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Excess Molar Volume, Viscosity, and Heat Capacity for the Mixtures of 1,4-Butanediol + Water at Different Temperatures

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Experimental densities, viscosities, and heat capacities were measured over the entire mole fraction range for the binary mixture of 1,4-butanediol + water mixtures over a temperature range. From these data, excess molar volumes, deviations in viscosity, and excess molar heat capacities were computed. The V^E, $\Delta\eta$, and C_p^E were fitted to the Redlich−Kister equation using a multiparametric nonlinear regression analysis. Estimated coefficients and standard error values for the mixing quantities are presented. V^E is negative for 1,4-butanediol + water mixtures at all temperatures and over the entire compositions. $\Delta\eta$ vs x_1 shows sinusoidal shape. The values of C_p^E are positive in the whole range of mole fraction and increase with raising temperature at constant x_1. The C_p^E curve has large maximum values located in the $x_1 = 0.23$.

Introduction

Glycols are generally accepted as compounds having two hydroxyl groups attached to separate carbon atoms in an aliphatic carbon chain. Glycols find widespread application in automotive, aviation, explosives, textile, surface coatings, food, cosmetic, pharmaceutical, tobacco, petroleum, and other industries. Examples of these glycols are ethylene glycol, propylene glycol, butylenes glycols (1,2-, 1,3-, and 1,4-butanediol). Up to now, we have investigated viscosities, excess molar volumes, and heat capacities for binary mixtures of ethylene glycol + water[1] and propylene glycol + water.[2] From the point of the use and manufacture, the physical properties of diol + water mixtures are, therefore, extremely important. The 1,4-butanediol is an important starting material for many types of polyesters. The density and viscosity data of binary mixture are important from the point of the use and manufacture. The excess molar volume, deviation of viscosity, and excess molar heat capacity are significant for the design of new processes and the study of molecular interactions in binary liquid systems. In the literature, Czechowski et al.[3] investigated the densities about a number of diols + water, including 1,4-butanediol, at 293.15 K, 303.15 K, and 313.15 K. Sun et al.[4] determined densities and viscosities of pure 1,4-butanediol between (293 to 463) K. Their density measurements were reproducible to ±0.1%, and the absolute accuracy was estimated to be within ±0.25%. Viscosities were estimated accuracy of ±1.0%. Grineva et al.[5] measured the densities of 1,4-butanediol and its solution with 10 mol % water and compared their results with literature detailed. Lech et al.[6] reported the viscosities of pure 1,4-butanediol at different temperatures. George et al.[7] measured the densities and viscosities of the binary mixtures of 1,4-butanediol + water at (298.15 to 338.15) K, and Hawrylak et al.[8] measured viscosities for this binary mixture at (298.15 to 318.15) K. Riddick et al.[9] gave viscosities at 293.15 K and 298.2 K. The data of heat capacity are few in the literature. Nistratov et al.[10] and Van Miltenburg et al.[11] presented heat capacities of pure substance at 298.13 K. In this paper, the experimental data on ρ, η, and C_p are presented over the temperature range from 293.15 K to 353.15 K and the entire mole fraction range of the mixture. The present values of density, viscosity, and heat capacity were compared with literature values. From density, ρ, viscosity, η, and heat capacity, C_p, measurements, excess molar volume V^E, viscosity deviations, $\Delta\eta$, and excess molar heat capacities, C_p^E, have been calculated. The Redlich−Kister equation was used to correlate and fit the experimental values.

Experimental Section

Materials. 1,4-Butanediol used is of analytical grade (better than 99.5%) and obtained from Tianjin reagent company and dried with anhydrous sodium sulfate. The purity of the liquid was further ascertained by measuring its densities and viscosities at 298.15 K and atmospheric pressure and compared with its corresponding literature values, as shown in Table 1. Binary mixtures were prepared by mass on an analytical BP 210 S balance with ±0.01-mg accuracy. The possible error in the mole fraction is estimated to be around ±0.0001.

