(16) Michailin, B. V.; Vorobev, A. F.; Vasilev, V. A. *Zh. Fiz. Khim.* **1982**, *56*, 1937.
(17) Spedding, F. H.; Shiers, L. E.; Brown, M. A.; Derer, J. L.; Swanson, D. L.; Habenschuss, A. *J. Chem. Eng. Data* **1975**, *20*, 81.
(18) Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1976**, *21*, 95.
(19) Freier, R. K. *Aqueous Solutions*; W. de Gruyter: Berlin, 1976; Vol. II.
(20) Spedding, F. H.; Shiers, L. E.; Brown, M. A.; Derer, J. L.; Swanson, D. L.; Habenschuss, A. *J. Chem. Eng. Data* **1975**, *20*, 72.
(21) Kartzmark, E. M. *J. Chem. Eng. Data* **1982**, *27*, 38.
(22) Linke, W. F. *Solubilities of Inorganic and Metal—Organic Compounds*; van Nostrand: New York, 1958.
(23) Drucker, C. *Arkiv. Kem. Min. Geol.* **1946**, *22A*(21), 17.
(24) Bendaoud, S.; Thourey, J.; Perachon, G. *J. Fluorine Chem.* **1984**, *25*, 395.
(25) Morris, K. B.; Nelson, J. J.; Nizko, H. S. *J. Chem. Eng. Data* **1985**, *10*, 120.
(26) Vorobev, A. F.; Vasilev, V. A.; Michailin, B. V.; Malkov, I. V. *Zh. Fiz. Khim.* **1979**, *53*, 2493.
(27) Campbell, A. N.; Singh, K. P. *Can. J. Chem.* **1959**, *37*, 1959.
(28) Haase, R.; Lenhert, G.; Janse, H.-J. *Z. Phys. Chem.* (*Frankfurt/Main*) **1969**, *42*, 32.
(29) Klochko, M. A.; Ururchanov, M. M. *Izv, Sekt. Fiz. Khim. Anal. Akad. Nauk SSSR* **1953**, *22*, 298.
(30) Mazzucchelli, A.; Rossi, A. *Gazz. Chim. Ital.* **1927**, *57*, 383.
(31) Hantzch, A.; Düringen, F. *Z. Phys. Chem.* **1928**, *A136*, 1.
(32) Högnäs, H. *An. Acad. Sci. Fennicae* **1969**, *145*, 1.
(33) Silva, J. W.; Chenevey, J. E. *Ind. Eng. Chem.* **1945**, *37*, 1017.
(34) Gupples, H. L. *J. Phys. Chem.* **1946**, *50*, 257.
(35) Rodnanskii, I. M.; Korobkov, V. I.; Galinker, I. S. *Zh. Fiz. Khim.* **1962**, *36*, 2216.
(36) Baranowski, B.; Jacob, H. P.; Sarnowski, M. *Z. Phys. Chem.* **1961**, *216*, 215.
(37) Ewing, W. W.; Mikovsky, R. J. *J. Am. Chem. Soc.* **1950**, *72*, 1390.
(38) Pearce, J. N.; Blackman, L. E. *J. Am. Chem. Soc.* **1935**, *57*, 24.
(39) Hering, H. *Ann. Chim.* **1936**, *5*, 483.
(40) Ewing, W. W.; Herty, Ch. H. *J. Phys. Chem.* **1953**, *57*, 245.
(41) Söhnel, O.; Novotný, P.; Šolc, Z. *J. Chem. Eng. Data* **1984**, *29*, 379.
(42) Isono, T. *J. Chem. Eng. Data* **1984**, *29*, 45.
(43) Spitzer, J. J.; Olofsson, I. V.; Singh, P. P.; Hepler, L. G. *J. Chem. Thermodyn.* **1979**, *11*, 233.
(44) Lengyel, S. *Magy. Kem. Foly.* **1963**, *69*, 117.
(45) Tamás, J. *Acta Chim. Acad. Sci. Hung.* **1964**, *40*, 117.
(46) Berchiesi, M. A.; Berchiesi, G.; Lobia, G. C. *J. Chem. Eng. Data* **1974**, *19*, 326.
(47) Charpy, G. *Ann. Chim. Phys.* **1893**, *5*, 29.
(48) Jones, H. C.; Getman, F. H. *J. Am. Chem. Soc.* **1904**, *31*, 303.
(49) Jones, H. C.; Getman, F. H. *J. Am. Chem. Soc.* **1904**, *32*, 308, 398.
(50) Jones, H. C.; Getman, F. H. *Z. Phys. Chem.* **1904**, *A49*, 385.
(51) Jones, H. C.; Bassett, H. P. *J. Am. Chem. Soc.* **1905**, *33*, 534.
(52) Jones, H. C.; Bassett, H. P. *J. Am. Chem. Soc.* **1905**, *34*, 290.
(53) Berthier, P.; Courty, C. *Compt. Rend. Acad. Sci.* **1952**, *234*, 604, 2525.
(54) Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans: London, 1957.
(55) Söhnel, O.; Novotný, P.; Wurzelová, J. *Chem. Listy* **1982**, *76*, 979.
(56) Haase, R.; Sauermann, P.-F.; Dücker, K.-H. *Z. Phys. Chem.* (*Frankfurt/Main*) **1965**, *47*, 224.
(57) Akerlöf, G.; Teare, J. W. *J. Am. Chem. Soc.* **1938**, *60*, 1226.
(58) Clark, L. H.; Putnam, G. L. *J. Am. Chem. Soc.* **1949**, *71*, 3445.
(59) D'Ans/Lax; *Taschenbuch für Chemiker und Physiker*; Springer: Berlin 1967; Band I.
