Excess Molar Volumes of 1,3-Diethyl Propanedioate with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-2-ol, 2-Methyl-propan-1-ol, and Pentan-1-ol at T = (288.15, 298.15, 313.15, and 328.15) K

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Densities of binary mixtures of 1,3-diethyl propanedioate with methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, 2-methyl-propan-1-ol, and pentan-1-ol have been measured at temperatures of (288.15, 298.15, 313.15, and 328.15) K using an Anton Paar model DMA 5000 M oscillating densimeter. Excess molar volumes were calculated from these densities. The experimental data were fitted to the Redlich−Kister equation.

Introduction

The excess properties of binary liquid mixtures are very important to understand the properties and the interactions of different molecules.[1−3] These excess properties are used to express the deviations of the mixing process from ideality. In addition, these properties can also be used in the development and design of the chemical engineering process. The excess molar volume (V^E) is one of the important excess properties which can be used in the understanding of molecular interactions between different components of mixtures[4−6] and also in engineering applications.

In our studies on the thermodynamic properties of the mixtures including 1,3-diethyl propanedioate (DEM) and alcohols,[7,8] some correlations between the excess molar enthalpies and the temperatures as well as structures of the components have been found. In this work, the excess molar volumes for seven binary systems of DEM + methanol, + ethanol, + propan-1-ol, + propan-2-ol, + butan-2-ol, + 2-methyl-propan-1-ol, and + pentan-1-ol at T = (288.15, 298.15, 313.15, and 328.15) K were determined by a vibrating-tube densimeter. The V^E data were correlated by the Redlich−Kister equation.

Experimental Section

Materials. 1,3-Diethyl propanedioate (guaranteed grade, w = 0.999) was purchased from Shanghai Jiachen Chemical. Methanol (high-performance liquid chromatography (HPLC) grade, w = 0.999) and propan-2-ol (HPLC grade, w = 0.995) were provided by Tianjin Siyou. Ethanol (analytical grade, w = 0.997) was provided by Sinopharm Chemical Reagent. Propan-1-ol (HPLC grade, w = 0.995), butan-2-ol, and pentan-1-ol (HPLC grade, w = 0.998) were purchased from Tianjin Saifu. 2-Methyl-propan-1-ol (HPLC grade, w = 0.995) was provided by Aladdin. All chemicals above were dried with molecular sieves of (3 to 4) Å and filtrated through a Millipore filter (0.45 μm). The mass fraction purities of these compounds were determined by gas chromatography and were found to be between w = 0.995 and 0.999. Before use, all chemicals were degassed in an ultrasonic bath.

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Table 1. Experimental Densities (ρ) of the Pure Component Liquids Together with Literature Values at T = 298.15 K

	ρ/g·cm^{-3}			ρ/g·cm^{-3}	
solvent	exptl	lit.	solvent	exptl	lit.
water	0.997068	0.99705[10]	propan-2-ol	0.780990	0.78085[16]
methanol	0.786987	0.78664[11]			0.78126[13]
		0.7868[12]	butan-2-ol	0.806137	0.80576[17]
		0.78637[13]			0.80575[13]
ethanol	0.785489	0.78504[11]	2-methyl-propan-1-ol	0.797916	0.7978[12]
		0.78520[14]			0.79980[13]
		0.78493[13]	pentan-1-ol	0.811465	0.811001[18]
propan-1-ol	0.800973	0.79960[13]			0.8109[19]
		0.799666[14]			0.81083[20]
		0.79958[15]			

Apparatus and Procedure. Binary mixtures were prepared in airtight stopped glass bottles. Mole fractions of these samples were determined by measuring the mass of each component with a precision balance (Sartorius, model CP 225D, ± 0.01 mg). The uncertainty of the composition on a mole fraction basis was 0.0001. The densities of pure components and binary mixtures at different temperatures were obtained with a vibrating-tube densimeter (Anton Paar DMA 5000 M). The uncertainty of density is ± 0.000005 g·cm^{-3}. The densimeter was calibrated with ultrapure water, and the densities have been listed in Table 1, compared with literature. Two integrated Pt 100 platinum thermometers (uncertainty: 0.01 K) together with Peltier elements provide an extremely precise thermostatting of the sample. The estimated uncertainty is about 0.001 cm^3·mol^{-1} for V^E.

Results and Discussion

Table 1 gives the experimental densities ρ of pure components compared with literature values at T = 298.15 K. Densities of the pure components and binary mixtures (see Table S1 in the Supporting Information) were used to determine the excess molar volumes V^E given in Table 2 by using the equation

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \quad (1)$$

where x_i, ρ_i, and M_i represent the mole fraction, the density, and the molar mass of the pure component and ρ represents the density of mixture.

