T_i^0	boiling temperature of pure component i, K
t	temperature, °C
x_i, y_i	mole fraction of component i in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation

Registry No. Methanol, 67-56-1; propyl bromide, 106-94-5; methyl methacrylate, 80-62-6.

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Excess Enthalpies for Binary Mixtures of 2,5,8-Trioxanonane or 2,5,8,11,14-Pentaoxapentadecane with *n*-Alkanes at 298.15 K

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Excess enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the binary systems formed by mixing 2,5,8-trioxanonane with *n*-hexane, *n*-decane, and *n*-dodecane, and by mixing 2,5,8,11,14-pentaoxapentadecane with *n*-hexane, *n*-heptane, and *n*-decane. All of the excess enthalpies are strongly positive, with maxima which are located near the equimolar concentration.

Introduction

Previously we reported thermodynamic properties of oligo(oxyethylene) alkyl ether–*n*-alkane mixtures containing 2,5-dioxahexane (*1*, *2*), 3,6-dioxaoctane (*3–5*), 2,5,8-trioxanonane (*1*, *6*, *7*), and 2,5,8,11-tetraoxadecane (*8*, *9*). Systems of this type have also been studied by Kehiaian et al. (*10*), and more recently by Booth and co-workers (*11*, *12*).

The present paper extends our previous investigations by describing measurements of the excess enthalpies for binary mixtures of 2,5,8-trioxanonane (diethylene glycol dimethyl ether) with *n*-hexane, *n*-decane, and *n*-dodecane, and of 2,5,8,11,14-pentaoxapentadecane (tetraethylene glycol dimethyl ether) with *n*-hexane, *n*-heptane, and *n*-decane. Data for such series of mixtures are needed in the development of lattice and equation of state theories for this class of systems.

Experimental Section

In the course of the present work, the 2,5,8-trioxanonane (Aldrich Chemical Co., labeled 99 mol %) was purified by fractional distillation from sodium. The 2,5,8,11,14-pentaoxapentadecane (purum, >98 mol %) was obtained from Fluka. Prior to their use, both ethers were stored over molecular sieve beads, Type 3A. The *n*-alkanes were obtained from the Phillips Petroleum Co. and were stored over Type 4A molecular sieve beads. The *n*-hexane was Research Grade (purity exceeding 99.9 mol %); the *n*-heptane, *n*-decane, and *n*-dodecane were Pure Grade (purity exceeding 99 mol %). Densities, ρ, characterizing the component liquids at 298.15 K are compared in Table I with data from the literature (*11*, *13–16*).

Table I. Densities, ρ, for the Component Liquids at 298.15 K

component	ρ, kg m^{-3} obsd	ρ, kg m^{-3} lit.
2,5,8-trioxanonane	939.52	944.0,[a] 938.4,[b] 942[c]
2,5,8,11,14-pentaoxapentadecane	1006.51	1004.7,[d] 1007[c]
n-hexane	654.99	654.84[e]
n-heptane	679.71	679.46[e]
n-decane	726.25	726.35[e]
n-dodecane	745.35	745.18[e]

[a] Reference *13*. [b] Reference *14*. [c] Estimated from density (measured within ±2 kg m^{-3}) at 304.15 K in ref *11*, using thermal expansivity. [d] Reference *15*. [e] Reference *16*.

Molar excess enthalpies, H^E_m, were determined in a LKB flow microcalorimeter (Model 10700-1) thermostated to ±0.002 K at 298.15 K. Details of this equipment and its operation have been described previously (*17*, *18*). Over most of the mole fraction range, the errors in H^E_m and in the mole fraction x are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

The experimental values of H^E_m are listed in Table II, where in all cases x is the mole fraction of the polyether. The results for 2,5,8-trioxanonane are plotted in Figure 1; those for 2,5,8,11,14-pentaoxapentadecane are shown in Figure 2. The equation

$$H^E_m/\mathrm{J\ mol^{-1}} = x(1-x)\sum_{j=1}^{k} h_j(1-2x)^{j-1} \qquad (1)$$

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients, h_j, and the standard deviations, s, for these representations are given in Table III. Curves calculated from eq 1 are shown

