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Excess molar enthalpies of some 2,2-dimethyl-3,6-dioxaheptane + *n*-alkane binary mixtures at 298.15 K

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Abstract

Flow microcalorimetric measurements of excess molar enthalpies at 298.15 K are reported for $x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_{v-2}CH_3$ with v being 6, 7, 8, 10 or 12. Smooth representations of the results are presented and analyses in terms of the Flory theory are described.

Keywords: Alkane; Binary system; Dimethyldioxaheptane; Excess molar enthalpy; Flory; Microcalorimetry

1. Introduction

Previous papers from our laboratory have reported excess molar enthalpies of several systems formed by mixing a symmetrical diether (2,4-dioxapentane [1] or 2,5-dioxahexane [1] or 3,6-dioxaoctane [2]) with various *n*-alkanes. Here we describe the results of a similar investigation in which the unsymmetrical diether 2,2-dimethyl-3,6-dioxaheptane (DMDOH) was mixed at 298.15 K with each of the normal alkanes: hexane, heptane, octane, decane and dodecane.

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2. Experimental

2.1. Materials

The DMDOH, octane, decane and dodecane were obtained from Aldrich Chemical Co. The hexane and heptane were Pure Grade materials from Phillips Chemical Co. All of the components had stated purities of at least 99 mol% and were used without further purification. Their densities, measured at 298.15 K in an Anton-Paar digital densimeter, were 840.61, 655.11, 679.75, 698.70, 726.37 and 745.28 kg m^{-3} for DMDOH, hexane, heptane, octane, decane and dodecane, respectively.

2.2. Equipment and technique

Excess molar enthalpies H_m^E were measured at 298.15 K in an LKB flow microcalorimeter (Model 10700-1) maintained within ± 0.002 K of the operating temperature. This equipment and its operating procedure have been described previously [3,4]. Over most of the mole fraction range, the errors in H_m^E and the ether mole fraction x are estimated to be less than 0.5% and 5×10^{-4}, respectively.

3. Results and discussion

The experimental values of x and H_m^E for the five binary mixtures are summarized in Table 1, and plotted in Fig. 1. The smoothing equation

$$H_m^E/(\mathrm{J\ mol^{-1}}) = x(1-x) \sum_{j=1}^{m} h_j(1-2x)^{j-1} \tag{1}$$

was fitted to each set of results. Values of the parameters h_j, determined by the method of least squares with all points weighted equally, are listed in Table 2, along with the standard deviation s of each representation.

The solid curves shown in Fig. 1 were calculated from Eq. (1) using the values of the parameters given in Table 2. For a fixed value of x, H_m^E increases fairly regularly with increasing chain length of the *n*-alkane. The curve for hexane is nearly symmetrical about $x = 0.5$, but the curves for the longer *n*-alkanes show an increasing skew towards $x = 1$. We are not aware of any directly comparable studies of the present systems. However, the shapes and changing symmetry of the curves are similar to those reported previously for a number of monoether + *n*-alkane systems: diethyl ether [5], di-*n*-propyl ether [6], diisopropyl ether [7], di-*n*-butyl ether [8], di-*n*-pentyl ether [9], methyl *n*-butyl ether [10], methyl *tert*-butyl ether [11] and methyl *tert*-amyl ether [12].

Previously [5–12], it was found that the Flory theory [13,14] provided a good basis for the correlation of the excess molar enthalpies of many ether + *n*-alkane mixtures. The same treatment was applied to the present set of systems. The characteristic pressures p^*, molar volumes V_m^* and temperatures T^* of the components are listed in Table 3. The values of these parameters for DMDOH were

