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HEAT CAPACITIES OF BINARY MIXTURES OF 1-HEXANOL WITH HEXANE ISOMERS AT 298.15 K *

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ABSTRACT

Volumetric heat capacities were determined for binary mixtures of 1-hexanol with *n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane at 298.15 K in a Picker flow microcalorimeter The results were combined with previously published excess molar volumes to obtain excess isobaric heat capacities

INTRODUCTION

This work is part of a program to provide accurate experimental information about changes in the thermodynamic properties which result from isomeric variations in the molecular configuration of one of the components of a binary mixture. Previous papers have reported the excess enthalpies [1], excess volumes [2,3], and ultrasonic speeds and isentropic compressibilities [4,5] for binary mixtures of 1-hexanol with the five isomeric hexanes: *n*-hexane (*n*-C6), 2-methylpentane (2-MP), 3-methylpentane (3-MP), 2,2-dimethylbutane (2,2-DMB), and 2,3-dimethylbutane (2,3-DMB). As an extension of those studies, the present paper describes measurements of the heat capacities of the same set of mixtures.

EXPERIMENTAL

1-Hexanol (95 mole% practical grade from Matheson Coleman and Bell) was purfied by preparative gas chromatography using two columns, each 1.8 m long, connected in series and containing 10% by weight OV-17 and Apiezon L, respectively. The substrate in both columns was 60/80 mesh Chromosorb W. In the course of the work, the supply of 1-hexanol was

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TABLE 1

Densities, ρ, and molar isobaric heat capacities, $C_{p,m}$, of the component liquids at 298.15 K

Component	ρ(kg m^{-3})			$C_{p,m}$(J K^{-1} mole^{-1})		
	Obs		Lit.	Obs	Lit	
1-Hexanol	815.90 [a]	815.39 [b]	816.2 [c]	240.65	236.8 [c]	240.2 [d]
n-Hexane	654.88		654.84 [e]	195.80	195.48 [f]	
2-Methylpentane	648.50		648.52 [g]	193.84	193.91 [f]	
3-Methylpentane	659.78		659.76 [g]	190.77	190.67 [f]	
2,2-Dimethylbutane	644.46		644.46 [g]	189.14	188.7 [f]	
2,3-Dimethylbutane	657.09		657.02 [g]	188.77	188.8 [f]	188.80 [h]

[a] Sample I

[b] Sample II

[c] Ref 6

[d] Ref 10

[e] Ref 7, see Table 23-2-(1 101)-a dated October 31, 1977

[f] Ref 7, see Table 23-2-(1 201)-vc dated October 31, 1975

[g] Ref 7, see Table 23-2-(1 201)-a dated October 31, 1952

[h] Ref 11

exhausted and a second preparation starting from different initial material (Aldrich Chemical Co., 98 mole%) was carried out. These samples are identified as I and II. Sample I was used for mixtures with *n*-C6 and 2-MP, and sample II for mixtures with the three other hexanes. Prior to their use, the 1-hexanol samples were stored over a molecular sieve (BDH Type 3A). The hexane isomers were Research Grade materials from Phillips Petroleum Co. They were used without further purification.

Densities characterizing the samples used in the calorimetric measurements were determined at 298.15 K in an Anton Paar densimeter. These are listed in Table 1 along with values from the literature [6,7].

Heat capacities were obtained from measurements in a Picker flow microcalorimeter, using a temperature increment of about 1.5 K centred on 298.15 K. This apparatus and its operational procedure have been described previously [8,9]. The measurement yielded the difference between the isobaric heat capacities per unit volume of the liquids flowing in the test and reference cells. Pure grade *n*-heptane (Phillips Petroleum Co.) was used as the initial reference liquid, and a value of 224.764 J K^{-1} mole^{-1} was adopted for its heat capacity. Heat capacities of the hexanes were determined from comparisons with *n*-heptane, using the single reference procedure [8]. The hexanes were in turn used as initial reference liquids in stepwise measurements [9] on their mixtures were 1-hexanol. In the latter procedure, each liquid (pure component or mixture) after measurement, served as a reference for the subsequent liquid. Corrections were applied for power losses. In order to minimize errors due to mixing effects and errors inherent in the stepwise procedure, measurements on mixtures were repeated with the test and reference liquids interchanged. Some difficulty was experienced due to the formation of bubbles while the liquids were flowing through the calorimeter. This was evidenced by a relatively large difference between the results of measurements before and after interchanging the liquids. Such results were rejected.

Mixtures were prepared by weighing, and an allowance for the effect of buoyancy was included in calculating their mole fractions. The error of the mole fractions is estimated to be less than 5×10^{-5}. Molar isobaric heat capacities $C_{p,m}$ were obtained from the volumetric heat capacities $C_{p,m}/V_m$ using molar volumes V_m calculated from the densities of the components and our previous results for the excess molar volumes V_m^E [2,3]. Excess molar isobaric heat capacities were obtained from the relation

$$C_{p,m}^E = C_{p,m} - xC_{p,1}^* - (1-x)C_{p,2}^* \qquad (1)$$

where x is the mole fraction of 1-hexanol, and $C_{p,1}^*$ and $C_{p,2}^*$ are the molar isobaric heat capacities of the pure component liquids, alcohol and hexane isomer, respectively. The error of $C_{p,m}^E$ is estimated to be less than 0.05 J K^{-1} mole^{-1}.

