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EXCESS ENTHALPIES AND HEAT CAPACITIES FOR 2,5,8-TRIOXANONANE + *n*-HEPTANE MIXTURES *

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ABSTRACT

Flow calorimetric techniques were used to determine excess enthalpies and volumetric heat capacities of 2,5,8-trioxanonane + *n*-heptane mixtures at 25°C. The molar excess enthalpies are positive over the entire mole fraction range. The molar excess isobaric heat capacities are negative and exhibit a maximum and two minima.

INTRODUCTION

A recent publication [1] from our laboratory reported excess volumes and isentropic compressibilities for mixtures of 2,5,8-trioxanonane (bis-2-methoxyethyl ether) with *n*-heptane at 25°C. The present paper describes direct calorimetric measurements of excess enthalpies and volumetric (isobaric) heat capacities for the same system.

EXPERIMENTAL

2,5,8-Trioxanonane with a stated purity of 99%, obtained from the Aldrich Chemical Co., was used as received. At 25°C the density of this material was 938.70 kg m^{-3} and its refractive index (n_D) was 1.40579. Both these values are lower than those for the samples used in our previous studies [1] but are close to those reported by Wallace and Mathews [2]. Phillips Petroleum Co. pure grade *n*-heptane was also used without further purification. At 25°C its density and refractive index were 679.60 kg m^{-3} and 1.38505, respectively.

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Excess enthalpies were determined in an LKB flow microcalorimeter using a Keithley 180 Nanovoltmeter to measure the thermopile output. Further details of the equipment and operational procedure have been described by Tanaka et al. [3]. Over most of the mole fraction range, the errors of the molar excess enthalpy, H_m^E, and the mole fraction, x, are estimated to be less than 1 J mole^{-1} and 5×10^{-4}, respectively.

A Picker flow microcalorimeter was used to determine the difference of volumetric (isobaric) heat capacities between pairs of liquids flowing in the test and reference cells. This apparatus has been described previously [4,5]. Mixtures were prepared by mass, and in calculating the mole fractions, corrections for the effect of buoyancy were applied. The error of the mole fraction is estimated to be less than 5×10^{-5}. A stepwise procedure [5] was adopted for most of the measurements and the pure grade *n*-heptane was used as the initial reference liquid. Comparison of the latter with an NBS standard sample of *n*-heptane gave a value of 274.764 J K^{-1} mole^{-1} for its molar isobaric heat capacity at 25°C. The results were corrected for power losses, and errors due to mixing effects were minimized by averaging measurements with the test and reference liquids interchanged. Volumetric heat capacities, $C_{p,m}/V_m$, were converted into molar isobaric heat capacities, $C_{p,m}$, using molar volumes, V_m, calculated from the densities of the component liquids and our previous results for the molar excess volumes [1]. The error of the molar excess isobaric heat capacities, $C_{p,m}^E$, is estimated to be less than 0.05 J K^{-1} mole^{-1}.

RESULTS AND DISCUSSION

The experimental values of H_m^E and $C_{p,m}^E$ for $xC_6H_{14}O_3 + (1-x)C_7H_{16}$ at 25°C are listed in Tables 1 and 2, and plotted in Figs. 1 and 2. These results

TABLE 1

Molar excess enthalpies for $xC_6H_{14}O_3 + (1-x)C_7H_{16}$ mixtures at 25°C

x	H_m^E (J mole^{-1})	x	H_m^E (J mole^{-1})	x	H_m^E (J mole^{-1})
0.05	372.79	0.40	1586.26	0.70	1352.74
0.10	683.78	0.45	1618.28	0.75	1215.99
0.15	937.56	0.50	1620.65	0.80	1042.56
0.20	1143.92	0.50	1620.41	0.85	834.82
0.25	1307.55	0.55	1596.17	0.90	594.81
0.30	1432.07	0.60	1543.55	0.95	316.53
0.35	1527.40	0.65	1462.27		

