Excess Molar Volumes and Excess Molar Heat Capacities of Mixtures Containing (Mono and Poly)ethers + Ethyl Acetate

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Excess molar volumes were obtained from density measurements for binary mixtures of ethyl acetate [$CH_3COOCH_2CH_3$] with glymes [$CH_3O(CH_2CH_2O)_nCH_3$, $n = 1$, 2, 3, and 4] and dibutyl ether [$(CH_3CH_2CH_2CH_2)_2O$] at (278.15, 288.15, 298.15, and 308.15) K and atmospheric pressure using a Kyoto Electronics DA-210 vibrating-tube densimeter. In addition, excess molar isobaric heat capacities were determined for ethyl acetate with glymes ($n = 2$, 4) and dibutyl ether at 298.15 K using a micro DSC II differential scanning calorimeter.

Introduction

During the last several years, many studies on the thermodynamic properties of mixtures containing a strongly polar liquid and a nonpolar substance (usually an alkane) have been carried out. Interactions between ester + alkane (Jiménez *et al.*, 1986, 1994), monoether + alkane (Berti *et al.*, 1989), and polyether + alkane (Romaní *et al.*, 1994; Peleteiro *et al.*, 1993, 1994; Tovar *et al.*, 1997a) have been extensively studied while the interaction between (monoether or polyether) + ester is not well-known. The aim of our work is to provide experimental data of the volumetric and thermal properties of binary mixtures containing two strongly polar substances such as (ether or polyether + ester) systems.

In this work, we report excess molar volumes V^E obtained from density measurements at (278.15, 288.15, 298.15, and 308.15) K and atmospheric pressure for mixtures containing ethyl acetate [$CH_3COOCH_2CH_3$] with glymes [$CH_3O(CH_2CH_2O)_nCH_3$: $n = 1$, monoglyme; $n = 2$, diglyme;

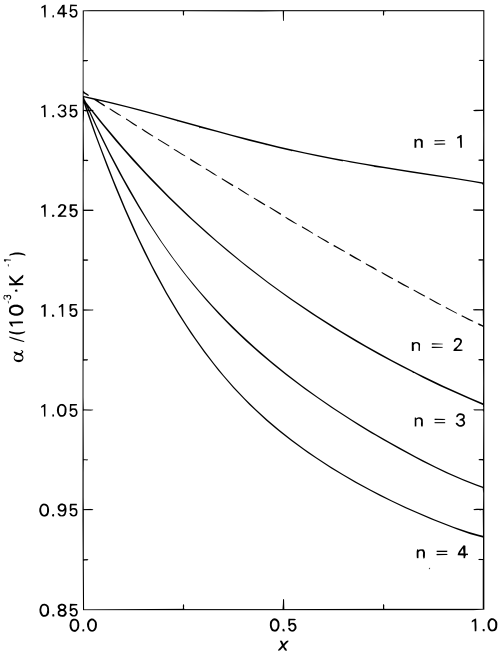

Figure 1. Isobaric thermal expansivities α at 298.15 K: (—) $x CH_3O(CH_2CH_2O)_nCH_3 + (1 - x)$ethyl acetate; (- - -) $x$dibutyl ether + $(1 - x)$ethyl acetate.

Table 1. Densities ρ, Isobaric Thermal Expansivities α, and Isobaric Heat Capacities C_p for the Pure Liquids at the Temperature T

component	T/K	this work	literature	ref
		ρ/g·cm^{-3}		
monoglyme	278.15	0.882 92		
	288.15	0.872 18	0.870 21	Sikora (1985)
	298.15	0.861 24	0.861 32	Muhuri and Hazra (1994)
	308.15	0.850 19	0.850 24	Sikora (1985)
diglyme	278.15	0.954 83		
	288.15	0.948 64		
	298.15	0.938 73	0.938 82	Nakai *et al.* (1991)
	308.15	0.928 80	0.929 5	Aminabhavi *et al.* (1993)
triglyme	278.15	0.999 64		
	288.15	0.990 31		
	298.15	0.980 67	0.980 01	Treszszanowicz *et al.* (1990)
	308.15	0.971 18		
tetraglyme	278.15	1.024 17		
	288.15	1.014 96		
	298.15	1.005 64	1.006 62	Treszszanowicz *et al.* (1990)
	308.15	0.996 42	0.997 61	Sikora (1985)
dibutyl ether	278.15	0.781 01		
	288.15	0.772 55	0.772 5	Obama *et al.* (1985)
	298.15	0.763 96	0.764 14	Berti *et al.* (1989)
	308.15	0.755 25	0.755 1	Obama *et al.* (1985)
ethyl acetate	278.15	0.918 56		
	288.15	0.906 62		
	298.15	0.894 49	0.894 28	Jiménez *et al.* (1986)
			0.894 38	Jiménez *et al.* (1994)
			0.894 37	Baluja *et al.* (1985)
	308.15	0.882 24	0.881 4	Aminabhavi *et al.* (1994)
		$\alpha/10^{-3}$·K^{-1}		
monoglyme	298.15	1.277	1.267 4	Treszszanowicz *et al.* (1990)
diglyme	298.15	1.055	1.060 2	Treszszanowicz *et al.* (1990)
triglyme	298.15	0.972	0.977 1	Treszszanowicz *et al.* (1990)
tetraglyme	298.15	0.922	0.919	Sikora (1985)
dibutyl ether	298.15	1.133	1.14	Obama *et al.* (1985)
ethyl acetate	298.15	1.364		
		C_p/J·mol^{-1}·K^{-1}		
diglyme	298.15	279.58	279.05	Kimura *et al.* (1983)
tetraglyme	298.15	458.42	457.10	Trejo *et al.* (1991)
dibutyl ether	298.15	279.46	278.16	Cobos *et al.* (1987)
ethyl acetate	298.15	170.58	169.30	Jiménez *et al.* (1986)