(60) Domke, J.; Bein, W. *Z. Anorg. Chem.* **1905**, *43*, 125.
(61) Curthoys, G.; Mathieson, J. G. *J. Chem. Eng. Data* **1977**, *22*, 225.
(62) Mýl, J.; Solc, Z.; Kvapil, J. *Sci. Pap. Univ. Chem. Technol. Pardubice* **1963**, No. 1, 89.
(63) Weast, R. C. *Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1981.
(64) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1941**, *63*, 288.
(65) Malatesta, F.; Zambonini, R. *J. Chem. Soc. Faraday Trans. 1* **1980**, *76*, 2510.
(66) Kearley, R. A. *J. Chem. Eng. Data* **1984**, *9*, 548.
(67) Jones, G.; Ray, W. A. *J. Am. Chem. Soc.* **1941**, *63*, 290.
(68) Mullin, J. W.; Amatavivadhana, A. *J. Appl. Chem.* **1967**, *17*, 151.
(69) Akerlöf, G.; Bender, P. *J. Am. Chem. Soc.* **1941**, *63*, 1085.
(70) Than, M. K.; Gubbins, K. E.; Walker, R. D. *J. Chem. Eng. Data* **1967**, *12*, 525.
(71) Ishi, T.; Fujita, S. *J. Chem. Eng. Data.* **1976**, *23*, 19.
(72) Gildseth, W. M.; Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1975**, *20*, 292.
(73) Haase, P.; Dücker, K. U. *Z. Phys. Chem.* (*Frankfurt/Main*) **1985**, *46*, 140.
(74) Puchkov, L. V.; Matashkin, V. G.; Matveeva, R. P. *Zh. Prikl. Khim.* **1979**, *52*, 1167.
(75) Hitchcock, L. B. *Ind. Eng. Chem.* **1937**, *29*, 302.
(76) Mikhailov, I. G.; Zhau, F. *Vestn. LGU* **1960**, *15*(16), 22.
(77) Fabuss, B. M.; Korosi, A.; Huq, A. K. M. S. *J. Chem. Eng. Data* **1966**, *11*, 325.
(78) Korosi, A.; Fabuss, B. M. *J. Chem. Eng. Data* **1968**, *13*, 548.
(79) Chen, Ch-T.; Chen, J. H.; Millero, F. J. *J. Chem. Eng. Data* **1980**, *25*, 307.
(80) Phang, S. *Aust. J. Chem.* **1980**, *33*, 413.
(81) Deckwer, W. D. *J. Chem. Eng. Data* **1980**, *25*, 75.
(82) Chomjakow, K.; Jaworowskaja, S.; Schirikich, P. *Z. Phys. Chem.* **1933**, *A167*, 35.
(83) Ranken, C.; Taylor, W. W. *Trans. R. Soc. Edinburgh* **1906**, *45*(15), 11.
(84) Getman, F. M. *J. Am. Chem. Soc.* **1908**, *30*, 721, 1077.
(85) Söhnel, O.; Novotný, P.; Solc, Z. *Sci. Pap. Univ. Technol. Pardubice* **1985**, *47*, 43.
(86) Mullin, J. W.; Osman, M. M. *J. Chem. Eng. Data* **1967**, *12*, 516.
(87) Miller, M. L.; Doran, M. *J. Phys. Chem.* **1956**, *60*, 186.
(88) Kelly, W. R.; Morgan, T. R. *J. Chem. Eng. Data* **1965**, *10*, 290.
(89) Millero, F. J.; Knox, J. H. *J. Chem. Eng. Data* **1973**, *18*, 407.
(90) Payne, J. H. *J. Am. Chem. Soc.* **1937**, *59*, 947.
(91) Desnoyers, J. E.; Perron, A. G.; Jolicoeur, C. *J. Phys. Chem.* **1969**, *73*, 3346.
(92) Millero, F. J. *J. Phys. Chem.* **1967**, *71*, 4567.
(93) Khara, P. L. *Trans. Faraday Soc.* **1962**, *58*, 359.
(94) Masom, C. M. *J. Am. Chem. Soc.* **1949**, *71*, 2387.
(95) Bonner, O.; Gable, R. W. *J. Chem. Eng. Data* **1970**, *15*, 499.
(96) White, J. C.; Miller, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3282.
(97) Günther, F.; Perschke, W. *J. Chem. Soc.* **1934**, 100.
(98) Akerlöf, G.; Kegeles, G. *J. Am. Chem. Soc.* **1939**, *61*, 1027.
(99) Krings, W. *Z. Anorg. Chem.* **1946**, *255*, 294.
(100) Hayward, A. M.; Permann, E. P. *Trans. Faraday Soc.* **1931**, *27*, 59.
(101) Stokes, R. H.; Phang, S.; Mills, R. *J. Solution Chem.* **1979**, *8*, 489.
(102) Chernenkaya, E. I.; Kuznetova, O. M. *Zh. Prikl. Khim.* **1972**, *52*, 1255.
(103) Masterton, W. L.; Welles, H.; Knox, J. H.; Millero, F. J. *J. Solution Chem.* **1974**, *3*, 91.
(104) Grant, W. E.; Darch, W. J.; Bowden, S. J.; Jones, W. I. *J. Phys. Chem.* **1948**, *52*, 1227.
(105) Kapustinskii, A. F.; Lipilina, I. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1956**, 649.
(106) Jain, S. K. *J. Chem. Eng. Data* **1976**, *23*, 170.

