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Excess enthalpies for binary mixtures formed by 2,5,8,11-tetraoxadodecane with homologous *n*-alkanes

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Abstract

Excess enthalpies, measured at 298.15 K, are reported for binary mixtures of 2,5,8,11-tetraoxadodecane with some homologous *n*-alkanes from C_7 to C_{12}. The excess enthalpies are positive with maximum values between 1.7 and 2.3 kJ mol^{-1}, located near the equimolar concentration. Use of the Flory theory to correlate the data is examined.

INTRODUCTION

A recent paper [1] from our laboratory presented (among other data) excess volumes for binary mixtures of 2,5,8,11-tetraoxadodecane (TODD) with *n*-heptane, *n*-octane, *n*-decane and *n*-dodecane. The present paper describes measurements of the excess enthalpies of the same set of mixtures. The data resulting from these studies should be useful in modelling the thermodynamic properties of polyethylene glycol dimethyl ether + *n*-alkane mixtures using equation of state theories.

EXPERIMENTAL

TODD from the Aldrich Chemical Co. with a stated purity of 99 mol.% was stored over molecular sieve beads (Type 4A) and used without further purification. Its density at 298.15 K, determined in an Anton–Paar densimeter, was 980.57 kg m^{-3}. The samples of the *n*-alkanes were the same as used in our previous work [1].

Excess molar enthalpies, H_m^E, were determined in an LKB flow microcalorimeter (Model 10700-1) thermostated to ±0.002 K at 298.15 K. Details of the equipment and its operation have been described previously [2,3].

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TABLE 1

Experimental results for excess molar enthalpies H_m^E (J mol^{-1}) of $x CH_3(OCH_2CH_2)_3OCH_3 + (1-x)C_nH_{2n+2}$ mixtures at 298.15 K

x	H_m^E	x	H_m^E	x	H_m^E	x	H_m^E	x	H_m^E
$n=7$									
0.0500	477.5	0.2492	1482.0	0.4450	1717.6	0.5995	1548.8	0.7506	1030.5
0.0999	846.5	0.2997	1606.5	0.4451	1714.3	0.6497	1421.7	0.7998	790.9
0.1498	1105.5	0.3496	1672.8	0.4995	1717.4	0.6993	1258.9	0.8504	620.8
0.2014	1322.6	0.3994	1703.1	0.5496	1636.1				
$n=8$									
0.1000	912.8	0.3499	1800.8	0.4502	1864.8	0.5999	1778.8	0.7002	1539.0
0.1500	1192.2	0.3500	1802.4	0.4999	1883.7	0.5999	1780.8	0.7499	1363.8
0.1999	1408.8	0.4000	1852.2	0.5000	1888.4	0.6500	1701.7	0.8000	1182.6
0.2501	1581.7	0.4500	1874.4	0.5498	1845.0	0.7001	1568.3	0.9001	637.7
0.2998	1706.7								
$n=10$									
0.0500	501.8	0.2997	1878.5	0.5053	2111.1	0.6352	1971.6	0.7499	1652.2
0.1000	922.1	0.3499	1992.3	0.5343	2100.4	0.6499	1919.4	0.8002	1434.7
0.1499	1272.6	0.4007	2059.7	0.5456	2078.0	0.6828	1845.3	0.8506	1161.5
0.1995	1523.1	0.4508	2104.3	0.5873	2048.1	0.6997	1804.9	0.8999	843.0
0.2504	1717.8	0.4958	2110.1	0.5998	2029.5	0.7306	1694.2	0.9500	435.8
$n=12$									
0.0500	479.4	0.3536	2100.3	0.4964	2212.8	0.5981	2142.6	0.7490	1804.3
0.0997	904.1	0.3962	2157.1	0.4998	2218.4	0.6003	2159.2	0.7994	1593.9
0.1510	1282.5	0.3994	2177.5	0.5497	2202.2	0.6466	2046.7	0.8999	928.1
0.2499	1822.5	0.4508	2203.0	0.5499	2201.7	0.6923	1943.1	0.9500	529.6
0.2998	1971.3	0.4510	2211.1						

Some difficulties were experienced in achieving thorough mixing when the normal total flow rate (5.0×10^{-9} m^3 s^{-1}) was employed. It was found necessary to operate at a reduced flow rate of 7.5×10^{-10} m^3 s^{-1} to obtain reproducible results. Over most of the mole-fraction range, the errors in H_m^E and the mole fraction x are estimated to be less than 1% and 5×10^{-4}, respectively.