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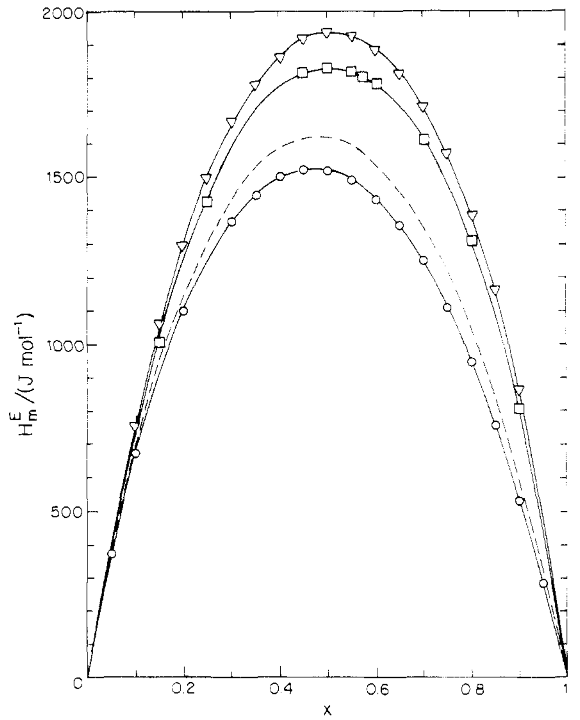

Figure 1. Molar excess enthalpies, H^E_m, of $\{xCH_3(OCH_2CH_2)_2OCH_3 + (1 - x)C_aH_{2a+2}\}$ mixtures at 298.15 K. Points are experimental results: (○) a = 6; (□) a = 10; (▽) a = 12. Curves: (—) calculated from eq 1 with coefficients from Table III; (- - -) a = 7 taken from ref *6*.

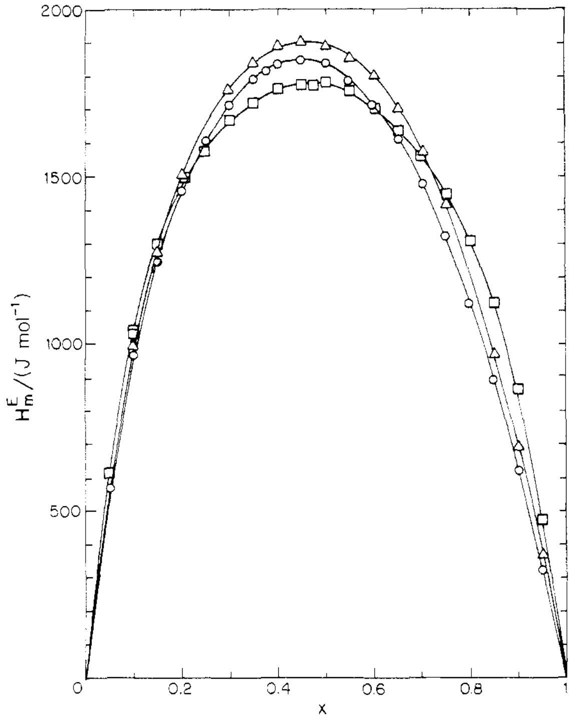

Figure 2. Molar excess enthalpies, H^E_m, of $\{xCH_3(OCH_2CH_2)_4OCH_3 + (1 - x)C_aH_{2a+2}\}$ mixtures at 298.15 K. Points are experimental results: (○) a = 6; (▽) a = 7; (□) a = 10. Curves: (—) calculated from eq 1 with coefficients from Table III.