Received for review May 21, 1986. Accepted August 3, 1987.

Excess Molar Volumes of Binary Mixtures of Diols and Water

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The excess molar volumes of binary mixtures of water and 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 1,3-propanediol, and 1,5-pentanediol have been determined at 293.15, 303.15, and 313.15 K.

Introduction

In a previous paper (*1*) we reported the excess molar volumes V_m^E measured in binary mixtures of dipolar compounds with nonpolar solvents. Here we report the results of measurements of the V_m^E carried out for binary mixtures of the strongly self-associated hydroxylic compounds: diols + water.

Table I. Densities ρ (g·cm^{-3}) of Pure Diols

	ρ		
diol	T = 293.15 K	T = 303.15 K	T = 313.15 K
1,2-Bu(OH)$_2$	1.003 47	0.995 44	0.987 87
1,3-Bu(OH)$_2$	1.005 79	0.999 04	0.992 39
1,4-Bu(OH)$_2$	1.016 22	1.010 11	1.004 15
1,3-Pr(OH)$_2$	1.053 70	1.047 44	1.041 10
1,5-Pen(OH)$_2$	0.992 79	0.986 73	0.981 25

0021-9568/88/1733-0055$01.50/0

Table II. Experimental Excess Molar Volumes V_m^E ($cm^3 \cdot mol^{-1}$) for Diol + Water Mixtures

