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EXCESS ENTHALPIES AND HEAT CAPACITIES FOR 3,6-DIOXAOCTANE + *n*-HEPTANE MIXTURES *

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ABSTRACT

Flow calorimetric measurements of excess enthalpies and excess isobaric heat capacities are reported for 3,6-dioxaoctane + *n*-heptane mixtures at 298.15 K. Throughout the composition range, the excess enthalpies are positive and the excess heat capacities are negative. The excess enthalpies are compared with the results of calculations using a model involving group surface interactions.

INTRODUCTION

In the course of our investigations of the thermodynamic properties of ether + *n*-alkane mixtures, we recently reported excess enthalpies and excess heat capacities for di-*n*-propylether ($C_6H_{14}O$) + *n*-heptane mixtures [1], and for 2,5,8-trioxanonane ($C_6H_{14}O_3$) + *n*-heptane mixtures [2]. The present paper describes similar direct calorimetric measurements of excess enthalpies and volumetric (isobaric) heat capacities for mixtures of 3,6-dioxaoctane ($C_6H_{14}O_2$, ethyleneglycol diethylether) with *n*-heptane at 298.15 K.

EXPERIMENTAL

3,6-Dioxaoctane from the Aldrich Chemical Co. (stated purity 95%) was repeatedly shaken with mercury until there was no evidence of a reaction. It was stored in the dark prior to its use in the experimental measurements. The density of this sample at 298.15 K was 0.84130 g cm^{-3}, which is somewhat higher than the value 0.8362 g cm^{-3} reported recently by Villamañan et al. [3]. Phillips Petroleum Co. Pure Grade *n*-heptane with a density of 0.67968 g cm^{-3} was used as received.

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The excess enthalpies were determined in an LKB flow microcalorimeter thermostated to ±0.002 K at 298.15 K. Details of the equipment and operating procedure have been described in previous papers from our laboratory [2,4]. Differences of the isobaric heat capacity per unit volume, $C_{p,m}/V_m$, were measured by a stepwise procedure [5,6] in a Picker flow microcalorimeter using a temperature interval of 1.4 K centred on 298.15 K. A value of 224.764 J K^{-1} mol^{-1} was adopted for the molar isobaric heat capacity of the *n*-heptane at 298.15 K [7] *. Binary mixtures were prepared by mass; the molar volumes of these were calculated from their excess molar volumes [8] and the densities of the component liquids.

RESULTS AND DISCUSSION

The molar isobaric heat capacity determined for 3,6-dioxaoctane at 298.15 K is (261.05 ± 0.12) J K^{-1} mol^{-1}. This is the average of results obtained in five stepwise runs and several direct comparisons with *n*-heptane. It is in close agreement with the value 261.08 J K^{-1} mol^{-1} reported by Villamañan et al. [9], despite the different densities noted above for the two samples.

The experimental results for the excess molar enthalpies, H_m^E, and the excess molar isobaric heat capacities, $C_{p,m}^E$, of x $C_6H_{14}O_2$ + $(1-x)$ C_7H_{16} mixtures at 298.15 K are summarized in Tables 1 and 2. The following smoothing equations were obtained from least-squares analyses in which each point was assigned unit weight

$$H_m^E/(\mathrm{J\ mol^{-1}}) = x(1-x)\left[3556.5 + 311.5(1-2x) + 436.0(1-2x)^2 + 222.4(1-2x)^3\right] \quad (1)$$

TABLE 1

Excess molar enthalpies for x $C_6H_{14}O_2 + (1-x)$ C_7H_{16} mixtures at 298.15 K

x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})
0.0528	221.3	0.3996	875.5	0.7003	731.0
0.1001	381.4	0.4503	893.4	0.7497	656.4
0.1501	514.3	0.5004	889.9	0.7996	555.8
0.2000	629.4	0.5501	871.7	0.8498	441.4
0.2499	724.5	0.6000	844.4	0.9000	316.0
0.3003	788.5	0.6502	791.1	0.9500	165.0
0.3502	837.4				

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* A misprint occurred in quoting this value in ref. 1.

TABLE 2

Excess molar isobaric heat capacities for $x\ C_6H_{14}O_2 + (1-x)C_7H_{16}$ mixtures at 298.15 K

x	$C^{E}_{p,m}$ (J K^{-1} mol^{-1})	x	$C^{E}_{p,m}$ (J K^{-1} mol^{-1})	x	$C^{E}_{p,m}$ (J K^{-1} mol^{-1})
0.05513	−0.228	0.27703	−0.519	0.69711	−0.669
0.07594	−0.277	0.30263	−0.480	0.74368	−0.652
0.09600	−0.281	0.32108	−0.574	0.80185	−0.578
0.09746	−0.238	0.34705	−0.571	0.84080	−0.483
0.12817	−0.313	0.39338	−0.617	0.87500	−0.457
0.12907	−0.346	0.43093	−0.609	0.89994	−0.393
0.15103	−0.370	0.55186	−0.677	0.91355	−0.328
0.19858	−0.424	0.59780	−0.673	0.94907	−0.235
0.22654	−0.422	0.64326	−0.676	0.96916	−0.140

and

$$C^{E}_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}}) = x(1-x)\left[-2.579 + 0.769(1-2x) - 1.684(1-2x)^2\right] \tag{2}$$