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Table 2. Excess Molar Volumes (V^E) of the Systems DEM (1) + Alcohols (2)

	V^E/cm^3·mol^{-1}					V^E/cm^3·mol^{-1}			
x_1	288.15 K	298.15 K	313.15 K	328.15 K	x_1	288.15 K	298.15 K	313.15 K	328.15 K
				DEM (1) + Methanol (2)					
0.0500	–0.072	–0.071	–0.066	–0.060	0.4503	–0.197	–0.188	–0.166	–0.132
0.1000	–0.125	–0.123	–0.116	–0.105	0.5004	–0.191	–0.182	–0.157	–0.124
0.1501	–0.160	–0.157	–0.147	–0.132	0.5497	–0.182	–0.171	–0.146	–0.111
0.2001	–0.184	–0.179	–0.167	–0.149	0.6000	–0.158	–0.147	–0.121	–0.086
0.2501	–0.198	–0.192	–0.177	–0.155	0.6495	–0.143	–0.133	–0.105	–0.072
0.3001	–0.210	–0.205	–0.188	–0.162	0.6997	–0.123	–0.112	–0.087	–0.054
0.3500	–0.209	–0.202	–0.183	–0.154	0.7978	–0.089	–0.080	–0.057	–0.032
0.4001	–0.206	–0.197	–0.175	–0.145	0.9009	–0.045	–0.038	–0.024	–0.011
				DEM (1) + Ethanol (2)					
0.0500	–0.010	0.001	0.017	0.036	0.4999	0.040	0.073	0.136	0.206
0.1001	–0.013	0.003	0.031	0.065	0.5501	0.042	0.075	0.134	0.203
0.0999	–0.014	0.002	0.029	0.063	0.6001	0.052	0.083	0.140	0.206
0.1500	–0.011	0.011	0.048	0.097	0.6453	0.054	0.086	0.138	0.200
0.2001	–0.003	0.022	0.066	0.119	0.6997	0.058	0.084	0.133	0.189
0.3000	0.010	0.040	0.094	0.159	0.7497	0.056	0.081	0.124	0.173
0.4000	0.018	0.051	0.111	0.181	0.8496	0.046	0.062	0.089	0.123
0.4499	0.029	0.064	0.122	0.193	0.8995	0.039	0.050	0.069	0.089
				DEM (1) + Propan-1-ol (2)					
0.1001	0.116	0.138	0.174	0.214	0.4999	0.247	0.292	0.370	0.452
0.2000	0.186	0.219	0.278	0.342	0.5446	0.245	0.289	0.362	0.444
0.2999	0.225	0.266	0.337	0.416	0.5997	0.239	0.281	0.351	0.425
0.3501	0.233	0.277	0.353	0.434	0.7003	0.211	0.247	0.306	0.369
0.4001	0.246	0.291	0.367	0.451	0.7998	0.165	0.190	0.233	0.279
0.4499	0.247	0.293	0.369	0.454	0.8996	0.098	0.113	0.135	0.159
				DEM(1) + Propan-2-ol (2)					
0.1001	0.141	0.176	0.227	0.274	0.5501	0.310	0.368	0.454	0.531
0.2000	0.226	0.278	0.356	0.427	0.5999	0.307	0.361	0.440	0.511
0.3000	0.280	0.341	0.432	0.516	0.6499	0.290	0.338	0.413	0.475
0.3501	0.290	0.353	0.448	0.533	0.7001	0.277	0.321	0.386	0.440
0.4000	0.308	0.372	0.466	0.552	0.8000	0.217	0.248	0.293	0.331
0.4550	0.317	0.380	0.472	0.557	0.8995	0.128	0.143	0.164	0.183
0.4999	0.318	0.379	0.470	0.551					
				DEM (1) + Butan-2-ol (2)					
0.1001	0.178	0.203	0.242	0.284	0.5000	0.369	0.420	0.501	0.589
0.2002	0.284	0.322	0.388	0.455	0.5501	0.354	0.401	0.481	0.565
0.3001	0.341	0.389	0.466	0.551	0.5999	0.342	0.389	0.464	0.545
0.3500	0.347	0.397	0.479	0.565	0.7000	0.297	0.337	0.399	0.465
0.4000	0.368	0.419	0.502	0.593	0.7998	0.228	0.254	0.300	0.346
0.4500	0.365	0.416	0.500	0.590	0.9001	0.126	0.141	0.164	0.190
				DEM (1) + 2-Methyl-propan-1-ol (2)					
0.1000	0.176	0.205	0.251	0.294	0.5001	0.365	0.423	0.511	0.599
0.2000	0.276	0.323	0.395	0.467	0.6001	0.341	0.393	0.472	0.550
0.3000	0.333	0.389	0.476	0.562	0.6999	0.298	0.339	0.404	0.468
0.3500	0.345	0.403	0.493	0.589	0.8003	0.226	0.256	0.299	0.345
0.3999	0.360	0.419	0.512	0.604	0.9000	0.126	0.140	0.164	0.187
0.4495	0.362	0.421	0.511	0.602					
				DEM (1) + Pentan-1-ol (2)					
0.0999	0.235	0.258	0.296	0.334	0.5501	0.473	0.525	0.608	0.696
0.1998	0.358	0.399	0.465	0.530	0.5990	0.457	0.505	0.584	0.666
0.2999	0.458	0.508	0.587	0.669	0.6500	0.440	0.485	0.558	0.634
0.3498	0.481	0.534	0.618	0.705	0.6997	0.406	0.449	0.514	0.581
0.3997	0.491	0.544	0.630	0.720	0.7997	0.309	0.340	0.389	0.436
0.4499	0.493	0.548	0.635	0.726	0.9000	0.174	0.188	0.212	0.239
0.4999	0.494	0.550	0.636	0.724					