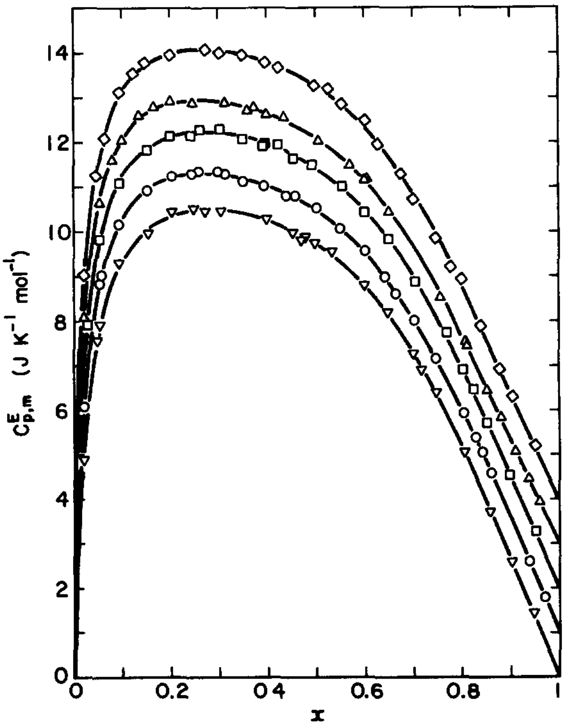

Fig 1. Excess molar heat capacities $C_{p,m}^E$ of $xC_6H_{13}OH + (1-x)\ C_6H_{14}$ mixtures at 298 15 K. Experimental results: ▽, *n*-C6; ○, 2-MP; □, 3-MP, △, 2,2-DMB, ◇, 2,3-DMB Curves calculated from eqn. (2) with coefficients from Table 3. Note that the results for the isomers in the order listed above have been increased by successive multiples of 1 J K^{-1} mole^{-1} to improve the clarity of their presentation

TABLE 2

Excess molar isobaric heat capacities for $x\mathrm{C_6H_{13}OH} + (1-x)\mathrm{C_6H_{14}}$ mixtures at 298.15 K

x	$C^E_{p,m}$ ($J\ K^{-1}\ mole^{-1}$)	x	$C^E_{p,m}$ ($J\ K^{-1}\ mole^{-1}$)	x	$C^E_{p,m}$ ($J\ K^{-1}\ mole^{-1}$)
1-Hexanol + *n*-C6					
0.01931	4.89	0.39862	10.29	0.69945	7.26
0.05024	7.59	0.45367	9.98	0.70163	7.23
0.05472	7.93	0.46981	9.82	0.71615	6.91
0.09432	9.32	0.47734	9.88	0.74674	6.40
0.15447	9.96	0.49734	9.76	0.80448	5.03
0.20376	10.45	0.53195	9.55	0.85831	3.71
0.24883	10.52	0.59901	8.80	0.90282	2.59
0.27227	10.47	0.64731	8.20	0.94709	1.44
0.30445	10.47				
1-Hexanol + 2-MP					
0.02133	5.08	0.31360	10.28	0.66303	7.59
0.05485	7.86	0.35140	10.12	0.70162	7.01
0.05851	8.02	0.39504	10.01	0.74607	6.13
0.09419	9.18	0.43990	9.79	0.80346	4.91
0.15351	9.92	0.45883	9.78	0.82814	4.37
0.20377	10.24	0.50188	9.52	0.84039	4.04
0.24530	10.29	0.54996	9.07	0.85925	3.57
0.26000	10.35	0.60028	8.55	0.93789	1.60
0.29822	10.33	0.64277	7.98	0.96958	0.79
1-Hexanol + 3-MP					
0.02873	5.94	0.34887	10.08	0.64802	7.83
0.05369	7.86	0.39060	9.92	0.70378	6.88
0.09581	9.09	0.39630	10.02	0.76761	5.75
0.15183	9.85	0.42079	9.95	0.80209	4.89
0.20107	10.15	0.45399	9.65	0.82432	4.47
0.24325	10.17	0.49335	9.50	0.85165	3.70
0.26079	10.29	0.55489	9.01	0.89633	2.55
0.30219	10.31	0.60013	8.43	0.94967	1.27
1-Hexanol + 2,2-DMB					
0.02162	5.08	0.35991	9.70	0.75564	5.53
0.05419	7.66	0.37287	9.77	0.80751	4.50
0.08147	8.62	0.39841	9.62	0.81082	4.44
0.10003	9.05	0.43545	9.56	0.85171	3.44
0.13616	9.60	0.50505	9.03	0.88038	2.83
0.16587	9.79	0.56903	8.48	0.90961	2.06
0.20144	9.90	0.60194	8.15	0.93705	1.46
0.24743	9.88	0.60631	8.16	0.95866	0.94
0.31398	9.89	0.64958	7.43		
1-Hexanol + 2,3-DMB					
0.02073	5.04	0.34722	9.95	0.70119	6.73
0.04808	7.26	0.39593	9.79	0.74705	5.86
0.06421	8.11	0.42283	9.66	0.77750	5.21
0.09559	9.12	0.49679	9.27	0.80103	4.92
0.12376	9.55	0.52573	9.19	0.83834	3.90
0.14745	9.80	0.55239	8.85	0.87812	2.91
0.20025	9.96	0.60080	8.48	0.90377	2.30
0.27283	10.08	0.62684	7.95	0.95019	1.17
0.30043	10.00	0.67569	7.29		

