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Densities and Viscosities of Four Butanediols between 293 and 463 K

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The densities of 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, and 2,3-butanediol were measured at atmospheric pressure and at temperatures ranging from 293 to 463 K with an accuracy of ±0.2%. Viscosities of the same butanediols were measured between 293 and 423 K with an estimated accuracy of ±1%. The low-temperature results for both density and viscosity were found to be in good agreement with data reported in the literature.

1. Introduction

In recent years, considerable attention has been paid to the design of absorption heat pumps and refrigeration equipment using a variety of working fluids. These working fluids include aqueous solutions of lithium bromide and mixtures of ammonia and butanediols (*1*). Since accurate values of thermophysical properties are indispensable for reliable design, we have measured the densities, viscosities, and thermal conductivities of several systems of interest in absorption refrigeration over a wide range of temperatures (*2–4*). The thermophysical properties of concentrated lithium bromide solutions were reported in our previous publications (*3*, *4*). The densities and viscosities of 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, and 2,3-butanediol are reported in this work. Literature data on densities of butanediols are limited to ambient conditions, whereas viscosity data for these liquids were found to be virtually nonexistent. The purpose of this work was, therefore, to measure new data and to extend the available data on butanediols to higher temperatures.

The study of the isomeric butanediols is also important from a fundamental point of view because it allows us to examine in detail the influence of the spacing of the OH groups on the thermophysical properties of the butanediols.

2. Experimental Section

2.1. ***Materials.*** The liquid samples used in the present work were obtained from Aldrich Chemical Co., Inc., and were used without further purification. According to the supplier, the purities of the materials were 98% for 1,2-butanediol, better than 99% for 1,3- and 1,4-butanediols, and 99% for 2,3-butanediol. In the case of 1,3- and 2,3-butanediols, which are hygroscopic, the water impurity was as low as <0.005%.

2.2. ***Density Measurements.*** Densities were measured using a high-pressure pycnometer designed for pressures up to 10 MPa and temperatures up to 473 K. The principle of operation of this pycnometer and its complete description have been given in a previous paper (*2*). Only a brief outline and a few remarks about the measurements are given below.

The high-pressure pycnometer consisted of a stainless steel cylinder and an isolation valve connected via steel capillary tubing to a high-pressure system. The pycnometer was placed into a fitted aluminum vessel with thick walls which, in turn, was immersed in a constant-temperature bath containing silicone oil. This arrangement provided sufficient thermal contact, while avoiding the wetting of the outside surface of the pycnometer by the silicone oil. The pycnometer was filled with the fluid to be measured and was weighed before and after filling. The density was readily calculated from the volume of the pycnometer (which was previously calibrated up to 423 K with pure liquid mercury) and the mass of the fluid in the pycnometer. The temperatures were measured by a thermocouple (which was calibrated against a platinum resistance thermometer) placed inside a thermowell with an accuracy estimated to be ±0.1 K up to 473 K.

A series of precautions were taken to eliminate dissolved gases in the experiment. First, the pycnometer was loaded with the test sample by means of a vacuum technique to minimize the amount of gases. Second, pure nitrogen gas was used for rinsing the pycnometer in order to prevent contamination by water vapor in the atmosphere. Finally, the liquid sample was degassed by using an alternating pressure cycle. This procedure was repeated about 10 times until the pressure increase attained a large and constant value.

2.3. ***Viscosity Measurement.*** Viscosities were measured using a commercial capillary viscometer of the Cannon–Ubbelohde type operating in the temperature range from 293 to 423 K. The kinematic viscosity (ν) is given by

$$\nu = \mu/\rho = C_1 t - C_2/t \qquad (1)$$

where μ is the absolute viscosity, ρ is the density, C_1 and C_2 are the viscometric constants, and t is the efflux time. The term C_2/t in eq 1 is the kinetic energy correction, and may usually be neglected if a properly sized viscometer is used ($C_1 > 0.05$). In this case, the viscosity data can be readily obtained from the measurements of the efflux times. The coefficients C_1 for several viscometers were provided by the manufacturer (International Research Glassware) and checked at room temperature by measurement of the viscosity of pure water. During the measurements, the viscometers were immersed in a silicone oil bath, controlled by a Haake temperature controller to within ±0.1 K. The temperature was measured by means of a calibrated platinum resistance thermometer with an estimated accuracy of ±0.1 K.

