m^E, and deviation in refractive index, $\Delta n(\phi)$, were fitted with the four-parameter Redlich–Kister equation and κ_s^E and $\Delta R(\phi)$ were fitted with a five-parameter Redlich–Kister equation.

The Lorentz–Lorenz (L–L) approximation [46] was also used to correlate the binary data of V_m^E and is given below:

$$V_m^E = (-\Delta n) \frac{3R(n^{\mathrm{id}} + n)}{(n^2 - 1)\left([n^{\mathrm{id}}]^2 - 1\right)} = (-\Delta n) f(R, n^{\mathrm{id}}, n) \tag{14}$$

V_m^E was calculated from $\Delta n(\phi)$ using Eq. 14, from pure component densities and refractive indices. In this work n^{id} was calculated from volume fraction instead of mole

Table 5 Coefficients A_i, and standard deviations, σ, obtained for the (butyric acid + hexanoic acid) at different temperatures for the Redlich–Kister equation

	T (K)	A_0	A_1	A_2	A_3	A_4	σ
V_m^E (cm^3·mol^{-1})	293.15	0.122	0.028	−0.069	−0.001	–	0.0005
	298.15	0.120	0.035	−0.068	−0.017	–	0.0006
	303.15	0.119	0.023	−0.074	0.009	–	0.0007
	308.15	0.119	0.023	−0.073	0.009	–	0.0007
	313.15	0.119	0.027	−0.085	0.007	–	0.0003
κ_s^E (TPa^{-1})	293.15	−143.1	−19.0	−5.9	−1.8	−8.0	0.1
	298.15	−145.0	−20.5	−3.9	2.5	−11.4	0.1
	303.15	−146.3	−20.7	−4.0	3.6	−13.3	0.1
	308.15	−147.9	−20.2	−2.8	2.7	−14.4	0.1
	313.15	−149.2	−20.2	−2.3	3.8	−16.3	0.1
$\Delta n(\phi)$	293.15	−0.00065	−0.00001	0.00019	−0.00026	–	0.00001
	298.15	−0.00,063	0.00000	0.00027	−0.00019	–	0.00001
	303.15	−0.00059	−0.00007	0.00022	−0.00002	–	0.00000
	308.15	−0.00058	−0.00004	0.00036	−0.00009	–	0.00000
	313.15	−0.00056	−0.00001	0.00030	−0.00014	–	0.00001
$\Delta R(\phi)$ (cm^3·mol^{-1})	293.15	−2.83	0.43	−0.14	−0.02	0.12	0.01
	298.15	−2.82	0.46	−0.22	−0.08	0.20	0.01
	303.15	−2.83	0.44	−0.11	−0.10	0.09	0.01
	308.15	−2.84	0.46	0.01	−0.10	−0.08	0.01
	313.15	−2.84	0.46	0.01	−0.10	−0.08	0.01

Table 6 Standard deviation, σ, between the experimental and correlated excess molar volumes, V_m^E, and also between the experimental and the predicted density, ρ, or refractive index, n, of the binary systems at different temperatures

Properties	σ (V_m^E, ρ and n)				
T (K)	293.15	298.15	303.15	308.15	313.15
V_m^E (cm^3·mol^{-1})	0.006	0.005	0.004	0.003	0.003
ρ (g·cm^{-3})	0.00005	0.00005	0.00006	0.00005	0.00004
n	0.00002	0.00,002	0.00003	0.00002	0.00002

fraction and gives good, consistent results for V_m^E [42, 46]. The experimental V_m^E and $\Delta n(\phi)$ are plotted in Figs. 1 and 2. These show that there is a strong correlation between V_m^E and $\Delta n(\phi)$, i.e. positive V_m^E corresponds to negative $\Delta n(\phi)$ [46]. Also, the maximum or minimum of both the properties occur at the same mole fraction [46]. The standard deviation (σ) between the correlated V_m^E and experimental V_m^E data are presented in Table 6. These results also show that there is very good correlation of V_m^E.

