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Effect of Temperature on W-Shaped Excess Molar Heat Capacities and Volumetric Properties: Oxaalkane–Nonane Systems

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Excess molar volumes V_m^E of the mixtures diglyme (2,5,8-trioxanonane; TON), triglyme (2,5,8,11-tetraoxadodecane; TODD), or tetraglyme (2,5,8,11,14-pentaoxapentadecane; POPD; E181) + *n*-nonane have been obtained from density measurements at 278.15, 288.15, 298.15, and 308.15 K. In addition, a micro DSC II differential scanning calorimeter was used to obtain excess molar heat capacities C_p^E at constant pressure for the same mixtures except for TON + *n*-nonane and at the same temperatures except for 278.15 K. These results allowed us to calculate the following mixing quantities in the complete range of concentration: α, $(\partial V_m^E/\partial T)_p$, and $(\partial H^E/\partial p)_T$ at 298.15 K. The excess molar volumes are positive with large maximum values located in the central concentration range with the exception of POPD + *n*-nonane at 278.15 K, which has a central miscibility gap. For these mixtures, C_p^E has a W-shaped concentration dependence: two minima separated by a maximum.

KEY WORDS: density; excess properties; molar heat capacity; nonane; 2,5,8,11,14-pentaoxapentadecane; 2,5,8,11-tetraoxadodecane; 2,5,8-trioxanonane.

1. INTRODUCTION

In previous works [1–3], we have studied the volumetric behavior of some mixtures $CH_3O(CH_2CH_2O)_\nu CH_3$ ($\nu = 1, 2, 3, 4$) (polyoxyetheneglycol dimethyl ethers; also called glymes) + alkane (heptane or cyclohexane). The aim of the present work is to study the effect of the systematic variation of the chain lengths of both components on the excess thermodynamic

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properties as well as their temperature dependence. We also investigate the behavior of the excess molar heat capacities C_p^E around the upper critical solution temperature (UCST). As a first step, we have measured the densities for diglyme (2,5,8-trioxanonane, TON), triglyme (2,5,8,11-tetraoxadodecane; TODD), or tetraglyme (2,5,8,11,14-pentaoxapentadecane, POPD) + *n*-nonane at 278.15, 288.15, 298.15, and 308.15 K. We also report molar isobaric heat capacities C_p for TODD or POPD + *n*-nonane at 288.15, 298.15, and 308.15 K. These results have allowed us to calculate excess molar volumes V_m^E, C_p^E, and the following values at 298.15 K: thermal expansivity α, $(\partial V_m^E/\partial T)_p$, and $(\partial H^E/\partial p)_T$; these quantities are related to randomness or nonrandomness in oxaalkane–alkane mixtures.

2. EXPERIMENTAL PROCEDURE

2.1. Materials

n-nonane and TODD were supplied from Aldrich (puriss, >99 mol%; TON was from Fluka (puriss; >99.5 mol%), and POPD was from Merck (zur Synthese; >98 mol%).

The chemicals were all partially degassed; some of them were dried over Fluka type 4-mm molecular sieves and, otherwise, used as supplied.

2.2. Equipment

Densities of the pure liquids and their mixtures were measured with a vibrating-tube densimeter (Kyoto Electronics). The vibrating-tube temperature was maintained to better than ±0.01 K with a Hetotherm PF-CB II thermostat. The experimental technique has been described previously [4]. Mole fractions were determined through weighing. The precision of the density measurements was $\pm 0.00001\ g \cdot cm^{-3}$, and that of the mole fractions ±0.00005.

Molar heat capacities C_p were measured at atmospheric pressure with a programmable differential temperature scanning calorimeter (micro DSC II, SETARAM, France). This apparatus has been described briefly elsewhere [5]. During an isobaric heat capacity measurement, the sample liquid, *x*, fills the measuring cell, and the reference liquid of known heat capacity, *n*-heptane [6] in our measurements, fills the reference cell. The calibration of the instruments is then performed in two runs: in the first run, the measuring cell is empty (E) and the reference cell is filled with *n*-heptane; in the second run, both cells are filled with *n*-heptane. To obtain the average differential calorimetric area of both measurements, the temperature is programmed linearly at a rate of 0.2 K/min in difference steps

of 1 K for both increasing and decreasing temperatures, this temperature increment is centered, respectively, at 288.15, 298.15, and 308.15 K.

