Densities and Viscosities of Binary Mixtures of Cyclopropanecarboxylic Acid with Methanol, Ethanol, Propan-1-ol, and Butan-1-ol at Different Temperatures

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Densities and viscosities of the binary mixtures of cyclopropanecarboxylic acid with methanol, ethanol, propan-1-ol, and butan-1-ol have been measured at different temperatures (298.15, 308.15, 318.15, 328.15, and 338.15) K and atmospheric pressure over the whole range of compositions. The excess molar volumes were calculated from the experimental data and correlated by the Redlich−Kister polynomial equation. McAllister's three-body and four-body interaction models are also used to correlate the kinematic viscosities of these binary mixtures.

Introduction

Densities and viscosities are important fundamental data for the chemical design and the optimization of chemical process. They are widely studied for many industrial interesting systems such as organic synthesis mixtures, ion extraction systems, and gas adsorption solvents, etc.[1−4] Furthermore, excess thermodynamic and transport properties of binary mixtures can provide important information concerning the deeper understanding of the molecular liquid structure and intermolecular interactions. Cyclopropanecarboxylic acid is an important industrial chemical that was widely used for the preparation of medicines and crop protection agents.[5] With respect to medicine, it is an indispensable intermediate in the synthesis of quinolone antibiotics such as Ciprofloxacin that belongs to the third generation of quinolones and has ranked in the top 10 of the world's highest sales of pharmaceuticals. The main economical industrial process for producing cyclopropanecarboxylic acid is the hydrolysis of cyclopropanecarboxylate esters into cyclopropanecarboxylic acid and corresponding alcohols.[6−8] So there is practical value in determining the densities and viscosities of the binary mixture of cyclopropanecarboxylic acid with different alkanols. On the other hand, alcohols are self-associated through hydrogen bonding, and this association decreases with an increase in molar mass of alkanols. In the last decades, much work has been devoted to studying the deviations from ideality for binary liquid mixtures containing a 1-alkanol and a second component.[9−12] A survey of the literature shows that there is no report on the densities and viscosities for cyclopropanecarboxylic acid with different alkanols.

In the present study, density and viscosity were measured for the binary mixtures of cyclopropanecarboxylic acid + methanol, + ethanol, + propan-1-ol, and + butan-1-ol at atmospheric pressure and temperatures ranging from (298.15 to 338.15) K. The excess molar volume has been calculated from the experimental data and correlated by the Redlich−Kister polynomial equation.[13] The kinematic viscosity data were correlated with McAllister's three-body and four-body interaction models.[14]

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Table 1. Comparison of Experimental Density and Viscosity of Pure Liquids with Literature Values at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s	
component	this paper	lit.	this paper	lit.
methanol	0.78701	0.7870[17]	0.556	0.546[17]
		0.78683[18]		0.550[18]
		0.7868[19]		0.557[19]
ethanol	0.78544	0.7854[19]	1.097	1.079[19]
		0.7854[20]		1.099[20]
		0.78546[21]		1.082[21]
propan-1-ol	0.79960	0.7992[19]	1.955	1.934[19]
		0.7995[22]		1.953[22]
		0.8000[23]		1.954[23]
butan-1-ol	0.80580	0.8057[22]	2.587	2.593[22]
		0.8063[23]		2.534[23]
		0.8060[24]		2.570[24]
cyclopropanecarboxylic acid	1.08292	------	3.306	------

Experimental Section

Materials. All chemicals used in this study were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. The claimed mass fraction purity for the chemicals was > 0.995. The purity of these pure samples was ascertained by gas chromatography (Agilent Technologyics 6890N). These pure samples were ascertained by MS (Thermo Finnigan Trace DSQ) too. The appendices 1-a, 2-a, 3-a, 4-a, and 5-a are the GC spectra of methanol, ethanol, propan-1-ol, butan-1-ol, and cyclopropanecarboxylic acid, respectively. The appendices 1-b, 2-b, 3-b, 4-b, and 5-b are the MS spectra of methanol, ethanol, propan-1-ol, butan-1-ol, and cyclopropanecarboxylic acid, respectively. All above-mentioned spectra are available as Supporting Information. These liquids were dried over 4 Å molecular sieves and partially degassed by ultrasound prior to use. The measured viscosity and density data of methanol, ethanol, propan-1-ol, and butan-1-ol were compared with the literature data and are shown in Table 1.