T, K	x	V_m^E	T, K	x	V_m^E	T, K	x	V_m^E	T, K	x	V_m^E	T, K	x	V_m^E
x1,2-Butanediol + $(1-x)$Water			x1,3-Butanediol + $(1-x)$Water			x1,4-Butanediol + $(1-x)$Water			x1,3-Propanediol + $(1-x)$Water			x1,5-Pentanediol + $(1-x)$Water		
293.15	0.0515	−0.2568	293.15	0.0532	−0.1649	293.15	0.0525	−0.1023	293.15	0.0617	−0.0815	293.15	0.0443	−0.1123
	0.0882	−0.4220		0.0971	−0.3361		0.0805	−0.1857		0.1034	−0.1597		0.0955	−0.2572
	0.1272	−0.5310		0.1403	−0.4708		0.1118	−0.2595		0.1534	−0.2395		0.1331	−0.3262
	0.1836	−0.6109		0.1918	−0.5869		0.1412	−0.3280		0.2080	−0.3198		0.1462	−0.3483
	0.2185	−0.6384		0.2309	−0.6519		0.2103	−0.4484		0.2673	−0.3778		0.1862	−0.4084
	0.2805	−0.6647		0.2707	−0.7014		0.2408	−0.4828		0.3084	−0.4054		0.2063	−0.4295
	0.3178	−0.6596		0.3263	−0.7363		0.2710	−0.5199		0.3519	−0.4294		0.2255	−0.4524
	0.3585	−0.6449		0.3619	−0.7415		0.3263	−0.5622		0.4078	−0.4447		0.2630	−0.4857
	0.3992	−0.6353		0.4402	−0.7427		0.3629	−0.5845		0.4533	−0.4429		0.3449	−0.5333
	0.4706	−0.5810		0.5002	−0.6963		0.4100	−0.6000		0.5197	−0.4254		0.3816	−0.5467
	0.5220	−0.5407		0.5286	−0.6812		0.4284	−0.5989		0.5571	−0.4110		0.4019	−0.5502
	0.5787	−0.4921		0.5511	−0.6668		0.4520	−0.5946		0.6132	−0.3786		0.4079	−0.5505
	0.6150	−0.4621		0.6097	−0.6210		0.5059	−0.5751		0.6584	−0.3459		0.4676	−0.5486
	0.6634	−0.4133		0.6231	−0.6076		0.6031	−0.5140		0.7030	−0.3053		0.5108	−0.5343
	0.7004	−0.3711		0.6673	−0.5594		0.6538	−0.4712		0.7539	−0.2599		0.5287	−0.5299
	0.7591	−0.2986		0.7117	−0.5080		0.7013	−0.4205		0.8085	−0.2040		0.6181	−0.4871
	0.8058	−0.2435		0.7135	−0.5009		0.7598	−0.3616		0.8476	−0.1640		0.6495	−0.4569
	0.8542	−0.1822		0.7581	−0.4434		0.7919	−0.3111		0.8955	−0.1175		0.6925	−0.4165
	0.9006	−0.1160		0.8169	−0.3497		0.8554	−0.2320		0.9429	−0.0653		0.7382	−0.3819
	0.9544	−0.0629		0.8567	−0.2793		0.9005	−0.1721	303.15	0.0617	−0.0835		0.7904	−0.3168
303.15	0.0515	−0.2408		0.9073	−0.1763		0.9444	−0.1083		0.1034	−0.1526		0.8294	−0.2738
	0.0882	−0.3895		0.9472	−0.1050	303.15	0.0525	−0.0970		0.1534	−0.2274		0.8784	−0.1943
	0.1272	−0.4913	303.15	0.0532	−0.1668		0.0805	−0.1683		0.2080	−0.2952		0.9314	−0.1217
	0.1836	−0.5659		0.0971	−0.3224		0.1118	−0.2360		0.3084	−0.3780		0.9597	−0.0719
	0.2185	−0.5952		0.1403	−0.4418		0.1412	−0.2952		0.3519	−0.3972	303.15	0.0443	−0.1013
	0.2805	−0.6192		0.1918	−0.5440		0.2103	−0.4019		0.4078	−0.4111		0.0955	−0.2228
	0.3178	−0.6232		0.2309	−0.6176		0.2408	−0.4390		0.4533	−0.4116		0.1331	−0.2884
	0.3585	−0.6134		0.2707	−0.6609		0.2710	−0.4669		0.5197	−0.3963		0.1862	−0.3590
	0.3992	−0.6033		0.3263	−0.6902		0.3263	−0.5084		0.5571	−0.3805		0.2063	−0.3830
