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Densities and Viscosities of Binary Mixtures of *n*-Butanol with 2-Butanol, Isobutanol, and *tert*-Butanol from (303.15 to 343.15) K

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This paper presents densities and viscosities for *n*-butanol, 2-butanol, isobutanol, *tert*-butanol, and for binary mixtures with *n*-butanol as a common component at temperatures between (303.15 and 343.15) K over the entire composition range. The experimental apparatuses are a vibrating-tube densimeter for the density measurements and two Cannon−Fenske viscosimeters for the viscosity measurements. We have calculated excess molar volumes, dynamic viscosities, and excess Gibbs energy of activation from the experimental measurements. A temperature-dependent Redlich−Kister equation represents the calculated excess molar volumes, viscosity deviations, and excess Gibbs energy of activation. The Grunberg−Nissan equation has been used to correlate the experimental kinematic viscosities of the binary liquid mixtures.

Introduction

The thermodynamic properties of alcohols and their mixtures are of great importance for food processing, pharmaceutical, and chemical industries. Density and viscosity are thermodynamic properties from which we can deduce the molecular interactions of these compounds as well as use them to optimize the processes of mass and energy exchange. Density data are available for butanol isomers in the literature in different temperature ranges: *n*-butanol,[1–9] 2-butanol,[5,8–15] isobutanol,[4,5,9,11,13,16] and *tert*-butanol.[4,5,13,14,17,18] The temperature ranges are (278.15 to 333.15) K, (283.15 to 343.15) K, (278.15 to 343.15) K, and (298.15 to 341.15) K for *n*-butanol, 2-butanol, isobutanol, and *tert*-butanol, respectively. Viscosity data are available for butanol isomers in the literature but again only at a few temperatures: *n*-butanol,[1–5,19,20] 2-butanol,[5,13–15,20–22] isobutanol,[4,5,13,16,23] and *tert*-butanol.[4,5,13,14,16] The temperature ranges are (278.15 to 333.15) K, (288.15 to 333.15) K, (288.15 to 323.15) K, and (298.15 to 323.15) K for *n*-butanol, 2-butanol, isobutanol, and *tert*-butanol, respectively. Surprisingly, density and viscosity data of binary mixtures of butanol isomers are not available in the literature.

This paper presents experimental density and viscosity data for *n*-butanol, 2-butanol, isobutanol, *tert*-butanol, and their binary mixtures, with *n*-butanol as a common component, at several temperatures between (303.15 and 343.15) K over the entire composition range. Redlich−Kister type equations provide excess molar volumes, viscosity deviations, and excess Gibbs activation energy of viscous flow. The Grunberg−Nissan equation has been used to correlate the kinematic viscosities of the binary mixtures.

Experimental Section

Apparatus and Procedures. A description of the vibrating-tube densimeter (Anton Paar DMA 5000) has appeared in the literature.[24] The standard deviations of the repeatability of density and temperature measurements provided by the manufacturer are ± $1.3 \cdot 10^{-6}$ $g \cdot cm^{-3}$ and ± 0.002 K, respectively. The uncertainties of the density measurements and thermometer are better than ± $3 \cdot 10^{-5}$ $g \cdot cm^{-3}$ and ± 0.01 K on ITS-90, respectively. The calibration of this equipment is performed using dry air and ultrapure degassed water at a given temperature to calculate two periodic constants. Then, the calibration is repeated at (313.15 and 333.15) K to obtain a temperature adjustment of the two characteristic parameters. The calibration is considered satisfactory if the density of water is less than ± $3 \cdot 10^{-5}$ $g \cdot cm^{-3}$ over a temperature range of (293.15 to 363.15) K. We have found a temporal stability of ± $6 \cdot 10^{-6}$ $g \cdot cm^{-3}$ over a month period. Two Cannon−Fenske viscosimeters provide the kinematic viscosities using sizes 25 and 50 with flow ranges of $(0.5 \text{ to } 2) \cdot 10^{-6}$ $m^2 \cdot s^{-1}$ and $(0.8 \text{ to } 4) \cdot 10^{-6}$ $m^2 \cdot s^{-1}$, respectively. Measurements follow ASTM Standard 445. The viscosimeters reside in a Polyscience constant-temperature water bath controlled within ± 0.01 K. A digital thermometer F250 (automatic system) measures the temperature with an uncertainty of 0.01 K. The efflux time has an uncertainty of ± 0.01 s. Each datum is an average of at least five measurements with a maximum deviation in the kinematic viscosity of $6 \cdot 10^{-10}$ $m^2 \cdot s^{-1}$, making the estimated uncertainty in the dynamic viscosity better than ± 0.004 mPa·s.

