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THERMODYNAMIC PROPERTIES FOR 2, 5, 8, 11-TETRAOXADODECANE + *n*-DODECANE MIXTURES AT 298.15 K *

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ABSTRACT

Flow calorimetric measurements of the excess molar enthalpy and excess molar isobaric heat capacity, dilatometric measurement of the excess molar volume, and pulse-echo-overlap determinations of the speed of sound were carried out over the whole composition range for mixtures of 2,5,8,11-tetraoxadodecane with *n*-dodecane at 298.15 K. The excess molar enthalpy and excess molar volume are positive at all mole fractions. The speed of sound shows negative deviations from linearity on a mole fraction basis. The excess molar isobaric heat capacity exhibits a maximum and two minima.

INTRODUCTION

In previous investigations of the thermodynamics of ether + *n*-alkane mixtures, we measured the excess molar enthalpy, excess molar volume, excess molar isobaric heat capacity, and the speed of sound for di-*n*-propylether + *n*-heptane [1,2], 3,6-dioxaoctane + *n*-heptane [3,4], and 2,5,8-trioxanonane + *n*-heptane [5,6]. We now report the results of similar measurements for 2,5,8,11-tetraoxadodecane (triglyme or triethylene glycol dimethylether) + *n*-dodecane.

EXPERIMENTAL

2,5,8,11-Tetraoxadodecane and *n*-dodecane, both from the Aldrich Chemical Co. with stated purities of 99 mol%, were stored over molecular sieve beads (Type 4A) and used without further purification. Their densities at

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298.15 K, determined in an Anton-Paar densimeter, were 979.81 and 745.22 kg m^{-3}, respectively.

The tilting dilution dilatometer described by Kumaran and McGlashan [7] was used to measure the excess molar volumes, V_m^E. Excess molar enthalpies, H_m^E, were determined in an LKB flow microcalorimeter [6,8].

Excess molar isobaric heat capacities, $C_{p,m}^E$, were obtained from differences of the isobaric heat capacity per unit volume, $C_{p,m}/V_m$, measured in a Picker flow microcalorimeter [9,10] using a temperature interval of 1.4 K centred at 298.15 K. A value of 367.30 ± 0.01 J K^{-1} mol^{-1} was obtained for the molar isobaric heat capacity, $C_{p,m}$, of 2,5,8,11-tetraoxadodecane from comparisons with *n*-heptane, assuming $C_{p,m} = 224.764$ J K^{-1} mol^{-1} for the latter material [3]. Binary mixtures were prepared by mass, and their molar volumes were calculated from their excess molar volumes and the densities of the component liquids. A stepwise procedure [10] was adopted, and six runs led to the average value 375.16 ± 0.41 J K^{-1} mol^{-1} for the molar isobaric heat capacity of *n*-dodecane, in reasonable agreement with 375.30 J K^{-1} mol^{-1} obtained recently from a comparison of *n*-dodecane with *n*-hexane [11].

A pulse-echo-overlap method [12,13] was used to measure the ultrasonic speeds, *u*, of 2 MHz waves in mixtures formed in a successive dilution cell [14]. Calibration of the cell was based on the value 1496.739 m s^{-1} for the speed of ultrasound in water at 298.15 K [15].

RESULTS AND DISCUSSION

The experimental results for V_m^E, H_m^E, and $C_{p,m}^E$ at 298.15 K are listed in Table 1, where x is the mole fraction of the ether. Table 2 summarizes the measurements of u, and also gives the corresponding values of the isentropic compressibility, κ_S, the excess isentropic compressibility, κ_S^E, and the differential coefficient, $(\partial V_m^E/\partial p)_S$, calculated from the relations

$$\kappa_S = \Big(V_m^E + \sum_i x_i V_i^*\Big) \Big/ \Big(u^2 \sum_i x_i M_i\Big) \tag{1}$$

$$\kappa_S^E = \kappa_S - \sum_i \phi_i \Big\{\kappa_{S,i}^* + T V_i^* \big(\alpha_{p,i}^*\big)^2 / C_{p,i}^*\Big\} + T\Big(\sum_i x_i V_i^*\Big)\Big(\sum_i \phi_i \alpha_{p,i}^*\Big)^2 \Big/ \Big(\sum_i x_i C_{p,i}^*\Big) \tag{2}$$

and

$$\big(\partial V_m^E/\partial p\big)_S = -V_m^E \kappa_S - \kappa_S^E \sum_i x_i V_i^* \tag{3}$$

