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EXCESS VOLUMES FOR BINARY MIXTURES FORMED BY 2,5,8,11-TETRAOXADODECANE OR 2,5,8,11,14-PENTAOXAPENTADECANE WITH HOMOLOGOUS *n*-ALKANES

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ABSTRACT

Excess volumes, measured at 298.15 K using a vibrating tube densimeter, are reported for binary mixtures of 2,5,8,11-tetraoxadodecane or 2,5,8,11,14-pentaoxapentadecane with some homologous *n*-alkanes from C_7 to C_{16}. The excess volumes are positive with large maximum values located in the central concentration range for all of the systems, with the exception of 2,5,8,11,14-pentaoxapentadecane with *n*-dodecane, which has a central miscibility gap. A correlation of the data by means of the Flory theory is described.

INTRODUCTION

The measurements presented here are an extension of our earlier work [1,2] which reported excess enthalpies for some polyethylene glycol dimethyl ether + *n*-alkane mixtures. In this paper, determinations of excess volumes for binary mixtures of 2,5,8,11-tetraoxadodecane (TODD) with *n*-heptane, *n*-octane, *n*-decane and *n*-hexadecane, and of 2,5,8,11,14-pentaoxapentadecane (POPD) with *n*-heptane, *n*-octane, *n*-decane and *n*-dodecane are described. Data for the excess volumes of mixtures formed by a polyether with a series of homologous *n*-alkanes are not available in the literature. Such data are needed in the development of equation of state theories. Polyethers containing three or more oxyethylene groups are of particular interest, since they are not completely miscible with long chain *n*-alkanes [2,3].

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EXPERIMENTAL

Sources of the component liquids and their densities measured at 298.15 K in an Anton Paar densimeter (model DMA 02C) are listed in Table 1, where densities from the literature [1,3–5] are cited for comparison. The liquids were used as received, since in all cases the manufacturers' specifications indicated purities of at least 99 mol%.

Mixtures were prepared by weighing in onion cells [6], specially designed to minimize evaporation effects. The error in the mole fraction is estimated to be less than 1×10^{-4}. Excess molar volumes, V_m^E, were obtained from densities measured at 298.15 ± 0.003 K in a vibrating tube densimeter (model 02D, Sodev Inc.) operated in a static mode [6]. For each system, the two constants characteristic of the densimeter were obtained from measurements on the pure liquids, and their densities as given in Table 1. The error in V_m^E is estimated to be less than 5×10^{-4} cm^3 mol^{-1}.

RESULTS AND DISCUSSION

The excess molar volumes of $\{xCH_3(OCH_2CH_2)_pOCH_3 + (1-x)C_nH_{2n+2}\}$ mixtures measured at 298.15 K are listed for $p = 3$, $n = 7$, 8, 10, 16 and $p = 4$, $n = 7$, 8, 10, 12 in Table 2, and plotted in Figs. 1 and 2. The smoothing equation

$$V_m^E(\mathrm{cm^3\ mol^{-1}}) = x(1-x)\sum_{j=1}^{m} v_j(1-2x)^{j-1} \qquad (1)$$

was fitted to the results for each system by the method of least squares with all points weighted equally. Values of the coefficients, v_j, and standard deviations, s, for these representations are listed in Table 3. Curves calculated from eqn. (1) are shown in Figs. 1 and 2. Also shown in Fig. 1 is a

TABLE 1

Sources and densities of component liquids at 298.15 K

Component	Source	Density (kg m^{-3})	
		Observed	Literature
TODD	Aldrich Chemical Co.	980.01	979.81 [1], 981.1 [a]
POPD	Aldrich Chemical Co.	1006.62	1004.7 [4], 1007.0 [a]
C_7H_{16}	Phillips Petroleum Co.	679.83	679.46 [5]
C_8H_{18}	Aldrich Chemical Co.	698.76	698.62 [5]
$C_{10}H_{22}$	Aldrich Chemical Co.	726.34	726.35 [5]
$C_{12}H_{26}$	Phillips Petroleum Co.	745.40	745.18 [5]
$C_{16}H_{34}$	Aldrich Chemical Co.	770.11	769.94 [5]

[a] Estimated from density at 304.15 K [3].

