Densities and Excess Molar Volumes for Binary Mixtures of 1,4-Butanediol + 1,2-Propanediol, + 1,3-Propanediol, and + Ethane-1,2-diol from (293.15 to 328.15) K

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Densities for binary mixtures of three alkanols (1,2-propanediol, 1,3-propanediol, and ethane-1,2-diol) with 1,4-butanediol over the whole composition range have been measured at temperatures from (293.15 to 328.15) K in 5 K intervals. From these data, the excess molar volumes (V^E) and their standard deviations $\sigma(V^E)$ were calculated. The experimental results were fitted to the Redlich–Kister equation using a multiparametric nonlinear regression analysis.

Introduction

Glycols are generally accepted as compounds having two hydroxyl groups attached to different carbon atoms in an aliphatic carbon chain. Glycols find widespread application in automotive, aviation, explosive, textile, surface coating, food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries.[1] 1,4-Butanediol is one of these glycols, which is the most widely used of all the four carbon-based diols in industry today. 1,4-Butanediol is used predominately as a polymer feedstock. For example, it is used in the production of both polyurethanes and polybutylene terephthalate. 1,4-Butanediol may also be converted to γ-butyrolactone and tetrahydrofuran, which can be employed as an intermediate for materials such as pyrrolidones and as a solvent, respectively.[2]

Knowledge of the elementary physicochemical properties such as density of these mixtures is essential in the modeling and design of chemical processes. We have measured the density and excess volumes of the binary mixture 1,4-butanediol + 1,2-propanediol, 1,3-propanediol, and ethane-1,2-diol at temperatures from (293.15 to 328.15) K over the whole composition range. The extensive experimental data reported in this work have been correlated with the Redlich–Kister model. The parameters of the model and deviations between experimental and calculated data are given.

Experimental Sections

Materials. Chemicals of high purity obtained from different suppliers were purified by simple vacuum fractionation. The purity was checked by gas chromatography (GC). In Table 1, the specifications of the experimental chemicals (molecular weight, CASRN, purity) are summarized, and literature data (if available) for comparison are also presented.

Apparatus and Procedure. We used an apparatus similar to that described in the literature[3] and described briefly here. The densities of the pure components and binary mixtures were measured using an approximately 50 cm^3 Gay-Lussac pycnometer which was calibrated by using pure water. The pycnometer containing the solutions was immersed in a constant-temperature bath. The temperature was controlled within ± 0.05 K of the desired temperature through a thermostat water bath. Once the solutions reached the desired temperature, they were weighed to within ± 0.0001 g with an analytical balance (Sartorius CP124S, Germany). Each reported value was the average of at

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Table 1. Pure Compound Specification: Molecular Weight, CAS Registry Number (CASRN), Purity, Densities at Different Temperatures and Comparison with Literature Data

					ρ/g·cm^{-3}	
compound	mol wt.	CASRN	purity	*T*/K	this work	lit.
1,4-butanediol	90.122	110-63-4	>99.9 %	293.15	1.01637	1.01622[a]
				298.15	1.01304	1.0127[b]
				303.15	1.00996	1.01011[a]
				308.15	1.00675	1.00643[c]
				313.15	1.00355	1.0034[b]
				318.15	1.00072	1.00076[d]
				323.15	0.99780	0.9972[b]
				328.15	0.99441	0.99402[c]
ethane-1,2-diol	62.068	107-21-1	>99.5 %	293.15	1.11355	1.1135[e]
				298.15	1.10986	1.1099[f]
				303.15	1.10682	1.1066[g]
				308.15	1.10320	1.103084[h]
				313.15	1.09980	
				318.15	1.09623	1.096301[h]
				323.15	1.09259	
				328.15	1.08866	1.088314[h]
1,2-propanediol	76.095	5-55-6	>99.6 %	293.15	1.03657	
				298.15	1.03286	1.0328[i]
				303.15	1.02915	1.0292[j]
				308.15	1.02557	1.02540[d]
				313.15	1.02144	1.0215[j]
				318.15	1.01759	1.01732[d]
				323.15	1.01374	1.014[j]
				328.15	1.00971	1.00956[d]
1,3-propanediol	76.095	504-63-2	>99.4 %	293.15	1.05366	
				298.15	1.05029	1.04999[d]
				303.15	1.04709	1.0470[j]
				308.15	1.04392	1.04371[d]
				313.15	1.04061	1.0408[j]
				318.15	1.03760	1.03737[d]
				323.15	1.03451	1.0348[j]
				328.15	1.03100	1.03096[d]

