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Molar heat capacities for (1-butanol + 1,4-butanediol, 2,3-butanediol, 1,2-butanediol, and 2-methyl-2,4-pentanediol) as function of temperature

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Abstract

The isobaric molar heat capacities for the binary mixtures (1-butanol + 1,4-butanediol) were determined in the temperature range from (293 to 353) K from measurements of isobaric specific heat capacity in a differential scanning calorimeter. The composition dependencies of the excess molar isobaric heat capacities obtained from the experimental results were fitted by the Redlich–Kister polynomials. Above $T = 303.15$ K, the excess isobaric molar heat capacities are negative over the whole composition range and absolute values increase with temperature. For temperatures (293.15 and 298.15) K, the excess values show S-shaped character. These excesses are however in general very small; at the temperature 298.15 K smaller than 0.1 $J \cdot K^{-1} \cdot mol^{-1}$.

Additionally, the isobaric molar heat capacities of 2,3-butanediol, 1,2-butanediol, and 2-methyl-2,4-pentanediol were determined over a similar temperature range. The experimental data for all diols are compared with available literature data and values estimated from group additivity.

Keywords: Isobaric heat capacity; DSC; Excess; Binary system; Alcohols

1. Introduction

As known, the isobaric heat capacity (which is a so-called Gibbsian property, *i.e.* a second derivative of Gibbs free energy G with respect to the temperature) is one of the main thermophysical quantities for any material, and its accurate values are needed in many areas of physics, chemistry and engineering sciences. A literature survey shows that much attention has been devoted to mixtures. However, it appears that in contrast with (alcohol + inert solvent) or (alcohol + water) systems, only a limited results are available in the literature for mixtures of alcohols.

Rather scarce are also data for pure alkanediols, however, alkanediols are very interesting from both a practical and fundamental point of view. Among others, alkanediols can be treated as model substances (model structural units), which exhibit two donor and two acceptor functions. Now then, the structure and properties of alkanediols are determined mainly by hydrogen bonds (inter- and intramolecular). Simultaneously, such interactions are often prominent forces in biological materials.

In this paper which is a continuation of earlier works related to the study of binary mixtures of 1-butanol with isomeric butanediols, the molar isobaric heat capacities $C_{p,m}$ for {1-butanol (1BU) + 1,4-butanediol (1,4BD)} over the temperature range from (293 to 353) K were determined. From these experimental data, the excess isobaric molar heat capacities $C^{E}_{p,m}$ have been calculated. These data are analyzed and discussed together with the results of the earlier investigations for {1-butanol (1BU) + 1,3-butanediol (1,3BD)} [1,2]. Moreover, the data on molar isobaric

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heat capacity for 2,3-butanediol (2,3BD), 1,2-butanediol (1,2BD), and 2-methyl-2,4-pentanediol (2MPD2,4) in the similar temperature range for 2,3BD and 2MPD2,4 from (296 to 354) K, whereas in the case of 1,2BD from (283 to 359) K are presented and compared as well with very scarce literature data (when available) as the heat capacity values estimated by means of reported recently amended group additivity [3].

It must be pointed out here that 1,4BD is one of the very interesting α,ω-alkanediols which are intramolecularly associated [4,5]. In the case of 1,4 positions of the OH groups, a rather strong internal hydrogen bond will be formed because the seven-membered associate ring is energetically favoured [5]. Unfortunately, 1,4BD is also used as an illicit drug known by recreational users as "One Comma Four" or "One Four Bee". It is interesting also that all investigated diols can be used as so-called cryoprotectant agents (first of all in cryobiology), *i.e.* antifreeze substance that prevents or reduces ice-crystal formation [6,7]. This group of cryoprotectants, *i.e.* polyols penetrate the cells and is mostly used in cell, tissues and organ cryopreservations as well as in protein crystal stabilization (RNA crystal as well). To be a cryoprotectant, a compound must be amongst other things of very low toxicity, soluble in water, and lowers the temperature of ice crystallisation at the thermodynamic equilibrium.