Density Measurements. The densities, ρ, of the pure liquids and their binary mixtures were measured by a vibrating tube digital densimeter (Density/Specific Gravity Meter DA 505) with precision of 10^{-5} g·cm^{-3}. The instrument has a built-in thermostat for maintaining the desired temperatures in the range (273.15 to 393.15) K. The uncertainty in the temperature during the measurements is ±0.01 K. The instrument was calibrated with dry air and both deionized double-distilled water. The uncertainty in density measurements was $\pm 5 \times 10^{-5}$ g·cm^{-3}.

Viscosity Measurements. Viscosity was measured using an Ubbelohde suspended-level viscometer, calibrated with double-distilled water. An electronic digital stopwatch with a readability of ±0.01 s was used for flow time measurements. Experiments were repeated a minimum of four times at each temperature for all compositions and the results were averaged. The viscosity, η, of the liquid was

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Table 1. Comparison of Measured Densities, ρ, Viscosities, η, and Heat Capacities, C_p, of the 1,4-Butanediol with Literature Values

	ρ/g·cm^{-3}		η/mPa·s		C_P/J·mol^{-1}·K^{-1}	
T/K	exp	lit	exp	lit	exp	lit
293.15	1.01576	1.01622^{3} 1.01573^{5}	90.327	84.26^{6}(293.4 K) 89.24^{9}		
298.15	1.01268	1.0127^{5} 1.01257^{7}	71.149	71.13^{4}(298.5 K) 67.03^{6} 72.618^{7} 71 × 10^{8} 71.5^{9}	200.9	200.1^{11} 178.2^{12}
303.15	1.00954	1.01011^{3} 1.0114^{4} (303.3 K) 1.0096^{5}	55.983	54.93^{4} (303.9 K) 53.21^{6} (302.8 K) 50.53^{8}		
308.15	1.00643	1.00640^{7}	44.435	43.14^{6} (307.5 K) 44.871^{7} 45.24^{8}		
313.15	1.00337	1.00411^{3} 1.0034^{5}	35.741	35.61^{6} (312.2 K) 37.03^{8}		
318.15	1.00045	1.00076^{7}	29.114	28.56^{4} (318.5 K) 29.071^{7} 30.12^{8}		
323.15	0.99714	0.9990^{4} (322.1K) 0.9972^{5}	23.630	24.19^{6} (321.6 K)		
328.15	0.99402	0.98414^{7}	19.679	19.480^{7}		
333.15	0.99093	0.9910^{5}	16.171	16.09^{4} (333.4 K)		
338.15	0.98793	0.98793^{7}	13.649	13.487^{7}		
343.15	0.98481	0.9864^{4} (343.0K) 0.9848^{5}	11.449			
348.15	0.98170		9.778	9.787^{4} (348.4 K)		
353.15	0.97859		8.280			
363.15	0.97271	0.9733^{4} (363.6K)	6.213	6.243^{4} (363.2 K)		

then calculated from the following relationship

$$\nu = \frac{\eta}{\rho} = k(t - \theta) \tag{1}$$

where t is the flow time, ν is the kinetic viscosity, and k and θ are the viscometer constant and the Hagenbach correction factor, respectively.

The overall uncertainty of the viscosity measurements is dependent on the equilibrium stability of the viscometer, the time of flow, and the change of concentration, which is in the order of 1×10^{-2}, 1×10^{-2}, and 1×10^{-4}, respectively; viscosity values are uncertain to within the range ±0.003 mPa·s. All measurements were carried out in a well-stirred water bath with temperature controlled to within ±0.1 K.

Heat Capacity Measurements. The differential scanning calorimeter (NETZSCH Producer, mode DSC-204, Phoeuix, Germany) used for this study consists of a differential scanning calorimeter (DSC) and a thermal analysis controller from TA Instruments. The DSC operating range was from (−113.15 to 973.15) K. Both the temperature and the heat flow associated with materials can be easily and rapidly measured with the system. The DSC features temperature reproducibility within 0.1 K. The purge gas was nitrogen with a flow rate of 70 mL·min^{-1}. By use of the sample-encapsulating press, the liquid sample was prepared within a hermetic sample pan. Hermetically sealed thermal contact between sample, pan, and constant disk reduced the thermal gradient in the sample and an airtight seal that can resist higher internal pressures up to 0.3 MPa. These hermetic pans were used for volatile liquids, subliming materials, and those in a self-generated atmosphere. The internal volume of the hermetic pan was approximately 10 mm^3. The sample mass is in the range of (8 to 15) mg.