Following this procedure isobaric heat capacities are obtained from

$$Cp_x = Cp_{ref} \frac{\rho_{ref}}{\rho_x} \frac{S_{x\text{-ref}} - S_{E\text{-ref}}}{S_{ref\text{-ref}} - S_{E\text{-ref}}} \quad (1)$$

where $S_{x\text{-ref}}$ is the differential calorimetric area when the measuring cell is filled with the sample liquid and the reference cell with *n*-heptane, $S_{ref\text{-ref}}$ is

Table I. Densities ρ and Molar Heat Capacities C_p for Pure Components

		ρ (g·cm^{-3})		C_p (J·K^{-1}·mol^{-1})	
Substance	T(K)	This work	Literature	This work	Literature
TON	278.15	0.95834			
	288.15	0.94859	0.94866[2]		
	298.15	0.93872	0.93872[2], 0.93870[7], 0.93882[8], 0.93892[9]		
	308.15	0.92868	0.92870[2]		
TODD	278.15	0.99953			
	288.15	0.99015	0.99028[2]	368.64	
	298.15	0.98064	0.98079[2], 0.98042[10], 0.98001[11], 0.98117[12], 0.98000[13]	369.52	367.78[14], 367.30[15], 366.58[16]
	308.15	0.97115	0.97127[12]	370.90	
POPD	278.15	1.02410			
	288.15	1.01484	1.01502[2]	458.48	
	298.15	1.00566	1.00569[2], 1.00651[17], 1.00662[11], 1.00627[12]	459.03	457.10[4]
	308.15	0.99634	0.99642[2]	460.34	
C_9H_{20}	278.15	0.72945			
	288.15	0.72179		280.01	
	298.15	0.71409	0.71400[18], 0.71391[14], 0.71392[19], 0.71389[20]	284.41	284.55[22], 284.34[14]
	308.15	0.70626	0.70642[18], 0.70596[21]	288.95	

the differential calorimetric area when both cells are filled with *n*-heptane, and $S_{E\text{-ref}}$ is the differential calorimetric area when the measuring cell is empty and the reference cell is filled with *n*-heptane. Under these conditions, the precision of the excess molar heat capacity value C_p^E was estimated to be $\pm 0.05\ J \cdot mol^{-1} \cdot K^{-1}$ [5].

3. RESULTS AND DISCUSSION

Experimental densities ρ and molar heat capacities C_p of the pure liquids at several temperatures and at atmospheric pressure, as well as some literature values, are reported in Table I. The experimental densities of the mixtures (Table II) were fitted as a function of the mole fraction and the temperature to a polynomial of the form

$$1/\rho = \sum_{i=1}^{5} \sum_{j=1}^{3} A_{ij} 10^{1-j} x^{i-1} (T - T_0)^{j-1} \tag{2}$$

where ρ is in $g \cdot cm^{-3}$, x is the mole fraction of the glyme, T is temperature in K, and $T_0 = 278.15$ K. The experimental excess molar volumes V_m^E (also in Table II) were determined from the densities of the pure liquids and their mixtures. They were fitted as a function of the mole fraction and temperature to a polynomial of the form

$$V_m^E = x(1-x) \sum_{i=1}^{5} \sum_{j=1}^{3} B_{ij} 10^{1-j} (2x-1)^{i-1} (T - T_0)^{j-1} \tag{3}$$

where V_m^E is in $cm^3 \cdot mol^{-1}$ and T is in K. The coefficients A_{ij} and B_{ij} and the standard deviations, given in Table III, were obtained by an optimization process, which employed Marquardt's algorithm [23]. Figures 1–3 show the experimental excess molar volumes and the fitted curves $V_m^E(x, T)$. The excess molar volumes are positive and parabolic. The V_m^E values decrease when the length of the glyme chain increases and are positive for all systems. The mixture POPD + *n*-nonane system has a central miscibility gap at 278.15 K; thus its UCST must take values between 278.15 and 288.15 K. However, the system TODD + *n*-nonane has a total miscibility at 278.15 K. The excess molar volumes for POPD + *n*-nonane at 298.15 K determined in this work agree closely with those obtained by Trejo et al. [19].

The values of α for pure liquids at 298.15 K obtained by analytical differentiation of Eq. (2) are given below: $\alpha_{nonane} = 1.087 \times 10^{-3}\ K^{-1}$, $\alpha_{TON} = 1.062 \times 10^{-3}\ K^{-1}$, $\alpha_{TODD} = 0.968 \times 10^{-3}\ K^{-1}$, and $\alpha_{POPD} = 0.922 \times 10^{-3}\ K^{-1}$. The literature values are $\alpha_{nonane} = 1.088 \times 10^{-3}\ K^{-1}$ [24] and

Table II. Experimental Densities ρ and Excess Molar Volumes V_m^E for $\{xCH_3O(CH_2CH_2O)_vCH_3 + (1-x)CH_3(CH_2)_7CH_3\}$ ($v = 2, 3, 4$)