[a] Ref 5. [b] Ref 6. [c] Ref 1. [d] Ref 7. [e] Ref 8. [f] Ref 9. [g] Ref 10. [h] Ref 11. [i] Ref 12. [j] Ref 3.

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Table 2. Densities and Molar Excess Volumes (V^E) for the 1,4-Butanediol (1) + 1,3-Propanediol (2) Binary Mixtures at Different Temperatures

x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
		T = 293.15 K			
0.0000	1.05366	0.000	0.5588	1.03127	−0.024
0.0858	1.04989	−0.006	0.6633	1.02752	−0.020
0.1743	1.04621	−0.016	0.7716	1.02377	−0.013
0.2657	1.04249	−0.022	0.8837	1.02005	−0.006
0.3602	1.03878	−0.027	1.0000	1.01637	0.000
0.4578	1.03505	−0.029			
		T = 298.15 K			
0.0000	1.05029	0.000	0.5588	1.02798	−0.029
0.0858	1.04656	−0.008	0.6633	1.02423	−0.024
0.1743	1.04287	−0.018	0.7716	1.02048	−0.017
0.2657	1.03920	−0.026	0.8837	1.01674	−0.008
0.3602	1.03548	−0.031	1.0000	1.01304	0.000
0.4578	1.03177	−0.034			
		T = 303.15 K			
0.0000	1.04709	0.000	0.5523	1.02489	−0.032
0.0858	1.04339	−0.010	0.6574	1.02116	−0.028
0.1743	1.03974	−0.021	0.7669	1.01741	−0.020
0.2657	1.03607	−0.030	0.8810	1.01368	−0.011
0.3602	1.03239	−0.036	1.0000	1.00996	0.000
0.4578	1.02869	−0.039			
		T = 308.15 K			
0.0000	1.04392	0.000	0.5588	1.02177	−0.038
0.0858	1.04026	−0.013	0.6633	1.01803	−0.034
0.1743	1.03661	−0.025	0.7716	1.01427	−0.025
0.2657	1.03295	−0.035	0.8837	1.01051	−0.014
0.3602	1.02926	−0.041	1.0000	1.00675	0.000
0.4578	1.02557	−0.045			
		T = 313.15 K			
0.0000	1.04061	0.000	0.5588	1.01861	−0.045
0.0858	1.03699	−0.015	0.6633	1.01487	−0.040
0.1743	1.03339	−0.030	0.7716	1.01108	−0.028
0.2657	1.02975	−0.041	0.8837	1.00733	−0.017
0.3602	1.02607	−0.047	1.0000	1.00355	0.000
0.4578	1.02239	−0.051			
		T = 318.15 K			
0.0000	1.03760	0.000	0.5588	1.01578	−0.051
0.0858	1.03404	−0.018	0.6633	1.01206	−0.046
0.1743	1.03048	−0.035	0.7716	1.00827	−0.033
0.2657	1.02688	−0.047	0.8837	1.00452	−0.020
0.3602	1.02321	−0.053	1.0000	1.00072	0.000
0.4578	1.01953	−0.056			
		T = 323.15 K			
0.0000	1.03451	0.000	0.5588	1.01286	−0.057
0.0858	1.03099	−0.020	0.6633	1.00917	−0.053
0.1743	1.02750	−0.041	0.7716	1.00536	−0.037
0.2657	1.02390	−0.052	0.8837	1.00161	−0.023
0.3602	1.02026	−0.059	1.0000	0.99780	0.000
0.4578	1.01660	−0.062			
		T = 328.15 K			
0.0000	1.03100	0.000	0.5588	1.00951	−0.064
0.0858	1.02753	−0.023	0.6633	1.00580	−0.058
0.1743	1.02408	−0.046	0.7716	1.00199	−0.041
0.2657	1.02050	−0.058	0.8837	0.99824	−0.026
0.3602	1.01686	−0.064	1.0000	0.99441	0.000
0.4578	1.01322	−0.068			

least three measurements. The uncertainties of the density were about ± 0.00003 g·cm^{-3}.