2. Experimental

Apart from partial degassing by means of ultrasound, the 1BU (GC > 0.998 mass fraction purity, Aldrich), 1,4BD (GC > 0.99+ mass fraction purity, Aldrich), 2,3BD (GC > 0.990 mass fraction purity, Fluka), 1,2BD (GC > 0.990 mass fraction purity, Aldrich), and 2MPD2,4 (GC > 0.990 mass fraction purity, Merck) were used without further purification. It should be noticed that according to the supplier specification, the mixture of racemic and *meso* forms of 2,3BD were used. The water content in the alcohols determined by the Karl Fischer method was $3.7 \cdot 10^{-4}$ (1BU), $3.9 \cdot 10^{-4}$ (1,4BD), $6.6 \cdot 10^{-4}$ (2,3BD), $3.0 \cdot 10^{-4}$ (1,2BD), and $6.5 \cdot 10^{-4}$ (2MPD2,4) mass fraction. Densities ρ ($T = 298.15$ K)/(kg · m^{-3}), measured with vibrating tube densimeters Anton Paar DMA 5000 (1BU, 1,4BD, and 1,2BD) and Unilab MG2 (2,3BD and 2MPD2,4), were 805.770, 1012.747, 998.408, 1000.40, and 918.22 for the 1BU, 1,4BD,1,2BD, 2,3-BU, and 2MPD2,4, respectively. These results are in reasonable agreement with the literature values [8]; deviations of $0.25 \cdot 10^{-2}$%, $1.4 \cdot 10^{-2}$%, and $1.3 \cdot 10^{-2}$% for 1BU, 1,4BD, and 2MPD2,4, respectively.

The mixtures were prepared by mass (precision $\pm 2 \cdot 10^{-8}$ kg) using a Sartorius RC 210D balance and the uncertainty in the mole fraction was estimated to be of $\pm 5 \cdot 10^{-5}$.

The specific isobaric heat capacity c_p was measured by using of a high sensitivity differential scanning calorimeter Micro DSC III, manufactured by Setaram and based on the Tian-Calvet's principle. The uncertainty of the measurements was estimated to be ±0.15% excluding the effects of sample impurities [9]. Details about the apparatus and the experimental procedure have been described elsewhere [9].

The uncertainty in the present investigations of $C_{p,\mathrm{m}}$ and $C^{\mathrm{E}}_{p,\mathrm{m}}$ are estimated to be about ±0.25% and ±1%, respectively. The molar masses are reported in terms of the 2001 IUPAC relative atomic masses [10]. The temperature scale used is the ITS-90.

3. Results and discussion

For clarity, only some selected (every 5 K) original experimental values of $C_{p,\mathrm{m}}$ ($C_{p,\mathrm{m}} = M \cdot c_p$, where M is molar mass) for pure compounds are shown in table 1. All the experimental values obtained for pure compounds and mixtures over the investigated temperature range (each time *ca.* 3000 recorded experimental points; in the case of 1,2BD *ca.* 3700) were approximated by the polynomials in form:

$$C_{p,\mathrm{m}}/R = \sum_{i=1}^{4} a_i \cdot (T/(100 \cdot \mathrm{K}))^{i-1}, \tag{1}$$

where $R = 8.314472\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ [11], a_i are fitting coefficients, and T is temperature. It must be pointed out that above equation is excellent for interpolation and scaling improve the numerical stability. The obtained a_i coefficients (unweighted least-square method), and the standard deviations from the regression lines δ are reported in table 2.

It must be pointed out here, that because the residual values of the above fit are small, the $C_{p,\mathrm{m}}$ values calculated from the obtained regression functions are equal to the raw data within the limits of the measurement uncertainty.

Comparison of our data for 1BU with the "best" recommended values obtained by temperature correlation of the

TABLE 1
The experimental $C_{p,\mathrm{m}}$ values for 1BU, 1,4BD, 2,3BD, 1,2BD, and 2MPD2,4 at various temperatures T

T/K	$C_{p,\mathrm{m}}$/(J · K^{-1} · mol^{-1})				
	1BU	1,4BD	2,3BD	1,2BD	2MPD2,4
288.15				225.51	
293.15	173.80	200.39		228.22	
298.15	177.10	203.06	236.67	230.94	263.09
303.15	180.61	205.82	239.28	233.64	267.10
308.15	184.28	208.65	241.85	236.32	271.31
313.15	188.02	211.57	244.35	238.97	275.53
318.15	192.10	214.55	246.82	241.59	279.94
323.15	196.13	217.61	249.23	244.18	284.50
328.15	200.40	220.72	251.60	246.72	289.17
333.15	204.72	223.90	253.91	249.20	293.90
338.15	209.16	227.12	256.17	251.63	298.68
343.15	213.57	230.40	258.39	254.00	303.35
348.15	218.10	233.72	260.55	256.29	308.44[a]
353.15	222.54	237.07	262.67	258.50	313.68
358.15				260.63	

[a] Calculated from equation (1).