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Excess enthalpies and excess volumes of methanol + *n*-decane mixtures at 298.15 K

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Abstract

Excess molar enthalpies, measured in a flow microcalorimeter, and excess molar volumes, derived from density determinations are reported for $x\mathrm{CH_3OH} + (1-x)\mathrm{C_{10}H_{22}}$ mixtures at 298.15 K. At this temperature, the components are only partially miscible for $0.107_7 < x < 0.973_7$.

INTRODUCTION

There have been many previous investigations of the excess thermodynamic properties of binary mixtures of methanol with *n*-hexane and with *n*-heptane. In comparison, mixtures of methanol with longer chain *n*-alkanes have received relatively little attention. This paper describes determinations of the excess enthalpies and the excess volumes of methanol + *n*-decane mixtures at 298.15 K.

EXPERIMENTAL

Materials

The methanol (A.C.S. HPLC grade, stated purity 99.9+ mol.%) and the *n*-decane (stated purity 99+ mol.%) were obtained from the Aldrich Chemical Co. Both materials were used as received.

Calorimetric measurements

Excess molar enthalpies $H^{\mathrm{E}}_{\mathrm{m}}$ were measured in an LKB flow microcalorimeter (Model 10700-1) thermostated at 298.150 ± 0.002 K. This equipment and its modifications have been described previously [1, 2].

The present system is only partially miscible over the central range of

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concentrations, and difficulties were experienced in obtaining reproducible results for mixtures with overall compositions close to or within the region of phase separation. The use of different total flow rates was investigated, but it was not possible to obtain reproducible values of H_m^E for mole fractions x of methanol in the range $0.08 < x < 0.3$. Usually our calorimeter produces results which are reproducible within about 0.5% over the central range of concentration. However, for the present system where the regions of complete miscibility are close to the ends of the mole fraction range, the estimated error of H_m^E is about 5%.

Density measurements

Excess molar volumes V_m^E were derived from densities measured at 298.150 ± 0.003 K in an Anton Paar densimeter (Model DMA 02C). Mixtures were prepared by weighing in "onion" cells [3], specially designed to minimize evaporation effects. The error of the overall mole fraction x is estimated to be less than 1×10^{-4}.

The contents of the cells were stirred and equilibrated in an air bath maintained at 298.150 ± 0.003 K. In cases where the contents separated into two layers, densities were measured for samples of the upper and/or lower layers, withdrawn with a hypodermic syringe. The error of V_m^E derived from densities in the regions of complete miscibility is estimated to be less than 1×10^{-3} cm^3 mol^{-1}.

RESULTS

Excess enthalpies

The experimental values of H_m^E are summarized in Table 1 and plotted in Fig. 1. The linearity of the results for mole fractions in the range $0.3 < x < 0.9$ can be interpreted as an indication of phase separation.

In the analysis of the data, the results were separated into three sets: A, B and C. A and B consisted of points in the regions of complete miscibility near $x = 0$ and $x = 1$, respectively. The third set, C, comprised points in the central region of partial miscibility. Polynomials of the form

$$H_m^E(x)/(\mathrm{J\ mol^{-1}}) = \sum_{j=0}^{n} c_j z^j \tag{1}$$

with $z = x$ for sets A and C, and $z = 1 - x$ for set B, were determined to

TABLE 1

Excess molar enthalpies $H_m^{E\,a}$ for xCH$_3$OH + $(1-x)$C$_{10}$H$_{22}$ mixtures at 298.15 K

Set	x	H_m^E/ J mol^{-1}	Set	x	H_m^E/ J mol^{-1}	Set	x	H_m^E/ J mol^{-1}
A	0.0200	237.4	C	0.4001	346.2	C	0.7499	242.8
A	0.0400	338.1	C	0.4501	334.0	C	0.8001	226.4
A	0.0400	342.9	C	0.5001	318.7	C	0.8501	209.5
A	0.0500	349.9	C	0.5500	303.0	C	0.9000	193.6
A	0.0500	352.1	C	0.6000	290.0	B	0.9800	120.2
A	0.0600	370.6	C	0.6500	275.2	B	0.9800	129.4
C	0.3499	360.2	C	0.6999	257.7	B	0.9800	127.6

[a] Representations of H_m^E by eqn. (1) and their standard deviations s: set A, $H_m^E/(\mathrm{J\,mol^{-1}}) = x(1.6826\times10^4 - 2.9857\times10^5x + 2.4729\times10^6x^2 - 7.4378\times10^6x^3)$; $s = 6.4$; set B, $H_m^E/(\mathrm{J\,mol^{-1}}) = 6288.2(1-x)$; $s = 4.9$; set C, $H_m^E/(\mathrm{J\,mol^{-1}}) = 469.78 - 304.00x$; $s = 2.1$.