RESULTS AND DISCUSSION

Our results for the molar isobaric heat capacities of the component liquids are listed in Table 1. These are in reasonable agreement with values from the literature [7,10,11]. In the case of 1-hexanol, the result is an average of 39 comparisons with *n*-heptane and the hexane isomers. No significant difference was observed between the heat capacities of the two alcohol samples.

The measurements on mixtures are summarized in Table 2, where $C_{\mathrm{p,m}}^{\mathrm{E}}$ is given for various mole fractions x of 1-hexanol. Each set of results was fitted with a skewed Redlich–Kister equation

$$C_{\mathrm{p,m}}^{\mathrm{E}}/(\mathrm{J\,K^{-1}\,mole^{-1}}) = \left[x(1-x)/\{1-k(1-2x)\}\right] \sum_{j=1}^{n} c_j(1-2x)^{j-1} \quad (2)$$

Values of the coefficients, c_j, and the skewing factors, k, determined by a least-squares analysis in which all points were weighted equally, are listed in Table 3 along with the standard deviations s of the representations.

The experimental results and their representations by eqn. (2) are plotted in Fig. 1. The curves are characterized by a steep rise from $x = 0$ to a shoulder near $x = 0.15$. This is followed by a relatively flat section containing a maximum near $x = 0.25$, and a more gradual descent towards $x = 1$. We are not aware of any directly comparable previous studies * of the present mixtures, but curves of similar shape have been reported for other *n*-alcohol + alkane mixtures: ethanol + *n*-heptane [9,12], 1-propanol + *n*-hexane [13], and 1-propanol + *n*-heptane [9,13,14].

The changes in $C_{\mathrm{p,m}}^{\mathrm{E}}$ resulting from variations in the molecular configuration of the hexane are relatively small. The curves for 2-MP and 3-MP are almost the same within their combined experimental uncertainties. At $x = 0.25$, the maximum difference between the results for the five mixtures is less than 0.6 J K^{-1} mole^{-1}. The curves fall in the order

n-C6 > 2-MP > 3-MP > 2,3-DMB > 2,2-DMB

TABLE 3

Coefficients, c_j, skewing factor, k, and standard deviation, s, for least-squares representation of $C_{\mathrm{p,m}}^{\mathrm{E}}$ for $x\mathrm{C_6H_{13}OH} + (1-x)\mathrm{C_6H_{14}}$ at 298.15 K by eqn. (2)

Hexane isomer	c_1	c_2	c_3	c_4	c_5	k	s
n-C6	38.903	−22.437	4.134	8.999	−7.933	0.9497	0.064
2-MP	37.915	−20.995	3.507	8.806	−6.587	0.9448	0.039
3-MP	37.702	−21.130	3.451	9.258	−7.180	0.9474	0.063
2,2-DMB	36.375	−19.779	2.306	10.884	−7.506	0.9455	0.052
2,3-DMB	37.076	−21.018	3.370	11.694	−9.498	0.9480	0.083

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* See Note Added in Proof.

This is the same as found previously for the excess molar enthalpies [1] but differs somewhat from the order found for the excess molar volumes [2,3] and the excess isentropic compressibilities [5]. However, for all of these properties, the limiting curves are *n*-C6 and 2,2-DMB as in the present work. Previously we suggested that *n*-C6 was more effective than 2,2-DMB in disrupting the H-bonds between alcohol molecules [1]. It appears from the present results that near 298.15 K, the disparity in this ability increases with temperature.

Finally, it must be pointed out that the present measurements were not extended to high enough dilutions of the alcohol to detect the presence of a negative minimum of $C_{p,m}^{E}$ such as has been reported for mixtures of 1-hexanol with longer *n*-alkanes [15].

NOTE ADDED IN PROOF

Since the submission of this paper we have learned of $C_{p,m}^{E}$ measurements for 1-hexanol + *n*-hexane at 298.15 K by Bravo et al. [16]. Their results are in excellent agreement with ours. We are indebted to Dr. J.-P.E. Grolier (Université de Clermont II, France) for bringing these data to our attention.

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