To obtain accurate results, the calibration must be checked periodically. The DSC calibrations consist of that for the baseline slope, the cell constant, and temperature calibrations. The baseline calibration involves heating an empty cell through the entire range of temperature expected in subsequent experiments. Both the cell constant and the temperature calibration are obtained from the run in which a calibration material (e.g., indium) is heated to its melting point. The enthalpy of fusion and the melting point of indium are utilized to obtain the cell constant and the temperature calibrations.

During the run, a temperature program was provided to cool the cell from ambient temperature to 283.15 K by liquid nitrogen and hold for 10 min. And then the cell was heated to 363.15 K at the heating rate 2 K·min^{-1}. Then the equipment was maintained at constant temperature for 10 min. For each sample, the average number of runs is four. On the basis of comparison with literature values for water,[12] the average error of C_p measurements was estimated to be less than ±1%. The C_p values were reproducible within ±0.02 J·g^{-1}·K^{-1}. The apparatus and the experimental procedure are the same as those described by Yang et al.[1]

The experimental results of density, viscosity, and heat capacity of the pure 1,4-butanediol and comparison with those from the literatures were listed in Table 1. For the densities, good agreement was found between the measured and literature values.[3,5,7] As shown in Table 1, there is an appreciable difference for the viscosity data among Lech,[6] Gorge,[7] Hawrylak,[8] and Riddick.[9] The viscosity values of 1,4-butanediol obtained in this study are in good agreement with those of Sun et al.;[7] the average percentage deviation is 1.1%.

Results and Discussion

The experimental densities, viscosities, and heat capacities for binary mixtures of 1,4-butanediol + water across the composition range and at (293.15 to 353.15) K are listed in Tables 2.