5 Predictions of Physical Properties

5.1 Prediction of Density

The framework of the Lorentz–Lorenz approximation is also helpful for predicting the density or refractive index data. The predictive expression for ρ can be obtained within the framework of the Lorentz–Lorenz approximation [46]:

$$\rho = \frac{\left(\frac{n^2-1}{n^2+2}\right)(x_1 M_1 + x_2 M_2)}{\left(\frac{n_1^2-1}{n_1^2+2}\right)\frac{x_1 M_1}{\rho_1} + \left(\frac{n_2^2-1}{n_2^2+2}\right)\frac{x_2 M_2}{\rho_2}} \tag{15}$$

The standard deviation (σ) between the measured densities and those predicted by Eq. 15 are presented in Table 6. The maximum standard deviation between the measured density and the predicted density of the mixtures is 0.00006 g·cm^{-3}. The standard deviation shows that densities predicted from the refractive indices agree well with the experimental values.

5.2 Prediction of Refractive Index

The inverse predictive expression for n can be obtained from Eq. 15 within the framework of the Lorentz–Lorenz approximation [46]:

$$n = \left(\frac{2\left[\left(\frac{n_1^2-1}{n_1^2+2}\right)x_1 \rho \frac{M_1}{\rho_1} + x_2 \left(\frac{n_2^2-1}{n_2^2+2}\right)\rho \frac{M_2}{\rho_2}\right] + [x_1 M_1 + x_2 M_2]}{[x_1 M_1 + x_2 M_2] - \left[\left(\frac{n_1^2-1}{n_1^2+2}\right)x_1 \rho \frac{M_1}{\rho_1} + x_2 \left(\frac{n_2^2-1}{n_2^2+2}\right)\rho \frac{M_2}{\rho_2}\right]}\right)^{1/2} \tag{16}$$

Equation 16 was used to predict refractive indices. The standard deviations (σ) between measured and predicted refractive indices are presented in Table 6. The maximum root mean square deviation is 0.00003. The standard deviation (σ) values show that the refractive indices predicted from the densities are also in excellent agreement with the experimental values. These results confirm that the Lorentz–Lorenz approximation is the most suitable equation for the prediction of density from the refractive index or refractive index from density.

6 Mixing Rules for Sound Velocity

Four sound velocity mixing rules were used to calculate the sound velocity of the binary mixtures from pure component data. The mixing rules applied here are the equations of Rao [47], Eq. 17, Wada [48], Eq. 18, Nomoto [49], Eq. 19, and Berryman [50], Eq. 20. The standard deviations calculated between experimental sound velocities and those calculated from the different mixing rules are presented in Table 7. These results show that the sound velocities calculated from the different mixing rules are quite good but the best results are obtained from the Berryman mixing rule. The largest standard deviation is 0.9 m·s^{-1}. The sound velocities calculated from the four sound velocity mixing rules used are given below:

Table 7 Standard deviation, σ, in sound velocity, u, at different temperatures for the studied mixing rules

Name	$\sigma(u)$				
T (K)	293.15	298.15	303.15	308.15	313.15
Rao	1.0	0.9	0.9	0.9	0.8
Wada	1.0	0.9	0.8	0.8	0.8
Nomoto	1.0	0.9	0.9	0.9	0.8
Berryman	0.5	0.4	0.4	0.3	0.3

$$u^{1/3} V_m = \sum_{i=1}^{2} u_i^{1/3} x_i V_i$$

$$\therefore \quad u = \left(\sum_{i=1}^{2} u_i^{1/3} x_i V_i / V_m \right)^3 \tag{17}$$

$$\kappa_s^{-1/7} V_m = \sum_{i=1}^{2} \kappa_{s,i}^{-1/7} x_i V_i$$

$$\therefore \quad u = \left(\sum_{i=1}^{2} u_i^{2/7} \rho_i^{1/7} x_i V_i \Big/ \left(\rho^{1/7} V_m \right) \right)^{7/2} \tag{18}$$

$$u = \left(\sum_{i=1}^{2} \varphi_i u_i^{1/3} \right)^3 \tag{19}$$

$$\kappa_s = \sum_{i=1}^{2} \varphi_i \kappa_{s,i}$$

$$\therefore \quad u = \left(\rho \sum_{i=1}^{2} \varphi_i \kappa_{s,i} \right)^{-1/2} \tag{20}$$

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.