	T							
	278.15 K		288.15 K		298.15 K		308.15 K	
x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
	$xCH_3O(CH_2CH_2O)_2CH_3 + (1-x)CH_3(CH_2)_7CH_3$							
0.01771	0.73222	0.115	0.72459	0.105	0.71685	0.112	0.70894	0.114
0.05205	0.73788	0.275	0.73015	0.279	0.72234	0.291	0.71434	0.304
0.06764	0.74055	0.330	0.73276	0.343	0.72486	0.372	0.71685	0.382
0.08173	0.74287	0.405	0.73506	0.417	0.72716	0.441	0.71914	0.449
0.09922	0.74579	0.491	0.73797	0.500	0.73007	0.518	0.72199	0.535
0.13848	0.74278	0.602	0.74485	0.623	0.73682	0.657	0.72864	0.683
0.17052	0.75840	0.729	0.75-39	0.757	0.74229	0.796	0.73406	0.823
0.17657	0.75953	0.739	0.75153	0.763	0.74338	0.811	0.73513	0.840
0.22100	0.76769	0.863	0.75956	0.900	0.75140	0.934	0.74305	0.969
0.26931	0.77691	0.959	0.76871	0.992	0.76042	1.035	0.75199	1.069
0.31226	0.78540	1.014	0.77705	1.063	0.76863	1.117	0.76005	1.167
0.37076	0.79723	1.085	0.78878	1.132	0.78022	1.191	0.77151	1.245
0.41490	0.80646	1.118	0.79789	1.171	0.78922	1.234	0.78042	1.288
0.45763	0.81568	1.126	0.80702	1.179	0.79828	1.238	0.78940	1.289
0.50390	0.82600	1.109	0.81725	1.160	0.80841	1.218	0.79940	1.274
0.55092	0.83669	1.095	0.82785	1.144	0.81890	1.202	0.80979	1.257
0.59623	0.84739	1.050	0.83846	1.096	0.82941	1.151	0.82023	1.199
0.64007	0.85794	1.010	0.84888	1.061	0.83977	1.108	0.83055	1.143
0.68929	0.87020	0.939	0.86104	0.986	0.85181	1.032	0.84241	1.078
0.73843	0.88285	0.850	0.87361	0.889	0.86429	0.927	0.85486	0.954
0.79182	0.89714	0.721	0.88778	0.756	0.87837	0.784	0.86872	0.825
0.83309	0.90845	0.623	0.89899	0.656	0.88954	0.672	0.87982	0.704
0.84923	0.91302	0.572	0.90360	0.591	0.89406	0.614	0.88445	0.619
0.89847	0.92721	0.416	0.91768	0.430	0.90805	0.443	0.89828	0.451
0.93557	0.93833	0.272	0.92868	0.287	0.91893	0.301	0.90905	0.309
0.96837	0.94850	0.122	0.93880	0.129	0.92897	0.139	0.91903	0.139
0.98470	0.95357	0.057	0.94386	0.058	0.93399	0.066	0.92399	0.067

Table II. *(Continued)*

	T							
	278.15 K		288.15 K		298.15 K		308.15 K	
x	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)	ρ ($g \cdot cm^{-3}$)	V_m^E ($cm^3 \cdot mol^{-1}$)
	$xCH_3O(CH_2CH_2O)_3CH_3 + (1-x)CH_3(CH_2)_7CH_3$							
0.00773	0.73142	0.028	0.72377	0.034	0.71600	0.041	0.70821	0.043
0.06727	0.74665	0.278	0.73885	0.296	0.73094	0.312	0.72301	0.325
0.10026	0.75467	0.507	0.74683	0.524	0.73882	0.553	0.73076	0.586
0.12983	0.76234	0.596	0.75445	0.612	0.74638	0.642	0.73827	0.676
0.17146	0.77302	0.742	0.76499	0.774	0.75683	0.809	0.74866	0.841
0.21815	0.78534	0.820	0.77719	0.860	0.76890	0.906	0.76058	0.953
0.24789	0.79303	0.902	0.78483	0.942	0.77651	0.983	0.76813	1.032
0.31349	0.81045	0.972	0.80207	1.025	0.79359	1.075	0.78511	1.121
0.33042	0.81494	0.990	0.80654	1.041	0.79802	1.093	0.78948	1.145
0.36844	0.82503	1.026	0.81652	1.086	0.80789	1.147	0.79927	1.202
0.40997	0.83614	1.043	0.82764	1.084	0.81894	1.142	0.81025	1.196
0.44740	0.84625	1.035	0.83760	1.093	0.82887	1.143	0.82013	1.193
0.49628	0.85952	1.008	0.85080	1.061	0.84195	1.117	0.83312	1.167
0.54890	0.87409	0.967	0.86525	1.024	0.85634	1.071	0.84740	1.124
0.56807	0.87887	0.992	0.87006	1.036	0.86105	1.098	0.85213	1.140
0.59147	0.88536	0.948	0.87643	1.008	0.86739	1.066	0.85843	1.108
0.63987	0.89857	0.899	0.88964	0.941	0.88057	0.986	0.87153	1.026
0.69107	0.91262	0.831	0.90361	0.869	0.89449	0.905	0.88540	0.936
0.71177	0.91823	0.816	0.90918	0.856	0.90001	0.895	0.89089	0.924
0.73425	0.92441	0.783	0.91538	0.810	0.90617	0.848	0.89701	0.878
0.78232	0.93771	0.694	0.92863	0.714	0.91942	0.735	0.91019	0.762
0.80492	0.94402	0.642	0.93495	0.652	0.92565	0.682	0.91641	0.702

