Densities and Dielectric Permittivities of Three Butanediols and Their Solutions with 10 mol % Water

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The densities of 1,3-butanediol, 1,4-butanediol, 2,3-butanediol, and their solutions with 10 mol % water were measured in the range $20 \leq t/°C \leq 70$. The dielectric permittivities of the same butanediols and their solutions were determined at 1 MHz between 10 °C and 90 °C. The results were compared with literature values.

Introduction

The density and dielectric permittivity are important properties of matter and of liquids in particular. The dielectric permittivity provides useful information on the intermolecular interactions in liquids. In our previous work (Zhuravlev, 1992) we used experimental densities and dielectric constants of pure propanediols and their solutions to calculate some related properties and then to discuss intermolecular association. Moreover density measurements may serve as a convenient and sufficiently accurate method to determine the purity of the investigated substance.

In this work we reported densities and dielectric permittivities of three butanediols. The substances under investigation are widely used in industry and scientific researches, and so there are some articles concerning their physical properties. However, literature information about densities of butanediols is discrepant, and it is rather difficult to determine the correct values. Possibly, the difference in the density values is due to the presence of water in some studied samples, as butanediols are hydroscopic liquids. To refine the influence of small additives of water on the density and dielectric permittivity of butanediols, we investigated pure butanediols and their solutions with 10 mol % (2.17 mass %) water.

Experimental Section

Materials. 1,3-Butanediol was from Merck-Schuchardt, and 2,3-butanediol was from Schuchardt-München. According to the supplier, the purities of the materials were better than 98% and 99%, respectively. 1,4-Butanediol was from Novocherkasskij zavod (USSR) with purity "rein".

Immediately prior to use the samples were fractionally distilled under reduced pressure. The middle fractions were used.

Apparatus and Procedures. For preparation of butanediol aqueous solutions, bidistilled deionized water was used. The solutions were made by mass with an estimated accuracy $\pm 5 \times 10^{-5}$ in the mole fraction. Each solution was prepared two to three times.

Densities were measured using glass monocapillar pycnometers which held approximately 20 cm^3 of liquid. The pycnometers were thermostated within ±0.02 deg. The temperatures were checked by a calibrated platinum resistance thermometer. The pycnometers were calibrated with bidistilled deionized water.

The density measurements were made in three to four pycnometers and repeated three to five times, so the total number of measurements was 12−15 at each temperature. The reproducibility of results was within $\pm 5 \times 10^{-5}$ $g \cdot cm^{-3}$. The absolute accuracy was estimated to be within $\pm 1 \times 10^{-4}$ $g \cdot cm^{-3}$.

Dielectric permittivity measurements were carried out at 1 MHz using a bridge scheme. The measuring cell was a coaxial capacitor type. It was equipped with an E7-12 digital device for measurements of L, C, and R. The cell, having a stainless steel jacket, was thermostated to within ±0.02 deg. The temperatures were measured by a calibrated platinum resistance thermometer.

The cell was calibrated with standard pure liquids: chlorobenzene ($\epsilon = 5.690$ at 20 °C and 5.612 at 25 °C), 1-butanol ($\epsilon = 17.8$ at 20 °C and 13.1 at 60 °C), acetone ($\epsilon = 20.7$ at 25 °C), ethanol ($\epsilon = 24.35$ at 25 °C and 22.8 at 35 °C), and bidistilled water ($\epsilon = 80.37$ at 20 °C and 78.54 at 25 °C). The dielectric constants for standards were taken from the literature (Akhadov, 1972).

Experiments were performed four to five times at each temperature. The reproducibility of dielectric permittivity measurements was better than ±0.3%, and the accuracy was estimated to be ±1%.

Results and Discussion

Density. Experimental density values for the three butanediols and their solutions with 10 mol % water are given in Table 1. We also listed some representative literature values.

Clendenning *et al.* (1950) investigated a number of glycol + water systems and showed that the density of aqueous solutions of butanediols, as well as of propanediols and 1,2- and 1,5-pentanediol, attain maximum values that are considerably above that of either the pure glycol or of water. So the purity of samples under investigation is very important considering that butanediols, especially 1,3- and 2,3-butanediol, are hydroscopic liquids.

Clendenning *et al.* (1950), Nakanishi *et al.* (1967), Durov *et al.* (1984), and authors of this work used a fractional distillation as a final stage of purification. Czechowski *et al.* (1988) stored the butanediols with 4 Å molecular sieves. Sun *et al.* (1992) used the commercial diols without further purification.