Airtight stoppered bottles were used for the preparation of the mixtures. The weight of the dry bottle was first determined. The less volatile component of the binary mixtures was introduced first in the sample tube followed by second component, and the weight at each step was taken using an electronic balance (BS224S, The Sartorias Group, Germany) accurate to

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Table 2. Densities (ρ), Viscosities (η), and Excess Molar Volumes V^E for the Binary Mixtures of Cyclopropanecarboxylic Acid (1) + 1-Alknaols (2) at Different Temperatures

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}
Cyclopropanecarboxylic Acid (1) + Methanol (2)							
T = 298.15 K							
0.0000	0.78701	0.556	0.000	0.4994	0.99621	2.189	−0.8242
0.1000	0.84650	0.773	−0.3546	0.5989	1.01949	2.557	−0.7619
0.2000	0.89502	1.052	−0.5918	0.7001	1.03941	2.887	−0.6346
0.3000	0.93516	1.392	−0.7466	0.8001	1.05617	3.139	−0.4636
0.3999	0.96842	1.778	−0.8184	0.9000	1.07057	3.298	−0.2529
				1.0000	1.08292	3.306	0.0000
T = 308.15 K							
0.0000	0.77754	0.484	0.0000	0.4994	0.98656	1.765	−0.8610
0.1000	0.83702	0.651	−0.3746	0.5989	1.00979	2.029	−0.7954
0.2000	0.88553	0.886	−0.6228	0.7001	1.02965	2.227	−0.6622
0.3000	0.92562	1.151	−0.7830	0.8001	1.04635	2.449	−0.4836
0.3999	0.95883	1.451	−0.8566	0.9000	1.06068	2.553	−0.2633
				1.0000	1.07297	2.603	0.0000
T = 318.15 K							
0.0000	0.76798	0.424	0.0000	0.4994	0.97686	1.440	−0.8979
0.1000	0.82745	0.572	−0.3928	0.5989	1.00006	1.641	−0.8294
0.2000	0.87584	0.753	−0.6533	0.7001	1.01987	1.825	−0.6899
0.3000	0.91600	0.965	−0.8194	0.8001	1.03653	1.963	−0.5041
0.3999	0.94918	1.199	−0.8952	0.9000	1.05081	2.047	−0.2746
				1.0000	1.06304	2.102	0.0000
T = 328.15 K							
0.0000	0.75828	0.372	0.0000	0.4994	0.96707	1.191	−0.9343
0.1000	0.81774	0.499	−0.4121	0.5989	0.99024	1.349	−0.8617
0.2000	0.86623	0.645	−0.6845	0.7001	1.01004	1.494	−0.7172
0.3000	0.90625	0.816	−0.8551	0.8001	1.02665	1.604	−0.5222
0.3999	0.93942	1.000	−0.9333	0.9000	1.04092	1.678	−0.2850
				1.0000	1.05312	1.739	0.0000
Cyclopropanecarboxylic Acid (1) + Ethanol (2)							
T = 298.15 K							
0.0000	0.78544	1.097	0.0000	0.4341	0.94780	2.279	−0.7669
0.0787	0.82026	1.272	−0.2913	0.5350	0.97675	2.562	−0.7197
0.1610	0.85387	1.469	−0.5116	0.6415	1.00467	2.818	−0.6162
0.2475	0.88651	1.711	−0.6737	0.7542	1.03156	3.035	−0.4548
0.3384	0.91774	1.985	−0.7517	0.8734	1.05773	3.204	−0.2582
				1.0000	1.08292	3.306	0.0000
T = 308.15 K							
0.0000	0.77678	0.908	0.0000	0.4341	0.93844	1.814	−0.7893
0.0787	0.81157	1.043	−0.3093	0.5350	0.96728	2.029	−0.7418
0.1610	0.84496	1.201	−0.5304	0.6415	0.99510	2.225	−0.6368
0.2475	0.87738	1.388	−0.6912	0.7542	1.02189	2.391	−0.4721
0.3384	0.90848	1.596	−0.7717	0.8734	1.04794	2.532	−0.2693
				1.0000	1.07297	2.603	0.0000
T = 318.15 K							
0.0000	0.76794	0.756	0.0000	0.4341	0.92898	1.470	−0.8126
0.0787	0.80261	0.865	−0.3202	0.5350	0.95774	1.636	−0.7653
0.1610	0.83592	0.990	−0.5518	0.6415	0.98547	1.789	−0.6578
0.2475	0.86810	1.136	−0.7085	0.7542	1.01217	1.895	−0.4886
0.3384	0.89910	1.299	−7924	0.8734	1.03812	2.024	−0.2790
				1.0000	1.06304	2.102	0.0000
T = 328.15 K							
0.0000	0.75892	0.634	0.0000	0.4341	0.91939	1.208	−0.8349
0.0787	0.79334	0.723	−0.3206	0.5350	0.94809	1.342	−0.7878
0.1610	0.82669	0.825	−0.5715	0.6415	0.97577	1.467	−0.6791
0.2475	0.85868	0.947	−0.7265	0.7542	1.00241	1.557	−0.5057
0.3384	0.88959	1.073	−0.8135	0.8734	1.0283	1.674	−0.2902
				1.0000	1.05312	1.739	0.0000
Cyclopropanecarboxylic Acid (1) + Propan-1-ol (2)							
T = 298.15 K							
0.0000	0.7996	1.955	0.0000	0.5001	0.95213	2.988	−0.5576
0.1000	0.83212	2.118	−0.2462	0.6000	0.97977	3.140	−0.5061
0.2000	0.86375	2.330	−0.4308	0.7000	1.00634	3.235	−0.3967
0.3000	0.89425	2.568	−0.5373	0.8000	1.03224	3.299	−0.2647
0.4138	0.92762	2.820	−0.5739	0.9000	1.05782	3.316	−0.1359
				1.0000	1.08292	3.306	0.0000