Experimental values of density are used to calculate V^E of the mixtures as

$$V^E = \frac{(x_1M_1 + x_2M_2)}{\rho} - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \qquad (1)$$

where M_1 and M_2 are the molecular weights of components 1 and 2; ρ_1 and ρ_2 are the densities; and x_1 an x_2 are the mole fractions of the respective components. The symbol ρ stands for the mixture density.

Table 3. Densities and Molar Excess Volumes (V^E) for the 1,4-Butanediol (1) + 1,2-Propanediol (2) Binary Mixtures at Different Temperatures

x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
		T = 293.15 K			
0.0000	1.03657	0.000	0.5588	1.02552	−0.093
0.0858	1.03490	−0.028	0.6633	1.02319	−0.069
0.1743	1.03319	−0.053	0.7716	1.02085	−0.042
0.2657	1.03146	−0.078	0.8837	1.01855	−0.017
0.3602	1.02977	−0.105	1.0000	1.01637	0.000
0.4578	1.02785	−0.116			
		T = 298.15 K			
0.0000	1.03286	0.000	0.5588	1.02217	−0.104
0.0858	1.03131	−0.034	0.6633	1.01988	−0.080
0.1743	1.02967	−0.062	0.7716	1.01757	−0.053
0.2657	1.02800	−0.088	0.8837	1.01525	−0.023
0.3602	1.02634	−0.116	1.0000	1.01304	0.000
0.4578	1.02448	−0.128			
		T = 303.15 K			
0.0000	1.02915	0.000	0.5588	1.01894	−0.113
0.0858	1.02773	−0.039	0.6633	1.01679	−0.095
0.1743	1.02621	−0.071	0.7716	1.01447	−0.062
0.2657	1.02462	−0.099	0.8837	1.01217	−0.028
0.3602	1.02301	−0.126	1.0000	1.00996	0.000
0.4578	1.02119	−0.137			
		T = 308.15 K			
0.0000	1.02557	0.000	0.5588	1.01576	−0.128
0.0858	1.02425	−0.044	0.6633	1.01364	−0.110
0.1743	1.02283	−0.081	0.7716	1.01133	−0.074
0.2657	1.02131	−0.112	0.8837	1.00903	−0.035
0.3602	1.01974	−0.139	1.0000	1.00675	0.000
0.4578	1.01800	−0.154			
		T = 313.15 K			
0.0000	1.02144	0.000	0.5588	1.01235	−0.141
0.0858	1.02028	−0.049	0.6633	1.01033	−0.124
0.1743	1.01900	−0.090	0.7716	1.00806	−0.084
0.2657	1.01764	−0.126	0.8837	1.00578	−0.041
0.3602	1.01612	−0.151	1.0000	1.00355	0.000
0.4578	1.01443	−0.162			
		T = 318.15 K			
0.0000	1.01759	0.000	0.5588	1.00928	−0.155
0.0858	1.01658	−0.053	0.6633	1.00733	−0.136
0.1743	1.01549	−0.101	0.7716	1.00516	−0.096
0.2657	1.01421	−0.135	0.8837	1.00294	−0.049
0.3602	1.01283	−0.163	1.0000	1.00072	0.000
0.4578	1.01122	−0.173			
		T = 323.15 K			
0.0000	1.01374	0.000	0.5588	1.00613	−0.167
0.0858	1.01291	−0.059	0.6633	1.00430	−0.150
0.1743	1.01197	−0.112	0.7716	1.00218	−0.107
0.2657	1.01078	−0.147	0.8837	1.00003	−0.058
0.3602	1.00947	−0.173	1.0000	0.99780	0.000
0.4578	1.00797	−0.184			
		T = 328.15 K			
0.0000	1.00971	0.000	0.5588	1.00263	−0.180
0.0858	1.00900	−0.064	0.6633	1.00083	−0.160
0.1743	1.00820	−0.123	0.7716	0.99881	−0.120
0.2657	1.00711	−0.161	0.8837	0.99669	−0.069
0.3602	1.00584	−0.185	1.0000	0.99441	0.000
0.4578	1.00439	−0.196			