TABLE 2

Experimental results for the excess molar volumes, V_m^E (cm^3 mol^{-1}), of $\{xCH_3(OCH_2CH_2)_pOCH_3+(1-x)C_nH_{2n+2}\}$ mixtures at 298.15 K

x	V_m^E	x	V_m^E	x	V_m^E	x	V_m^E	x	V_m^E
$p = 3$, $n = 7$									
0.0880	0.3832	0.3002	0.7356	0.5503	0.7154	0.7505	0.4806	0.8001	0.3945
0.1504	0.5460	0.4001	0.7700	0.5999	0.6775	0.7991	0.3969	0.8502	0.3133
0.2003	0.6336	0.5003	0.7478	0.7002	0.5466				
$p = 3$, $n = 8$									
0.0998	0.5003	0.3003	0.9239	0.5003	0.9700	0.6002	0.9061	0.7997	0.5907
0.1500	0.6645	0.3999	0.9866	0.5502	0.9389	0.7002	0.7796	0.9004	0.3326
0.2002	0.7849								
$p = 3$, $n = 10$									
0.1007	0.6085	0.3003	1.1847	0.5003	1.2717	0.6005	1.2199	0.8001	0.8416
0.1501	0.8099	0.3999	1.2820	0.5498	1.2481	0.7003	1.0635	0.9001	0.4776
0.2004	0.9774								
$p = 3$, $n = 16$									
0.0503	0.4016	0.2506	1.4389	0.4002	1.7145	0.5509	1.6816	0.8008	1.2110
0.1003	0.7364	0.3002	1.5830	0.4501	1.7394	0.7000	1.4644	0.9001	0.7704
0.1501	1.0189	0.3502	1.6576						
$p = 4$, $n = 7$									
0.1000	0.3923	0.3003	0.6239	0.4959	0.6048	0.6004	0.5381	0.7979	0.3190
0.1502	0.5047	0.3994	0.6339	0.5504	0.5738	0.7002	0.4414	0.8998	0.1701
0.2002	0.5662								
$p = 4$, $n = 8$									
0.1001	0.5097	0.3002	0.8383	0.4971	0.8476	0.5997	0.7704	0.8004	0.4644
0.1500	0.6419	0.4001	0.8687	0.5497	0.8143	0.6999	0.6452	0.9005	0.2448
0.2000	0.7318								
$p = 4$, $n = 10$									
0.0998	0.6457	0.2997	1.1243	0.4996	1.1882	0.6002	1.1217	0.7529	0.8831
0.1497	0.8368	0.4009	1.1880	0.5501	1.1668	0.7001	0.9870	0.8998	0.4314
0.1999	0.9741								
$p = 4$, $n = 12$									
0.0498	0.4056	0.1494	0.9232	0.2126	1.1407	0.7951	0.9771	0.9002	0.5797
0.0804	0.5996	0.1702	1.0236	0.2344	1.1930	0.8383	0.8118	0.9449	0.3186
0.1000	0.7045	0.1990	1.0867	0.7562	1.0630	0.8500	0.7878		

curve representing the results of our previous investigation of the TODD + *n*-dodecane system [1].

The V_m^E results for all of the present polyether + *n*-alkane systems are positive, with curves which are slightly skewed towards $x = 0$, and maxima which move to larger x values as the chain length of the alkane increases. V_m^E achieves relatively large values in the central mole fraction range, exceeding 1 cm^3 mol^{-1} for $p = 3$, $n = 10$, 12, 16 and $p = 4$, $n = 10$, 12.