0.84848	0.95638	0.503	0.94718	0.523	0.93783	0.546	0.92851	0.566
0.88730	0.96737	0.385	0.95813	0.398	0.94873	0.417	0.93936	0.433
0.93018	0.97964	0.232	0.97032	0.244	0.96086	0.259	0.95146	0.266
0.95668	0.98695	0.187	0.97771	0.176	0.96828	0.177	0.95886	0.178
			$xCH_3O(CH_2CH_2O)_4CH_3 + (1-x)CH_3(CH_2)_7CH_3$					
0.02406	0.73740	0.182	0.72966	0.179	0.72197	0.171	0.71411	0.168
0.03691	0.74171	0.253	0.73393	0.254	0.72614	0.265	0.71823	0.269
0.05651	0.74821	0.366	0.74039	0.367	0.73262	0.365	0.72467	0.369
0.08957	0.75928	0.494	0.75134	0.509	0.74345	0.520	0.73541	0.532
0.12044	0.76955	0.590	0.76152	0.612	0.75353	0.634	0.74542	0.649
0.15921	—	—	0.77413	0.734	0.76605	0.760	0.75781	0.789
0.16769	—	—	0.77682	0.769	0.76872	0.796	0.76049	0.820
0.21224	—	—	0.79130	0.829	0.78307	0.867	0.77470	0.905
0.26228	—	—	0.80719	0.902	0.79886	0.943	0.79040	0.981
0.31164	—	—	0.82269	0.934	0.81419	0.995	0.80562	1.038
0.36102	—	—	0.83790	0.958	0.82931	1.020	0.82067	1.060
0.39908	—	—	0.84943	0.970	0.84078	1.032	0.83211	1.065
0.44679	—	—	0.86367	0.975	0.85497	1.030	0.84618	1.074
0.49788	—	—	0.87865	0.969	0.86987	1.025	0.86109	1.048
0.53732	—	—	0.89003	0.958	0.88122	1.008	0.87237	1.033
0.58551	—	—	0.90377	0.926	0.89497	0.958	0.88606	0.982
0.63117	—	—	0.91648	0.911	0.90770	0.924	0.89876	0.940
0.67838	—	—	0.92946	0.877	0.92070	0.872	0.91179	0.867
0.73092	0.95297	0.745	0.94393	0.772	0.93512	0.762	0.92608	0.771
0.77356	0.96461	0.649	0.95556	0.665	0.94666	0.663	0.93756	0.674
0.82453	0.97831	0.529	0.96920	0.543	0.96024	0.541	0.95112	0.541
0.87266	0.99086	0.447	0.98178	0.443	0.97276	0.441	0.96367	0.422
0.87331	0.99121	0.407	0.98207	0.415	0.97305	0.413	0.96393	0.400
0.89604	0.99728	0.322	0.98809	0.334	0.97902	0.336	0.96989	0.319
0.94300	1.00947	0.186	1.00026	0.190	0.99118	0.182	0.98195	0.176
0.96979	1.01647	0.080	1.00724	0.081	0.99812	0.075	0.98888	0.064

Table III. Parameters A_{ij} and B_{ij} for Eqs. (2) and (3) and Standard Deviations (s)