Results and Discussion

The densities and excess molar volumes at temperatures between (293.15 and 328.15) K for the 1,4-butanediol + ethane-1,2-diol, 1,2-propanediol, and 1,3-propanediol binary mixtures

Table 4. Densities and Molar Excess Volumes (V^E) for the 1,4-Butanediol (1) + Ethane-1,2-diol (2) Binary Mixtures at Different Temperatures

x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x_1	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
		T = 293.15 K			
0.0000	1.11355	0.000	0.5081	1.05191	0.084
0.0711	1.10271	0.015	0.6164	1.04267	0.075
0.1469	1.09213	0.029	0.7337	1.03374	0.053
0.2279	1.08171	0.046	0.8611	1.02496	0.029
0.3147	1.07148	0.065	1.0000	1.01637	0.000
0.4078	1.06152	0.080			
		T = 298.15 K			
0.0000	1.10986	0.000	0.5081	1.04856	0.077
0.0711	1.09909	0.014	0.6164	1.03934	0.068
0.1469	1.08858	0.026	0.7337	1.03040	0.049
0.2279	1.07821	0.042	0.8611	1.02164	0.026
0.3147	1.06802	0.060	1.0000	1.01304	0.000
0.4078	1.05812	0.074			
		T = 303.15 K			
0.0000	1.10682	0.000	0.5081	1.04558	0.071
0.0711	1.09606	0.013	0.6164	1.03635	0.062
0.1469	1.08557	0.023	0.7337	1.02739	0.044
0.2279	1.07522	0.038	0.8611	1.01861	0.022
0.3147	1.06504	0.055	1.0000	1.00996	0.000
0.4078	1.05516	0.067			
		T = 308.15 K			
0.0000	1.10320	0.000	0.5081	1.04233	0.064
0.0711	1.09251	0.012	0.6164	1.03312	0.056
0.1469	1.08210	0.020	0.7337	1.02417	0.039
0.2279	1.07184	0.033	0.8611	1.01541	0.018
0.3147	1.06170	0.049	1.0000	1.00675	0.000
0.4078	1.05185	0.061			
		T = 313.15 K			
0.0000	1.09980	0.000	0.5081	1.03915	0.057
0.0711	1.08915	0.011	0.6164	1.02995	0.049
0.1469	1.07880	0.017	0.7337	1.02099	0.035
0.2279	1.06856	0.029	0.8611	1.01222	0.016
0.3147	1.05850	0.042	1.0000	1.00355	0.000
0.4078	1.04865	0.055			
		T = 318.15 K			
0.0000	1.09623	0.000	0.5081	1.03615	0.050
0.0711	1.08569	0.009	0.6164	1.02701	0.043
0.1469	1.07544	0.015	0.7337	1.01810	0.029
0.2279	1.06532	0.024	0.8611	1.00936	0.013
0.3147	1.05533	0.037	1.0000	1.00072	0.000
0.4078	1.04562	0.046			
		T = 323.15 K			
0.0000	1.09259	0.000	0.5081	1.03305	0.045
0.0711	1.08218	0.007	0.6164	1.02396	0.038
0.1469	1.07203	0.011	0.7337	1.01511	0.026
0.2279	1.06197	0.021	0.8611	1.00640	0.011
0.3147	1.05209	0.032	1.0000	0.99780	0.000
0.4078	1.04243	0.042			
		T = 328.15 K			
0.0000	1.08866	0.000	0.5081	1.02953	0.040
0.0711	1.07833	0.006	0.6164	1.02051	0.032
0.1469	1.06825	0.009	0.7337	1.01166	0.022
0.2279	1.05828	0.017	0.8611	1.00299	0.009
0.3147	1.04846	0.028	1.0000	0.99441	0.000
0.4078	1.03886	0.037			

are presented in Tables 2 to 4, respectively. The experimental excess molar volumes have been correlated by means of the well-known Redlich–Kister[4] polynomial equation

$$V^E/\mathrm{cm^3\cdot mol^{-1}} = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2) \qquad (2)$$