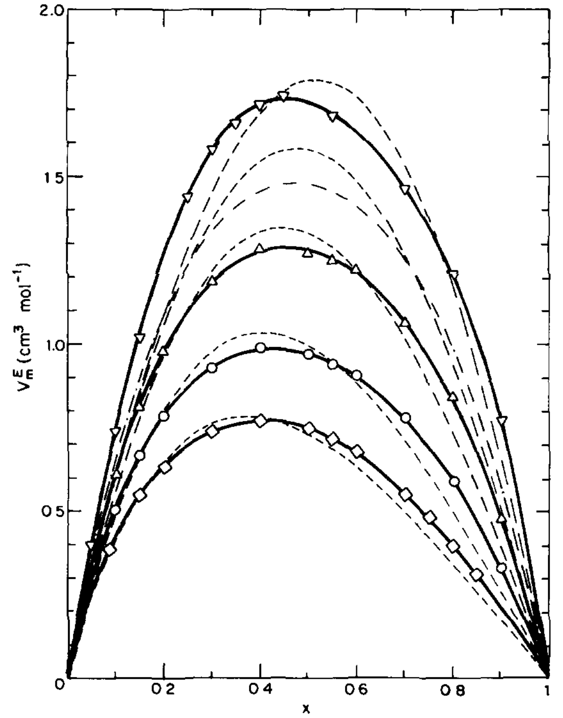

Fig. 1. Excess molar volumes for $\{xCH_3(OCH_2CH_2)_3OCH_3 + (1 - x)C_nH_{2n+2}\}$ mixtures at 298.15 K. Experimental results: ◇, $n = 7$; ○, $n = 8$; △, $n = 10$; ▽, $n = 16$. Curves: -·-·-, $n = 12$, from ref. 1; ——, least-squares representation by eqn. (1); ---, calculated from the Flory theory with X_{12} from eqn. (2).

Similar behavior was observed for the excess enthalpies of these systems which exceed 1.8 kJ mol^{-1} in the central range [1,2]. Such large excess volumes and enthalpies are attributable in part to changes in the correlation of molecular orientations associated with the high polarities of the polyethers (dipole moments > 2 D). This effect may also play a role in the partial immiscibility observed for mixtures of polyethers with the longer *n*-alkanes [3,7].

As shown in Fig. 2, the sytem POPD + *n*-dodecane has a miscibility gap in the central mole fraction range. The boundaries of this region, $0.234 < x < 0.756$, were established through measurements of the densities of the two liquid layers formed when mixtures with overall compositions within the gap were equilibrated in a thermostat at 298.15 ± 0.002 K. Analyses of the separate phases were based on the use of suitable polynomial forms for minor extrapolations of the densities measured in the single phase regions.

In the present investigation, the system POPD + *n*-decane was completely miscible at 298.15 K. This is in agreement with our previous findings [2], but at variance with those of Al-Kafaji and Booth [3], who reported immiscibil-

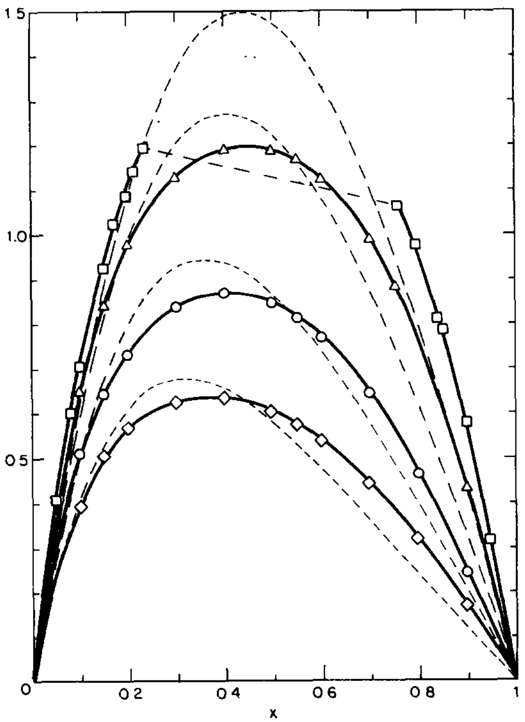

Fig. 2. Excess molar volumes for $\{x\mathrm{CH_3(OCH_2CH_2)_4OCH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+2}\}$ mixtures at 298.15 K. Experimental results: ◇, $n = 7$; ○, $n = 8$; △, $n = 10$; □, $n = 12$. Curves —— and ······, least-squares representations by eqn. (1); —·—·—, $n = 12$ miscibility gap; – – –, calculated from the Flory theory with X_{12} from eqn. (2).

ity at 304.15 K. Liquid–liquid studies, currently in progress [7], indicate that at atmospheric pressure the upper critical solution temperature is somewhat below 293 K for POPD + *n*-decane mixtures and ≈ 324 K for POPD + *n*-hexadecane.