Table 1
Experimental excess molar enthalpies H^E_m at 298.15 K

x	H^E_m/ (J mol^{-1})	x	H^E_m/ (J mol^{-1})	x	H^E_m/ (J mol^{-1})	x	H^E_m/ (J mol^{-1})
$x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_4CH_3$							
0.0500	179.9	0.2999	678.4	0.5004	755.5	0.7500	526.3
0.1002	316.0	0.3499	721.5	0.5501	740.9	0.8000	437.2
0.1500	438.2	0.4002	748.2	0.6002	708.3	0.8500	345.6
0.2000	536.2	0.4502	756.2	0.6505	662.2	0.9000	237.6
0.2499	615.2	0.4737	757.2	0.7000	603.7	0.9499	119.0
$x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_5CH_3$							
0.0500	180.4	0.3002	700.7	0.5506	803.4	0.8001	492.0
0.1000	320.3	0.3499	756.1	0.5998	771.5	0.8499	386.9
0.1501	441.4	0.4004	797.6	0.6501	724.7	0.9000	268.7
0.1997	544.3	0.4502	817.0	0.6995	663.5	0.9501	136.3
0.2500	630.4	0.5000	820.6	0.7502	581.4		
$x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_6CH_3$							
0.0499	181.7	0.3003	733.5	0.5497	858.6	0.8002	537.9
0.1001	331.2	0.3502	795.5	0.6000	825.5	0.8501	427.7
0.1501	457.2	0.3986	837.9	0.6499	778.6	0.9001	298.5
0.1996	565.1	0.4506	862.7	0.7001	715.5	0.9501	149.5
0.2500	662.1	0.4997	872.2	0.7502	631.8		
$x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_8CH_3$							
0.0501	190.5	0.3005	792.1	0.5502	959.7	0.8001	632.9
0.1000	345.4	0.3505	865.0	0.6000	931.7	0.8500	507.5
0.1500	482.2	0.4005	920.4	0.6505	885.5	0.9001	359.9
0.2000	598.8	0.4505	959.3	0.7005	822.4	0.9500	190.2
0.2502	706.8	0.5003	971.4	0.7500	739.9		
$x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_{10}CH_3$							
0.0500	209.0	0.3002	860.8	0.5503	1082.6	0.7502	851.9
0.1001	371.0	0.3510	934.9	0.5999	1053.8	0.7998	738.5
0.1500	518.8	0.4002	1003.6	0.6505	1007.7	0.8500	593.7
0.2001	649.2	0.4503	1050.7	0.7005	940.3	0.9001	425.6
0.2500	761.1	0.4993	1081.1	0.7499	851.3	0.9500	226.0

Table 2
Parameters h_j and standard deviations s for the representations of H^E_m for $x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_{v-2}CH_3$ at the temperature 298.15 K by Eq. (1)

v	h_1	h_2	h_3	h_4	h_5	h_6	s
6	3026.86	397.71	87.47	283.96			2.8
7	3277.99	253.63	−272.48	−165.96	422.65	560.79	1.4
8	3477.74	137.75	−196.26	−173.78	333.16	519.62	2.2
10	3873.97	−119.81	−246.02	−421.95	513.71	713.19	2.2
12	4302.74	−565.67	−193.57	324.08	650.17		3.8