In accordance with Czechowski *et al.* (1988) their density measurements were reproducible to $\pm 1 \times 10^{-5}$ $g \cdot cm^{-3}$. Sun *et al.* (1992) noted that the reproducibility of the density data was found to be ±0.1%, and the absolute accuracy was estimated to be within ±0.25%. The authors of the other

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Table 1. Densities ρ (g·cm^{-3}) of Butanediols (1) + Water (2)

ρ/g·cm^{-3}

1,3-Butanediol

	$x_1 = 1.0000$						$x_1 = 0.9073$	$x_1 = 0.8997$	$x_1 = 0.8217^b$
					Sun *et al.* (1992)				
t/°C	this work	Clendenning *et al.* (1950)	Nakanishi *et al.* (1967)	Czechowski *et al.* (1988)	t/°C	ρ	Czechowski *et al.* (1988)^a	this work	Nakanishi *et al.* (1967)
20.0	1.00342	d^{20}_4 1.0037		1.00579			1.00778	1.00558	
30.0	0.9966		0.99778	0.99904	29.2	1.0006	1.00106	0.9988	1.00162
40.0	0.9897			0.99239			0.99446	0.9918	
50.0	0.9827				49.9	0.9861		0.9847	
60.0	0.9756							0.9775	
70.0	0.9683				69.7	0.9708		0.9701	

1,4-Butanediol

	$x_1 = 1.0000$							$x_1 = 0.9005$	$x_1 = 0.9000$		$x_1 = 0.8598^b$
					Sun *et al.* (1992)						
t/°C	this work	Clendenning *et al.* (1950)	Nakanishi *et al.* (1967)	Czechowski *et al.* (1988)	t/°C	ρ	Bald *et al.* (1992)	Czechowski *et al.* (1988)^a	this work	Bald *et al.* (1992)	Nakanishi *et al.* (1967)
20.0	1.01573	d^{20}_4 1.0185		1.01622				1.01797	1.01733		
25.0	1.0127		1.01289				1.0129		1.0142	1.0143	1.01492
30.0	1.0096			1.01011	30.1	1.0114		1.01176	1.0111		
40.0	1.0034			1.00415				1.00564	1.0049		
50.0	0.9972				48.9	0.9990			0.9986		
60.0	0.9910								0.9923		
70.0	0.9848				69.8	0.9864			0.9859		

2,3-Butanediol

	$x_1 = 1.0000$				$x_1 = 0.9000$	
			Sun *et al.* (1992)			
t/°C	this work	Durov *et al.* (1984)	t/°C	ρ	this work	Durov *et al.* (1984)
20.0	0.99193	0.9921			0.99445	0.9953
30.0	0.9835	0.9847	30.1	0.9849	0.9860	0.9864
40.0	0.9750	0.9764			0.9774	0.9784
50.0	0.9664		49.7	0.9685	0.9688	
60.0	0.9577	0.9621			0.9601	0.9604
70.0	0.9489		70.4	0.9502	0.9513	

[a] Density values were calculated using excess molar volumes (V^{E}_{m}) given by Czechowski et al. (1988). [b] Calculated from the weight fraction.

cited works did not report information about the accuracy of their density measurements.

From Table 1, our density value for 1,3-butanediol at 20 °C is in good agreement ($\pm 3 \times 10^{-4}$ g·cm^{-3}) with that of Clendenning *et al.* (1950). The density measured at 30 °C by Nakanishi *et al.* (1967) is greater than ours by 1.2×10^{-3} g·cm^{-3}, while the density values for 1,3-butanediol determined by Czechowski *et al.* (1988) and Sun *et al.* (1992) are considerably greater than ours, by $(2.4-2.7) \times 10^{-3}$ g·cm^{-3} and by $(2.3-3.4) \times 10^{-3}$ g·cm^{-3}, respectively, and even somewhat greater, $(0.2-1.4) \times 10^{-3}$ g·cm^{-3}, than our values for 1,3-butanediol solution with 10 mol % water. These differences are much more than the experimental error given by Czechowski *et al.* (1988) and greater than the estimated accuracy given by Sun *et al.* (1992). Thus the water content in 1,3-butanediol samples used in both these works may be estimated as >2 mass %, although its purities according to the suppliers were better than 99 mass %. As 1,3-butanediol readily absorbs water during the storing or handling, we believe that to determine the correct values of physical properties it is necessary to do a fractional distillation immediately before the measurements.