TABLE 2

Molar excess isobaric heat capacities for $x\mathrm{C_6H_{14}O_3}+(1-x)\mathrm{C_7H_{16}}$ mixtures at 25°C

x	$C^{\mathrm{E}}_{\mathrm{p,m}}$ (J K^{-1} mole^{-1})	x	$C^{\mathrm{E}}_{\mathrm{p,m}}$ (J K^{-1} mole^{-1})	x	$C^{\mathrm{E}}_{\mathrm{p,m}}$ (J K^{-1} mole^{-1})
0.05159	−0.562	0.39780	−0.621	0.67355	−0.816
0.09329	−0.848	0.45157	−0.594	0.70015	−0.780
0.12307	−0.992	0.49663	−0.567	0.74786	−0.833
0.15223	−1.025	0.49793	−0.648	0.80295	−0.817
0.19730	−1.031	0.52603	−0.657	0.83496	−0.822
0.24686	−0.930	0.55308	−0.654	0.87445	−0.765
0.27273	−0.854	0.59823	−0.659	0.90292	−0.588
0.31043	−0.829	0.64992	−0.690	0.95075	−0.388
0.34799	−0.750	0.65058	−0.763		

were fitted with the smoothing function

$$X^{\mathrm{E}} = x(1-x)\sum_{j=1}^{n} a_j(1-2x)^{j-1} \tag{1}$$

where X^{E} is either $H^{\mathrm{E}}_{\mathrm{m}}$ or $C^{\mathrm{E}}_{\mathrm{p,m}}$. Values of the coefficients a_i, determined by

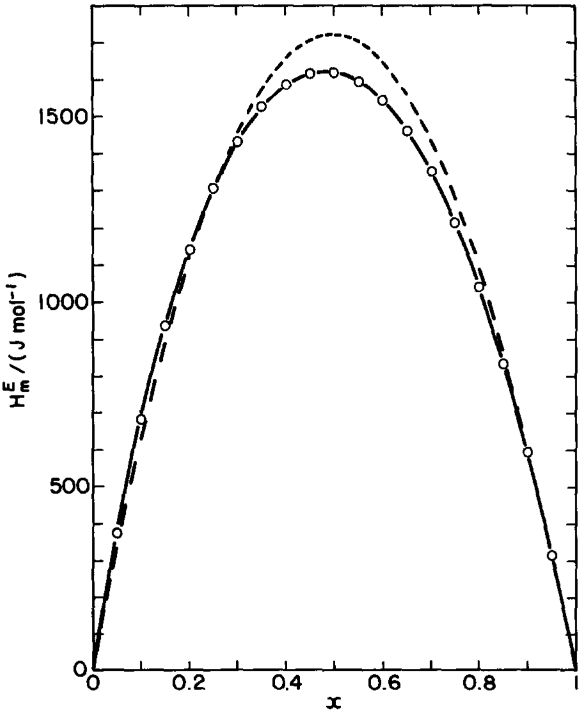

Fig. 1. Molar excess enthalpies of $x\mathrm{C_6H_{14}O_3}+(1-x)\mathrm{C_7H_{16}}$ mixtures at 25°C. (○) Our experimental results for $H^{\mathrm{E}}_{\mathrm{m}}$; (————) least-squares representation of $H^{\mathrm{E}}_{\mathrm{m}}$ by eqn. (1); (- - - - -) $H^{\mathrm{E}}_{\mathrm{m}}$ estimated from the theory described in ref. 10.

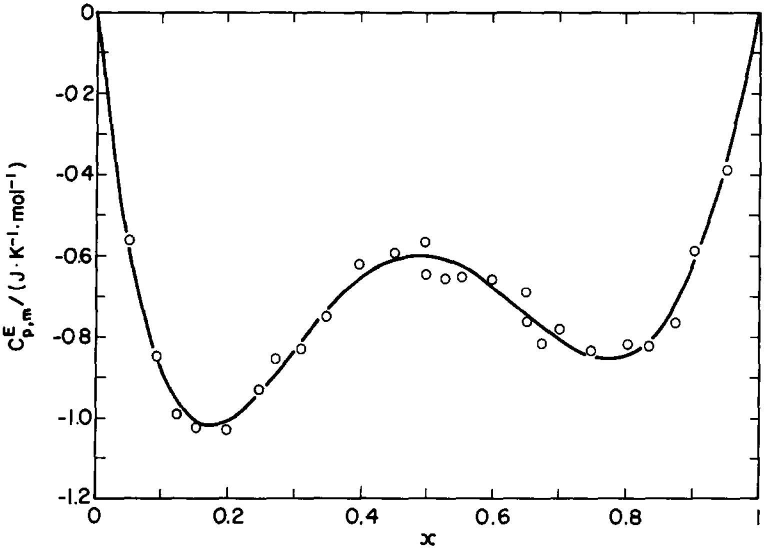

Fig. 2. Molar excess isobaric heat capacities of $xC_6H_{14}O_3+(1-x)C_7H_{16}$ mixtures at 25°C. (O) Our experimental results; (———) least-squares representation of $C^E_{p,m}$ by eqn. (1).

the method of least-squares with all points assigned unit weight, are given in Table 3 together with the standard deviations, s, of the representations. Curves calculated from these representations are also shown in Figs. 1 and 2.