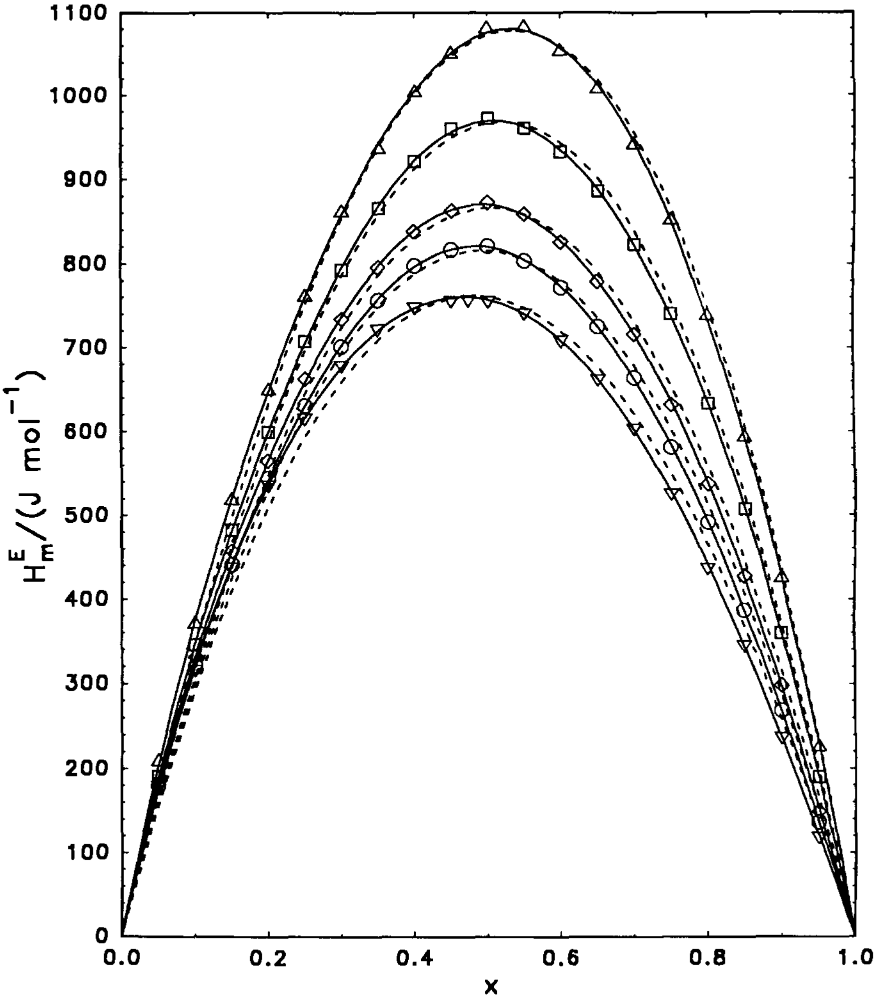

Fig. 1. Excess molar enthalpies H^E_m at 298.15 K for the mixtures $x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_{v-2}CH_3$. Experimental results: ▽, $v = 6$; ○, $v = 7$; ◇, $v = 8$; □, $v = 10$; △, $v = 12$. Curves: ——, calculated from Eq. (1) with coefficients from Table 2; – – –, calculated from the Flory theory with X_{12} from Eq. (2).

obtained from the Flory formalism [13,14] using the values of the thermodynamic properties given in the footnote of the table. The parameters for the n-alkanes were taken from our previous work [5–12]. Also listed in Table 3 is the ratio s_{12} of ether-to-alkane molecular surface areas of contact per segment, and the interchange-energy parameter X_{12} for each mixture. The values of s_{12} were calculated from the values of V^*_m for the components, assuming the molecules to be spherical. The values of X_{12} in the sixth column of the table were obtained from least squares analyses in which the Flory formula for H^E_m was fitted to the individual representa-

Table 3
Parameters used in Flory theory calculations for DMDOH + *n*-alkane mixtures at 298.15 K

Component	p^*/ (J cm^{-3})	V_m^*/ (cm^3 mol^{-1})	T^*/ K	s_{12}	X_{12}/(J cm^{-3})	
					Fit of H_m^E	Eq. (2)
DMDOH [a]	504.0	123.00	4846.1			
Hexane	424.2	99.52	4436.1	0.9318	25.421	25.428
Heptane	431.9	113.60	4648.1	0.9739	25.852	25.856
Octane	436.8	127.70	4827.0	1.0126	26.432	26.404
Decane	447.0	155.75	5091.4	1.0819	27.828	27.854
Dodecane	445.2	184.40	5351.4	1.1445	29.787	29.779

[a] Parameters were derived from the following thermodynamic properties at 298.15 K: molar volume V_m/(cm^3 mol^{-1}) = 157.27; isobaric expansivity α_p/kK^{-1} = 1.16 from measured densities; isothermal compressibility κ_T/TPa^{-1} = 1117 from an estimate of the thermal pressure coefficient by the molecular-group method of Manzini and Crescenzi [15].