Samples

Fischer supplied high performance liquid chromatography (HPLC) grade water with a mole fraction purity greater than 0.9995. Sigma-Aldrich provided the *n*-butanol and 2-butanol with a mole fraction purity greater than 0.999 and 0.995, respectively. Fermont supplied the isobutanol with a mole

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Table 1. Experimental Densities and Viscosities of Butanol Isomers

	$\rho/(\mathrm{g\cdot cm^{-3}})$			$\eta/(\mathrm{mPa\cdot s})$		
component	T/K	this work	literature	T/K	this work	literature
n-butanol	303.15	0.80221	0.80210[2]	303.15	2.296	2.226[1]
	308.15	0.79834	0.79830[2]	308.15	2.025	2.029[3]
	313.15	0.79442	0.79430[2]	313.15	1.795	1.720[1]
	318.15	0.79046		318.15	1.595	1.589[19]
	323.15	0.78645	0.78620[1]	323.15	1.417	1.343[1]
	328.15	0.78239		328.15	1.271	1.269[19]
	333.15	0.77828	0.77820[1]	333.15	1.138	1.064[1]
	338.15	0.77409		338.15	1.027	
	343.15	0.76984		343.15	0.930	
2-butanol	303.15	0.79835	0.79840[8]	303.15	2.606	2.567[14]
	308.15	0.79405	0.79398[5]	308.15	2.162	2.128[5]
	313.15	0.78965	0.78950[8]	313.15	1.840	1.785[13]
	318.15	0.78515	0.78500[5]	318.15	1.557	1.533[5]
	323.15	0.78055	0.78050[11]	323.15	1.332	1.315[13]
	328.15	0.77583		328.15	1.150	
	333.15	0.77099		333.15	1.001	1.025[15]
	338.15	0.76603		338.15	0.877	
	343.15	0.76096		343.15	0.776	
isobutanol	303.15	0.79406	0.79431[4]	303.15	2.648	2.842[4]
	308.15	0.79012	0.79026[4]	308.15	2.279	2.246[4]
	313.15	0.78612	0.78613[4]	313.15	1.965	2.080[4]
	318.15	0.78206	0.78220[5]	318.15	1.692	1.861[5]
	323.15	0.77793	0.77780[11]	323.15	1.482	1.602[13]
	328.15	0.77373		328.15	1.267	
	333.15	0.76944	0.76930[11]	333.15	1.116	
	338.15	0.76507		338.15	0.985	
	343.15	0.76061	0.76030[11]	343.15	0.876	
tert-butanol	308.15	0.77036	0.76975[4]	308.15	2.690	2.589[4]
	313.15	0.76507	0.76448[4]	313.15	2.142	2.047[4]
	318.15	0.75967	0.75941[5]	318.15	1.736	1.690[5]
	323.15	0.75419	0.75380[13]	323.15	1.428	1.409[13]
	328.15	0.74862	0.74861[18]	328.15	1.196	
	333.15	0.74295		333.15	1.015	
	338.15	0.73719		338.15	0.873	
	343.15	0.73131		343.15	0.760	

fraction purity greater than 0.998, and the *tert*-butanol came from J. T. Baker with a mole fraction purity greater than 0.997. We used the pure components as received. The mixtures were prepared gravimetrically using an analytical balance (Ohaus model AS120S) with a precision of ± 0.1 mg. The overall uncertainty in the mole fraction was better than ± 0.002. Binary mixtures were kept in airtight containers.

Results and Discussion

This paper reports densities of pure butanol isomers and some of their binary mixtures from (303.15 to 343.15) K at atmospheric pressure using a vibrating-tube densimeter. We check the temporal stability of the calibration of the densimeter measuring after each mixture composition and consider it satisfactory if a measured water density is within $\pm\ 3\cdot 10^{-5}$ $\mathrm{g\cdot cm^{-3}}$ of the value given by Wagner and Pruss.[25]

Densities of the pure liquids of this work and literature appear in Table 1. A comparison of the current results to literature values[1,2,4,5,8,11,13,18] indicates relative agreements of 0.02 % for *n*-butanol, 0.01 % for 2-butanol, 0.02 % for isobutanol, and 0.04 % for *tert*-butanol. These results give a verification of the results obtained by the densimeter.