7 Conclusions

In this paper density, sound velocity, and refractive index were measured over the entire composition range and at 293.15, 298.15, 303.15, 308.15 and 313.15 K for the binary system (butyric acid + hexanoic acid). Excess molar volume, isentropic compressibility, excess isentropic compressibility, deviation in refractive index, molar refraction and deviation in molar refraction were also calculated. The Redlich–Kister equation was used to fit the excess molar volume, excess isentropic compressibility, deviation in refractive index and deviation in molar refraction data. The Lorentz–Lorenz approximation was used to correlate the excess molar volume from the deviation in refractive index and to also predict the density from refractive index or the refractive index from density of the binary mixtures. Four sound velocity mixing rules were tested and the best result was obtained

from the Berryman mixing rule. The excess molar volumes are positive and excess isentropic compressibility, deviation in refractive index and deviation in molar refraction are negative.

References

1. King, C.J.: Amine-based systems for carboxylic acid recovery: tertiary amines and the proper choice of diluent allow extraction and recovery from water. ChemTech **5**, 285–291 (1992)
2. Clifford, S.L., Ramjugernath, D., Raal, J.D.: 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**, 1189–1192 (2004)
3. Hong, Y.K., Hong, W.H., Han, D.H.: Application of reactive extraction to recovery of carboxylic acids. Biotechnol. Bioprocess Eng. **6**, 386–394 (2001)
4. Lotero, E., Liu, Y., Lopez, D.E., Suwannakarn, K., Bruce, D.A., Goodwin Jr., J.G.: Synthesis of biodiesel via acid catalysis. Ind. Eng. Chem. Res. **44**, 5353–5363 (2005)
5. Letcher, T.M., Redhi, G.G.: Thermodynamic excess properties for binary mixtures of (benzonitrile + a carboxylic acid) at $T = 298.15$ K. Fluid Phase Equilib. **198**, 257–266 (1999)
6. Zhou, Z., Shi, Y., Zhou, X.: Theoretical studies on the hydrogen bonding interaction of complexes of formic acid with water. J. Phys. Chem. A **108**, 813–822 (2004)
7. Wei, D., Truchon, J.-F., Sirois, S., Salahub, D.: Solvation of formic acid and proton transfer in hydrated clusters. J. Chem. Phys. **116**, 6028–6038 (2002)
8. Velardez, G.F., Ferrero, J.C., Beswick, J.A., Daudey, J.P.: Ab initio study of the structures and $\pi^* \leftarrow n$ electronic transition in formic acid—(water) n ($n = 3, 4,$ and 5) hydrogen bonded complexes. J. Phys. Chem. A **105**, 8769–8774 (2001)
9. Fredlake, C.P., Crosthwaite, J.M., Hert, D.G., Akai, S.N.V.K., Brennecke, J.F.: Thermophysical properties of imidazolium-based ionic liquids. J. Chem. Eng. Data **49**, 954–964 (2004)
10. Abrman, P., Malijevská, I.: Solid–liquid equilibria in the acetic acid–propanoic acid and propanoic acid–trifluoroacetic acid systems. Fluid Phase Equilib. **166**, 47–52 (1999)
11. Tadie, M., Bahadur, I., Reddy, P., Naidoo, P., Deenadayalu, N., Ramjugernath, D., Ngema, P.: 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**, 485–492 (2013)
12. Clifford, S.L., Ramjugernath, D., Raal, J.D.: Vapour–liquid equilibrium of carboxylic acid systems: propionic acid + valeric acid and isobutyric acid + valeric acid. Fluid Phase Equilib. **237**, 89–99 (2005)
13. Narasigadu, C., Raal, J.D., Naidoo, P., Ramjugernath, D.: 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**, 735–738 (2009)
14. Arabi, A., Mahmoudi, J., Saradar, H., Jafarzade, A., Ghasemi, M.: Liquid + liquid equilibria of ternary water + carboxylic acid + solvent systems at 288.15 K. Korean J. Chem. Eng. Data **28**, 917–922 (2011)
15. Çehreli, S.: Liquid–liquid equilibria of ternary systems (water + carboxylic acid + cumene) at 298.15 K. Fluid Phase Equilib. **248**, 24–28 (2006)
16. Korpela, J.: The densities and compression isotherms of formic acid–, acetic acid–, propionic acid–, and isobutyric acid–water mixtures. Acta Chem. Scand. **25**, 2852–2864 (1971)
17. Majer, V., Sedlbauer, J., Hnedkovsky, L., Wood, R.H.: Thermodynamics of aqueous acetic and propionic acids and their anions over a wide range of temperatures and pressures. Phys. Chem. Chem. Phys. **2**, 2907–2917 (2000)
18. Criss, C.M., Wood, R.H.: Apparent molar volumes of aqueous solutions of some organic solutes at the pressure 28 MPa and temperatures to 598 K. J. Chem. Thermodyn. **28**, 723–741 (1996)