	0.4706	−0.5675		0.3619	−0.6954		0.3629	−0.5277		0.6132	−0.3513		0.2255	−0.3999
	0.5220	−0.5328		0.4402	−0.6859		0.4100	−0.5428		0.6584	−0.3214		0.2630	−0.4316
	0.5787	−0.4905		0.5002	−0.6569		0.4284	−0.5469		0.7030	−0.2835		0.3449	−0.4763
	0.6150	−0.4582		0.5286	−0.6408		0.4517	−0.5437		0.7539	−0.2412		0.4079	−0.4959
	0.6634	−0.4128		0.5511	−0.6240		0.5059	−0.5296		0.8085	−0.1938		0.5108	−0.4847
	0.7004	−0.3695		0.6097	−0.5809		0.6031	−0.4772		0.8476	−0.1539		0.6181	−0.4539
	0.7591	−0.3139		0.6231	−0.5660		0.6538	−0.4350		0.8955	−0.1094		0.6925	−0.3898
	0.8058	−0.2578		0.6673	−0.5310		0.7013	−0.3929		0.9429	−0.0601		0.7904	−0.3068
	0.8542	−0.2008		0.7117	−0.4709		0.7598	−0.3369	313.15	0.0617	−0.0817		0.8784	−0.1905
	0.9006	−0.1358		0.7135	−0.4698		0.7919	−0.2910		0.1034	−0.1461		0.9314	−0.1054
	0.9544	−0.0704		0.7581	−0.4165		0.8554	−0.2160		0.1534	−0.2154	313.15	0.0443	−0.0881
313.15	0.0515	−0.2286		0.8169	−0.3266		0.9005	−0.1599		0.2081	−0.2762		0.0955	−0.1837
	0.0882	−0.3594		0.8567	−0.2578		0.9444	−0.0968		0.3084	−0.3514		0.1331	−0.2410
	0.1272	−0.4560		0.9073	−0.1744	313.15	0.0525	−0.0933		0.3519	−0.3780		0.1862	−0.3056
	0.1836	−0.5258		0.9472	−0.0958		0.0805	−0.1543		0.4078	−0.3903		0.2063	−0.3290
	0.2185	−0.5557	313.15	0.0532	−0.1638		0.1118	−0.2168		0.4533	−0.3892		0.2255	−0.3463
	0.2805	−0.5823		0.0971	−0.3082		0.1412	−0.2685		0.5197	−0.3720		0.2630	−0.3725
	0.3178	−0.5869		0.1403	−0.4174		0.2103	−0.3685		0.5571	−0.3597		0.3449	−0.4130
	0.3585	−0.5780		0.1918	−0.5116		0.2408	−0.4006		0.6132	−0.3318		0.3816	−0.4290
	0.3992	−0.5645		0.2309	−0.5791		0.2710	−0.4273		0.6584	−0.3041		0.4079	−0.4363
	0.4706	−0.5319		0.2707	−0.6167		0.3263	−0.4634		0.7030	−0.2685		0.4676	−0.4394
	0.5220	−0.5083		0.3263	−0.6406		0.3629	−0.4831		0.7539	−0.2282		0.5287	−0.4266
	0.5787	−0.4695		0.3619	−0.6524		0.4100	−0.4976		0.8085	−0.1842		0.6495	−0.3652
	0.6150	−0.4340		0.4402	−0.6464		0.4284	−0.4996		0.8476	−0.1470		0.7382	−0.2950
	0.6634	−0.3914		0.5002	−0.6220		0.4517	−0.4995		0.8955	−0.1045		0.8294	−0.2061
	0.7004	−0.3536		0.5286	−0.6079		0.5059	−0.4833		0.9429	−0.0574		0.9597	−0.0464
	0.7591	−0.3044		0.5511	−0.5924		0.5528	−0.4664						
	0.8058	−0.2467		0.6097	−0.5516		0.6031	−0.4402						
	0.8542	−0.1895		0.6231	−0.5355		0.6538	−0.4057						
	0.9006	−0.1341		0.6673	−0.5000		0.7013	−0.3643						
	0.9544	−0.0686		0.7117	−0.4404		0.7598	−0.3082						
				0.7135	−0.4372		0.7919	−0.2747						
				0.7581	−0.3967		0.8554	−0.1995						
				0.8169	−0.3164		0.9005	−0.1441						
				0.8567	−0.2648		0.9444	−0.0862						
				0.9073	−0.1750									
				0.9472	−0.1061									