Table 2. Densities, ρ, Viscosities, η, Heat Capacities, C_p, Excess Molar Volumes, V^E, Viscosities Deviations, $\Delta\eta$, and Excess Molar Heat Capacities, C_p^E, for the Binary Mixtures of 1,4-Butanediol (1) + Water (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	C_p/J·mol^{-1}·K^{-1}	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	C_p^E/J·mol^{-1}·K^{-1}
293.15 K						
0.0000	0.99821	1.002	75.2			
0.0218	1.00144	1.792	88.5	−0.029	−1.158	10.6
0.0478	1.00597	2.650	97.3	−0.091	−2.622	16.2
0.0789	1.01098	3.889	103.9	−0.177	−4.161	19.0
0.1175	1.01571	5.788	111.8	−0.274	−5.709	22.1
0.1665	1.01986	8.755	120.1	−0.378	−7.119	24.3
0.2305	1.02286	11.860	129.0	−0.476	−9.731	25.4
0.3179	1.02432	19.072		−0.549	−10.326	
0.4441	1.02418	31.722	138.7	−0.578	−8.949	24.3
0.6426	1.02157	56.690	169.3	−0.471	−1.712	15.1
0.7917	1.01904	73.609		−0.303	1.888	
0.8663	1.01774	80.526		−0.196	2.142	
1.0000	1.01576	90.327	198.2			
303.15 K						
0.0000	0.99565	0.797	75.3			
0.0218	0.99853	1.418	89.3	−0.030	−0.582	11.2
0.0478	1.0024	1.957	97.7	−0.086	−1.478	16.3
0.0789	1.00662	2.756	104.8	−0.161	−2.396	19.3
0.1175	1.0106	3.954	112.7	−0.247	−3.328	22.4
0.1665	1.01411	5.775	121.3	−0.341	−4.211	24.6
0.2305	1.01662	7.633	130.4	−0.430	−5.885	25.6
0.3179	1.01788	12.089		−0.502	−6.252	
0.4441	1.01765	19.656	140.8	−0.533	−5.649	24.7
0.6426	1.01515	34.958	173.3	−0.441	−1.302	15.5
0.7917	1.01277	45.497		−0.289	1.009	
0.8663	1.01148	49.819		−0.186	1.214	
1.0000	1.00954	55.983	203.6			
313.15 K						
0.0000	0.99222	0.653	75.2			
0.0218	0.99486	1.176	88.8	−0.030	−0.241	10.6
0.0478	0.99821	1.522	98.1	−0.082	−0.807	16.5
0.0789	1.00179	2.053	105.5	−0.149	−1.368	19.7
0.1175	1.00516	2.835	113.8	−0.225	−1.941	22.8
0.1665	1.00813	4.008	122.4	−0.310	−2.487	24.9
0.2305	1.01028	5.198	131.8	−0.392	−3.542	25.7
0.3179	1.01136	8.018		−0.461	−3.789	
0.4441	1.01109	12.775	142.7	−0.495	−3.460	25.0
0.6426	1.00876	22.425	177.1	−0.418	−0.776	16.0
0.7917	1.0064	29.654		−0.271	1.222	
0.8663	1.00515	32.533		−0.173	1.483	
1.0000	1.00331	35.741	208.8			
323.15 K						
0.0000	0.98805	0.547	75.2			
0.0218	0.99045	0.981	88.9	−0.030	−0.069	10.6
0.0478	0.9934	1.222	98.5	−0.077	−0.428	16.6
0.0789	0.99645	1.573	106.2	−0.137	−0.795	20.0
0.1175	0.99934	2.124	114.8	−0.205	−1.135	23.2
0.1665	1.00187	2.909	123.5	−0.280	−1.481	25.2
0.2305	1.00372	3.683	133.1	−0.355	−2.184	25.9
0.3179	1.00468	5.573		−0.421	−2.312	
0.4441	1.00442	8.706	144.6	−0.456	−2.092	25.3
0.6426	1.00232	14.600	180.7	−0.392	−0.780	16.3
0.7917	1	19.293		−0.250	0.471	
0.8663	0.99884	21.115		−0.159	0.571	
1.0000	0.99714	23.630	214.0			
333.15 K						
0.0000	0.98321	0.467	75.2			
0.0218	0.9854	0.871	89.2	−0.029	0.061	10.7
0.0478	0.98796	1.042	99.1	−0.071	−0.176	16.8
0.0789	0.99059	1.281	107.3	−0.123	−0.425	20.5
0.1175	0.99309	1.652	116.0	−0.184	−0.660	23.6
0.1665	0.99527	2.191	125.0	−0.251	−0.890	25.4
0.2305	0.99689	2.705	135.1	−0.318	−1.382	26.1
0.3179	0.99778	4.017		−0.381	−1.442	
0.4441	0.99758	6.143	147.3	−0.415	−1.298	25.6
0.6426	0.99575	10.120	185.7	−0.365	−0.438	16.6
0.7917	0.9936	13.040		−0.233	0.140	
0.8663	0.99248	14.294		−0.146	0.223	
1.0000	0.99093	16.171	221.3			
343.15 K						
0.0000	0.97779	0.405	75.3			
0.0218	0.97961	0.783	89.1	−0.023	0.137	10.5
0.0478	0.98188	0.905	99.6	−0.060	−0.028	17.0

Table 2 (Continued)