19. Baltazar, A.E., Rodríguez, A.D.L., Hall, K.R., Estrada, M.R., Silva, G.A.I.: Experimental densities and excess volumes for binary mixtures containing propionic acid, acetone, and water from 283.15 K to 323.15 K at atmospheric pressure. J. Chem. Eng. Data **48**, 1425–1431 (2003)

20. Amigo, A., Granados, K., Fadrique, J.G., Bravo, R.: Refractive index, surface tension, and density of aqueous mixtures of carboxylic acids at 298.15 K. J. Chem. Eng. Data **51**, 1356–1360 (2006)

21. Sakurai, M.: Apparent molal volumes of some organic electrolytes in a dilute aqueous solution at 5, 25, and 45 °C. Bull. Chem. Soc. Jpn. **46**, 1596–1602 (1973)

22. Hoiland, H.: Additivity relations of partial molal volumes in carboxylic acid series. Acta Chem. Scand. **28**, 699–700 (1974)

23. Drabek, O., Cibulka, I.: Excess molar volumes of binary mixtures of acetic acid and propionic acid with some members of homologous series of alkanes. Collect. Czech. Chem. Commun. **56**, 736–744 (1991)

24. Hales, J.L., Gundry, H.A., Ellender, J.H.: Liquid densities from 288 to 490 K of four organic oxygen compounds. J. Chem. Thermodyn. **15**, 211–215 (1983)

25. Romero, C.M., Suarez, F.: Effect of temperature on the solubility of short-chain carboxylic acids in water. J. Solution Chem. **38**, 315–320 (2009)

26. Thermodynamic Research Center: TRC Thermodynamic Tables: Hydrocarbons. Thermodynamics Research Center, College Station (1994)

27. Vong, W.-T., Tsai, F.-N.: 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**, 1116–1120 (1997)

28. Sewnarain, R., Raal, J.D., Ramjugernath, D.: 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**, 603–607 (2002)

29. Clifford, S.C., Bolton, K., Ramjugernath, D.: Monte Carlo simulation of carboxylic acid phase equilibria. J. Phys. Chem. B **110**, 21938–21943 (2006)

30. Bahadur, I., Deenadayalu, N., Naidoo, P., Ramjugernath, D.: 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 to 313.15) K. J. Chem. Thermodyn. **57**, 203–211 (2013)

31. Riddick, J.A., Bunger, W.B., Sakano, T.K.: Organic Solvents: Physical Properties and Methods of Purification. Wiley-Interscience, New York (1986)