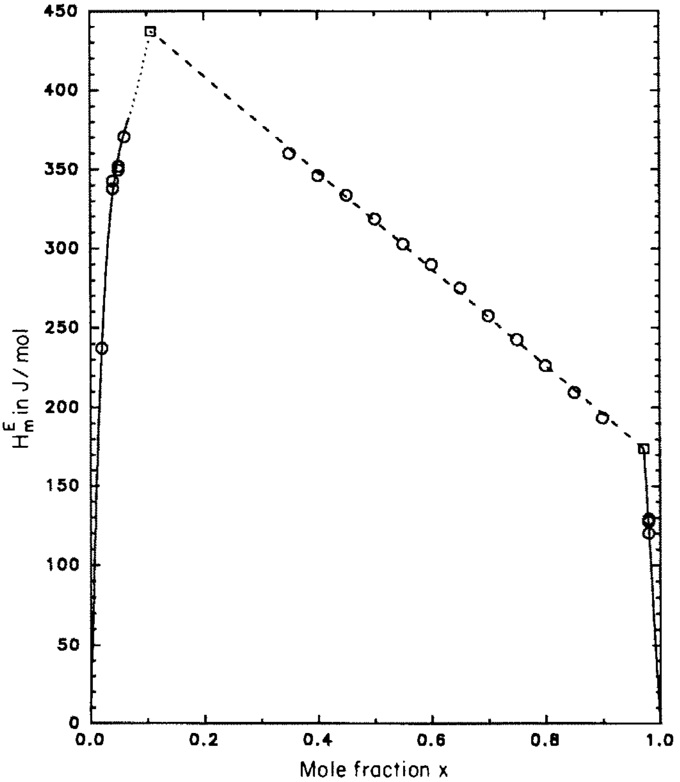

Fig. 1. Excess molar enthalpies H_m^E for xCH$_3$OH + $(1-x)$C$_{10}$H$_{22}$ mixtures at 298.15 K: ○, experimental results; □, limits of region of partial miscibility. Curves calculated from the representations given in the footnote of Table 1.

represent the data in each set. In order to obtain a form suitable for extrapolating the results of set A to larger values of x, it was necessary to draw a reasonable spline fit of the data and to use this in determining the values of the coefficients in eqn. (1). Coefficients for the three representations of the results by eqn. (1) are listed in the footnote of Table 1, along with the standard deviations s of the representations. Plots of these representations are shown in Fig. 1, where the limiting points for phase separation at $x = 0.1074$ and $x = 0.9723$ are also indicated. The latter were obtained by solving for the intersections of the representation of set C with the representations of sets A and B, respectively.

Excess volumes

The experimental values of the densities, measured for various overall mole fractions x, are listed in Table 2, where the results are again separated into three sets. Two values are reported for set C in cases where the densities of both the upper and lower layers were determined.

TABLE 2

Densities ρ and excess molar volumes V_m^E [a] for $x CH_3OH + (1 - x) C_{10}H_{22}$ mixtures at 298.15 K

Set	x	ρ/ (g cm^{-3})	V_m^E/ (cm^3 mol^{-1})	Set	x	ρ/(g cm^{-3})	
						Upper layer	Lower layer
A	0.0	0.726262	0.0	C	0.1185	0.726604	
A	0.0194	0.726191	0.0847	C	0.1192	0.726580	
A	0.0202	0.726194	0.0867	C	0.1288	0.726583	
A	0.0381	0.726240	0.1350	C	0.1299	0.726593	
A	0.0498	0.726303	0.1583	C	0.1499	0.726603	
A	0.0507	0.726312	0.1589	C	0.1701	0.726601	
A	0.0696	0.726408	0.1987	C	0.1701	0.726615	
A	0.0799	0.726440	0.2261	C	0.1805	0.726602	
A	0.0994	0.726554	0.2646	C	0.1999	0.726608	
B	0.9800	0.778855	0.1396	C	0.1999	0.726606	
B	0.9800	0.778838	0.1406	C	0.4999	0.726652	
B	0.9900	0.782655	0.0697	C	0.6959	0.726638	0.777054
B	1.0	0.786742	0.0	C	0.7999	0.726631	0.777083
				C	0.9000	0.726716	0.777054
				C	0.9201		0.777204
				C	0.9300		0.777125
				C	0.9401		0.777135
				C	0.9499		0.777094
				C	0.9700		0.777105

[a] Representations of V_m^E by eqn. (3) and their standard deviations s: set A, V_m^E (cm^3 mol^{-1}) $= x(5.8061 - 93.1982x + 1005.9x^2 - 3884.5x^3)$; $s = 0.0018$; set B, V_m^E (cm^3 mol^{-1}) $= 7.0011(1 - x)]; s = 0.0005$.