			$x\mathrm{CH_3O(CH_2CH_2O)_2CH_3} + (1-x)\mathrm{C_9H_{20}}$			
$1/\rho$	$A_{11} = 1.370930$	$A_{12} = 0.014187$	$A_{13} = 0.000273$	$A_{21} = -0.298678$	$A_{22} = -0.002362$	
	$A_{23} = -0.000028$	$A_{31} = -0.058985$	$A_{32} = -0.000309$	$A_{33} = -0.000057$	$A_{41} = 0.052355$	
	$A_{42} = -0.002212$	$A_{43} = -0.000142$	$A_{51} = -0.022217$	$A_{52} = 0.001228$	$A_{53} = 0.000148$	$s = 0.000060$
V_m^E	$B_{11} = 4.4590$	$B_{12} = 0.2184$	$B_{13} = 0.0017$	$B_{21} = -0.4978$	$B_{22} = -0.0198$	
	$B_{23} = -0.0044$	$B_{31} = 0.8292$	$B_{32} = -0.0198$	$B_{33} = -0.0254$	$B_{41} = -0.0370$	
	$B_{42} = 0.0542$	$B_{43} = -0.0185$	$B_{51} = -0.2325$	$B_{52} = -0.0125$	$B_{53} = 0.0269$	$s = 0.0084$
			$x\mathrm{CH_3O(CH_2CH_2O)_3CH_3} + (1-x)\mathrm{C_9H_{20}}$			
$1/\rho$	$A_{11} = 1.370789$	$A_{12} = 0.014285$	$A_{13} = 0.000235$	$A_{21} = -0.467524$	$A_{22} = -0.005986$	
	$A_{23} = 0.000134$	$A_{31} = 0.091883$	$A_{32} = 0.005100$	$A_{33} = -0.001376$	$A_{41} = 0.029342$	
	$A_{42} = -0.008335$	$A_{43} = 0.002129$	$A_{51} = -0.024104$	$A_{52} = 0.004317$	$A_{53} = -0.000999$	$s = 0.00013$
V_m^E	$B_{11} = 4.0366$	$B_{12} = 0.2335$	$B_{13} = -0.0057$	$B_{21} = -0.8601$	$B_{22} = -0.0398$	
	$B_{23} = -0.0118$	$B_{31} = 1.8978$	$B_{32} = -0.2047$	$B_{33} = 0.0385$	$B_{41} = 0.0913$	
	$B_{42} = -0.0489$	$B_{43} = -0.0124$	$B_{51} = -1.6739$	$B_{52} = 0.1110$	$B_{53} = -0.0060$	$s = 0.017$
			$x\mathrm{CH_3O(CH_2CH_2O)_4CH_3} + (1-x)\mathrm{C_9H_{20}}$			
$1/\rho$	$A_{11} = 1.371105$	$A_{12} = 0.014370$	$A_{13} = 0.000205$	$A_{21} = -0.633571$	$A_{22} = -0.009618$	
	$A_{23} = 0.000240$	$A_{31} = 0.344635$	$A_{32} = 0.003848$	$A_{33} = 0.000226$	$A_{41} = -0.120448$	
	$A_{42} = 0.004429$	$A_{43} = -0.002412$	$A_{51} = -0.014669$	$A_{52} = -0.004355$	$A_{53} = 0.001865$	$s = 0.00011$
V_m^E	$B_{11} = 3.6274$	$B_{12} = 0.2964$	$B_{13} = -0.0355$	$B_{21} = 0.1012$	$B_{22} = -0.4839$	
	$B_{23} = 0.0480$	$B_{31} = 1.5871$	$B_{32} = 0.0787$	$B_{33} = -0.0430$	$B_{41} = -2.4650$	
	$B_{42} = 0.6460$	$B_{43} = -0.1020$	$B_{51} = -0.3427$	$B_{52} = -0.4692$	$B_{53} = 0.0763$	$s = 0.011$

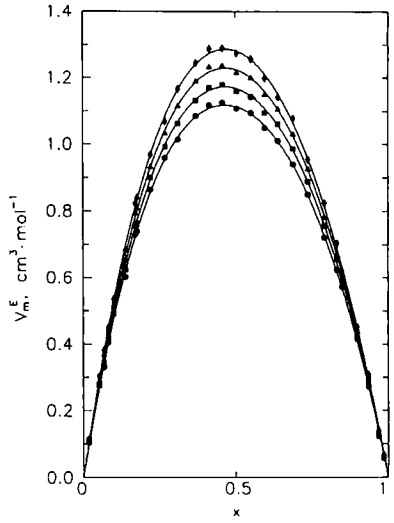

Fig. 1. Excess molar volumes V_m^E for $\{x\text{TON} + (1-x)\,n\text{-nonane}\}$ at 278.15 K (●), 288.15 K (■), 298.15 K (▲), and 308.15 K (◆). (——) Calculated from Eq. (3).

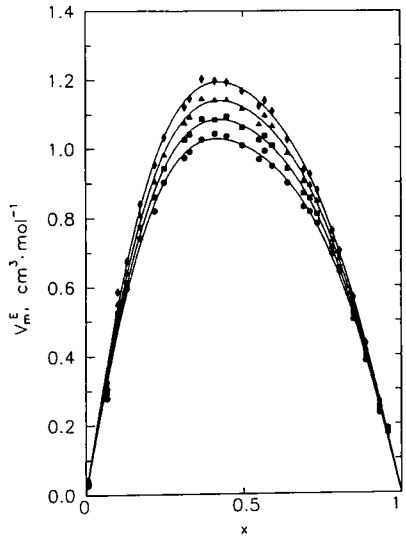

Fig. 2. Excess molar volumes V_m^E for $\{x\text{TODD} + (1-x)\,n\text{-nonane}\}$ at 278.15 K (●), 288.15 K (■), 298.15 K (▲), and 308.15 K (◆). (——) Calculated from Eq. (3).