In these equations, x_i, V_i^*, M_i, $\kappa_{S,i}^*$, $\alpha_{p,i}^*$, and $C_{p,i}^*$ are, respectively, the mole fraction, molar volume, molar mass, isentropic compressibility, isobaric thermal expansivity, and molar isobaric heat capacity of component i, and

$$\phi_i = x_i V_i^* / \sum_j x_j V_j^* \tag{4}$$

TABLE 1

Experimental results, ΔX, for $xC_8H_{18}O_4 + (1-x)C_{12}H_{26}$ at 298.15 K

x	ΔX	x	ΔX	x	ΔX	x	ΔX	x	ΔX
$\Delta X \equiv V_m^E$ (cm^3 mol^{-1})									
0.1031	0.6760	0.4755	1.4814	0.5619	1.4445	0.6401	1.3570	0.8058	0.9692
0.2336	1.1867	0.5235	1.4675	0.5899	1.4209	0.6892	1.2741	0.8580	0.7707
0.4100	1.4650	0.5396	1.4615	0.5973	1.4121	0.7353	1.1736	0.9326	0.4125
$\Delta X \equiv H_m^E$ (J mol^{-1})									
0.0500	526.5	0.2499	1695.6	0.4494	1991.0	0.6497	1858.1	0.8496	1224.9
0.0999	945.0	0.3002	1815.6	0.5002	1996.7	0.6986	1768.3	0.8997	931.9
0.1499	1279.4	0.3507	1908.8	0.5495	1970.5	0.7495	1624.9	0.9499	527.3
0.1997	1516.0	0.4005	1966.0	0.5982	1935.0	0.7997	1449.3		
$\Delta X \equiv C_{p,m}^E$ (J K^{-1} mol^{-1})									
0.0221	−0.38	0.2451	−0.60	0.4678	2.88	0.6353	2.44	0.8377	−0.78
0.0295	−0.71	0.2720	−0.12	0.4996	3.17	0.6494	2.13	0.8492	−1.02
0.0699	−1.40	0.3184	0.59	0.5449	3.06	0.6846	1.81	0.8746	−0.95
0.1294	−1.40	0.3455	1.29	0.5566	3.12	0.7118	1.21	0.8976	−1.15
0.1349	−1.38	0.3899	1.92	0.5844	3.07	0.7468	0.82	0.9121	−1.01
0.1479	−1.45	0.3972	2.07	0.5985	2.98	0.7489	0.67	0.9329	−0.98
0.1880	−1.44	0.4359	2.94	0.6091	2.87	0.7838	0.01	0.9563	−0.85
0.2239	−0.69	0.4530	2.59	0.6201	2.79	0.7997	−0.26	0.9770	−0.51

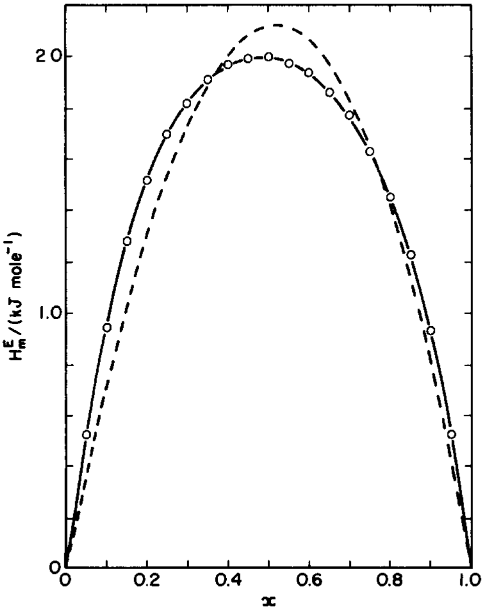

Fig. 1. Excess molar enthalpies for $xC_8H_{18}O_4 + (1-x)C_{12}H_{26}$ at 298.15 K. (○) Experimental results; (———) least-squares representation by eqn. (5); (- - - - -) calculated from Flory theory.

TABLE 2

Ultrasonic speed, u, isentropic compressibility, κ_S, excess isentropic compressibility, κ_S^E, and the differential coefficient, $(\partial V_m^E/\partial p)_S$, for $xC_8H_{18}O_4+(1-x)C_{12}H_{26}$ at 298.15 K