x_1	ρ/g·cm^{-3}	η/mPa·s	C_p/J·mol^{-1}·K^{-1}	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	C_p^E/J·mol^{-1}·K^{-1}
			343.15 K			
0.0789	0.98416	1.081	108.3	−0.105	−0.195	20.9
0.1175	0.98637	1.338	117.2	−0.158	−0.365	23.9
0.1665	0.98829	1.719	126.5	−0.217	−0.525	25.7
0.2305	0.98974	2.055	137.0	−0.276	−0.895	26.4
0.3179	0.9906	2.991		−0.332	−0.925	
0.4441	0.99049	4.471	149.9	−0.364	−0.839	25.9
0.6426	0.98897	7.211	190.8	−0.321	−0.291	17.0
0.7917	0.98721	9.223		−0.212	0.074	
0.8663	0.98617	10.106		−0.130	0.134	
1.0000	0.98481	11.449	228.6			
			353.15 K			
0.0000	0.97183	0.356	75.4			
0.0218	0.97352	0.723	89.3	−0.021	0.194	10.5
0.0478	0.97553	0.809	100.2	−0.053	0.075	17.2
0.0789	0.97747	0.940	109.3	−0.090	−0.041	21.3
0.1175	0.9793	1.108	118.5	−0.133	−0.179	24.2
0.1665	0.98105	1.381	128.1	−0.183	−0.294	25.9
0.2305	0.98241	1.804	139.2	−0.236	−0.379	26.7
0.3179	0.9833	2.283		−0.287	−0.593	
0.4441	0.98333	3.358	152.9	−0.317	−0.517	26.3
0.6426	0.98214	5.276	196.4	−0.283	−0.172	17.3
0.7917	0.98068	6.743		−0.190	0.114	
0.8663	0.97977	7.321		−0.116	0.5523	
1.0000	0.97859	8.280	236.9			

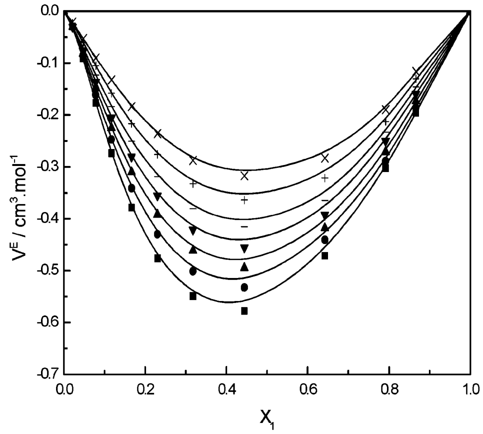

Figure 1. Excess volume variation with mol fraction for 1,4-butanediol (1) + water (2): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; −, 333.15 K; +, 343.15 K; ×, 353.15 K; solid curves, calculated with Redlich-Kister equations; symbols, experimental values.

The excess molar volume, V^E, was calculated from density measurement according to the following equation[13−15]

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

where ρ is the density of the mixture and x_1, ρ_1, M_1, x_2, ρ_2, and M_2 are the mole fraction, densities, and molecular weights of pure components 1 and 2, respectively. The results of V^E are given in Table 2 and displayed in Figure 1.

The viscosity derivations all were calculated from the following relation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

Where η is the viscosity of mixtures and η_1 and η_2 are the viscosities of components 1 and 2, respectively. The viscosity deviation of the system at different temperature is presented in Table 2.

The excess molar heat capacity C_p^E are calculated as following[16,17]

$$C_p^E = C_p - (x_1C_{p,1} + C_{p,2}) \tag{4}$$

where C_p is the heat capacity of mixtures and $C_{p,i}$ is the molar heat capacity of the pure component i. The obtained excess molar heat capacities, C_p^E, from eq 4 are also listed in Table 2 and shown in Figure 3.

The well-known Redlich−Kister polynomial equation,[18−20] which has the following form

$$V^E = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2)^i \tag{5}$$

$$\Delta\eta = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2)^i \tag{6}$$

$$C_p^E = x_1x_2\sum_{i=0}^{n} b_i(x_1 - x_2)^i \tag{7}$$

was used to correlate the experimental data. The coefficients b_i were determined by a multiple regression analysis based on the least-squares method and were given along with the standard deviations between the experimental and fitted values of the corresponding function in Table 3.

In each case, the optimum number of coefficients b_i was determined from an examination of the variation of the standard derivation

$$\sigma(Y) = [\sum (Y_{cal} - Y_{exp})^2/(n - m)]^{1/2} \tag{8}$$

where n is the total number of experimental values and m is the number of parameters.