The regression was performed by means of the maximum likelihood method using a program with the possibility to select the number of adjustable parameters and to input estimated standard deviations for the measured properties. The conclusion was to use just three parameters for the Redlich–Kister equation and to find the source of possible errors. Therefore, the input estimated standard deviation for the composition determinations (in more fractions) was set to 0.001 for all mixtures under investigation.

Table 5. Redlich–Kister Parameters, b_i, and Standard Deviations of Molar Excess Volumes, $\sigma(V^E)$, for the Investigated Systems at Different Temperatures

T/K	b_0	b_1	b_2	$\sigma(V^E)$ / cm^3·mol^{-1}
	1,4-Butanediol (1) + 1,3-Propanediol (2)			
293.15	−0.1082	−0.0336	0.0526	0.001
398.15	−0.1278	−0.0349	0.0515	0.001
303.15	−0.1463	−0.0354	0.0454	0.002
308.15	−0.1685	−0.0358	0.0299	0.002
313.15	−0.1939	−0.0387	0.0259	0.001
318.15	−0.2187	−0.0429	0.0078	0.001
323.15	−0.2443	−0.0452	−0.0008	0.002
328.15	−0.2675	−0.0489	−0.0143	0.002
	1,4-Butanediol (1) + 1,2-Propanediol (2)			
293.15	−0.4201	−0.1575	0.3145	0.005
398.15	−0.4661	−0.1577	0.2864	0.005
303.15	−0.5086	−0.1586	0.2434	0.004
308.15	−0.5713	−0.1556	0.2329	0.005
313.15	−0.6208	−0.1553	0.1985	0.003
318.15	−0.6695	−0.1470	0.1546	0.003
323.15	−0.7151	−0.1386	0.0899	0.003
328.15	−0.7643	−0.1353	0.0214	0.002
	1,4-Butanediol (1) + Ethane-1,2-diol (2)			
293.15	0.3303	0.0030	−0.1957	0.002
398.15	0.3035	0.0082	−0.1867	0.002
303.15	0.2774	0.0102	−0.1826	0.002
308.15	0.2509	0.0126	−0.1825	0.002
313.15	0.2229	0.0073	−0.1723	0.002
318.15	0.1937	0.0056	−0.1575	0.002
323.15	0.1726	0.0034	−0.1572	0.002
328.15	0.1528	0.0028	−0.1569	0.002

The Redlich–Kister parameters obtained from the correlation of V^E−composition data are summarized in Table 5 together with the resulting standard deviations in excess molar volume $\sigma(V^E)$. The standard deviation was calculated by

$$\sigma(V^E) = \left[\frac{\Sigma(V^E_{exptl} - V^E_{calcd})^2}{N - n}\right]^{0.5} \qquad (3)$$

where N and n are the number of experimental points and parameters, respectively. It was shown that the experimental data

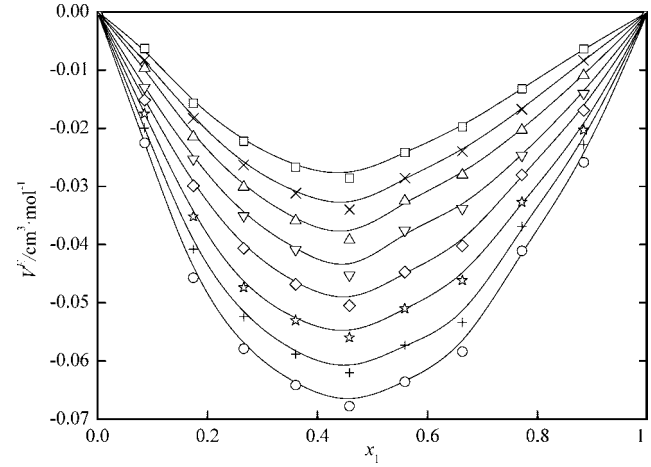

Figure 1. Excess molar volumes (V^E) for the 1,4-butanediol (1) + 1,3-propanediol (2) mixture at different temperatures: □, 293.15 K; ×, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; ☆, 318.15 K; +, 323.15 K; ○, 328.15 K.