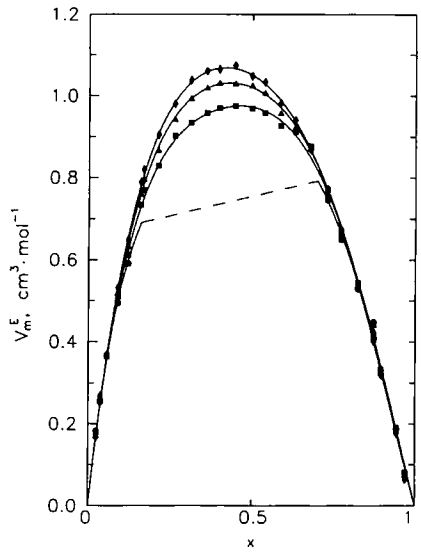

Fig. 3. Excess molar volumes V_m^E for $\{x\text{POPD} + (1-x)\,n\text{-nonane}\}$ at 278.15 K (●), 288.15 K (■), 298.15 K (▲), and 308.15 K (◆). (——) Calculated from Eq. (3).

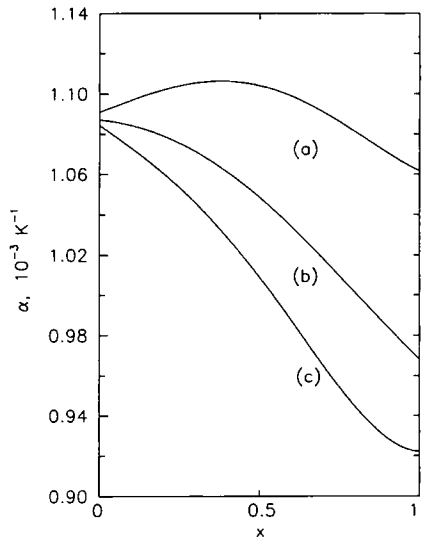

Fig. 4. Thermal expansivities α calculated from Eq. (2) at 298.15 K: (a) $\{x\text{TON} + (1-x)\,n\text{-nonane}\}$; (b) $\{x\text{TODD} + (1-x)\,n\text{-nonane}\}$; (c) $\{x\text{POPD} + (1-x)\,n\text{-nonane}\}$.

Table IV. Experimental Excess Molar Heat Capacities C_p^E for $\{x CH_3O(CH_2CH_2O)_\nu CH_3 + (1-x)CH_3(CH_2)_7CH_3\}$ ($\nu = 3, 4$)

T: 288.15 K		T: 298.15 K		T: 308.15 K	
x	C_p^E ($J \cdot mol^{-1} \cdot K^{-1}$)	x	C_p^E ($J \cdot mol^{-1} \cdot K^{-1}$)	x	C_p^E ($J \cdot mol^{-1} \cdot K^{-1}$)
		$x CH_3O(CH_2CH_2O)_3CH_3 + (1-x)CH_3(CH_2)_7CH_3$			
0.05081	−0.93	0.04788	−0.74	0.05081	−0.87
0.09922	−1.04	0.09904	−1.21	0.09922	−1.36
0.19865	−0.06	0.14854	−0.98	0.19865	−1.00
0.24858	1.03	0.19685	−0.63	0.24858	−0.47
0.30138	1.41	0.24840	−0.02	0.30138	−0.32
0.39745	2.18	0.29470	0.29	0.39745	0.05
0.51240	2.45	0.34557	0.69	0.51240	0.29
0.59715	1.74	0.39600	1.10	0.59715	0.00
0.64542	1.21	0.46101	1.26	0.64542	−0.24
0.69924	0.45	0.51235	1.13	0.69924	−0.69
0.79958	−0.53	0.56493	0.98	0.84854	−1.24
0.89953	−0.80	0.61300	0.45	0.89953	−0.94
0.94800	−0.47	0.66323	0.18		
		0.71056	−0.33		
		0.76025	−0.68		
		0.81088	−1.02		
		0.85636	−1.00		
		0.95049	−0.60		
		$x CH_3O(CH_2CH_2O)_4CH_3 + (1-x)CH_3(CH_2)_7CH_3$			
0.05052	−1.01	0.05052	−1.02	0.05052	−1.44
0.09941	−0.51	0.09941	−0.96	0.09941	−1.34
0.14781	1.26	0.14781	0.07	0.14781	−0.51
0.19374	4.29	0.19374	1.65	0.24776	0.48
0.24776	7.89	0.24776	2.93	0.29999	1.73
0.29661	13.5	0.29999	4.46	0.34740	2.12
0.29999	13.99	0.34740	4.99	0.41508	2.73
0.34740	16.3	0.41508	5.83	0.42050	2.51
0.42050	17.94	0.42050	5.59	0.45134	2.39
0.44185	17.09	0.45134	5.23	0.50183	2.33
0.45134	17.33	0.50183	5.06	0.50753	2.04
0.50183	14.87	0.50753	4.67	0.54584	1.18
0.50753	13.41	0.54584	3.11	0.59660	0.52
0.59660	6.07	0.59660	2.17	0.64669	−0.08
0.64669	4.45	0.64669	0.95	0.69523	−0.51
0.69523	1.19	0.69523	0.26	0.79710	−1.17
0.84841	−1.13	0.79710	−1.01	0.84841	−1.26
0.94727	−0.53	0.84841	−1.26	0.89820	−1.05
		0.89820	−1.12	0.94727	−0.65
		0.94727	−0.68		