Viscosities of the pure liquids and literature values are also in Table 1. A comparison of current results to literature values[1,3–5,13–15,19] indicates average percentage deviations of 2.8 % for *n*-butanol, 1.8 % for 2-butanol, 6.5 % for isobutanol, and 3.0 % for *tert*-butanol. Even though the highest average deviation is for isobutanol, our viscosity values are randomly distributed with positive and negative deviations from the literature values. We believe the discrepancy is due to the accuracy of the different experimental methods.

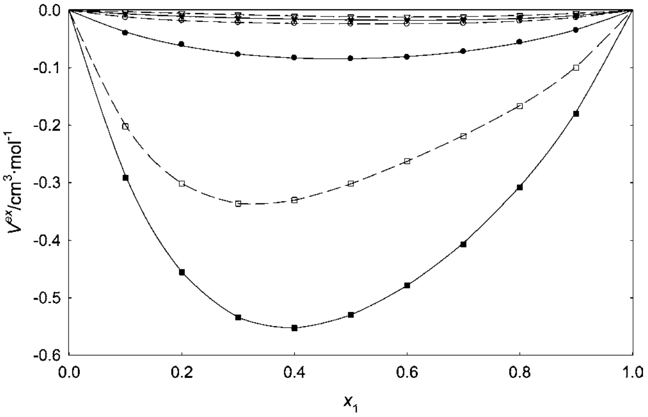

Figure 1. Comparison of excess molar volumes of butanol isomer mixtures. *n*-butanol + 2-butanol: ○, 308.15 K; ●, 343.15 K. *n*-butanol + isobutanol: ▽, 308.15 K; ▼, 343.15 K. *n*-butanol + *tert*-butanol: □, 308.15 K; ■, 343.15 K. Solid and dashed lines represent the Redlich−Kister equation.

The densities of the binary mixtures of *n*-butanol with 2-butanol, isobutanol, and *tert*-butanol measured here in the range (303.15 to 343.15) K cannot be compared to data in the literature because these systems apparently are unmeasured previously. Table 2 presents the experimental densities of these systems. Excess molar volumes have been calculated from these data, and all of the mixtures present negative deviations from ideality; the uncertainties of molar excess volumes are $\pm\ 0.003\ \mathrm{cm^3\cdot mol^{-1}}$. Mixtures of *n*-butanol + isobutanol and *n*-butanol + 2-butanol form ideal solutions at the conditions considered in this work as shown in Figure 1. Mixtures of *n*-butanol + *tert*-butanol do not present ideal solution behavior in the molar volume probably caused by the isomeric form of *tert*-butanol. Redlich−Kister type equations represent the excess volumes, viscosity deviations, and excess Gibbs energy of viscous flow:

$$J = x_1 x_2 \sum_{i=0}^{2} a_i (x_1 - x_2)^i \qquad (1)$$

with

$$a_0 = \sum_{j=1}^{13} a_{0,j} (T - 273.15)^{(j-1)/2} \qquad (2)$$

$$a_1 = \sum_{j=1}^{13} a_{1,j} (T - 273.15)^{(j-1)/2} \qquad (3)$$

$$a_2 = \sum_{j=1}^{13} a_{2,j} (T - 273.15)^{(j-1)/2} \qquad (4)$$

where J is the excess molar volume, the viscosity deviation, or the excess Gibbs energy of activation of viscous flow,[26] a_i are the adjusted coefficients for the calculated property, and x_i are the mole fractions. We have used a stepwise procedure to select the terms that contribute most to the curve-fitting. Table 4 contains the parameters a_{ij} of eq 1 for the calculated excess molar volumes. All digits of the parameters should be included to have a calculated value within the given standard deviation. The correlations are only valid in the temperature range.