Table 2. Continued

x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	η / mPa·s	V^E / cm^3·mol^{-1}
			T = 308.15 K				
0.0000	0.79149	1.538	0.0000	0.5001	0.94295	2.317	−0.5638
0.1000	0.82373	1.667	−0.2456	0.6000	0.97045	2.437	−0.5145
0.2000	0.85512	1.833	−0.4314	0.7000	0.99688	2.517	−0.4055
0.3000	0.88541	2.002	−0.5395	0.8000	1.02280	2.574	−0.2852
0.4138	0.91858	2.190	−0.5787	0.9000	1.04815	2.617	−0.1482
				1.0000	1.07297	2.603	0.0000
			T = 318.15 K				
0.0000	0.78322	1.224	0.0000	0.5001	0.93370	1.834	−0.5714
0.1000	0.81519	1.325	−0.2447	0.6000	0.96107	1.929	−0.5236
0.2000	0.84635	1.451	−0.4315	0.7000	0.98737	2.002	−0.4142
0.3000	0.87646	1.583	−0.5425	0.8000	1.0318	2.060	−0.2942
0.4138	0.90945	1.733	−0.5845	0.9000	1.03838	2.092	−0.1534
				1.0000	1.06304	2.102	0.0000
			T = 328.15 K				
0.0000	0.77473	0.986	0.0000	0.5001	0.92434	1.481	−0.5806
0.1000	0.80646	1.068	−0.2452	0.6000	0.95161	1.560	−0.5347
0.2000	0.83742	1.169	−0.4340	0.7000	0.97781	1.626	−0.4252
0.3000	0.86736	1.276	−0.5473	0.8000	1.00351	1.678	−0.3033
0.4138	0.90017	1.396	−0.5899	0.9000	1.02860	1.713	−0.1596
				1.0000	1.05312	1.739	0.0000
			T = 338.15 K				
0.0000	0.76598	0.801	0.0000	0.5001	0.91485	0.211	−0.5920
0.1000	0.79748	0.870	−0.2450	0.6000	0.94203	1.282	−0.5467
0.2000	0.82826	0.953	−0.4361	0.7000	0.96816	1.342	−0.4371
0.3000	0.85807	1.041	−0.5533	0.8000	0.99378	1.392	−0.3132
0.4138	0.89075	1.141	−0.5987	0.9000	1.01878	1.429	−0.1654
				1.0000	1.04320	1.459	0.0000
			Cyclopropanecarboxylic Acid (1) + Butan-1-ol (2)				
			T = 298.15 K				
0.0000	0.80580	2.588	0.0000	0.5000	0.93930	3.217	−0.4592
0.1000	0.83184	2.672	−0.1928	0.6000	0.96697	3.319	−0.4130
0.2000	0.85824	2.782	−0.3340	0.6987	0.99472	3.386	−0.3386
0.3000	0.88497	2.936	−0.4263	0.7996	1.02360	3.401	−0.2397
0.4000	0.91203	3.091	−0.4693	0.9000	1.05300	3.362	−0.1247
				1.0000	1.08292	3.306	0.0000
			T = 308.15 K				
0.0000	0.79808	1.991	0.0000	0.5000	0.93044	2.475	−0.4607
0.1000	0.82384	2.064	−0.1881	0.6000	0.95792	2.558	−0.4169
0.2000	0.85001	2.145	−0.3301	0.6987	0.98550	2.616	−0.3460
0.3000	0.87651	2.260	−0.4227	0.7996	01.01415	2.634	−0.2457
0.4000	0.90336	2.374	−0.4677	0.9000	1.04331	2.628	−0.1283
				1.0000	1.07297	2.603	0.0000
			T = 318.15 K				
0.0000	0.79022	1.555	0.0000	0.5000	0.92151	1.944	−0.4630
0.1000	0.81572	1.615	−0.1844	0.6000	0.94881	2.016	−0.4212
0.2000	0.84164	1.689	−0.3238	0.6987	0.97622	2.079	−0.3523
0.3000	0.86795	1.779	−0.4198	0.7996	1.00468	2.110	−0.2522
0.4000	0.89460	1.863	−0.4664	0.9000	1.03363	2.109	−0.1332
				1.0000	1.06304	2.102	0.0000
			T = 328.15 K				
0.0000	0.78217	1.228	0.0000	0.5000	0.91247	1.556	−0.4659
0.1000	0.80743	1.289	−0.1815	0.6000	0.93961	1.620	−0.4260
0.2000	0.83315	1.339	−0.3223	0.6987	0.96686	1.671	−0.3582
0.3000	0.85926	1.416	−0.4189	0.7996	0.99517	1.708	−0.2596
0.4000	0.88574	1.488	−0.4684	0.9000	1.02394	1.723	−0.1390
				1.0000	1.05312	1.739	0.0000
			T = 338.15 K				
0.0000	0.77388	0.981	0.0000	0.5000	0.90333	1.266	−0.4739
0.1000	0.79892	1.031	−0.1792	0.6000	0.93034	1.324	−0.4363
0.2000	0.82446	1.081	−0.3219	0.6987	0.95746	1.370	−0.3696
0.3000	0.85039	1.145	−0.4194	0.7996	0.98560	1.410	−0.2681
0.4000	0.87673	1.207	−0.4729	0.9000	1.01421	1.432	−0.1447
				1.0000	1.04320	1.459	0.0000