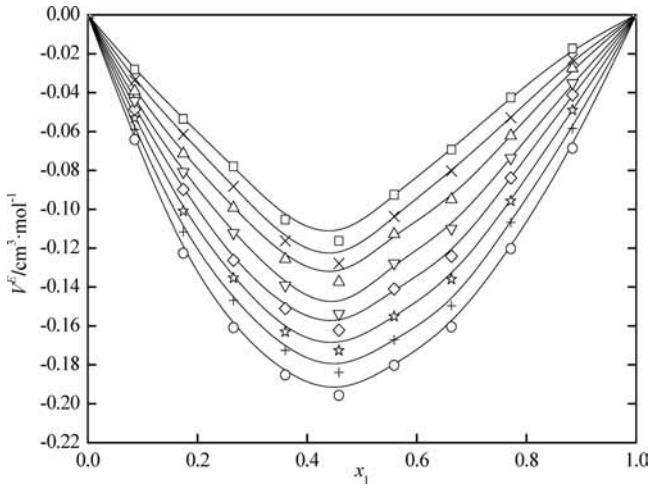

Figure 2. Excess molar volumes (V^E) for the 1,4-butanediol (1) + 1,2-propanediol (2) mixture at different temperatures: □, 293.15 K; ×, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; ☆, 318.15 K; +, 323.15 K; ○, 328.15 K.

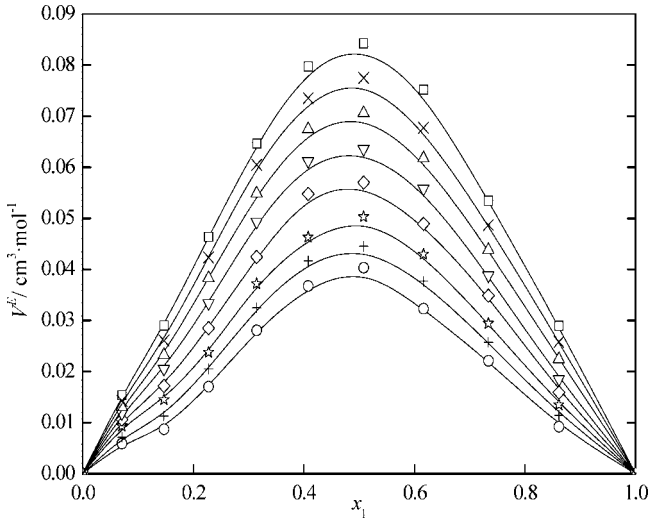

Figure 3. Excess molar volumes (V^E) for the 1,4-butanediol (1) + ethane-1,2-diol (2) mixture at different temperatures: □, 293.15 K; ×, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K; ☆, 318.15 K; +, 323.15 K; ○, 328.15 K.

provided previously were reliable. From the inspection of Table 1, one may conclude that the pure compound densities at different temperatures are in good agreement with the available literature values.

The results presented in Tables 2 to 4 and Figures 1 to 3 indicate that V^E values are negative for (1,4-butanediol + 1,2-propanediol, 1,3-propanediol) and are positive for (1,4-butanediol + ethane-1,2-diol) mixtures over the entire mole fraction range and at all temperatures investigated for each binary system under study.

Conclusions

Densities of the three binary mixtures of glycols (1,4-butanediol + 1,2-propanediol, 1,3-propanediol, and ethane-1,2-diol) have been measured at different temperatures under atmospheric pressure over the whole concentration range. The values of excess molar volumes are calculated by the densities and have been correlated well using the Redlich–Kister polynomial equation.

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