As shown in Figure 1, V^E is negative for 1,4-butanediol + water mixtures at all temperatures and over the entire range of compositions. Excess molar volumes decrease with rising temperature from 293.15 K to353.15 K. The excess molar volumes, V^E, appear to be in good agreement with Cezchowski et al.[3] and George et al.,[7] and the curve shape of V^E to x_1 for this study concur with the literature.[3,7] The present of large negative V^E results can be interpreted

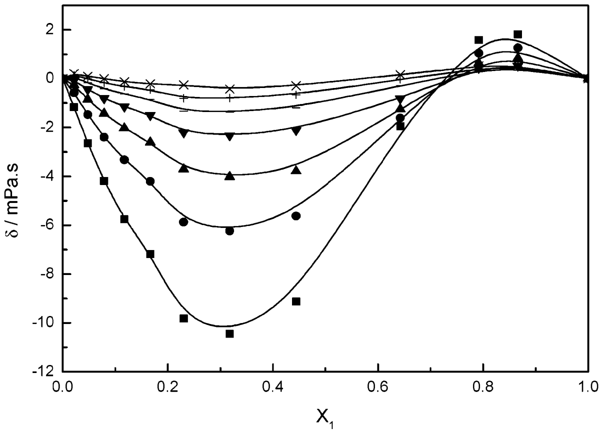

Figure 2. Viscosity deviation with mol fraction for 1,4-butanediol (1) + water (2): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; −, 333.15 K; +, 343.15 K; ×, 353.15 K; solid curves, calculated with Redlich-Kister equations; symbols, experimental values.

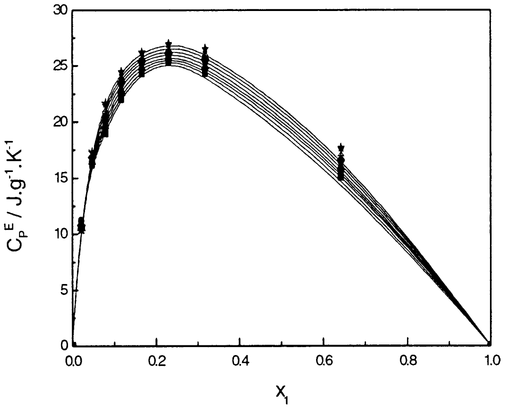

Figure 3. Excess molar heat capacity C_p^E of 1,4-butanediol (1) + water (2): ■, 293.15 K; ●, 303.15 K; ▲, 313.15 K; ▼, 323.15 K; −, 333.15 K; +, 343.15 K; ×, 353.15 K; solid curves, calculated with Redlich−Kister equations; symbols, experimental values.

qualitatively by taking into account the several expansions and contraction process simultaneously. The following

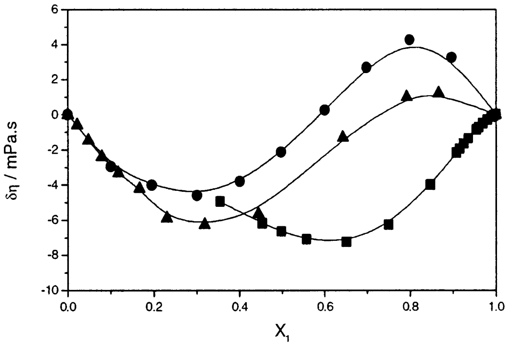

Figure 4. Comparison of experimental values from literatures for the viscosity deviation: ■, George[7] (298.15 K); ●, Hawrylak[8] (303.15 K); ▲, this study (303.15 K).

effects were considered (1) expansion due to disruption of hydrogen bond in water and 1,4-butanediol, (2) contraction due to free volume difference of unlike molecules, and (3) contraction due to mutual association through hydrogen bond formation between water and 1,4-butanediol. The negative V^E value can be explained by the three mentioned effects.