Diols were selected in such a way as to enable us to estimate the influence of distance between the OH groups substituted to the same hydrocarbon (1,2-butanediol, 1,3-butanediol, and 1,4-butanediol) and at the ends of successive hydrocarbons (1,3-propanediol, 1,4-butanediol, and 1,4-pentanediol) on the excess molar volumes of their mixtures with water.

Experimental Section

The diols were supplied by Aldrich (purity better than 99%) and stored with 4A molecular sieves. Table I contains the measured density of pure diols. Water was double distilled and degassed before use.

Table III. Coefficients A_i, and Standard Deviation S, for Least-Squares Representations by Eq 1

	T, K	A_0	A_1	A_2	A_3	A_4	S
x1,2-butanediol + (1 − x)water	293.15	−2.2295	1.6943	−1.4684	0.7545		0.008
	303.15	−2.1651	1.4236	−1.4273	0.6777		0.007
	313.15	−2.0435	1.2774	−1.3459	0.6623		0.006
x1,3-butanediol + (1 − x)water	293.15	−2.7823	1.3838	−1.5430	−0.6881	2.0037	0.008
	303.15	−2.6253	1.2734	−1.2935	−0.5274	1.5684	0.006
	313.15	−2.4805	1.1784	−1.0271	−0.5866	0.9119	0.006
x1,4-butanediol + (1 − x)water	293.15	−2.3215	0.9913	0.1654	−1.0556		0.008
	303.15	−2.1266	0.7714	0.1551	−0.7584		0.006
	313.15	−1.9546	0.6391	0.1400	−0.5571		0.005
x1,3-propanediol + (1 − x)water	293.15	−1.7522	0.6975	0.4667	−0.6908		0.005
	303.15	−1.6250	0.6060	0.3796	−0.5111		0.004
	313.15	−1.5335	0.5540	0.3299	−0.4410		0.003
x1,5-pentanediol + (1 − x)water	293.15	−2.1752	0.6852	−0.2502	−0.1782		0.007
	303.15	−1.9972	0.4609	−0.1528	−0.0091		0.007
	313.15	−1.7413	0.4119	0.0637	0.1073		0.004

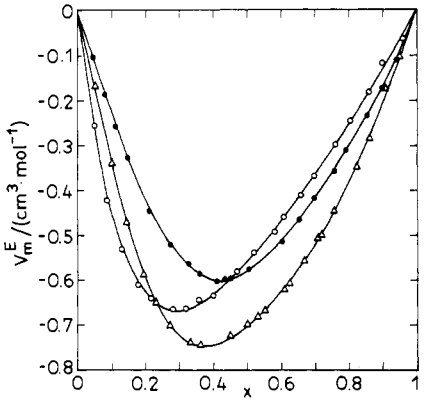

Figure 1. Excess molar volumes of {$x$butanediol + (1 − x)water} at 298.15 K: O, 1,2-Bu(OH)$_2$; Δ, 1,3-Bu(OH)$_2$; ●, 1,4-Bu(OH)$_2$.