Table V. Parameters A_i for Eq. (4) and Standard Deviations (s)

			$x\mathrm{CH_3O(CH_2CH_2O)_3CH_3} + (1-x)\mathrm{C_9H_{20}}$			
			$T = 288.15$ K			
C_p^E	$A_1 = 9.6446$	$A_2 = -8.1719$	$A_3 = -30.6549$	$A_4 = -15.2150$		$s = 0.13$
			$T = 298.15$ K			
	$A_1 = 4.6399$	$A_2 = -5.0439$	$A_3 = -25.7916$	$A_4 = 9.4318$		$s = 0.075$
			$T = 308.15$ K			
	$A_1 = 1.1882$	$A_2 = -3.2515$	$A_3 = -21.4493$	$A_4 = 7.5400$		$s = 0.12$
			$x\mathrm{CH_3O(CH_2CH_2O)_4CH_3} + (1-x)\mathrm{C_9H_{20}}$			
			$T = 288.15$ K			
C_p^E	$A_1 = 57.038$	$A_2 = -141.264$	$A_3 = -136.318$	$A_4 = 550.164$	$A_5 = -37.744$	
	$A_6 = -803.772$	$A_7 = 239.392$	$A_8 = 432.280$	$A_9 = -151.555$		$s = 0.62$
			$T = 298.15$ K			
	$A_1 = 18.366$	$A_2 = -38.903$	$A_3 = -49.386$	$A_4 = 82.949$	$A_5 = 6.296$	
	$A_6 = -37.883$					
			$T = 308.15$ K			
	$A_1 = 7.985$	$A_2 = -19.698$	$A_3 = -33.330$	$A_4 = 34.989$		$s = 0.23$

$1.091 \times 10^{-3}\ K^{-1}$ [18], $\alpha_{TON} = 1.062 \times 10^{-3}\ K^{-1}$ [16], and $\alpha_{TODD} = 0.977 \times 10^{-3}\ K$ [16] and $\alpha_{POPD} = 0.919 \times 10\ K^{-1}$ (estimated from density measurements of Ref. 25). Figure 4 shows the α values at 298.15 K calculated from Eq. (2).

Results for the excess molar heat capacities C_p^E are given in Table IV. For each mixture and each temperature, the C_p^E values were fitted to a Redlich–Kister function of the form

$$C_p^E = x(1-x) \sum_{i=0} A_i (2x-1)^i \tag{4}$$

where C_p^E is in $J \cdot K^{-1} \cdot mol^{-1}$ and x is the mole fraction of the glyme. The coefficients A_i and the corresponding standard deviations s are given in Table V and they were used to obtain the curves in Figs. 5 and 6. The excess molar heat capacities show a W-shaped-concentration dependence at several temperatures. The excess molar heat capacities at constant pressure for POPD + *n*-nonane at 298.15 K determined in this work agree closely with those obtained by Trejo et al. [26].

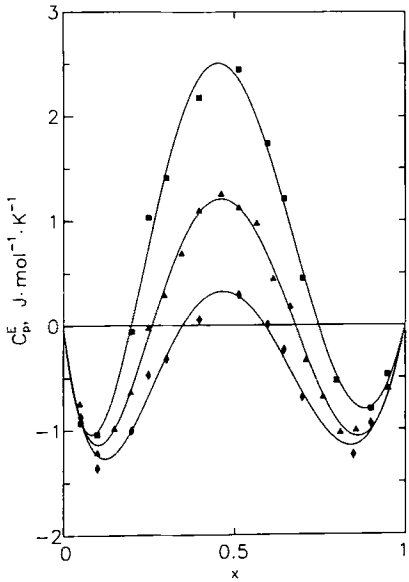

Fig. 5. Excess molar heat capacities C_p^E for $\{x\text{TODD} + (1-x)\ n\text{-nonane}\}$ at 288.15 K (■), 298.15 K (▲), and 308.15 K (◆). (——) Calculated from Eq. (4).

It is observed for both systems that, as the temperature increases, C_p^E decreases. This tendency is stronger at the maximum in C_p^E. It was verified that the mixture POPD + *n*-nonane exhibits a miscibility gap at 283.15 K; at the same time, the maximum of the C_p^E curve is strongly enhanced. The system TODD + *n*-nonane is miscible at 298.15 K, and the temperature dependence of C_p^E is regular. The behavior of both mixtures at $x = 0.5$ is represented in Fig. 7. These experimental results agree with Patterson's hypothesis about nonrandomness in the mixture by concentration fluctuations in the UCST proximities [27, 28].