Viscosity measurements of the binary mixtures of *n*-butanol + 2-butanol, + isobutanol, and + *tert*-butanol appear in this work. These measurements appear to be the only ones existing

Table 2. Experimental Densities for Binary Mixtures of *n*-Butanol + 2-Butanol, + Isobutanol, and + *tert*-Butanol

	$\rho/(g\cdot cm^{-3})$								
x_1	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$	$T/K = 328.15$	$T/K = 333.15$	$T/K = 338.15$	$T/K = 343.15$
	n-Butanol (1) + 2-Butanol (2)								
0.1008	0.79881	0.79458	0.79026	0.78585	0.78132	0.77670	0.77196	0.76711	0.76216
0.2005	0.79924	0.79505	0.79080	0.78645	0.78201	0.77746	0.77282	0.76805	0.76319
0.3002	0.79964	0.79551	0.79131	0.78703	0.78266	0.77820	0.77364	0.76898	0.76421
0.4006	0.80004	0.79595	0.79179	0.78757	0.78327	0.77888	0.77440	0.76983	0.76515
0.5004	0.80043	0.79639	0.79227	0.78811	0.78387	0.77955	0.77514	0.77064	0.76604
0.6005	0.80082	0.79682	0.79276	0.78864	0.78445	0.78019	0.77586	0.77143	0.76691
0.6999	0.80120	0.79724	0.79322	0.78915	0.78502	0.78081	0.77653	0.77217	0.76772
0.7989	0.80156	0.79763	0.79365	0.78962	0.78553	0.78138	0.77716	0.77285	0.76848
0.8988	0.80190	0.79801	0.79406	0.79008	0.78604	0.78193	0.77776	0.77353	0.76921
	n-Butanol (1) + Isobutanol (2)								
0.1010	0.79489	0.79096	0.78697	0.78293	0.77881	0.77463	0.77036	0.76602	0.76157
0.2029	0.79574	0.79181	0.78784	0.78380	0.77970	0.77553	0.77129	0.76696	0.76254
0.3008	0.79655	0.79264	0.78867	0.78464	0.78055	0.77640	0.77217	0.76787	0.76347
0.4000	0.79738	0.79347	0.78951	0.78549	0.78141	0.77728	0.77306	0.76877	0.76440
0.5000	0.79820	0.79430	0.79034	0.78634	0.78227	0.77815	0.77396	0.76968	0.76533
0.5999	0.79902	0.79513	0.79118	0.78718	0.78313	0.77902	0.77484	0.77059	0.76626
0.6999	0.79983	0.79595	0.79201	0.78802	0.78398	0.77989	0.77573	0.77149	0.76718
0.7993	0.80063	0.79675	0.79282	0.78885	0.78482	0.78074	0.77659	0.77237	0.76808
0.8995	0.80142	0.79755	0.79363	0.78967	0.78565	0.78158	0.77745	0.77325	0.76898
	n-Butanol (1) + *tert*-Butanol (2)								
0.1017		0.77475	0.76969	0.76454	0.75928	0.75392	0.74845	0.74288	0.73720
0.2006		0.77829	0.77343	0.76848	0.76342	0.75825	0.75297	0.74758	0.74208
0.3008		0.78131	0.77666	0.77190	0.76703	0.76206	0.75698	0.75179	0.74649
0.4005		0.78406	0.77956	0.77497	0.77027	0.76548	0.76057	0.75556	0.75044
0.5011		0.78665	0.78228	0.77784	0.77330	0.76867	0.76394	0.75911	0.75416
0.6002		0.78911	0.78488	0.78056	0.77616	0.77169	0.76711	0.76243	0.75765
0.6975		0.79152	0.78738	0.78318	0.77890	0.77454	0.77010	0.76556	0.76094
0.7987		0.79395	0.78989	0.78579	0.78161	0.77737	0.77305	0.76865	0.76416
0.8978		0.79624	0.79226	0.78824	0.78415	0.78000	0.77579	0.77152	0.76715

for these systems. Table 3 contains the dynamic viscosities of the systems. Also, viscosity deviations calculated from the experimental measurements are represented with eq 1. Table 4 contains the parameters a_{ij} of eq 1. Viscosity deviations can be

Table 3. Dynamic Viscosities for Binary Mixtures of *n*-Butanol + 2-Butanol, + Isobutanol, and + *tert*-Butanol