Table II. Experimental Results for the Molar Excess Enthalpies, H^E_m, of $\{xCH_3(OCH_2CH_2)_nOCH_3 + (1 - x)C_aH_{2a+2}\}$ Mixtures 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}
		n = 2, a = 6			
0.0500	371.5	0.4503	1524.2	0.7504	1110.8
0.1000	674.3	0.5002	1520.9	0.8001	947.3
0.2001	1101.1	0.5501	1491.5	0.8501	757.1
0.3002	1367.8	0.6001	1433.5	0.9001	531.3
0.3500	1449.2	0.6504	1356.3	0.9501	283.2
0.4005	1503.0	0.6996	1250.6		
		n = 2, a = 10			
0.1500	1007.5	0.5498	1817.3	0.7040	1615.4
0.2503	1426.9	0.5751	1797.8	0.8026	1309.6
0.4506	1813.1	0.6046	1782.4	0.9016	806.8
0.5003	1827.2				
		n = 2, a = 12			
0.1001	755.6	0.4004	1861.6	0.7001	1713.8
0.1500	1060.7	0.4506	1916.8	0.7503	1573.3
0.2001	1298.4	0.5005	1936.3	0.7999	1386.6
0.2502	1501.2	0.5507	1924.8	0.8501	1163.8
0.3001	1669.7	0.6001	1887.0	0.9000	866.9
0.3499	1779.3	0.6501	1814.9		
		n = 4, a = 6			
0.0501	569.6	0.3758	1818.7	0.6999	1478.8
0.1000	966.4	0.3998	1837.6	0.7503	1324.4
0.1500	1247.4	0.4498	1851.3	0.7997	1123.6
0.2006	1456.3	0.4999	1838.1	0.8498	891.4
0.2506	1606.9	0.5493	1785.5	0.8996	619.4
0.3000	1714.9	0.5983	1719.2	0.9493	325.1
0.3500	1793.0	0.6500	1613.8		
		n = 4, a = 7			
0.0501	575.1	0.4000	1887.3	0.6999	1571.1
0.1000	993.1	0.4500	1903.4	0.7501	1415.5
0.1501	1272.4	0.5003	1895.3	0.8499	968.0
0.2009	1506.9	0.5012	1891.5	0.8998	685.7
0.3005	1762.7	0.5495	1862.8	0.9000	694.4
0.3504	1841.0	0.5497	1857.6	0.9499	368.7
0.3506	1842.7	0.5999	1802.1		
0.3995	1890.5	0.6495	1701.9		
		n = 4, a = 10			
0.0500	618.4	0.3501	1722.0	0.6500	1641.0
0.1000	1034.3	0.4001	1765.2	0.6998	1557.4
0.1001	1043.2	0.4499	1775.6	0.7499	1447.9
0.1502	1301.0	0.4746	1774.2	0.8000	1308.9
0.2000	1473.8	0.4996	1782.6	0.8500	1123.4
0.2502	1576.4	0.4998	1784.8	0.9000	865.2
0.2999	1671.4	0.5499	1760.1	0.9500	475.9
0.3500	1726.2	0.5996	1704.7	0.9500	475.0

Table III. Coefficients, h_j, and Standard Deviations, s, for Least-Squares Representations of H^E_m for $\{xCH_3(OCH_2CH_2)_nOCH_3 + (1 - x)C_aH_{2a+2}\}$ Mixtures at 298.15 K by Eq 1

h_j	n = 2 a = 6	n = 2 a = 10	n = 2 a = 12	n = 4 a = 6	n = 4 a = 7	n = 4 a = 10
h_1	6085.3	7309.3	7743.7	7336.1	7586.4	7121.6
h_2	632.8	−163.1	−157.9	1233.8	834.5	584.4
h_3	848.9	1934.6	1742.1	1580.0	2122.0	2335.0
h_4	502.4	−743.0	−900.0	731.5	1904.4	166.3
h_5	177.9		394.3	1126.8	888.2	7215.5
h_6				1703.1		1405.1
h_7						−4080.9
s	2.2	3.8	4.5	2.7	5.2	6.1

in Figures 1 and 2. The smooth representation of our previous results for 2,5,8-trioxanonane-n-heptane (*6*) is also included in Figure 1 for comparison. [In Table 3 of ref *6*, the coefficient a_3 for H^E_m is misprinted. The corrected value is 964.58.]