Figure 8 shows, for each mixture, the values of $(\partial V_m^E/\partial T)_p$ and $(\partial H^E/\partial p)_T = V_m^E - T(\partial V_m^E/\partial T)_p$ at $x = 0.5$ and 298.15 K computed by analytical differentiation of Eq. (3). Patterson and co-workers suggested [28] that the parameters, $(\partial V_m^E, \partial T)_p$ and $(\partial H^E/\partial p)_T$, can be employed as indicators of nonrandomness in the solution. Randomness in the solution implies a negative contribution to $(\partial V_m^E/\partial T)_p$ and a positive contribution to $(\partial H^E/\partial p)_T$. $(\partial V_m^E/\partial T)_p$ is positive for all mixtures with values that decrease slightly with the glyme chain length. Inversely, values for $(\partial H^E/\partial p)_T$ are negative, and they are enhanced with the glyme chain length. Similarities have been found between the behavior of these systems

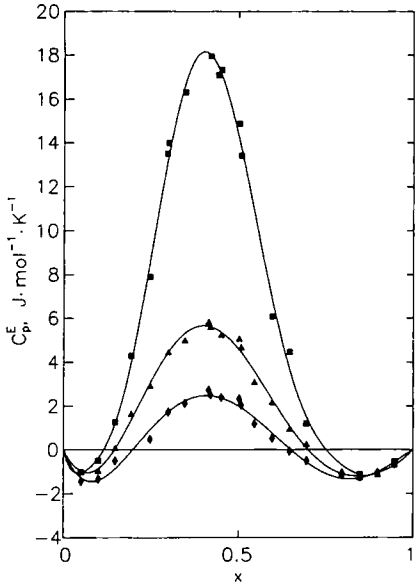

Fig. 6. Excess molar heat capacities C_p^E for $\{x\text{POPD} + (1-x)\,n\text{-nonane}\}$ at 288.15 K (■), 298.15 K (▲), and 308.15 K (◆). (——) Calculated from Eq. (4).

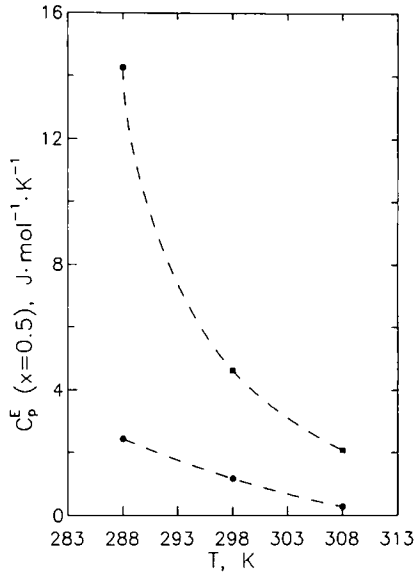

Fig. 7. Excess molar heat capacities C_p^E at $x = 0.5$ and 288.15, 298.15, and 308.15 K calculated from Eq. (4): (■) POPD + *n*-nonane; (●) TODD + *n*-nonane.

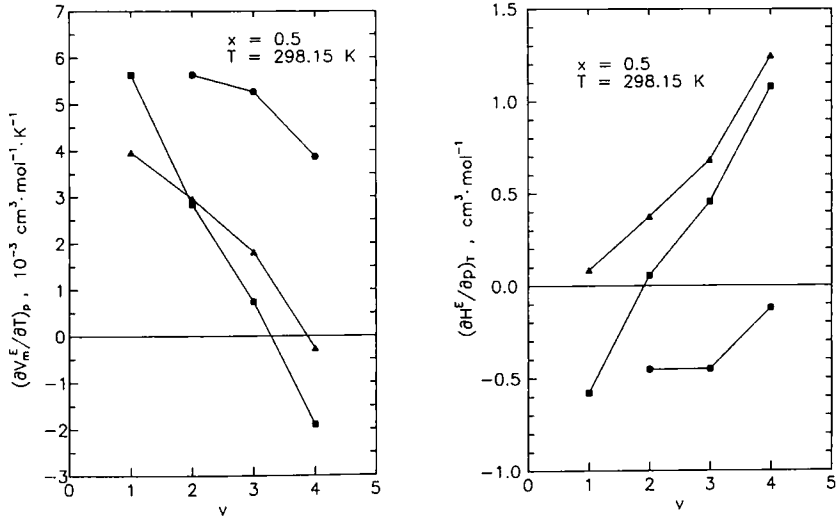

Fig. 8. Differential coefficients, $(\partial V_m^E/\partial T)_p$, and $(\partial H^E/\partial p)_T$ at $x = 0.5$ and 298.15 K calculated from Eq. (3) (■) {$CH_3O(CH_2CH_2O)_vCH_3$ + *n* − heptane} ($v = 1, 2, 3, 4$) [1, 3]; (▲) {$CH_3O(CH_2CH_2O)_vCH_3$ + *n* − cyclohexane} ($v = 1, 2, 3, 4$) [2]; (●) {$CH_3O(CH_2CH_2O)_vCH_3$ + *n*-nonane} ($v = 2, 3, 4$), this work.

and glyme + n-heptane and glyme + cyclohexane mixtures [1–3]. These results agree with nonrandomness in the mixtures investigated.

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