A comparison between the present results for H^E_m and those of other investigators [6,7] is given in Fig. 3, where deviations from our smoothing function are plotted. For the most part, our results fall between the two sets reported previously but are closer to those of Kehiaian et al. [6]. Deviations between our results and those of Villamañan et al. [7] are relatively large and exceed 5% for an equimolar mixture. This is larger than the inherent errors of the calorimetric determinations and must be attributed to differences in the purities of the 2,5,8-trioxanonane used in the two investigations.

TABLE 3

Coefficients, a_j, and standard deviations, s, for representations of H^E_m and $C^E_{p,m}$ by eqn. (1)

	H^E_m (J mole^{-1})	$C^E_{p,m}$ (J K^{-1} mole^{-1})
a_1	6482.64	−2.403
a_2	430.72	0.360
a_3	968.58	−9.422
a_4	283.22	−3.346
s	1.04	0.032

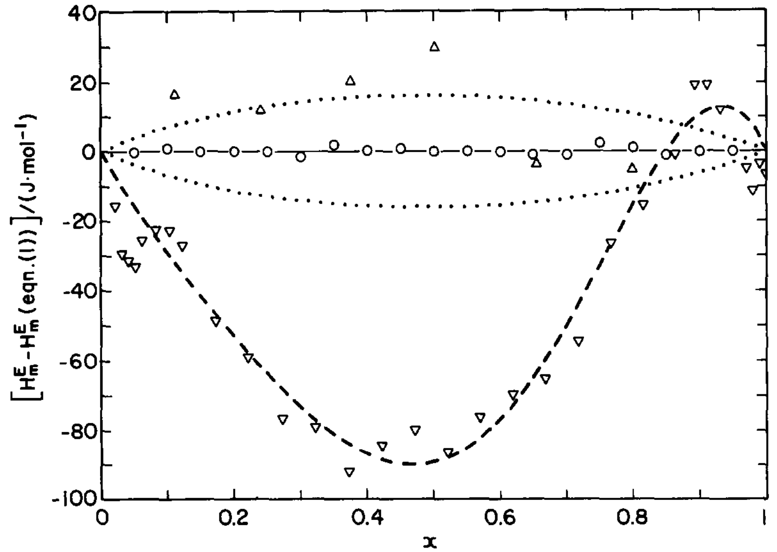

Fig. 3. Difference plot for molar excess enthalpies of $xC_6H_{14}O_3+(1-x)C_7H_{16}$ mixtures at 25°C. (○) Our experimental results; (△) Kehiaian et al. [6]; (▽) Villamañan et al. [7]; (······)±1% deviation; (------) calculated from the smoothing function given in ref. 7.

During the course of our studies, five stepwise runs were carried out in the Picker microcalorimeter. The mean value of the molar isobaric heat capacity of 2,5,8-trioxanonane derived from these was (279.05 ± 0.05) J K^{-1} mole^{-1}. This is ~2% higher than the result, 274 J K^{-1} mole^{-1}, determined by Beaumont et al. [8], but differs by less than 0.3% from the value 279.84 J K^{-1} mole^{-1} reported more recently by Villamañan et al. [9].

Recently the excess enthalpies of ether + *n*-alkane mixtures have been interpreted in terms of a group surface interaction theory [10]. For the present mixture, parameters describing the geometry of the groups and their interactions were taken from ref. 10, and the broken curve in Fig. 1 was calculated. The agreement with the experimental curve (i.e., within ~ 100 J mole^{-1} for $x = 0.5$) seems reasonable in view of the simple assumptions of the model.

In Fig. 2, the unusual shape of the curve for $C_{p,m}^E$ suggests that the variation of the group interactions with temperature is probably rather complex. Similar W-shaped $C_{p,m}^E$ curves have been reported for binary mixtures of 1,4-dioxane with *n*-alkanes [11] and it appears that they may be a characteristic of polyether + *n*-alkane mixtures.

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