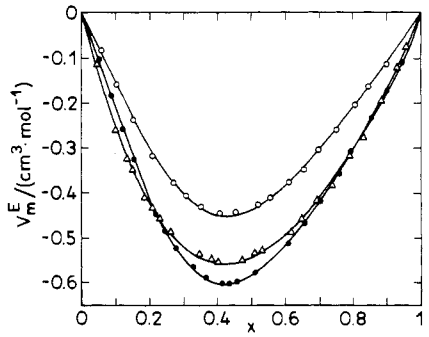

Figure 2. Excess molar volumes of {x1,n-diol + (1 − x)water} at 298.15 K: O, 1,3-Pr(OH)$_2$; ●, 1,4-Bu(OH)$_2$; Δ, 1,5-Pen(OH)$_2$.

Density measurements were carried out with an A. Paar DMA 60/602 vibrating tube densimeter. The measuring cell was thermostated (±0.02 K) by using a Heto Birkeroad ultrathermostat. The density measurements were reproducible to ±1 × 10^{-5} g·cm^{-3}.

Results and Discussion

The excess molar volumes V_m^E for five mixtures, {$x$diol + (1 − x)water}, measured at 293.15, 303.15, and 313.15 K are collected in Table II.

Functions of the form

$$V_m^E = x(1-x)\sum_i A_i(2x-1)^i \qquad (1)$$

have been fitted to the experimental data by the least-squares method, for each mixture and at each temperature. The value of the coefficients A_i and the standard deviation s of the fits are listed in Table III.

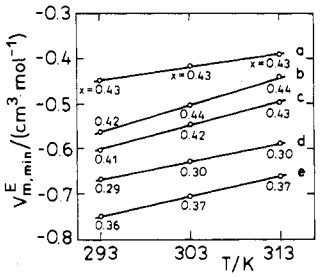

Figure 3. $V^E_{m,min}$ vs temperature for the mixtures of {$x$diol + (1 − x)water}. V_m^E reaches its minimal value for the value of x indicated in the figure. (a) 1,3-Pr(OH)$_2$; (b) 1,5-Pen(OH)$_2$; (c) 1,4-Bu(OH)$_2$; (d) 1,2-Bu(OH)$_2$; (e) 1,3-Bu(OH)$_2$.

Figure 1 shows the concentration dependence of V_m^E for the mixtures of 1,2-, 1,3-, and 1,4-butanediol + water, and Figure 2 for the mixtures of 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol + water.

While mixing diols with water one observes, like in the case of diol + alkohol mixtures (*2*), a contraction of the molar volume (V_m^E < 0), which is caused by breaking the intramolecular hydrogen bonds in diols (*3*–*5*) and formation of the intermolecular hydrogen bonds with water molecules. Minimum values of V_m^E occur within the range 0.3–0.4 mole fraction of the studied diols. Figure 3 shows the dependence of $V^E_{m,min}$ on temperature.

Registry No. 1,2-Bu(OH)$_2$, 584-03-2; 1,3-Bu(OH)$_2$, 107-88-0; 1,4-Bu(OH)$_2$, 110-63-4; 1,3-Pr(OH)$_2$, 504-63-2; 1,5-Pen(OH)$_2$, 111-29-5; H$_2$O, 7732-18-5.

Literature Cited

(1) Diguet, R.; Jadżyn, J. *J. Chem. Eng. Data* **1982**, *27*, 86.
(2) Awwad, A. M. *J. Chem. Thermodyn.* **1986**, *18*, 443.
(3) Kuhn, L. P. *J. Am. Chem. Soc.* **1958**, *80*, 5950.
(4) Schleyer, P. R. *J. Am. Chem. Soc.* **1961**, *83*, 1368.
(5) Kuhn, L. P.; Schleyer, P. R.; Baltinger, W. F., Jr.; Eberson, L. *J. Am. Chem. Soc.* **1964**, *86*, 650.

Received for review May 12, 1987. Accepted October 7, 1987. This work was supported by the Polish Academy of Sciences within the framework of Project CPBP 01.12.