From Table 1, our density values for pure 1,4-butanediol and its solution with water at 25 °C are in excellent agreement ($\pm 2 \times 10^{-4}$ g·cm^{-3}) with those of Nakanishi *et al.* (1967) and Bald *et al.* (1992). The density of 1,4-butanediol measured by Clendenning *et al.* (1950) at 20 °C is higher than ours by 2.8×10^{-3} g·cm^{-3}. It is rather suprising, because our results for 1,3-butanediol (this work) and 1,2- and 1,3-propanediol (Zhuravlev, 1992) agree within $\pm 4 \times 10^{-4}$ g·cm^{-3} with those of Clendenning *et al.* (1950). We cannot suggest any reasonable explanation for this discrepancy. The density values for 1,4-butanediol and its solution with 10 mol % water by Czechowski *et al.* (1988) are greater than ours by $(5-7) \times 10^{-4}$ g·cm^{-3}. The densities of 1,4-butanediol measured by Sun *et al.* (1992) are greater than ours by $(1.2-1.8) \times 10^{-3}$ g·cm^{-3}.

2,3-Butanediol can exist in several isomeric forms (*d*, *l*, and *meso*) or as a mixture of these stereoisomers. The physico-chemical properties of these isomers are quite different. In this as well as in the cited works the samples of commercial 2,3-butanediol with an unknown stereoisomeric composition were investigated. The density value of pure 2,3-butanediol measured by Durov *et al.* (1984) at 20 °C is in very good agreement with ours ($+2 \times 10^{-4}$ g·cm^{-3}); for 30 °C to 40 °C their results are greater than ours by $(1.2-1.4) \times 10^{-3}$ g·cm^{-3} and at 60 °C by 4.4×10^{-3} g·cm^{-3}. At the same time the densities of 2,3-butanediol solution with 10 mol % water determined by Durov *et al.* (1984) are greater than ours by $(3-10) \times 10^{-4}$ g·cm^{-3} in all temperature ranges, and the minimum difference (3×10^{-4} g·cm^{-3}) is at 60 °C. So we assume that the density value for 2,3-butanediol at 60 °C given by Durov *et al.* (1984) is incorrect due to experimental or typographical error. The densities measured by Sun *et al.* (1992) are greater than ours by $(1.4-2) \times 10^{-3}$ g·cm^{-3}. As in the case of 1,4-butanediol these differences (up to 0.21%) are within the estimated absolute density accuracy given by Sun *et al.* (1992). Nevertheless, we assume that the samples used by Sun *et al.* (1992) contained some water impurities because for all three diols their densities are considerably greater than ours. On the other hand, one may suppose that there is a systematic experimental error in Sun's work.

Table 2. Dielectric Permittivities ϵ of Butanediols (1) + Water (2)

1,3-Butanediol

	$x_1 = 1.0000$				$x_1 = 0.9000$
t/°C	this work	Sagal (1962)	McDuffie and Litovitz (1962)[a]	Rajyam *et al.* (1977)	this work
10.0	30.77		32.0$^{10.3}$		32.42
15.0	29.98	30.25			31.56
20.0	29.20				30.73
25.0	28.43	28.8			29.93
30.0	27.71			28.18	29.14
35.0	26.94	27.25			28.40
40.0	26.29				27.64
45.0	25.62				26.92
50.0	24.95	25.25			26.20
55.0	24.33				25.53
60.0	23.68				24.85
65.0	23.09				24.17
70.0	22.49				23.57
75.0	21.92				22.97
80.0	21.35				22.36
85.0	20.78				21.78
90.0	20.24				21.23

1,4-Butanediol

	$x_1 = 1.0000$				$x_1 = 0.9000$		
t/°C	this work	Sagal (1962)	Safonova *et al.* (1980)	Bald *et al.* (1992)	this work	Safonova *et al.* (1980)	Bald *et al.* (1992)
10.0	33.43				35.15		
15.0	32.54	32.5	33.8		34.10	34.8	
20.0	31.70		32.9		33.14	34.0	
25.0	30.84	30.8	31.9	30.33	32.25	33.0	31.84
30.0	30.05		30.9		31.39	32.0	
35.0	29.26	29.2	30.0		30.58	31.0	
40.0	28.46		29.0		29.70	30.1	
45.0	27.74		28.2		28.98	29.3	
50.0	27.00	27.0	27.3		28.14	28.4	
55.0	26.32		26.5		27.43	27.7	
60.0	25.62				26.67		
65.0	24.94				25.99		
70.0	24.30				25.26		
75.0	23.66				24.63		
80.0	23.04				23.96		
85.0	22.42				23.33		
90.0	21.83				22.76		