	$\eta/(mPa\cdot s)$								
x_1	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$	$T/K = 328.15$	$T/K = 333.15$	$T/K = 338.15$	$T/K = 343.15$
	n-Butanol (1) + 2-Butanol (2)								
0.1008	3.156	2.679	2.311	1.982	1.723	1.506	1.327	1.177	1.054
0.2005	3.080	2.650	2.298	1.981	1.736	1.525	1.349	1.201	1.079
0.3002	3.027	2.625	2.287	1.980	1.750	1.543	1.368	1.223	1.102
0.4006	2.987	2.609	2.283	1.981	1.762	1.560	1.387	1.241	1.121
0.5004	2.955	2.595	2.278	1.985	1.772	1.575	1.404	1.258	1.138
0.6005	2.932	2.583	2.274	1.992	1.782	1.590	1.421	1.274	1.155
0.6999	2.911	2.570	2.271	1.999	1.789	1.602	1.434	1.289	1.170
0.7989	2.894	2.557	2.268	2.006	1.794	1.612	1.446	1.302	1.183
0.8988	2.875	2.544	2.264	2.012	1.797	1.620	1.456	1.315	1.197
	n-Butanol (1) + Isobutanol (2)								
0.1010	3.446	2.987	2.590	2.236	1.963	1.680	1.506	1.342	1.203
0.2029	3.442	2.982	2.587	2.233	1.957	1.691	1.523	1.362	1.226
0.3008	3.389	2.938	2.561	2.219	1.951	1.689	1.520	1.360	1.229
0.4000	3.313	2.871	2.511	2.190	1.930	1.684	1.510	1.356	1.227
0.5000	3.236	2.803	2.462	2.157	1.910	1.673	1.499	1.351	1.224
0.5999	3.166	2.751	2.424	2.129	1.889	1.668	1.489	1.343	1.218
0.6999	3.101	2.707	2.390	2.111	1.877	1.661	1.487	1.341	1.215
0.7993	3.040	2.669	2.363	2.093	1.863	1.657	1.483	1.338	1.213
0.8995	2.970	2.620	2.326	2.068	1.842	1.650	1.479	1.334	1.210
	n-Butanol (1) + *tert*-Butanol (2)								
0.1017		3.438	2.786	2.299	1.921	1.635	1.405	1.221	1.069
0.2006		3.373	2.763	2.301	1.941	1.666	1.439	1.253	1.102
0.3008		3.302	2.732	2.298	1.955	1.690	1.465	1.282	1.130
0.4005		3.220	2.692	2.284	1.956	1.704	1.486	1.306	1.155
0.5011		3.125	2.640	2.257	1.950	1.709	1.499	1.323	1.176
0.6002		3.021	2.577	2.223	1.933	1.703	1.504	1.334	1.190
0.6975		2.912	2.507	2.181	1.909	1.692	1.501	1.339	1.200
0.7987		2.790	2.429	2.130	1.876	1.672	1.492	1.340	1.206
0.8978		2.666	2.347	2.076	1.840	1.650	1.477	1.334	1.208

Table 4. Redlich−Kister Temperature Dependent Parameters for Excess Molar Volume, Viscosity Deviations, and Excess Gibbs Energy of Activation