3. Results and Discussion

3.1. ***Density.*** The densities of the butanediols were measured at atmospheric pressure and at temperatures from 303 to 463 K in 20 K increments. The experimental data are presented in Table I. The reproducibility of the density data was found to be ±0.1%, and the absolute accuracy was estimated to be ±0.25%. The density data for each liquid were smoothed by fitting the data to several empirical or semiempirical equations. The best equation for representing the experimental data was found to be a polynomial function in temperature given by

$$\rho/(\text{kg m}^{-3}) = A_0 + A_1(T/\text{K}) + A_2(T/\text{K})^2 + A_3(T/\text{K})^3 \qquad (2)$$

where the values of A_0 to A_3 are given in Table II. The average absolute deviations (AAD) for the best fit were found to be 0.02% for 1,4-butanediol, 0.03% for 1,3-butanediol, and 0.04% for 1,2- and 2,3-butanediols. The maximum absolute deviations (MAD) of the results from the smooth curves are mostly in the range 0.05–0.08%, which is less than the ex-

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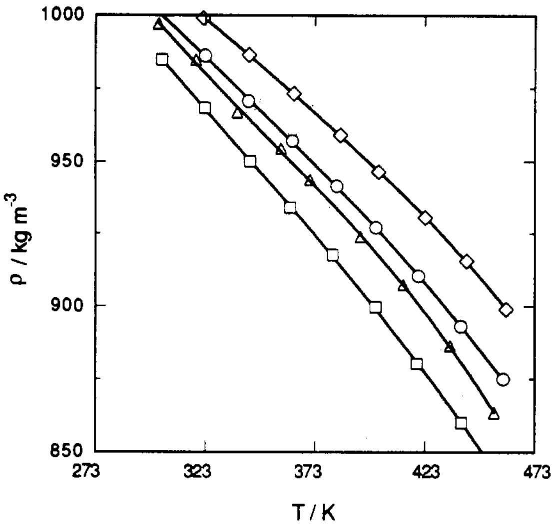

Figure 1. Experimental and correlated (eq 2) densities of butanediols as a function of temperature: △, 1,2-butanediol; ○, 1,3-butanediol; ◇, 1,4-butanediol; □, 2,3-butanediol.

Table I. Experimental Densities of Butanediols

this work		lit.	
T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
	1,2-Butanediol		
301.8	997.1	ref 5	
318.8	984.8	293.2	1003.47
337.7	970.0	303.2	995.44
357.7	954.7	313.2	987.87
370.9	943.7	ref 6	
393.9	923.9	293.2	1002.4
413.5	907.4	298.2	998.7
434.6	886.5		
454.7	863.4		
	1,3-Butanediol		
302.4	1000.6	ref 5	
323.1	986.1	293.2	1005.79
342.9	970.8	303.2	999.04
363.0	957.2	313.2	992.39
383.2	941.5	ref 6	
400.9	927.0	293.2	1005.3
420.3	910.4		
439.6	893.1		
458.9	874.8		
	1,4-Butanediol		
303.3	1011.4	ref 5	
322.1	999.0	293.2	1016.22
343.0	986.4	303.2	1010.11
363.6	973.3	313.2	1004.15
384.8	959.3	ref 6	
402.2	946.5	293.2	1017
423.3	930.5	298.2	1015
442.3	915.6		
460.3	899.0		
	2,3-Butanediol		
303.3	984.9	ref 6	
322.9	968.5	298.2	987.1
343.6	950.2		
361.7	934.0		
381.2	917.7		
400.6	899.8		
419.5	880.2		
439.7	860.0		
452.2	847.1		

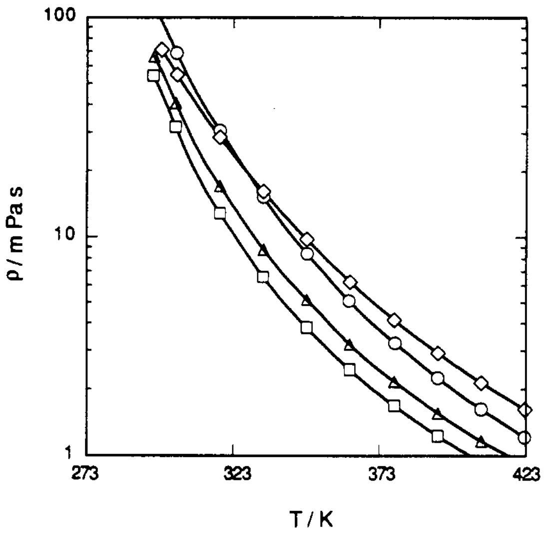

Figure 2. Experimental and correlated (eq 3) viscosities of butanediols as a function of temperature: △, 1,2-butanediol; ○, 1,3-butanediol; ◇, 1,4-butanediol; □, 2,3-butanediol.

perimental uncertainty of the measurements. It should be added that eq 2 is useful for interpolating the measured data sets in temperature; extrapolation in temperature is not recommended.

The density data for the butanediols at 1 bar were found to be in very good agreement with the data of Czechowski et al. (*5*) at temperatures of 293, 303, and 313 K and with those of TRC table (*6*) at ambient temperature. All the literature data are also given in Table I. No data were available at high temperatures.

3.2. ***Viscosity.*** The experimental kinematic viscosities of the butanediols were measured at ambient pressure and temperatures from 293 to 423 K in 15 K increments. At least three measurements were made at each temperature, and the average values are reported in Table III. The reproducibility of the results was better than 1%, and the accuracy of the data was estimated to be ±1%. The viscosity data of each butanediol could be described by a three-parameter equation of the type

$$\ln(\mu/(\mathrm{mPa\ s})) = A + B/((T/\mathrm{K}) - C) \tag{3}$$

where μ is the viscosity. The values of the coefficients A, B, and C obtained by a least-squares analysis are given in Table IV. The absolute average deviations (AAD) were 0.4% for 1,4-butanediol, 0.5% for 2,3-butanediol, 0.6% for 1,2-butanediol, and 0.9% for 1,3-butanediol. The maximum absolute deviations (MAD) for the butanediols ranged from 1.1% to 1.8%.