TABLE 3

Coefficients, v_j, and standard deviations, s, for least-squares representations of V_m^E for $\{x\mathrm{CH_3(OCH_2CH_2)}_p\mathrm{OCH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+2}\}$ mixtures at 298.15 K by eqn. (1)

p	n	v_1	v_2	v_3	v_4	v_5	v_6	v_7	s
3	7	2.9945	0.9980	0.2820	0.6297	0.9329			0.0031
3	8	3.8800	0.7899	1.1658	0.5910				0.0034
3	10	5.1219	0.6408	1.4640	0.2850				0.0080
3	16	6.8778	0.9298	2.3202	−1.8630				0.0066
4	7	2.4091	0.9441	0.7393	0.9834	0.6307			0.0027
4	8	3.3807	0.9950	0.9243	0.8369	−0.1719	0.7325	1.1227	0.0010
4	10	4.7479	0.5941	1.7556	1.4095	0.2889			0.0024
4	12	5.5635	0.5406	2.3719	0.6858				0.0122

TABLE 4

Component properties and parameters used in calculations for $\{x\mathrm{CH_3(OCH_2CH_2)}_p\mathrm{OCH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+2}\}$ mixtures at 298.15 K by the Flory theory

Component	V_m (cm^3 mol^{-1})	α_p (kK)	κ_T (TPa^{-1})	p^* (J cm^{-3})	V_m^* (cm^3 mol^{-1})	T^* (K)	TODD + n-alkane			POPD + n-alkane		
							s_{12}	X_{12} (J cm^{-3})		s_{12}	X_{12} (J cm^{-3})	
								Fit of V_m^E	Eqn. (2)		Fit of V_m^E	Eqn. (2)
TODD [a]	181.86	0.929	694.88	605.9	147.50	5452.0						
POPD	220.82	0.830 [b]	589.6 [c]	616.3	182.23	5825.1						
C_7H_{16} [d]	147.45	1.256	1460.6	431.9	113.60	4648.1	0.9166	62.587	61.996	0.8543	75.091	74.690
C_8H_{18} [d]	163.50	1.164	1302.4	436.8	127.70	4827.0	0.9531	61.550	61.566	0.8882	72.337	73.009
$C_{10}H_{22}$ [d]	195.94	1.051	1109.6	447.0	155.75	5091.4	1.0183	60.737	60.706	0.9490	69.991	69.648
$C_{12}H_{26}$ [d]	228.55	0.960	987.6	445.2	184.40	5351.4	1.0773	58.501	59.846	1.0040	66.215	66.286
$C_{16}H_{34}$ [d]	294.07	0.883	862.0	457.0	240.41	5614.7	1.1768	58.865	58.126			

[a] α_p and κ_T from ref. 1. [b] Estimated by extrapolation of α_p values for $\mathrm{CH_3(OCH_2CH_2)}_p\mathrm{OCH_3}$ with $p = 1$, 2 and 3. [c] Obtained from α_p and an estimate of the thermal pressure coefficient based on the group contributions of Manzini and Crescenzi [15]. [d] Thermodynamic data for the n-alkanes are the same as in our previous work [10].

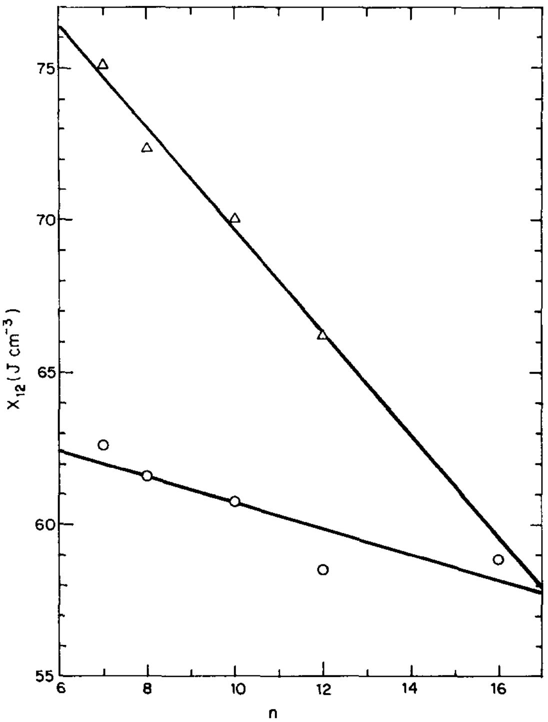

Fig. 3. Flory interchange-energy parameter, X_{12}, for $\{xCH_3(OCH_2CH_2)_pOCH_3+(1-x)C_nH_{2n+2}\}$ mixtures at 298.15 K plotted against the number, n, of carbon atoms in the alkane molecule. Results from fitting V_m^E: ○, $p = 3$; △, $p = 4$. Lines: ———, calculated from eqn. (2).