± 0.1 mg. Each mixture was immediately used after it was well mixed by shaking. The uncertainty in the mole fraction is estimated to be lower than ± $1 \cdot 10^{-4}$. All mole quantities were based on the IUPAC relative atomic mass table.[15]

Apparatus and Procedure. The density of these pure compounds and the binary mixtures was measured by an Anton Paar DMA 4500 oscillating U-tube densitometer at (298.15 to 338.15) K. The temperature in the cell was regulated to ± 0.01

Table 3. Coefficients of the Redlich−Kister Equation and Standard Deviation for Excess Molar Volumes of the Binary Mixtures

T/K	property	A_0	A_1	A_2	σ
	Cyclopropanecarboxylic Acid (1) + Methanol (2)				
298.15	V^E/cm^3·mol^{-1}	−3.2849	0.6683	−0.0807	0.0033
308.15	V^E/cm^3·mol^{-1}	−3.43281	0.7242	−0.1083	0.0034
318.15	V^E/cm^3·mol^{-1}	−3.5816	0.7762	−0.1390	0.0035
328.15	V^E/cm^3·mol^{-1}	−3.7268	0.8368	−0.1664	0.0037
	Cyclopropanecarboxylic Acid (1) + Ethanol (2)				
298.15	V^E/cm^3·mol^{-1}	−2.9750	1.0846	−0.2011	0.0041
308.15	V^E/cm^3·mol^{-1}	−3.0558	1.1165	−0.3200	0.0045
318.15	V^E/cm^3·mol^{-1}	−3.1453	1.1385	−0.3679	0.0040
328.15	V^E/cm^3·mol^{-1}	−3.2376	1.1435	−0.3813	0.0050
	Cyclopropanecarboxylic Acid (1) + Propan-1-ol (2)				
298.15	V^E/cm^3·mol^{-1}	−2.2466	0.8233	0.1872	0.0047
308.15	V^E/cm^3·mol^{-1}	−2.2718	0.7442	0.1110	0.0040
318.15	V^E/cm^3·mol^{-1}	−2.3026	0.7034	0.1207	0.0042
328.15	V^E/cm^3·mol^{-1}	−2.3381	0.6649	0.1176	0.0044
338.15	V^E/cm^3·mol^{-1}	−2.3831	0.6263	0.1382	0.0045
	Cyclopropanecarboxylic Acid (1) + Butan-1-ol (2)				
298.15	V^E/cm^3·mol^{-1}	−1.8400	0.5087	0.1271	0.0026
308.15	V^E/cm^3·mol^{-1}	−1.8469	0.4511	0.1348	0.0022
318.15	V^E/cm^3·mol^{-1}	−1.8548	0.3902	0.1439	0.0026
328.15	V^E/cm^3·mol^{-1}	−1.8674	0.3440	0.1347	0.0032
338.15	V^E/cm^3·mol^{-1}	−1.8990	0.2886	0.1538	0.0030