The Redlich–Kister[9] polynomial was used to describe the composition dependence of experimental V^E data:

$$V_m^E = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \qquad (2)$$

where x_1 is the mole fraction of DEM, A_i is the adjustable parameter, and n is the number of fitted parameters.

The Redlich−Kister parameters were obtained by using a least-squares fit method and are listed in Table 3 together with the root-mean-square deviations (rmsd). The rmsd is defined as

$$\text{rmsd} = \sqrt{\frac{1}{N}\sum_{i}^{N}(V_{\text{cal}(i)}^E - V_{\text{exp}(i)}^E)^2} \qquad (3)$$

where $V_{\text{cal}(i)}^E$ and $V_{\text{exp}(i)}^E$ are the calculated and experimental values of excess molar volume and N is the number of data points for each data set.

As examples, the V^E values for binary systems at 298.15 K and for methanol + DEM were plotted in Figures 1 and 2, respectively. The V^E values are considered to consist of two contributions resulting from two types of interactions between components: (1) dissociation of the H-bonds of the alcohols and physical interaction consisting mainly of dispersive force, which contributes to the increase of the volume, and (2) association of two different components resulting in the decrease of the volume. Results presented in Table 2 and Figure 1 indicate that V^E values are positive except for that of the methanol mixture. This phenomenon may result from the decrease in volume due to the association of DEM with alcohol molecules which is less than the increase in volume due to the dissociation of the H-bonds of alcohols and physical interaction of the pure components. Figure 1 also indicates that the V^E values increase with the increasing branch and carbon number of alcohols at the same

Table 3. Parameters, A_i, of the Redlich−Kister Equation with the Root-Mean-Square Deviation (σ)

T / K	A_0 / cm^3·mol^{-1}	A_1 / cm^3·mol^{-1}	A_2 / cm^3·mol^{-1}	A_3 / cm^3·mol^{-1}	σ / cm^3·mol^{-1}
		DEM (1) + Methanol (2)			
288.15	–0.7520	0.4663	–0.2939	0.1347	0.002
298.15	–0.7141	0.4914	–0.2747	0.1457	0.003
313.15	–0.6184	0.5516	–0.2394	0.1153	0.003
328.15	–0.4813	0.6001	–0.2373	0.0711	0.003
		DEM (1) + Ethanol (2)			
288.15	0.1575	0.2463	–0.0328	0.1779	0.002
298.15	0.2901	0.2459	0.0023	0.1157	0.002
313.15	0.5305	0.2268	0.0303	0.0399	0.002
328.15	0.8137	0.1865	0.0651	–0.0400	0.002
		DEM (1) + Propan-1-ol (2)			
288.15	0.9901	–0.0760	0.2967	–0.0792	0.001
298.15	1.1699	–0.1068	0.3305	–0.1074	0.001
313.15	1.4753	–0.1726	0.3543	–0.1609	0.001
328.15	1.8070	–0.2575	0.3856	–0.1955	0.001
		DEM (1) + Propan-2-ol (2)			
288.15	1.2625	0.0031	0.3732	–0.1659	0.003
298.15	1.5054	–0.0899	0.4198	–0.2355	0.003
313.15	1.8666	–0.2309	0.4884	–0.3381	0.003
328.15	2.1892	–0.3906	0.5429	–0.3873	0.003
		DEM (1) + Butan-2-ol (2)			
288.15	1.4547	–0.2031	0.3853	–0.2453	0.003
298.15	1.6552	–0.2509	0.4134	–0.2808	0.004
313.15	1.9855	–0.3365	0.4393	–0.3207	0.003
328.15	2.3357	–0.4400	0.4769	–0.3394	0.004
		DEM (1) + 2-Methyl-propan-1-ol (2)			
288.15	1.4422	–0.1624	0.3585	–0.2988	0.002
298.15	1.6735	–0.2419	0.3763	–0.3240	0.002
313.15	2.0265	–0.3747	0.4222	–0.3639	0.002
328.15	2.3812	–0.5175	0.4462	–0.3597	0.002
		DEM (1) + Pentan-1-ol (2)			
288.15	1.9633	–0.2432	0.4647	–0.2661	0.006
298.15	2.1810	–0.2917	0.4555	–0.2917	0.006
313.15	2.5257	–0.3699	0.4615	–0.3128	0.006
328.15	2.8827	–0.4574	0.4611	–0.3147	0.005