The dependence of $\Delta\eta$ on mole fraction x_1 is displayed in Figure 2. The viscosity derivations are negative at lower mole fractions and positive at higher mole fractions. The absolute values of $\Delta\eta$ decrease with rising temperature from 293.15 K to 353.15 K. For the viscosities of the 1,4-butanediol + water mixture, literature values show quite inconsistent results. For the purpose of comparison, the dependence of $\Delta\eta$ to mole fraction for our results along with the literature values is shown in Figure 4. Though the viscosity deviations have different values, there are similar sinusoidal shape curves of $\Delta\eta$ vs x_1 for this study and Hawrylak et al.[8] It is different from George et al.[7] whose results are U-shaped curves.

The plot of C_p^E vs x_1 is presented in Figure 3. The values of C_p^E are positive in the whole range of x. The excess molar heat capacities increase as the temperature increases at constant x_1. The C_p^E curve has large maximum values located in the $x_1 = 0.23$.

Table 3. Coefficients (b_i) of the Redlich−Kister Equation and Standard Deviations (σ) for V^E (cm^3·mol^{-1}), $\Delta\eta$ (mPa·s), and C_p^E (J·mol^{-1}·K^{-1}) of 1,4-Butanediol (1) + Water (2)

T/K		b_0	b_1	b_2	b_3	b_4	s
293.15	V^E/cm^3·mol^{-1}	−2.119	0.838	−1.921	−0.260	3.482	0.013
	$\Delta\eta$/mPa·s	−46.63	4.78	63.46	56.32		0.781
	C_p^E/ J·mol^{-1}·K^{-1}	192.0	−34.1	−1054	−1375		3.21
303.15	V^E/cm^3·mol^{-1}	−1.984	0.663	−1.483	−0.177	−2.760	0.010
	$\Delta\eta$/mPa·s	−18.24	36.99	14.28	−13.07		0.162
	C_p^E/ J·mol^{-1}·K^{-1}	207.6	−32.0	−1183	−1519		3.82
313.15	V^E/cm^3·mol^{-1}	−1.877	0.514	−1.050	−0.041	2.121	0.007
	$\Delta\eta$/mPa·s	−12.63	24.66	12.08	−11.73		0.166
	C_p^E/ J·mol^{-1}·K^{-1}	188.7	−30.1	−991.2	−1322.		2.91
323.15	V^E/cm^3·mol^{-1}	−1.753	0.398	−0.733	0.069	1.659	0.006
	$\Delta\eta$/mPa·s	−7.73	16.08	7.99	−10.63		0.167
	C_p^E/ J·mol^{-1}·K^{-1}	186.2	−29.2	−955.9	−1290.		2.75
333.15	V^E/cm^3·mol^{-1}	−1.622	0.266	−0.512	0.194	1.337	0.004
	$\Delta\eta$/mPa·s	−4.15	12.88	5.35	−12.93		0.184
	C_p^E/ J·mol^{-1}·K^{-1}	188.1	−28.2	−963.3	−1306		2.72
343.15	V^E/cm^3·mol^{-1}	−1.415	0.174	−0.588	0.219	1.407	0.004
	$\Delta\eta$/mPa·s	−2.36	10.81	5.34	−12.66		0.195
	C_p^E/ J·mol^{-1}·K^{-1}	179.5	−27.0	−865.9	−1209		2.18
353.15	V^E/cm^3·mol^{-1}	−1.253	0.098	−0.320	0.206	0.943	0.003
	$\Delta\eta$/mPa·s	−1.02	9.35	5.47	−12.17		0.214
	C_p^E/ J·mol^{-1}·K^{-1}	177.8	−26.5	−856.9	−1182		2.03

Conclusion

New experimental values of density and viscosity for the system of 1,4-butanediol + water at different temperatures and compositions are measured. In addition, the heat capacities are measured at the same temperature range with a DSC. The excess molar volume and viscosity deviations as well as the excess molar heat capacity were correlated using the Redlich−Kister polynomial equation. The excess molar volumes V^E were negative for 1,4-butanediol + water mixtures at all temperatures and over the entire range of compositions and increase in absolute value with rising temperature from 293.15 K to 353.15 K. The viscosity deviation vs x_1 shows sinusoidal shapes. The values of C_p^E are positive in the whole range of x and increase as the temperature increases at constant x_1. The C_p^E curve has large maximum values located in the $x_1 = 0.23$.

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