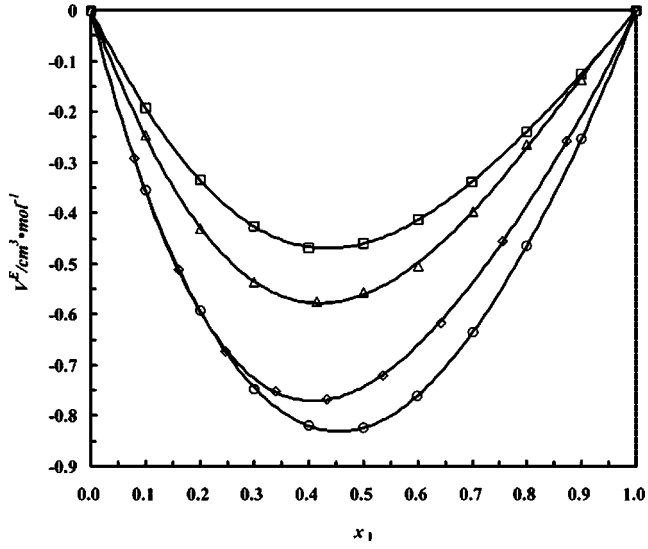

Figure 1. Excess mole volume V^E at 298.15 K for (x_1) cyclopropanecarboxylic acid + (1 − x_1) alkanols: ○, methanol; ◇, ethanol; △, propan-1-ol; □, butan-1-ol. The symbols represent experimental values, and solid curves were correlated by the Redlich−Kister equation.

K with a solid-state thermostat (Peltier). The temperature in the cell was measured by means of two integrated Pt 100 platimun thermometers. The densitometer was calibrated once a day with dry air and double-distilled freshly degassed water. The density of water was taken from the literature.[16] The uncertainty in density measurements was ± 5·10^{-5} g·cm^{-3}.

The viscosities of pure liquids and the binary mixtures were measured at atmospheric pressure and different temperatures using an Ubbelohde capillary viscometer (Shanghai Glass Instruments Factory, China). The viscometer was filled with experimental liquid and immersed vertically in a DF-02 transparent thermostatic water bath (Fangao Scientific Co., Ltd., Nanjing, China) with temperature regulated within ± 0.01 K. An electronic digital stopwatch with a readability of ± 0.01 s was used for flow time measurement. Experiments were repeated at least four times at each temperature for all mixtures, and the results were averaged. The viscosity (η) of these pure liquids and binary mixtures was then calculated from the following relationship

$$\upsilon = \frac{\eta}{\rho} = At - \frac{B}{t} \tag{1}$$

where t is the flow time; ν is the kinematic viscosity; and A and B are the viscometer constants. The values of these constants A and B were obtained by using double-distilled water at 5 K intervals from (293.15 to 338.15) K. During the heating, to minimize the evaporation losses, the viscometer's limbs are closed with Teflon caps. During the measurements of flow time, the caps of the limps were removed. The uncertainty of viscosity measurements was found to be within ± 0.003 mPa·s.

Results and Discussion

The densities and viscosities of pure liquid at 298.15 K are shown in Table 1. It could be found that the measured density and viscosity data are in agreement with those in the literature.

The experimental values of density and viscosity for the binary mixtures at different temperatures and at atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from the measured density data according to the following equation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \left(\frac{x_1M_1}{\rho_1} + \frac{x_2M_2}{\rho_2}\right) \tag{2}$$

where x_1 and x_2 are mole fractions; M_1 and M_2 are the molar masses; and ρ_1 and ρ_2 are the densities of pure components 1 and 2, respectively. Quantities without subscripts refer to the mixture. The numerical values of excess molar volume are shown in Table 2.

