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Molar heat capacities for {isomer of butanediol + methanol} as function of mixture composition and temperature

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ABSTRACT

Isobaric specific heat capacities for the binary mixtures {isomer of butanediol + methanol} were measured using a differential scanning calorimeter. The isobaric molar heat capacities were determined in the temperature range from (293 to 324) K. The excess molar isobaric heat capacities of mixtures and its components were calculated. The composition dependencies of the excess molar isobaric heat capacities at $T = 298.15$ K and at $T = 323.15$ K were fitted by the Redlich–Kister polynomials. The obtained results were analyzed from point of view of the influence of distance of —OH groups in butanediol molecule.

1. Introduction

Alkanediols are very interesting bi-functional compounds, frequently used in different fields of technics as well as in everyday life e.g. as antifreeze substances, cryoprotectant agents, biocides and many others [1–3]. They are also interesting from scientific point of view, as they are treated as model substances, which properties are determined by inter- and intra-molecular hydrogen bonds. However, the literature data concerning the behavior of alkanediols in different molecular surroundings are rather scarce, which indicates the necessity of the widely planned studies of such systems. The systematic examinations of binary mixtures of alkanediols with water and methanol were undertaken in our laboratory several years ago. Among others the densities and the heat capacities of dilute solutions of several alkanediols in methanol were measured and from these data the appropriate apparent and partial molar functions of the diols were determined. The behavior of the diols in methanol was compared with that observed in aqueous solutions [4]. As it is known, the volumetric properties of solutions are directly connected with a structure of solvent while the heat capacity defines the susceptibility of the solution structure on temperature changes hence, it provides information about its stability. For this reason, in the mentioned work the obtained results were analyzed from the point of view of molecular interactions using the scaled particle theory (SPT) for determination of the heat capacity "cavity formation" term, $C_{p,cav}$ and the "(solute + solvent) interaction" term, $C_{p,int}$ [4]. The obtained results have inspired us to extent the examinations of (alkanediol + methanol) mixtures on the whole range of the mixtures composition at several temperatures. In the present work we have examined the heat capacities of binary mixtures of isomeric butanediols i.e. 1,2-butanediol (1,2BD), 1,3-butanediol (1,3BD), 1,4-butanediol (1,4BD) and 2,3-butanediol (2,3BD) with methanol. We have expected that these studies show us the influence of distance of —OH groups in the butanediol molecule on the heat capacity of the investigated mixtures.

The specific isobaric heat capacities c_p for the examined systems have been determined within the whole range of the mixture composition and within the (293 to 324) K temperature range. The molar isobaric heat capacities $C_{p,m}$, the excess molar isobaric heat capacities $C^E_{p,m}$ as well as the excess partial molar isobaric heat capacities $C^E_{p,mi}$ of isomeric butanediols and methanol in the mixtures have been calculated and analyzed as function of temperature and the mixture composition.

2. Experimental

Methanol and isomeric butanediols used in this work, their source and purity are presented in table 1.

Methanol was dried prior to distillation, using freshly roasted molecular sieves of 3A type. For butanediols the 4A type molecular sieves were applied. All solvents were degassed before use.

The mixtures were prepared by mass in a glove box in a dry atmosphere. The components were weighed with an accuracy of

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TABLE 1
Sample table.

Chemicals	Source	Purity[a]
Methanol (MeOH)	Chempur	⩾0.99
1,2-butanediol (1,2BD)	Aldrich	⩾0.999
1,3-butanediol (1,3BD)	Aldrich	⩾0.997
1,4-butanediol (1,4BD)	Aldrich	⩾0.998
2,3-butanediol (2,3BD)	Aldrich	⩾0.995

[a] Assay in mass fraction.

±2 · 10^{-8} kg using a Sartorius RC 210D balance. The mole fraction was estimated with accuracy ±5 · 10^{-5}.

The specific isobaric heat capacity c_p was measured using a differential scanning calorimeter Micro DSC III (Setaram). The "continuous with reference" method was applied with the use *n*-heptane as a reference. The uncertainty of the measurements was estimated to be ±0.15%. Details about the apparatus and the experimental procedure have been described by Góralski et al. [5] In the present work the measurements of specific isobaric heat capacities c_p were made within the (293 to 324) K temperature range. The experiment was repeated two or three times for each composition of the mixture and the obtained values were agree to within $\delta c_p = \pm 0.003\ \text{J}\text{g}^{-1} \cdot \text{K}^{-1}$. The uncertainties of determined $C_{p,m}$ and $C^E_{p,m}$ values are estimated to be about (±0.25 and ±1)%, respectively.

3. Results and discussion

The measured experimental values of specific isobaric heat capacity, c_p for pure components and their mixtures over the whole examined temperature range were approximated by the polynomials in form:

$$c_p = \sum_{i=0}^{2} a_i \cdot T^i, \tag{1}$$

where a_i are fitting coefficients and T is temperature. The obtained a_i values are collected in table 2.