RESULTS AND DISCUSSION

The excess molar enthalpies of $x CH_3(OCH_2CH_2)_3OCH_3 + (1-x) C_nH_{2n+2}$ mixtures at 298.15 K are listed in Table 1 for $n = 7$, 8, 10 and 12, and are plotted in Fig. 1. The smoothing function

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

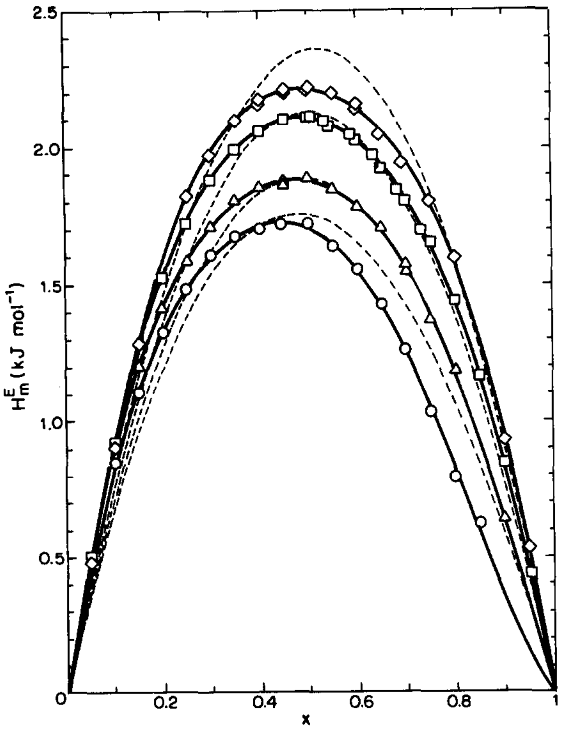

Fig. 1. Excess molar enthalpies, H_m^E (kJ mol^{-1}), for $x CH_3(OCH_2CH_2)_3OCH_3 + (1-x)C_nH_{2n+2}$ mixtures at 298.15 K. Experimental results: ○, $n = 7$; △, $n = 8$; □, $n = 10$, ◇, $n = 12$. Curves: ———, least-squares representation by eqn. (1); — — —, calculated from the Flory theory with X_{12} given by eqn. (3).

was fitted to the results for each mixture. Values of the coefficients, h_j, determined by a least-squares analysis with all points weighted equally, are given in Table 2, together with the standard deviations s of the representations. Curves calculated from eqn. (1) are shown in Fig. 1.

The excess molar enthalpies of the present systems are positive at all mole fractions. The curves in Fig. 1 are nearly symmetric about $x = 0.5$ and, as in

TABLE 2

Coefficients, h_j, and standard deviations, s, for representations of H_m^E (J mol^{-1}) for $x CH_3(OCH_2CH_2)_3OCH_3 + (1-x)C_nH_{2n+2}$ mixtures at 298.15 K by eqn. (1)

n	h_1	h_2	h_3	h_4	h_5	s
7	6797.0	1665.3	−222.0	2598.1		16.1
8	7509.7	611.3	1614.3	1894.9		10.6
10	8432.2	385.5	2151.9	342.0		9.5
12	8858.7	352.0	3312.5	−963.4	−1610.6	13.6

the case of the excess molar volumes [1], the maxima increase with increasing chain length of the n-alkane.

Excess molar enthalpies at 298.15 K have been reported previously for TODD + n-heptane [4] and for TODD + n-dodecane [5]. In the case of the mixture with n-heptane, our results agree reasonably well with those of Marongiu et al. [4]: for an equimolar mixture, the difference is ≈ 5 J mol^{-1}. However, the present results for the mixture with n-dodecane are all significantly higher than those published previously [5]; for an equimolar mixture, the difference is ≈ 220 J mol^{-1}. In view of the difficulties noted in the preceding section, it is possible that the discrepancies can be attributed to incomplete mixing in the earlier work.

In studying the excess volumes of the present systems [1], it was found that the results could be correlated reasonably well by the Flory theory [6,7] with the interchange-energy parameter, X_{12}, expressed by the linear function

$$X_{12}\ (\mathrm{J\ cm^{-3}}) = 65.0054 - 0.4299n \qquad (2)$$

Using this relation and the values of the characteristic pressures, volumes and temperatures given in ref. 1, yields estimates of H_m^E which are considerably higher than the observed values: at $x = 0.5$, the discrepancies are 453, 361, 259 and 246 J mol^{-1} for the systems with $n = 7$, 8, 10 and 12, respectively.

In contrast to eqn. (2), values of X_{12} adjusted to give the best overall fit of the Flory formula for H_m^E to each system separately tend to increase with n, and are approximated by the function

$$X_{12}\ (\mathrm{J\ cm^{-3}}) = 41.3717 + 1.3278n \qquad (3)$$

H_m^E curves calculated from the Flory theory using X_{12} values given by eqn. (3) are shown in Fig. 1. The discrepancies between the theoretical and experimental curves are considerably less than when eqn. (2) is used. This behaviour is not unusual, as it is often found that Flory analyses of excess enthalpy and excess volume data lead to different values of X_{12}.

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