The values of V^E for the four binary mixtures were fitted to the Redlich−Kister equation

$$Y = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \tag{3}$$

where $Y = V^EA_i$ are the adjustable parameters, and x_1 is the mole fraction of component 1. In each case, the optimum numerical values of coefficients (A_i) were selected from an examination of the variation of the standard deviation

$$\sigma(Y) = \left[\sum (Y_{cal} - Y_{exp})^2/(n - m)\right]^{(1/2)} \tag{4}$$

where n is the total number of number of data points and m is the number of parameters. The subscripts "cal" and "exp" denote correlated and experimental values. Table 3 lists the values of the parameters A_i together with the standard deviations.

We have calculated the V^E at several temperatures, but graphically the results are shown only at 298.15 K since at other temperatures the variation of curves is similar. The variation of V^E with the mole fraction of cyclopropanecarboxylic acid for the four binary mixtures at 298.15 K is presented in Figure 1. It is seen that the V^E values are negative for binary mixtures of cyclopropanecarboxylic acid with methanol, ethanol, propan-1-ol, and butan-1-ol over the whole composition range at a particular temperature (Figure 1). It appears that the magnitude of negative deviation is sensitive to the lengths of alkanol molecules. The absolute V^E values at equimolar concentration of cyclopropanecarboxylic acid and 1-alkanols in the binary mixtures follow the order: methanol > ethanol > propan-1-ol > butan-1-ol. For the binary mixtures in this article, the minimum V^E values exist at x_1 = (0.4 to 0.5) within the whole region of experimental temperatures. The absolute V^E values

Table 4. Parameters of McAllister's Model together with the Standard Deviations (σ) at Different Temperatures

	four-body interaction model				three-body interaction model		
	ν_{1112}	ν_{1122}	ν_{222}	σ	ν_{12}	ν_{21}	σ
T/K	(mm^2·s^{-1})	(mm^2·s^{-1})	(mm^2·s^{-1})	(mm^2·s^{-1})	(mm^2·s^{-1})	(mm^2·s^{-1})	(mm^2·s^{-1})
Cyclopropanecarboxylic Acid (1) + Methanol (2)							
298.15	3.2327	2.7483	1.4375	0.0091	3.4811	1.9555	0.0135
308.15	2.4161	2.3543	1.1681	0.0075	2.6818	1.6274	0.0193
318.15	1.9547	1.8583	1.0243	0.0037	2.1079	1.3841	0.0670
328.15	1.5947	1.5220	0.8884	0.0035	1.6925	1.1811	0.0600
Cyclopropanecarboxylic Acid (1) + Ethanol (2)							
313.15	3.0241	3.0321	1.9291	0.0047	3.2759	2.3227	0.0212
318.15	2.4308	2.3560	1.5982	0.0049	2.5848	1.8801	0.0124
323.15	1.9048	1.9494	1.3161	0.0072	2.0357	1.5616	0.0147
328.15	1.5914	1.5761	1.1174	0.0072	1.6693	1.3044	0.0104
Cyclopropanecarboxylic Acid (1) + Propan-1-ol (2)							
298.15	3.2358	3.6321	2.6586	0.0063	3.5853	2.9730	0.0286
308.15	2.5836	2.7357	2.1426	0.007	2.7870	2.3395	0.0159
318.15	2.0688	12.1743	1.7117	0.0038	2.2164	1.8631	0.0119
328.15	1.6812	1.7744	1.3924	0.0021	1.7912	1.5207	0.0102
338.15	1.4080	1.4483	1.1542	0.0013	1.4817	1.2532	0.0071
Cyclopropanecarboxylic Acid (1) + Butan-1-ol (2)							
298.15	3.4588	3.7656	3.0972	0.0045	3.8062	3.2298	0.0213
308.15	2.6956	2.8722	2.4413	0.0046	2.9234	2.5180	0.0140
318.15	2.2110	2.1860	1.9869	0.0051	2.3286	2.0008	0.0061
328.15	1.7557	1.8046	1.5778	0.003	1.8468	1.6292	0.0066
338.15	1.4518	1.4723	1.2990	0.0028	1.5083	1.3438	0.0050

of each binary system increase slightly with an increase in temperature from (298.15 to 338.15) K.