x	u ($m\ s^{-1}$)	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})	$(\partial V_m^E/\partial p)_S$ ($cm^3\ mol^{-1}\ GPa^{-1}$)	x	u ($m\ s^{-1}$)	κ_S (TPa^{-1})	κ_S^E (TPa^{-1})	$(\partial V_m^E/\partial p)_S$ ($cm^3\ mol^{-1}\ GPa^{-1}$)
0.0000	1278.96	820.36	0.00	0.000	0.5139	1272.33	729.92	23.16	−5.813
0.0540	1274.58	816.26	6.54	−1.798	0.5536	1274.58	719.44	22.74	−5.654
0.0971	1271.91	811.73	10.68	−2.916	0.6107	1278.56	703.63	21.78	−5.340
0.1529	1269.36	804.43	14.91	−4.032	0.6776	1284.53	683.89	20.02	−4.828
0.2309	1267.29	791.99	19.10	−5.095	0.7478	1292.47	661.73	17.44	−4.132
0.3096	1266.81	777.12	21.69	−5.697	0.8099	1301.21	640.75	14.40	−3.358
0.3870	1267.71	760.65	23.07	−5.959	0.8751	1312.41	617.21	10.37	−2.377
0.4353	1269.00	749.49	23.40	−5.979	0.9223	1322.07	599.11	6.83	−1.548
0.4653	1270.11	742.18	23.39	−5.938	0.9630	1331.53	582.81	3.41	−0.763
0.5066	1271.95	731.80	23.23	−5.839	1.0000	1341.11	567.45	0.00	0.000

TABLE 3

Coefficients, a_j, and standard deviations, s, for least-squares representations of V_m^E, H_m^E, $C_{p,m}^E$, Δu, κ_S^E and $(\partial V_m^E/\partial p)_S$ for $xC_8H_{18}O_4+(1-x)C_{12}H_{26}$ at 298.15 K by eqn. (1)

	V_m^E (cm^3 mol^{-1})	H_m^E (J mol^{-1})	$C_{p,m}^E$ (J K^{-1} mol^{-1})	Δu (m s^{-1})	κ_S^E (TPa^{-1})	$(\partial V_m^E/\partial p)_S$ (cm^3 mol^{-1} GPa^{-1})
a_1	5.9093	7976.2	12.52	−153.64	93.13	−23.448
a_2	0.5215	303.7	−8.10	28.56	11.77	−5.711
a_3	1.6373	3341.1	−52.65	−28.80	23.96	−6.242
a_4	−0.1453	578.1	9.29		7.23	−2.260
a_5	−0.1530	720.6	16.79			
a_6	0.2883	−1239.6				
s	0.0009	4.2	0.12	0.02	0.03	0.006

is the volume fraction of component i, expressed in terms of the unmixed components. For n-dodecane at 298.15 K, $\alpha_p^* = 0.953$ kK^{-1} was adopted from our previous work [11]; measurements of the density of 2,5,8,11-tetraoxadodecane at temperatures near 298.15 K yielded $\alpha_p^* = 0.929$ kK^{-1}.

Equations of the form

$$\Delta X = x(1-x)\sum_{j=1}^{n} a_j(1-2x)^{j-1} \tag{5}$$

were fitted to the results for V_m^E, H_m^E, $C_{p,m}^E$, κ_S^E, $(\partial V_m^E/\partial p)_S$, and also to the deviation of u from mole fraction linearity

$$\Delta u = u - 1341.11x - 1278.96(1-x) \tag{6}$$

Values of the coefficients a_j, determined by the method of least-squares with unit weight assigned to each point, are listed in Table 3 together with the standard deviation, s, of each representation.

The experimental results for H_m^E, V_m^E, $C_{p,m}^E$, and $(\partial V_m^E/\partial p)_S$ and their representations by eqn. (5) are plotted in Figs. 1–4. We are not aware of any directly comparable earlier studies of the present mixture. The shapes of the curves for H_m^E and V_m^E are similar to those found for other ether + n-alkane mixtures [1–6,16]. Previously we reported a W-shaped $C_{p,m}^E$ curve for 2,5,8-trioxanonane + n-heptane [6], and similar shaped curves have been observed for mixtures of 1,4-dioxane with n-alkanes [17] and cyclohexane [18]. The appearance of the curve in Fig. 3 is more unusual in view of its negative–positive–negative excursions.

In our previous studies [1,4] we found that the Flory theory [19,20] provided a useful basis for correlating the excess functions of some ether + n-alkane mixtures. For the components of the present mixture, the Flory characteristic volume, V^*, pressure, p^*, and temperature, T^*, calculated from the values of the physical properties given above, are, respectively: 147.53 cm^3 mol^{-1}, 606.0 J cm^{-3}, and 5452 K for 2,5,8,11-tetraoxadodecane;

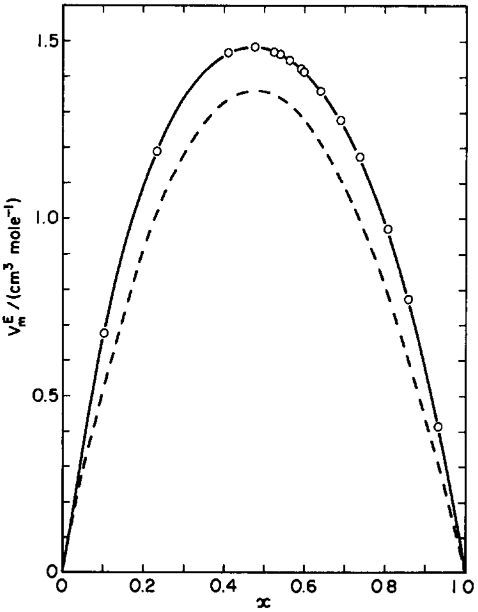

Fig. 2. Excess molar volumes for $xC_8H_{18}O_4 + (1 - x)C_{12}H_{26}$ at 298.15 K. (○) Experimental results; (———) least-squares representation by eqn. (5); (- - - - - -) calculated from Flory theory.