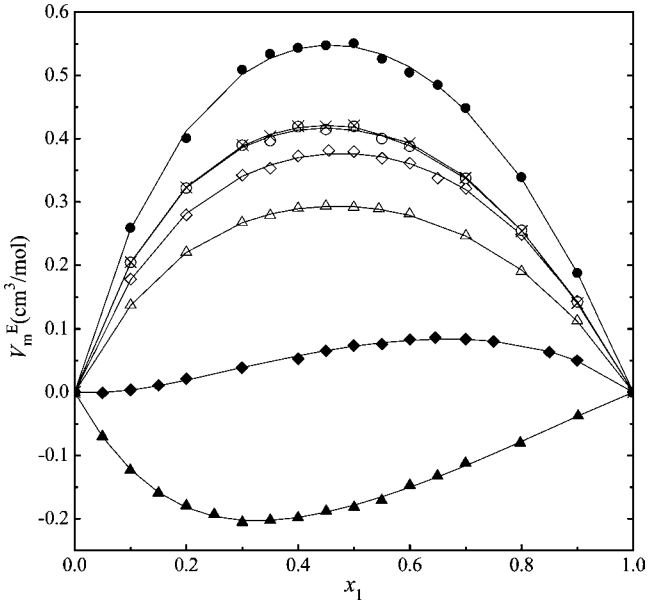

Figure 1. Excess molar volumes for the system DEM (1) + alcohols (2) as a function of mole fraction, x_1, at $T = 298.15$ K: ▲, DEM (1) + methanol (2); ◆, DEM (1) + ethanol (2); △, DEM (1) + propan-1-ol (2); ◇, DEM (1) + propan-2-ol (2); ○, DEM (1) + butan-2-ol (2); ×, DEM (1) + 2-methyl-propan-1-ol (2); ●, DEM (1) + pentan-1-ol (2). The curves were calculated by the Redlich−Kister equation (parameters taken from Table 3).

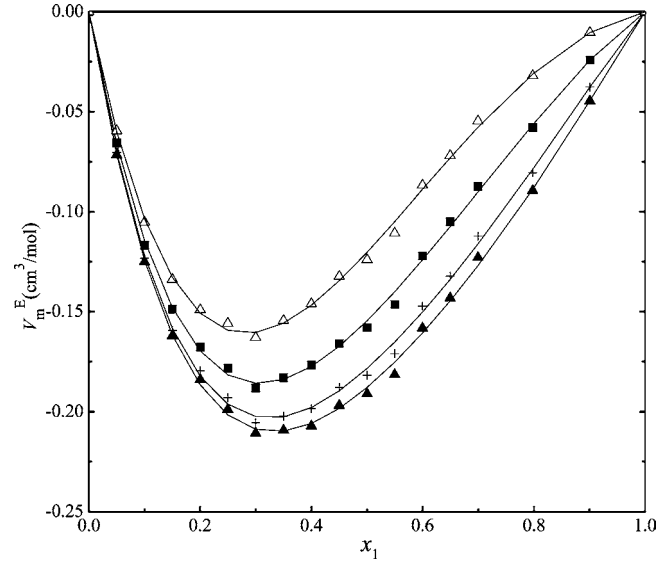

Figure 2. Excess molar volumes of the system DEM (1) + methanol (2) as a function of mole fraction, x_1: ▲, 288.15 K; +, 298.15 K; ■, 313.15 K; △, 328.15 K. The curves were calculated by the Redlich−Kister equation (parameters taken from Table 3).

molar fraction. It may be due to the increasing difficulty to form crossed associations between different molecules with increasing steric hindrance and aliphatic chain of alcohol. Figure 2 indicates that V^E values increase with temperature. It may be due to the reduction of H-bonds probably between methanol and DEM with the increase of temperature.

Supporting Information Available:

Densities for DEM (1) + alcohol (2) (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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