McAllister's multibody interaction model, which takes into account interactions of both like and unlike molecules, is widely used for correlating the kinematic viscosity (ν) of binary mixtures with mole fraction. The three-body model is defined as

$$\ln \upsilon = x_1^3 \ln \upsilon_1 + 3x_1^2 x_2 \ln \upsilon_{12} + 3x_1 x_2^2 \ln \upsilon_{21} + x_2^3 \ln \upsilon_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 3x_1^2 x_2 \ln\left(\frac{2 + M_2/M_1}{3}\right) + 3x_1 x_2^2 \ln \times \left(\frac{1 + 2M_2/M_1}{3}\right) + x_2^3 \ln\left(\frac{M_2}{M_1}\right) \quad (5)$$

and the four-body model is given by

$$\ln \upsilon = x_1^4 \ln \upsilon_1 + 4x_1^3 x_2 \ln \upsilon_{1112} + 6x_1^2 x_2^2 \ln \upsilon_{1122} + 4x_1 x_2^3 \ln \upsilon_{2221} + x_2^4 \ln \upsilon_2 - \ln\left(x_1 + \frac{x_2 M_2}{M_1}\right) + 4x_1^3 x_2 \times \ln\left(\frac{3 + M_2/M_1}{4}\right) + 6x_1^2 x_2^2 \ln\left(\frac{1 + M_2/M_1}{2}\right) + 4x_1 x_2^3 \times \ln\left(\frac{1 + 3M_2/M_1}{4}\right) + x_2^4 \ln\left(\frac{M_2}{M_1}\right) \quad (6)$$

where ν, ν_1, and ν_2 are the kinematic viscosities of the mixture and the kinematic viscosities of pure components 1 and 2, respectively. ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters. The calculated results are presented in Table 4. The correlating ability of eqs 5 and 6 was tested by calculating the standard deviation (σ) between the experimental and calculated kinematic viscosities. From Table 4, it is clear that McAllister's four-body interaction model gives a better result than the three-body model for correlating the kinematic viscosities of the four binary mixtures in this study.

Conclusion

This paper reports new experimental data for the densities and viscosities of the binary mixtures of cyclopropanecarboxylic acid + methanol, + ethanol, + propan-1-ol, and + butan-1-ol over the whole composition range at different temperatures ranging from (298.15 to 338.15) K and atmospheric pressure. Excess molar volumes V^E for the binary mixtures were derived from the experimental data. The magnitude of V^E values of each binary mixture increases at each temperature with an increase of alkyl chain length in the molecule of 1-alkanols and becomes more negative with the rise of temperature. The values of V^E were correlated by using the Redlich−Kister equation. The binary kinemaic viscosities were correlated by the McAllister three- and four-body interaction equations. Both the Redlich−Kister equation and the McAllister equation can represent data very well.

Supporting Information Available:

GC and MS spectra for the pure components. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Wang, L. C.; Xu, H. S.; Zhao, J. H.; Song, C. Y.; Wang, F. A. Densities and Viscosities of Niacin + 3-Picoline + Water Mixtures from (293.15 to 343.15) K. *J. Chem. Eng. Data* **2005**, *50*, 254–257.

(2) Schmid, B.; Doker, M.; Gmehling, J. Measurement of the Thermodynamic Properties for the Reactive System Ethylene glycol-acetic acid. *Fluid Phase Equilib.* **2007**, *258*, 115–124.

(3) Fang, S.; Zhao, C. X.; He, C. H. Densities and Viscosities of Binary Mixtures of Tris(2-ethylhexyl) Phosphate + Cyclohexane or *n*-Hexane at T = (293.15, 298.15, and 303.15) K and p = 0.1 MPa. *J. Chem. Eng. Data* **2008**, *53*, 2718–2720.

(4) Álvarez, E.; Gómez-Díaz, D.; Dolores La Rubia, D.; Navaza, J, M. Densities and Viscosities of Aqueous Ternary Mixtures of 2-(Methylamino)ethanol and 2-(Ethylamino)ethanol with Diethanolamine, Triethanolamine, N-Methyldiethanolamine, or 2-Amino-1-methyl-1-propanol from 298.15 to 323.15 K. *J. Chem. Eng. Data* **2006**, *51*, 955–962.

(5) Tatsuya, M.; Kazuya, U.; Osamu, M.; Kazunori, Y.; Noritada, M. Synthetic studies of fluorine-containing compounds for household insecticides. *J. Fluorine Chem.* **2007**, *128*, 1174–1181.

(6) Pinnick, H. W.; Brown, S. P.; McLean, E. A.; Zoller, L. W. Fridel-Crafts Reactions of Ethyl Cyclopropanecarboxylate. *J. Org. Chem.* **1981**, *46*, 3758–3760.