a_{ij}	*n*-butanol (1) + 2-butanol (2)	a_{ij}	*n*-butanol (1) + isobutanol (2)	a_{ij}	*n*-butanol (1) + *tert*-butanol (2)
			$V^{ex}/(cm^3 \cdot mol^{-1})$		
a_{05}	$-1.0240 \cdot 10^{-5}$	a_{01}	$-8.7900 \cdot 10^{-3}$	a_{02}	$-3.8885 \cdot 10^{-2}$
a_{10}	$6.1220 \cdot 10^{-11}$	a_{02}	$1.7917 \cdot 10^{-4}$	a_{04}	$1.2186 \cdot 10^{-4}$
a_{13}	$-2.7590 \cdot 10^{-2}$	a_{10}	$-5.0152 \cdot 10^{-12}$	a_{14}	$1.3005 \cdot 10^{-1}$
a_{16}	$6.6340 \cdot 10^{-5}$	a_{14}	$-3.4500 \cdot 10^{-3}$	a_{18}	$-7.5059 \cdot 10^{-6}$
a_{27}	$-1.5210 \cdot 10^{-2}$	a_{22}	$3.8182 \cdot 10^{-11}$	a_{27}	$-2.0060 \cdot 10^{-1}$
a_{39}	$-2.1670 \cdot 10^{-2}$	a_{35}	$-1.0225 \cdot 10^{-9}$	a_{28}	$1.3072 \cdot 10^{-2}$
		a_{37}	$1.2338 \cdot 10^{-11}$		
$\sigma/(cm^3 \cdot mol^{-1})$	$1.2156 \cdot 10^{-5}$		$1.6635 \cdot 10^{-6}$		$1.2059 \cdot 10^{-5}$
			$\Delta\eta/(mPa \cdot s)$		
a_{00}	$-1.0397 \cdot 10^{+3}$	a_{00}	$3.2720 \cdot 10^{+2}$	a_{00}	$-4.6604 \cdot 10^{+1}$
a_{01}	$7.0259 \cdot 10^{+2}$	a_{01}	$-2.2712 \cdot 10^{+2}$	a_{01}	$2.2003 \cdot 10^{+1}$
a_{02}	$-1.8056 \cdot 10^{+2}$	a_{02}	$6.1457 \cdot 10^{+1}$	a_{02}	$-2.8322 \cdot 10^{+0}$
a_{03}	$2.0996 \cdot 10^{+1}$	a_{03}	$-7.8542 \cdot 10^{+0}$	a_{05}	$2.9200 \cdot 10^{-3}$
a_{04}	$-9.3713 \cdot 10^{-1}$	a_{04}	$4.2150 \cdot 10^{-1}$	a_{08}	$-5.9080 \cdot 10^{-6}$
a_{11}	$1.9758 \cdot 10^{-8}$	a_{06}	$-5.6666 \cdot 10^{-4}$	a_{09}	$4.1355 \cdot 10^{-7}$
a_{12}	$-1.5416 \cdot 10^{-9}$	a_{17}	$-1.8500 \cdot 10^{-3}$	a_{15}	$-8.7649 \cdot 10^{-3}$
a_{13}	$1.3028 \cdot 10^{+1}$	a_{20}	$1.0790 \cdot 10^{-5}$	a_{21}	$3.9002 \cdot 10^{-6}$
a_{14}	$-5.3391 \cdot 10^{+0}$	a_{24}	$-6.2507 \cdot 10^{-9}$	a_{22}	$-1.3701 \cdot 10^{-6}$
a_{15}	$7.3046 \cdot 10^{-1}$	a_{25}	$5.5942 \cdot 10^{-10}$	a_{23}	$1.6396 \cdot 10^{-7}$
a_{16}	$-3.3350 \cdot 10^{-2}$	a_{30}	$2.8700 \cdot 10^{-3}$	a_{24}	$-6.6400 \cdot 10^{-9}$
a_{26}	$-1.5968 \cdot 10^{+0}$	a_{34}	$-8.2500 \cdot 10^{-6}$	a_{27}	$-6.9600 \cdot 10^{-3}$
a_{27}	$4.1960 \cdot 10^{-1}$	a_{35}	$1.2500 \cdot 10^{-6}$	a_{34}	$1.4000 \cdot 10^{-9}$
a_{28}	$-2.7050 \cdot 10^{-2}$	a_{37}	$-4.7729 \cdot 10^{-9}$		
$\sigma/(mPa \cdot s)$	$4.6518 \cdot 10^{-5}$		$2.0695 \cdot 10^{-4}$		$6.1310 \cdot 10^{-4}$
			$\Delta G^{ex}/(J \cdot mol^{-1})$		
a_{00}	$-2.6798 \cdot 10^{+4}$	a_{01}	$9.8417 \cdot 10^{+1}$	a_{03}	$1.2987 \cdot 10^{+1}$
a_{01}	$-3.5799 \cdot 10^{+4}$	a_{10}	$-3.0370 \cdot 10^{-5}$	a_{06}	$-1.1009 \cdot 10^{-1}$
a_{02}	$1.7140 \cdot 10^{+4}$	a_{11}	$6.9000 \cdot 10^{-6}$	a_{10}	$2.1604 \cdot 10^{-4}$
a_{03}	$-2.3622 \cdot 10^{+3}$	a_{12}	$-3.9445 \cdot 10^{-7}$	a_{11}	$-3.9790 \cdot 10^{-5}$
a_{05}	$1.4682 \cdot 10^{+1}$	a_{20}	$-4.5710 \cdot 10^{-2}$	a_{12}	$1.9300 \cdot 10^{-6}$
a_{10}	$-1.3904 \cdot 10^{-4}$	a_{21}	$9.7100 \cdot 10^{-3}$	a_{13}	$-6.6125 \cdot 10^{+3}$
a_{12}	$9.7986 \cdot 10^{-7}$	a_{24}	$-2.0260 \cdot 10^{-5}$	a_{14}	$3.2269 \cdot 10^{+3}$
a_{14}	$1.2482 \cdot 10^{+2}$	a_{25}	$1.5500 \cdot 10^{-6}$	a_{15}	$-5.1394 \cdot 10^{+2}$
a_{22}	$-2.3700 \cdot 10^{-3}$	a_{26}	$1.0319 \cdot 10^{+3}$	a_{16}	$2.6646 \cdot 10^{+1}$
a_{23}	$8.5284 \cdot 10^{-4}$	a_{29}	$-1.0606 \cdot 10^{+0}$	a_{29}	$-2.4240 \cdot 10^{-1}$
a_{24}	$-1.0333 \cdot 10^{-4}$				
a_{25}	$4.2000 \cdot 10^{-6}$				
a_{26}	$-4.8216 \cdot 10^{+2}$				
a_{27}	$7.0830 \cdot 10^{+1}$				
$\sigma/(J \cdot mol^{-1})$	$2.3912 \cdot 10^{+8}$		$3.3891 \cdot 10^{+2}$		$1.9970 \cdot 10^{+2}$