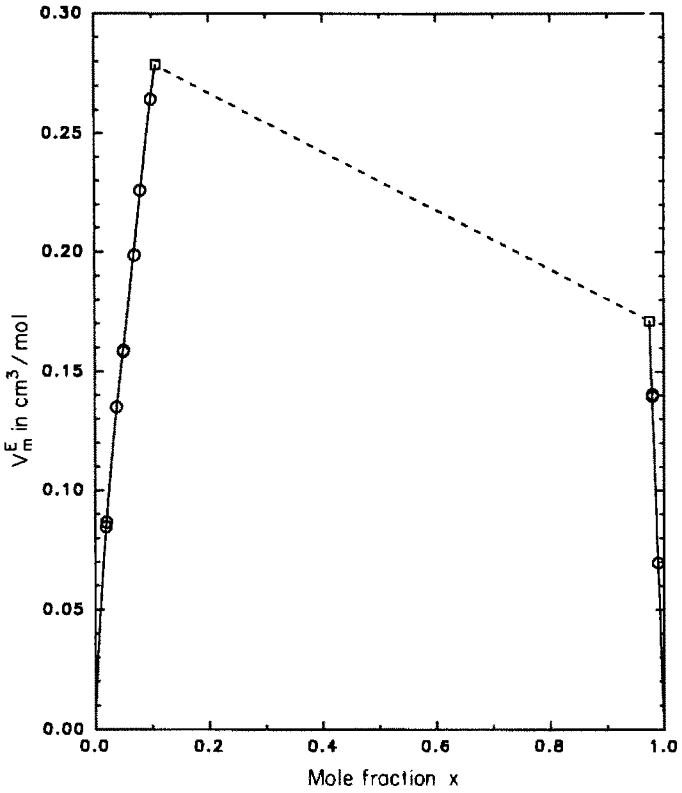

Fig. 2. Excess molar volumes V_m^E for $x\text{CH}_3\text{OH} + (1-x)\text{C}_{10}\text{H}_{22}$ mixtures at 298.15 K: ○, experimental results; □, limits of region of partial miscibility. Curves calculated from the representations given in the footnote of Table 2.

Values of V_m^E were obtained from the densities in sets A and B, using the relationship

$$V_m^E = [xM_1 + (1-x)M_2]/\rho - [xV_1^0 + (1-x)V_2^0] \tag{2}$$

where M_i and V_i^0 are respectively the molar mass and molar volume of component i (1 for methanol, and 2 for n-decane). The results of these calculations are included in Table 2 and are plotted in Fig. 2. Coefficients for the representations of V_m^E by the form

$$V_m^E(x)/(\text{cm}^3\,\text{mol}^{-1}) = \sum_{j=0}^{n} c_j z^j \tag{3}$$

with $z = x$ and $z = 1 - x$ for set A and set B, respectively, are listed in the footnote of Table 2, along with their standard deviations. These representations are also plotted in Fig. 2.

The limiting mole fractions for phase separation were obtained by solving eqns. (2) and (3) simultaneously for x, using the average values for the densities from set C. For the upper layer, $\rho_{av} = 0.726617 \pm 0.000034$ g cm^{-3} leads to $x = 0.1080$; for the lower layer, $\rho_{av} = 0.777105 \pm 0.000044$ g cm^{-3} leads to $x = 0.9751$.

DISCUSSION

We are not aware of any directly comparable excess enthalpies or excess volumes for this system. H_m^E for methanol + n-hexane at 298.15 K has been reported by Van Ness and Abbott [4]; V_m^E for methanol + n-heptane at 298.15 K was investigated by Treszczanowicz and Benson [5]. In both cases, the region of partial miscibility is not as broad as was found for the n-decane system, and although the absolute slopes of the curves in the miscible regions are not as great, the curves rise to higher values before phase separation occurs. Near $x = 0$, these differences are attributable in part to greater disruption of the orientational order of the alkane molecules in the case of n-decane; near $x = 1$, the longer n-decane molecule is more effective in disrupting the H-bonded structure of the methanol.

The miscibility limits obtained from the present calorimetric and density determinations agree well, and their averages yield $0.107_7 < x < 0.973_7$ for the range of partial miscibility of $x\text{CH}_3\text{OH} + (1-x)\text{C}_{10}\text{H}_{22}$ at 298.15 K. Sorensen and Arlt [6] and Macedo and Rasmussen [7] have compiled liquid–liquid equilibrium data for some methanol + n-alkane mixtures. The value given for the solubility of n-decane in methanol at 298.15 K corresponds to $x = 0.9753$. No value is available for the solubility of methanol in n-decane, but the values for n-hexane, n-heptane, n-tetradecane, and n-hexadecane correspond to $x = 0.2322$, 0.137, 0.05887, and 0.0475, respectively. Our values for the miscibility limits are reasonable in comparison with these data.

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