The standard deviations of these representations are 3.2 J mol^{-1} and 0.027 J

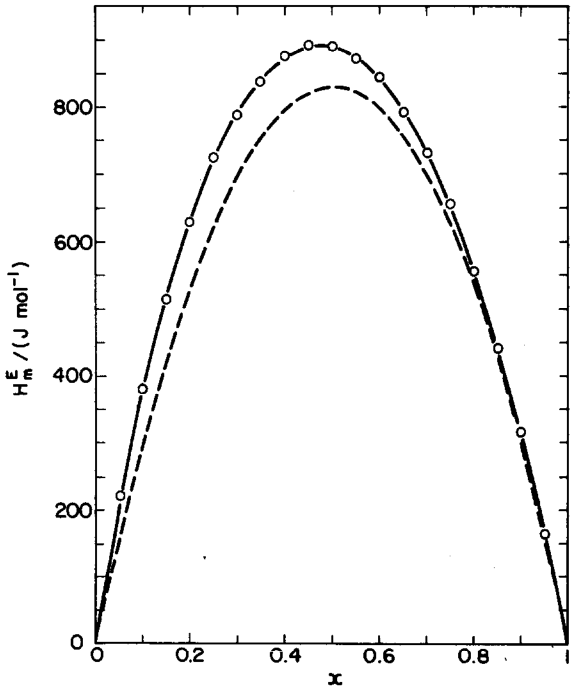

Fig. 1. Excess molar enthalpies of $x\ C_6H_{14}O_2 + (1-x)\ C_7H_{16}$ mixtures at 298.15 K. (○) Our experimental results for H^{E}_{m}; (———) least-squares representation of H^{E}_{m} by eqn. (1); (- - - - -) H^{E}_{m} estimated from the theory described in ref. 10.

K^{-1} mol^{-1}, respectively. Plots of the experimental results and their smoothing equations are shown in Figs. 1 and 2.

In our work to date we have studied mixtures of the type x $C_6H_{14}O_p$ + $(1-x)$ C_7H_{16} for the cases $p = 1$ (di-*n*-propylether) [1], $p = 2$ (3,6-dioxaoctane) reported here, and $p = 3$ (2,5,8-trioxanonane) [2]. The shapes of the excess enthalpy curves are similar in all three cases, and the magnitude of H_m^E increases with the number of etheric linkages. A generalized quasichemical theory of mixtures in terms of group surface interactions [10] provides a semi-quantitative interpretation of the enthalpy results. For the present mixture the formula for H_m^E becomes

$$H_m^E = x(1-x)q_1q_2\alpha_{e1}^2h_{ae}/[xq_1 + (1-x)q_2] \qquad (3)$$

where q_1 and q_2 are the molecular surface areas of 3,6-dioxaoctane and *n*-heptane, respectively, α_{e1} is the surface ratio of etheric oxygen in 3,6-dioxaoctane, and h_{ae} is the molar interchange enthalpy for surface contacts between aliphatic and etheric groups. Using values of q_1, q_2, α_{e1} and h_{ae} from ref. 10, the broken curve in Fig. 1 was calculated. At $x = 0.5$ it falls 59 J mol^{-1} (about 6.6%) below the experimental curve. Previously we found for the di-*n*-propylether mixture [1] and the 2,5,8-trioxanonane mixture [2] that the theoretical estimates at $x = 0.5$ exceeded the experimental results by

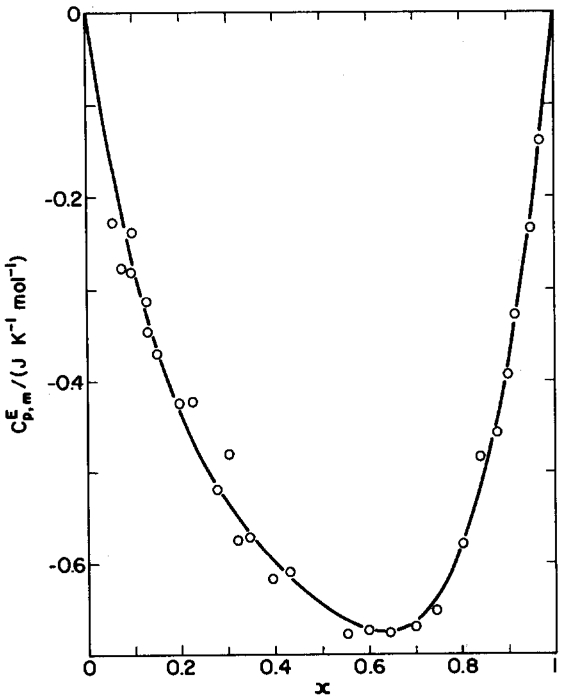

Fig. 2. Excess molar isobaric heat capacities of x $C_6H_{14}O_2 + (1-x)$ C_7H_{16} mixtures at 298.15 K. (○) Our experimental results; (————) least-squares representation of $C_{p,m}^E$ by eqn. (2).

10.6% and 6.2%, respectively. Agreement within about 10% of the experimental results is reasonable in view of the simple assumptions of the theory.

The values of $C^{E}_{p,m}$ for 3,6-dioxaoctane + *n*-heptane are negative at all compositions, as are those for the di-*n*-propylether mixture [1] and the 2,5,8-trioxanonane mixture [2] studied previously. The curve of $C^{E}_{p,m}$ for the present mixture is most similar to that for the monoether but is more skewed towards high mole fractions of the ether. It shows no sign of the double minimum observed for the triether and thus is contrary to our earlier suggestion [2] that such behaviour might be a characteristic of polyether + *n*-alkane mixtures.

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