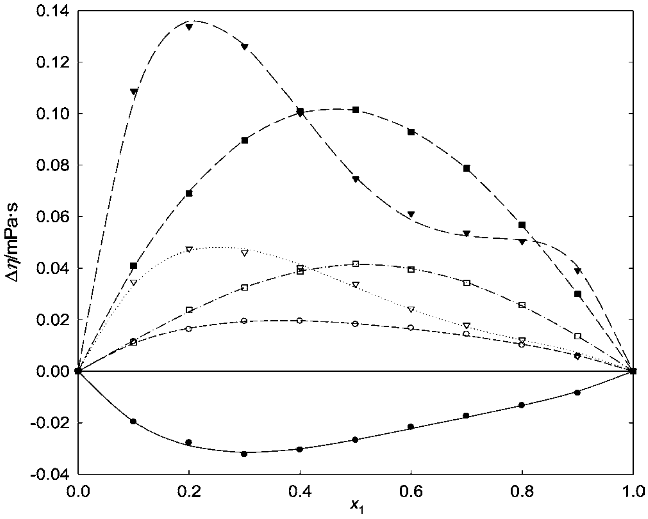

Figure 2. Comparison of viscosity deviations of butanol isomer mixtures. ●, 308.15 K; ○, 343.15 K for *n*-butanol + 2-butanol. ▼, 308.15 K; ▽, 343.15 K for *n*-butanol + isobutanol. ■, 308.15 K; □, 343.15 K for *n*-butanol + *tert*-butanol. Solid and dashed lines represent the Redlich−Kister equation.

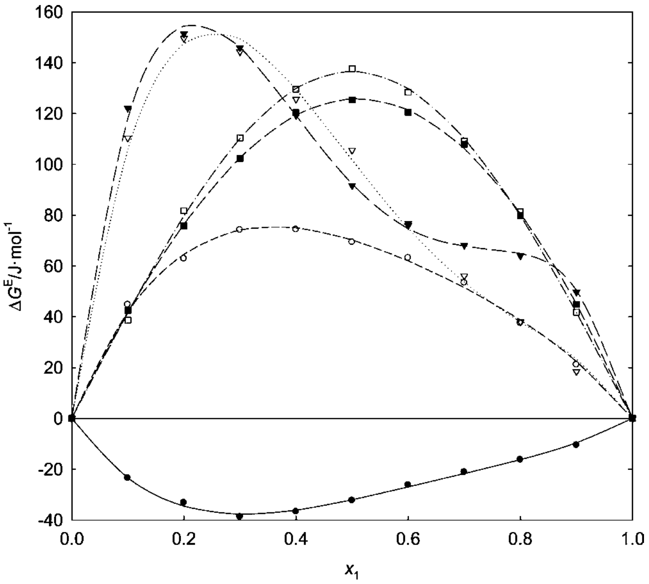

Figure 3. Comparison of excess Gibbs energy of activation of butanol isomer mixtures. ●, 308.15 K; ○, 343.15 K for *n*-butanol + 2-butanol. ▼, 308.15 K; ▽, 343.15 K for *n*-butanol + isobutanol. ■, 308.15 K; □, 343.15 K for *n*-butanol + *tert*-butanol. Solid and dashed lines represent the Redlich−Kister equation.