The molar excess enthalpy curves are all nearly symmetrical about x = 0.5. The maxima of H^E_m for mixtures with 2,5,8-trioxanonane increase as the size of the n-alkane increases, and $H^E_m(x_{max})$ is nearly linear in the number of C atoms in the alkane. For the 2,5,8,11,14-pentaoxapentadecane systems, $H^E_m(x_{max})$ increases on going from n-hexane to n-heptane, but then decreases for n-decane. Al-Kafaji and Booth (*11*) found that, at 304.15 K, this ether is incompletely miscible with n-alkanes in the range C_{10} to C_{17}. Immiscibility was not observed in the present work at 298.15 K, but the broader curve for H^E_m and the lower value of $H^E_m(x_{max})$ may be precursors of immiscibility at higher temperatures.

The only literature data, which are directly comparable with the present results, are those of Kehiaian et al. (*10*) for 2,5,8-trioxanonane–*n*-decane. Near $x = 0.5$, these are about 3% higher than our curve.

Excess enthalpies at 304.15 K have been reported for binary mixtures of 2,5,8-trioxanonane with *n*-decane and with *n*-dodecane (*11*). For equimolar mixtures, these are ~250 J mol^{-1} higher than our results at 298.15 K. In combination with our results, they indicate unrealistically large positive molar excess isobaric heat capacities (~40 J K^{-1} mol^{-1}), which are in sharp contrast to the small negative values obtained from direct measurements of the heat capacities of mixtures of the same ether with *n*-heptane (*6*).

Registry No. 2,5,8-Trioxanonane, 111-96-6; 2,5,8,11,14-pentaoxapentadecane, 143-24-8; *n*-hexane, 110-54-3; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; *n*-heptane, 142-82-5.

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Vapor Pressures of Ammonium Bromide + Ammonia and Ammonium Iodide + Ammonia Solutions

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Vapor pressures for ammonium bromide + ammonia and ammonium iodide + ammonia solutions were measured in the concentration ranges of 10–65 wt % and 10–75 wt % at various temperatures, respectively. The observed vapor pressures were fitted to Antoine's equation, using the method of least squares. Furthermore, Antoine's constants for both solutions were expressed as fourth-degree functions of concentration of ammonium halides. In addition, vapor pressures for saturated ammonia solutions of ammonium halide were measured over the temperature range of 0–80 °C. The calculated vapor pressures by these equations at 25 °C were compared with Hunt's data, and good agreement was obtained. Vapor pressure measurements were carried out by using a strain gauge transducer (up to 2.0 MPa), and the accuracy of this measurement was ±0.001 MPa. The vapor pressures calculated by Antoine's equation agreed with the observed values within a deviation of ±2.7%.

Introduction

Reaction products from ammonium halides and liquid ammonia are referred as ammine complexes or ammoniated salts. Recently, these complexes in the liquid phase have been utilized as a working system for chemical energy storage and chemical heat pumps (*1*, *2*, *3*).

Table I. Vapor Pressure of Saturated Ammonia Solution of Ammonium Halide

temp, °C	press., MPa	temp, °C	press., MPa
	NH_4Br–NH_3 System		
0.5	0.094	47.3	0.456
5.8	0.115	50.0	0.491
10.6	0.138	54.5	0.564
16.0	0.162	59.1	0.647
20.3	0.190	63.8	0.740
25.5	0.231	69.0	0.855
30.9	0.267	73.5	0.967
34.3	0.294	78.6	1.098
41.6	0.374	83.2	1.255
	NH_4I–NH_3 System		
0.6	0.043	44.6	0.182
8.5	0.053	48.3	0.198
14.5	0.066	50.4	0.212
16.0	0.074	53.8	0.226
19.1	0.080	59.0	0.259
25.0	0.101	60.1	0.261
28.4	0.110	63.8	0.286
35.8	0.138	68.9	0.315
39.6	0.158	82.6	0.469

Ammonium bromide + ammonia and ammonium iodide + ammonia solutions were valuable as the working system (*4*). However, the physical properties of these systems, especially the observed values for vapor pressure, were not reported sufficiently. Vapor pressures of these two systems at 25 °C

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