2,3-Butanediol

	$x_1 = 1.0000$		$x_1 = 0.9000$
t/°C	this work	Venkateswara Rao and Bhanumathi (1978)	this work
10.0	22.77		24.38
15.0	22.14		23.74
20.0	21.55		23.10
25.0	20.98		22.48
30.0	20.46	20.15	21.90
35.0	19.95		21.33
40.0	19.46		20.78
45.0	18.96		20.26
50.0	18.52	18.65	19.77
55.0	18.07		19.28
60.0	17.63		18.81
65.0	17.20		18.35
70.0	16.81	16.86	17.89
75.0	16.41		17.45
80.0	16.03		17.02
85.0	15.65		16.58
90.0	15.32		16.18

[a] Superscript indicates temperature at which dielectric measurement was carried out.

Dielectric Permittivity. Experimental values for the dielectric permittivity (ϵ) are given in Table 2. We also listed literature values in the temperature range.

Dielectric measurements were performed at 1 MHz in this work as well as by Rajyam *et al.* (1977), Safonova *et al.* (1980), Venkateswara Rao and Bhanumathi (1978) and at 100 kHz by Sagal (1962).

Sagal (1962) reported that static dielectric constants were measured to ±1%. In accordance with Safonova *et al.* (1980) the accuracy of their dielectric permittivity measurements was within ±0.5%. Other investigators did not report on the accuracy of their dielectric data.

The dielectric permittivities of 1,3-butanediol determined by Sagal (1962) are in good agreement with ours (greater by 0.9−1.2%), and ϵ measured at 30 °C by Rajyam *et al.* (1977) is greater than ours by 1.7%. In both cited works the distillation of samples before investigation was used. The dielectric constant of 1,3-butanediol determined at 10.3 °C by McDuffie and Litovitz (1962) is greater than ours by 4% as in the case of other polyhydric alcohols (Grineva *et al.*, 1996). McDuffie and Litovitz (1962) boiled the samples under vacuum for 8 h to 10 h to dehydrate them and estimated their water contents on the order of 1 mass %. On the basis of our experiments we believe that the water content in above samples was about 2 mass %.

According to Curme and Johnston (1953), 1,4-butanediol freezes at 16 °C. Possibly, this is the correct value because in the range 18 °C to 20 °C we did not observe any solidification. However, it is known that 1,4-butanediol can be easily supercooled. Hinopoulos and Sakellaridis (1977) measured dielectric constants of 1,4-butanediol, and in their experiments glycol solidified at 5 °C. Sagal (1962) and Safonova *et al.* (1980) measured the dielectric permittivity of 1,4-butanediol in the liquid state at 15 °C. From our experiments, the temperature of freezing of 1,4-butanediol depends not only on water content but also on some other conditions. We did not undertake a special investigation of this question, but several times we could measure the dielectric constants of pure 1,4-butanediol and its solution with 10 mol % water at 10 °C in the liquid state and several times the solidification began at the same temperature (dielectric permittivity decreased). For all samples the difference in ϵ above 20 °C was within ±0.1% (better than for other investigated diols).

Our results for 1,4-butanediol are in excellent agreement with those of Sagal (1962) (±0.2%). The dielectric constants of pure 1,4-butanediol and its water solution measured at 25 °C by Bald *et al.* (1992) are lower than ours by 1.3 to 1.7%. At the same time the densities measured by Bald *et al.* (1992) are in very good agreement with ours. So we connect the differences in ϵ as a result of the dielectric cell calibration. Safonova *et al.* (1980) detected the water content in investigated 1,4-butanediol as <0.02 mass %. At the same time dielectric permittivities determined by Safonova *et al.* (1980) were greater than ours and differences at 15 °C reached 3.8% for pure 1,4-butanediol and 2% for solution. With increasing temperature the differences between our and Safonova *et al.* (1980) ϵ values decrease and constitute 0.8 to 1% at 55 °C. For explanation of these discrepancies we may suspect only an incorrect dielectric measurement technique in Safonova *et al.* (1980).

Our dielectric constants of 2,3-butanediol are in satisfactory agreement (±1.5%) with those of Venkateswara Rao and Bhanumathi (1978).

Author Supplied Registry Nos.: 1,3-Butanediol, 107-88-0; 1,4-butanediol, 110-63-4; 2,3-butanediol, 513-85-9; water, 7732-18-5.

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