The calculated molar heat capacities of pure solvents, $C^*_{p,m}$ ($C^*_{p,m} = c_p M$ where M is molar mass) at $T = 298.15$ K are given in table 3. As it is seen, our results agree very well with the appropriate literature data (table 3). The same concerns the molar volumes at other temperatures when compared with the compilation of the appropriate data given in the paper of Zorębski et al. [10].

The excess molar heat capacities, $C^E_{p,m}$ were calculated from equation (2):

$$C^E_{p,m} = C_{p,m} - \left((1 - x) \cdot C^*_{p,m1} + x \cdot C^*_{p,m2}\right), \tag{2}$$

where x, $C^*_{p,m1}$, $C^*_{p,m2}$ are mole fraction of butanediol and molar heat capacity of methanol (1) and butanediol (2) as the pure solvents.

The $C^E_{p,m}$ values were fitted to the Redlich–Kister's equation:

$$C^E_{p,m} = x(1 - x) \cdot \sum_{i=1}^{n} A_i (1 - 2x)^{i-1}. \tag{3}$$

Partial molar heat capacities of components, $C_{p,mi}$ were calculated using following relationships:

$$C_{pi,\Phi} = C^*_{p,m,i} + \frac{C^E_{p,m}}{x_i}, \tag{4}$$

$$C_{p,mi} = C_{pi,\Phi} + x_i(1 - x_i)\left(\frac{\partial C_{pi,\Phi}}{\partial x_i}\right)_{p,x_{j \neq i}}, \tag{5}$$

where $C_{pi,\Phi}$ is the apparent molar heat capacity of i component ($i = 1$ for methanol and $i = 2$ for butanediol).

TABLE 2
The coefficients a_i of equation (1) for the {xBD + (1 − x)MeOH} mixtures in the temperature range from (293 to 323) K at atmospheric pressure p = 0.1 MPa.[a]

x	a_0	$a_1 \cdot 10^3$	$a_2 \cdot 10^5$	x	a_0	$a_1 \cdot 10^3$	$a_2 \cdot 10^5$
	x1,2BD + (1 − x)MeOH				*x1,3BD + (1 − x)MeOH*		
0	4.42476	−18.6661	4.14017	0	4.42476	−18.6661	4.14017
0.0476	3.27431	−11.3170	2.96145	0.0970	3.88549	−15.3258	3.57812
0.2098	2.52778	−6.35736	2.13529	0.1924	2.95668	−9.58620	2.66514
0.2964	1.53504	0.04734	1.10435	0.2893	2.67084	−7.82687	2.37455
0.3913	1.47853	0.58414	1.00254	0.3902	1.91085	−3.03448	1.61151
0.4706	1.09831	3.20701	0.54431	0.4943	1.93764	−3.20752	1.63043
0.6016	0.52863	7.05630	−0.09431	0.6067	1.55430	−0.79821	1.24837
0.6991	0.51045	7.26814	−0.14995	0.7843	1.45358	−0.19426	1.15504
0.8042	0.86830	5.24815	1.37406	0.9064	1.01997	2.58002	0.71169
0.8917	0.18426	9.70016	−0.59137	0.9165	1.30297	7.81306	0.99554
0.9224	0.69583	6.44199	−0.06979	0.9242	1.10524	2.01009	0.80585
0.9627	0.49142	7.85597	−0.31449	0.9624	1.08483	2.13749	0.78814
1	0.69849	6.51876	−0.09088	1	1.04517	2.38280	0.75734
	x1,4BD + (1 − x)MeOH				*x2,3BD + (1 − x)MeOH*		
0	4.42476	−18.6661	4.14017	0	4.42476	−18.6661	4.14017
0.1009	3.72736	−14.4242	3.41073	0.0456	3.39943	−12.2312	3.12521
0.1972	2.49506	−6.72071	2.15414	0.0847	2.81447	−8.51990	2.54172
0.2955	3.00804	−10.2748	2.72396	0.1972	2.38269	−5.80873	2.12019
0.4144	3.06293	−10.7682	2.78839	0.2792	1.56511	−0.28913	1.20248
0.5093	2.92504	−9.95675	2.64917	0.3824	1.30743	1.33684	0.95390
0.6240	1.85211	−3.13694	1.54661	0.4673	1.32011	1.60053	0.87497
0.6996	2.44740	−7.04178	2.17332	0.5862	1.10061	3.04619	0.64033
0.8004	2.35962	−6.51537	2.08290	0.7041	1.38177	1.53804	0.84576
0.8591	2.17148	−5.32416	1.89073	0.8094	3.38271	−1.15020	2.96158
0.9043	1.99469	−4.25198	1.71840	0.8169	0.48924	7.44705	−0.11604
0.9565	2.25532	−5.97474	2.00252	0.8832	0.87084	5.35196	0.15956
1	2.26261	−6.04548	2.02622	0.9271	1.06725	3.86600	0.44421
				0.9501	1.46098	1.65972	0.74040
				1	0.87842	5.72762	0.04455

[a] x is molar fraction of butanediol. Standard uncertainties u are $u(x) = 0.0001$; $u(T) = 0.01$ K; $u(p) = 10$ kPa.