Previously, we found for dialkyl ether + n-alkane mixtures that the excess enthalpies [8–11] and excess volumes [12] could be correlated by the Flory theory [13,14] using interchange-energy parameters, X_{12}, which were linear functions of the number of carbon atoms in the alkane molecules. A similar treatment of the present mixtures was investigated. The calculations used the molar volumes, V_m, isobaric thermal expansivities, α_p, and isothermal compressibilities, κ_T, listed for the components in Table 4. The characteristic pressures, $p^\star$, molar volumes, $V_m^\star$, and temperatures, $T^\star$, obtained from the Flory formalism, are also listed in Table 4, together with the ratio, s_{12}, of ether/alkane molecular surface areas of contact per segment and the interchange-energy parameter, X_{12}, for each mixture. The values of s_{12} are based on the simple assumption that the molecules are spherical. The values of X_{12} given in columns 9 and 12 were obtained from least-squares analyses in which the Flory formula for the excess molar volume was fitted to the representation of the experimental results by eqn. (1).

In Fig. 3, the values of X_{12} obtained from fitting V_m^E are plotted against n, the number of carbon atoms in the alkane molecule. As in our previous work

[8–12], the variation of X_{12} for a given ether is nearly linear with n. The least-squares lines, shown in Fig. 3, were plotted from the equation

$$X_{12}\ (\mathrm{J\ cm^{-3}}) = 0.6545 + 21.4503p + (3.3228 - 1.2509p)n \qquad (2)$$

Values of X_{12} calculated from this equation are given in columns 10 and 13 of Table 4, and curves obtained from the Flory theory with these values are shown in Figs. 1 and 2. It can be seen that the Flory theory, as applied here, tends to underestimate V_m^E for ether-rich mixtures and overestimate V_m^E for alkane-rich mixtures. Nevertheless, the agreement with the experimental curves is reasonable and suggests that eqn. (2) in combination with the Flory theory can provide useful estimates of V_m^E for mixtures of TODD and POPD with other n-alkanes.

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REFERENCES

1 G.C. Benson, M.K. Kumaran, T. Treszczanowicz, P.J. D'Arcy and C.J. Halpin, Thermochim. Acta, 95 (1985) 59.
2 T. Treszczanowicz, G.C. Benson and B.C.-Y. Lu, J. Chem. Eng. Data, 33 (1988) 379.
3 J.K.H. Al-Kafaji and C. Booth, J. Chem. Soc., Faraday Trans. 1, 79 (1983) 2695.
4 R.L. McGee, W.J. Wallace and R.D. Rataiczak, J. Chem. Eng. Data, 28 (1983) 305.
5 TRC Thermodynamic Tables—Hydrocarbons, Thermodynamics Research Center, Texas A & M University System, College Station, TX, 1986.
6 M. Takenaka, R. Tanaka and S. Murakami, J. Chem. Thermodyn., 12 (1980) 849.
7 T. Treszczanowicz and D. Cieślak, personal communication.
8 B. Luo, G.C. Benson and B.C.-Y. Lu, J. Chem. Thermodyn., 20 (1988) 267.
9 L. Wang, G.C. Benson and B.C.-Y. Lu, J. Chem. Thermodyn., 20 (1988) 975.
10 G.C. Benson, B. Luo and B.C.-Y. Lu, Can. J. Chem., 66 (1988) 531.
11 L. Wang, G.C. Benson and B.C.-Y. Lu, Fluid Phase Equilibria, 46 (1989) 211.
12 L. Wang, G.C. Benson and B.C.-Y. Lu, J. Chem. Thermodyn., 21 (1989) 147.
13 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
14 A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
15 G. Manzini and V. Crescenzi, Gazz. Chim. Ital., 104 (1974) 51.