32. Suarez, F., Romero, C.M.: Apparent molar volume and surface tension of dilute aqueous solutions of carboxylic acids. J. Chem. Eng. Data **56**, 1778–1786 (2011)

33. Lieben, A., Rossi, A.J.L.: Normal amyl alcohol and hexanoic acid. Ann. Chem. **159**, 70 (1871)

34. Gabrijela, B.-G., Mercedes, E., Albertina, R.: Densities and refractive indices of pure organic acids as a function of temperature. J. Chem. Eng. Data **35**, 202–204 (1990)

35. Rubio, J.E.F., Arsuaga, J.M., Taravillo, M., Cáceres, M.: Refractive index temperature and wavelength dependencies of normal saturated fatty acids in liquid state. Exp. Thermal Fluid Sci. **29**, 681–684 (2005)

36. Rodríguez, A., Canosa, J., Tojo, J.: Density, refractive index, and speed of sound of binary mixtures (diethyl carbonate + alcohols) at several temperatures. J. Chem. Eng. Data **46**, 1506–1515 (2001)

37. Douhéret, G., Davis, M.I., Reis, J.C.R.: Excess isentropic compressibilities and excess ultrasound speeds in binary and ternary liquid mixtures. Fluid Phase Equilib. **231**, 246–249 (2005)

38. Von Reis, M.A.K.E.: The specific heat of liquid organic compounds and their relationship with their molecular weight. Annia. Phys. **13**, 447–464 (1881)

39. Konicek, J., Wadso, I.: Thermochemical properties of some carboxylic acids, amines and N-substituted amides in aqueous solution. Acta Chem. Scand. **25**, 1541–1551 (1971)

40. Roy, M.N., Ekka, D.T., Dewan, R.R.: Physico-chemical studies of some bioactive solutes in pure ethanoic acid. Acta Chim. Slov. **58**, 792–796 (2011)

41. Zafarani-Moattar, M.T., Shekaari, H.: Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at T = (298.15 to 318.15) K. J. Chem. Thermodyn. **37**, 1029–1035 (2005)

42. Brocos, P., Piñeiro, Á., Bravo, R., Amigo, A.: Refractive indices, molar volumes and molar refractions of binary liquid mixtures: concepts and correlations. Phys. Chem. Chem. Phys. **5**, 550–557 (2003)

43. Tasic, A.Z., Djordjevic, B.D., Grozdanic, D.K., Radojkovic, N.: Use of mixing rules in predicting refractive indexes and specific refractivities for some binary liquid mixtures. J. Chem. Eng. Data **37**, 310–313 (1992)

44. Toumi, A., Bouanz, M.: Volumetric and refractive index properties of isobutyric acid–water binary mixtures at temperatures ranging from 300.15 to 313.15 K. J. Mol. Liq. **139**, 55–60 (2008)

45. Redlich, O., Kister, A.T.: Algebraic representation of thermodynamic properties and the classification of solutions. Ind. Eng. Chem. **40**, 345–348 (1948)

46. Iglesias-Otero, M.A., Troncoso, J., Carballo, E., Romani, L.: Density and refractive index in mixtures of ionic liquids and organic solvents: correlations and predictions. J. Chem. Thermodyn. **40**, 949–956 (2008)
47. Rao, M.R.: Velocity of sound in liquids and chemical constitution. J. Chem. Phys. **9**, 682–686 (1941)
48. Wada, Y.: On the relation between compressibility and molal volume of organic liquids. J. Phys. Soc. Jpn. **4**, 280–283 (1949)
49. Nomoto, O.: Empirical formula for sound velocity in liquid mixtures. J. Phys. Soc. Jpn. **13**, 1528–1532 (1958)
50. Berryman, J.G.: Analysis of ultrasonic velocities in hydrocarbon mixtures. J. Acoust. Soc. Am. **93**, 2666–2668 (1993)