Table 5. Adjustable Parameters of the Grunberg−Nissan Equation

	G_{12}								
	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15	T/K = 323.15	T/K = 328.15	T/K = 333.15	T/K = 338.15	T/K = 343.15
				n-Butanol (1) + 2-Butanol (2)					
G_{12}	−0.139	−0.054	−0.029	−0.024	0.045	0.063	0.082	0.089	0.108
σ	$1.11 \cdot 10^{-4}$	$2.44 \cdot 10^{-5}$	$1.21 \cdot 10^{-5}$	$3.67 \cdot 10^{-6}$	$3.70 \cdot 10^{-7}$	$1.04 \cdot 10^{-6}$	$3.00 \cdot 10^{-6}$	$2.65 \cdot 10^{-5}$	$4.03 \cdot 10^{-5}$
				n-Butanol (1) + Isobutanol (2)					
G_{12}	0.225	0.191	0.185	0.164	0.150	0.127	0.147	0.155	0.166
σ	$6.80 \cdot 10^{-4}$	$8.20 \cdot 10^{-4}$	$7.04 \cdot 10^{-4}$	$4.84 \cdot 10^{-4}$	$3.09 \cdot 10^{-4}$	$1.83 \cdot 10^{-4}$	$5.44 \cdot 10^{-4}$	$6.10 \cdot 10^{-4}$	$6.73 \cdot 10^{-4}$
				n-Butanol (1) + *tert*-Butanol (2)					
G_{12}		0.206	0.204	0.212	0.230	0.247	0.248	0.232	0.206
σ		$8.31 \cdot 10^{-7}$	$4.44 \cdot 10^{-6}$	$1.07 \cdot 10^{-5}$	$1.74 \cdot 10^{-5}$	$3.01 \cdot 10^{-5}$	$1.56 \cdot 10^{-5}$	$6.32 \cdot 10^{-6}$	$6.16 \cdot 10^{-6}$

positive or negative for the mixtures of *n*-butanol + 2-butanol as shown in Figure 2. For the other mixtures, the viscosity deviations are negative at all temperatures considered in this work and the uncertainty of viscosity deviation ± 0.001 mPa·s. The systems that show a small departure from ideality (viscosity of the mixture equal to the sum of the product of the pure viscosity of the constituents in the mixture times the corresponding mole fraction) are *n*-butanol with isobutanol and *tert*-butanol at low temperatures. This observation indicates that ideal solutions for equilibrium properties differ from those of transport properties. We have calculated the excess Gibbs energy of activation of viscous flow with an uncertainty of ± 2 J·mol^{-1}, and Table 4 presents the parameters a_{ij} of eq 1. The excess Gibbs energy of activation has a similar functional behavior of the deviation of viscosity as shown in Figure 3. The only mixture that shows a change in sign is *n*-butanol + 2-butanol. This is an indication of solute−solute association as suggested by Meyer et al.[27] Table 5 contains the interaction parameter, G_{12}, which is proportional to the interchange energy. Additionally, we have correlated our viscosity values to the Grunberg−Nissan[28] equation. Following the analysis of Grunberg and Nissan,[28] the parameters indicate that the mixture *n*-butanol + 2 butanol has positive deviations from ideality at low temperatures which diminish as the temperature increases until they become negative. Also, the systems of *n*-butanol + isobutanol and + *tert*-butanol present negative deviations from ideality in the temperatures considered in this work. These observations agree with our results.

Conclusions

Liquid densities and viscosities of pure butanol isomers and binary mixtures (*n*-butanol + 2-butanol, + isobutanol, + *tert*-butanol) have been measured from (303.15 to 343.15) K over the entire range of mole fractions. The new density and viscosity measurements of the pure liquids agree within an average percentage deviation of 0.02 % and 3.5 %, respectively, with respect to the literature values. The experimental densities and viscosities for mixtures of butanol isomers presented here appear to be the only ones in existence.

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