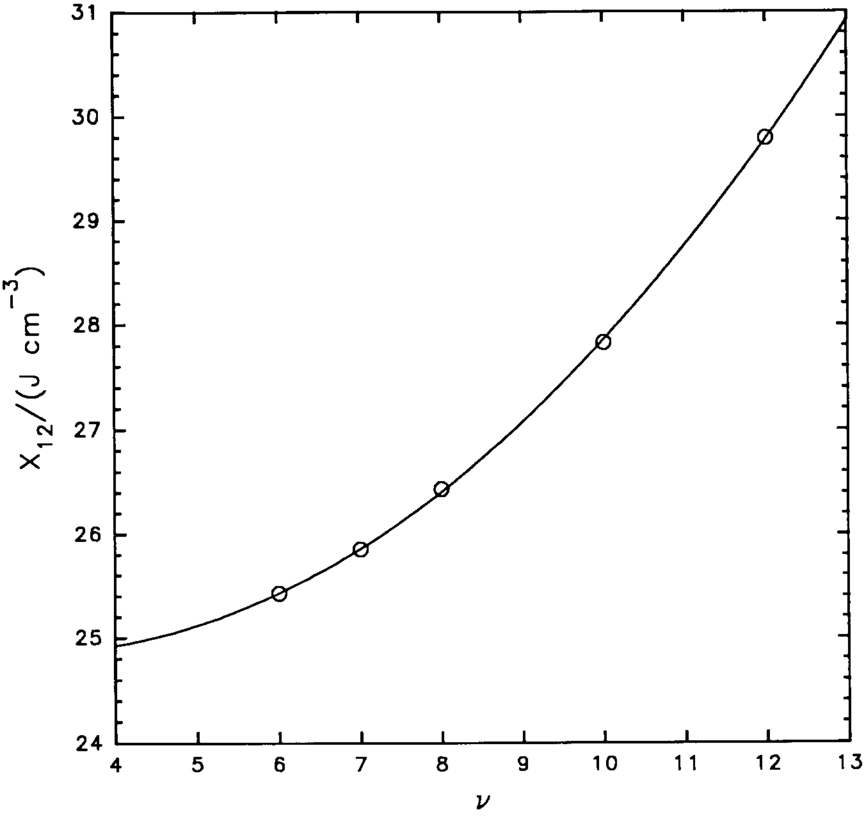

Fig. 2. Flory interchange-energy parameter X_{12} for $x(CH_3)_3COCH_2CH_2OCH_3 + (1-x)CH_3(CH_2)_{\nu-2}CH_3$ mixtures at 298.15 K plotted against the number ν of carbon atoms in the *n*-alkane. Points: ○, from fit of H_m^E (column 6 in Table 3). Curve: ——, plotted from Eq. (2).

tions of the experimental results by Eq. (1). A plot of these values of X_{12} against the number v of carbon atoms in the n-alkane is shown in Fig. 2.

It can be seen from Fig. 2 that X_{12} increases with increasing v and is approximated closely by the quadratic form

$$X_{12}/(\mathrm{J\ cm^{-3}}) = 25.3479 - 0.3426v + 0.0593v^2 \tag{2}$$

Values of X_{12} calculated from this equation are listed in the last column of Table 3; these were used in the Flory formula for H_m^E to calculate the broken curves in Fig. 1. Although these curves are slightly more skewed towards $x = 1$, the general good agreement with the experimental curves indicates that Eq. (2), used in conjunction with the Flory theory, can provide useful estimates of H_m^E for mixtures of DMDOH with other n-alkanes having chain lengths between 6 and 12, for which experimental results are unavailable.

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