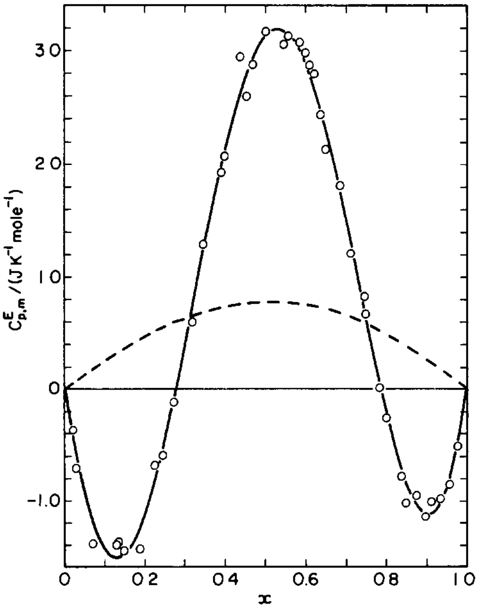

Fig. 3. Excess molar isobaric heat capacities for $xC_8H_{18}O_4 + (1 - x)C_{12}H_{26}$ at 298.15 K. (○) Experimental results; (———) least-squares representation by eqn. (5); (- - - - - -) calculated from Flory theory.

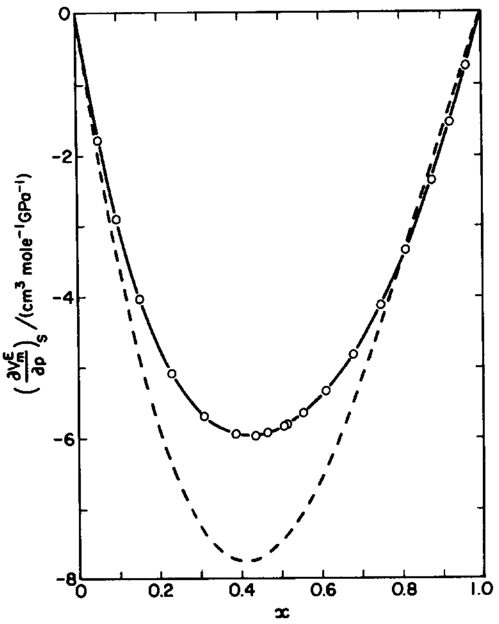

Fig. 4. Differential coefficients, $(\partial V_m^E/\partial p)_S$, for $xC_8H_{18}O_4+(1-x)C_{12}H_{26}$ at 298.15 K. (○) Experimental results; (———) least-squares representation by eqn. (5); (- - - - - -) calculated from Flory theory.

and 184.63 cm^3 mol^{-1}, 442.2 J cm^{-3}, and 5374 K for *n*-dodecane. The ratio of the molecular surface areas of contact was estimated from the Flory characteristic volumes, assuming that the molecules were approximately spherical. The value of the interchange energy parameter, X_{12}, was adjusted to give a least-squares fit between the theoretical and experimental excess molar enthalpies at 298.15 K. This analysis led to $X_{12}=51.50$ J cm^{-3}. The broken curves in Figs. 1–4 were calculated from the Flory theory with this value, assuming for $C_{p,m}^E$ and $(\partial V_m^E/\partial p)_S$ that X_{12} was independent of the temperature. In view of the relatively simple form of the theory, the estimates of V_m^E and its isentropic pressure derivative seem reasonable. The estimate of $C_{p,m}^E$ is less satisfactory. Previously for binary alkane mixtures [21], we noted that better agreement between theoretical and experimental values of $C_{p,m}^E$ could be achieved by treating $(\partial X_{12}/\partial T)_p$ as an adjustable parameter. However, for the present mixture it is clear that assigning a constant non-zero value to $(\partial X_{12}/\partial T)_p$ will not greatly improve the estimate of $C_{p,m}^E$, and that it would be necessary to consider $(\partial X_{12}/\partial T)_p$ as a function of x in order to reproduce more closely the complex variation of $C_{p,m}^E$ with mole fraction.

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