Agreement of the viscosity data with data from the literature compiled by Riddick et al. (*7*) was very good at room temperature (see Table I). No data were available for comparison at high temperatures.

3.3. ***Discussion.*** The method proposed by Hankinson et al. (*8*) can be used to predict the volumetric properties as a function of temperature for the butanediols. The density is given by

$$1/\rho = V_c\sum_{i=0}^{4}a_i(1 - T_r)^{i/3}[1 - (\omega/(T_r - 1.00001))\sum_{j=0}^{3}b_jT_r^{\,j}] \tag{4}$$

Table II. Coefficients of Equation 2

substance	A_0	A_1	$A_2 \times 10^3$	$A_3 \times 10^6$	AAD/%	MAD/%
1,2-butanediol	1519.054	−3.435 384	8.163 260	−8.307 652	0.04	0.08
1,3-butanediol	1323.893	−1.787 522	3.560 611	−3.919 230	0.03	0.08
1,4-butanediol	1396.844	−2.432 001	5.549 931	−5.682 449	0.02	0.05
2,3-butanediol	1375.06	−2.102 106	3.962 518	−4.195 231	0.04	0.07

Table III. Experimental Viscosities of Butanediols

this work		lit.	
T/K	μ/(mPa s)	T/K	μ/(mPa s)
	1,2-Butanediol		
296.0	66.47		
303.4	40.72		
318.5	17.04		
333.5	8.782		
348.4	5.155		
363.0	3.204		
378.3	2.165		
393.2	1.555		
408.0	1.169		
422.8	0.914		
	1,3-Butanediol		
295.2	116.4	ref 7	
303.7	68.79	293.2	130.3
318.5	30.60	298.2	98.3
333.5	15.16		
348.5	8.397		
362.9	5.077		
378.6	3.243		
393.2	2.247		
408.0	1.620		
422.8	1.212		
	1,4-Butanediol		
298.5	71.13	ref 7	
303.9	54.93	293.2	89.24
318.5	28.56	298.2	71.5
333.4	16.09		
348.4	9.787		
363.2	6.243		
378.3	4.149		
393.2	2.923		
408.0	2.137		
422.9	1.615		
	2,3-Butanediol		
295.6	54.51	ref 7	
303.3	31.87	293.2	107.9
318.5	12.83		
333.4	6.576		
348.4	3.832		
363.2	2.453		
378.3	1.683		
393.2	1.229		
408.1	0.940		
422.9	0.746		

Table IV. Coefficients of Equation 3

substance	A	B	C	AAD/ %	MAD/ %
1,2-butanediol	−3.875 713	902.3514	184.274	0.6	1.8
1,3-butanediol	−4.858 379	1351.236	154.9497	0.9	1.7
1,4-butanediol	−5.273 284	1797.808	110.0998	0.4	1.1
2,3-butanediol	−3.571 396	735.4572	198.5396	0.5	1.4

where V_c is the critical volume, T_r is the reduced temperature, T_c is the critical temperature, ω is the acentric factor, and a_i and b_j are empirical coefficients. Critical properties and acentric factors of the butanediols were estimated (*8*, *9*) using the experimental boiling temperatures found in the literature (*10*, *11*). The predicted values of the densities of butanediols were found to be systematically higher than the experimental data by about 10% at room temperature to 20% at 453 K.

No reliable methods were found for the prediction of the viscosities of butanediols. The method developed by Orrick and Erbar (*9*) is typical of the methods available. The viscosity in the Orrick and Erbar method is given by

$$\eta = \rho_0 M \exp(A + B/T) \qquad (5)$$

where η is the viscosity, ρ_0 is the density at 293 K, M is molecular weight, and A and B are coefficients obtained using a group contribution technique. Prediction errors using eq 5 were on the order of 100% at room temperature and about 50% at temperatures from 373 to 423 K.

It is interesting to note that the available prediction methods for viscosity give acceptable results for alcohols such as 1-butanol (*8*), but completely fail to predict the viscosities of butanediols.

It should also be noted that the viscosity–temperature curves of 1,3- and 1,4-butanediols intersect, and the estimation methods fail to account for this behavior. Clearly, improved estimation methods need to be developed for the diols.

4. Conclusion

The densities and viscosities of four isomeric butanediols were measured at ambient pressure and at temperatures ranging from 293 to 463 K. Very good agreement was obtained between the results obtained in this study and literature data at room temperature. However, no data could be found for comparison of the higher temperatures.

Registry No. 1,2-Butanediol, 584-03-2; 1,3-butanediol, 107-88-0; 1,4-butanediol, 110-63-4; 2,3-butanediol, 513-85-9.

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