(7) Periana, R. A.; Bergman, R. G.; Mater, M. R. Carbon-Carbon activation of Organic Small Ring Compounds by Arrangement of Cycloalkylhydridorhodium Complexes to Rhodacycloalkanes. Synthesis of Metallacyclobutane, Including One with a Tertiary Metal-Carbon Bond,

by Nucleophilic Addition to π-Allyl Complexes. *J. Am. Chem. Soc.* **1986**, *108*, 2425–2437.
(8) Langer, R.; Emde, H.; Wagner, P. Process for The Acid Hydrolysis of Methyl or Ethyl Cyclopropanecarboxylate Esters into Cyclopropanecarboxylic Acid and Methanol or Ethanol. *Eur. Pat. Appl.* EP 1707554 A1, 2006; 12pp.
(9) Mozo, I.; García de la Fuente, I.; González, J. A.; Cobos, J. C. Densities, Excess Molar Volumes, Speeds of Sound at (293.15, 298.15, and 303.15) K and Isentropic Compressibilities at 298.15 K for 1-Butanol, 1-Pentanol, or 1-Hexanol + Dibutylether Systems. *J. Chem. Eng. Data* **2008**, *53*, 857–862.
(10) Awwad, A. M.; Alsyouri, H. A.; Jbara, K. A. Viscosities and Densities of Binary Mixtures of (*N*-Acetylmorpholine + Alkanols) from (293.15 to 323.15) K. *J. Chem. Eng. Data* **2008**, *53*, 1655–1659.
(11) Chávez, H.; Piñeiro, A.; Brocos, P. Thermodynamics of Mixing Tetrahydrofuran with 1-Alkanols and Excess Enthalpies of Homomorphy-Related Systems. *J. Chem. Eng. Data* **2007**, *52*, 2298–2305.
(12) Al-Jimaz, A. S.; Al-Kandary, J. A.; Abdul-Latif, A. M. Acoustical and Excess Properties of (Chlorobenzene + 1-Hexanol, or 1-Heptanol, or 1-Octanol, or 1-Nonanol, or 1-Decanol) at (298.15, 303.15,308.15, and 313.15) K. *J. Chem. Eng. Data* **2007**, *52*, 206–214.
(13) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and The Classification of Solutions[J]. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
(14) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J.* **1960**, *6* (3), 427–431.
(15) IUPAC Commission on Atomic Weight and Isotopic Abundances, 1985. *Pure Appl. Chem.* **1986**, *58*, 1677−1692.
(16) *Perry's Chemical Engineering Handbook*, 8/E Section 1&2, 2007.
(17) Riddick, J. A.; Bunger, W. B. *Organic Solvents. Techniques of Chemistry*; Willey-Interscience: New York, 1970; Vol. Π.
(18) Yang, C. S; Lai, H. X.; Liu, Z.; Ma, P. S. Densities and Viscosities of Diethyl Carbonate + Toluene, + Methanol, and + 2-Propanol from (293.15 to 363.15) K. *J. Chem. Eng. Data* **2006**, *51*, 584–589.
(19) Nikam, P. S.; Jadhav, M. C.; Hasan, M. Density and Viscosity of Mixtures of Nitrobenzene with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at 298.15 and 303.15K. *J. Chem. Eng. Data* **1995**, *40*, 931–934.
(20) Aralaguppi, M. I.; Jadar, C. V.; Aminabhavi, T. M. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Acrylonitrile With Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, Hexan-1-ol, Heptan-1-ol, and Butan-2-ol. *J. Chem. Eng. Data* **1999**, *44*, 216–221.
(21) González, B.; Domínguez, A.; Tojo, J. Dynamic Viscosities, Densities, and Speed of Sound and Derived Properties of the Binary Systems Acetic Acid with Water, Methanol, Ethanol, Ethyl Acetate and Methyl Acetate at T = (293.15, 298.15, and 303.15) K at Atmospheric Pressure. *J. Chem. Eng. Data* **2004**, *49*, 1590–1596.
(22) Shan, Z. G.; Asfour, A. A. Viscosities and Densities of Nine Binary 1-Alkanol Systems at 293.15 and 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 118–123.
(23) Agarwal, D.; Singh, M. Densities and Viscosities of Binary Liquid Mixtures of Trichloroethylene and Tetrachloroethylene with Some Polar and Nonpolar Solvents. *J. Chem. Eng. Data* **2004**, *49*, 1218–1224.
(24) Sastry, N. V.; Valand, M. K. Densities, Speeds of Sound, Viscosities, and Relative Permittivities for 1-Propanol + and 1-Butanol + Heptane at 298.15 and 308.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1421–1425.

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