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Table 2. Excess Molar Volumes, V^E, for the Mixtures at (278.15, 288.15, 298.15, and 308.15) K

	V^E/cm^3·mol^{-1}					V^E/cm^3·mol^{-1}			
x	278.15 K	288.15 K	298.15 K	308.15 K	x	278.15 K	288.15 K	298.15 K	308.15 K
				xMonoglyme + (1 − x)Ethyl Acetate					
0.050 45			0.003		0.656 32	0.026	0.024	0.018	
0.153 40				0.008	0.710 92			0.017	
0.208 07	0.015				0.757 32	0.023	0.021	0.016	0.008
0.291 44	0.019		0.014	0.010	0.825 07	0.017	0.016	0.012	
0.370 48	0.024	0.021			0.856 50	0.014	0.014		0.005
0.500 39	0.026	0.023	0.018	0.011	0.892 64	0.008	0.008	0.009	
0.589 05		0.024	0.018	0.011	0.989 27	0.002	0.003		
				xDiglyme + (1 − x)Ethyl Acetate					
0.051 80	−0.016	−0.030	−0.035	−0.030	0.449 37	−0.082	−0.102	−0.121	−0.140
0.103 74	−0.036	−0.049	−0.058	−0.062	0.520 92	−0.082	−0.101	−0.119	−0.134
0.154 17	−0.049	−0.062	−0.075	−0.082	0.618 44			−0.102	−0.117
0.203 77		−0.080		−0.103	0.713 62	−0.058	−0.073	−0.091	−0.103
0.257 77		−0.082		−0.115	0.805 22	−0.048	−0.054	−0.066	−0.076
0.306 17	−0.072	−0.093	−0.113	−0.129	0.855 26	−0.033	−0.043	−0.050	−0.057
0.352 52	−0.079	−0.098	−0.117	−0.133	0.909 71	−0.014	−0.022	−0.035	−0.046
0.415 19	−0.081	−0.102	−0.120	−0.137	0.949 17	−0.009	−0.010	−0.015	−0.017
				xTriglyme + (1 − x)Ethyl Acetate					
0.020 33	−0.025	−0.047	−0.042	−0.029	0.461 50	−0.199	−0.230	−0.274	
0.047 47	−0.072	−0.083	−0.093	−0.099	0.512 99			−0.255	−0.283
0.092 39	−0.090	−0.111	−0.132	−0.149	0.591 79	−0.177	−0.201	−0.239	−0.270
0.177 26	−0.147	−0.171	−0.207	−0.231	0.715 95	−0.134	−0.151	−0.188	−0.197
0.194 34	−0.158	−0.193	−0.221	−0.244	0.816 16	−0.089	−0.100	−0.130	−0.127
0.262 46	−0.184	−0.216	−0.248	−0.277	0.905 11	−0.041	−0.045	−0.068	−0.079
0.326 02	−0.199	−0.237	−0.275	−0.304	0.952 58	−0.017	−0.015	−0.038	−0.042
0.404 33	−0.202	−0.236	−0.277	−0.308					
				xTetraglyme + (1 − x)Ethyl Acetate					
0.035 28	−0.065	−0.066	−0.071	−0.078	0.502 20	−0.295	−0.334	−0.370	−0.417
0.055 65	−0.103	−0.114	−0.124	−0.136	0.559 61	−0.275	−0.315	−0.353	−0.397
0.107 18	−0.167	−0.187	−0.210	−0.235	0.613 73				−0.379
0.158 51	−0.222	−0.251	−0.285	−0.323	0.657 38	−0.217	−0.248	−0.289	−0.328
0.253 43	−0.279	−0.316	−0.364	−0.421	0.706 72	−0.209	−0.237	−0.269	−0.303
0.312 87	−0.302	−0.343	−0.392	−0.446	0.773 20	−0.146	−0.164	−0.185	−0.222
0.375 20	−0.300	−0.344	−0.393	−0.449	0.804 68	−0.133	−0.148	−0.169	−0.191
0.423 03	−0.310	−0.355	−0.404		0.916 86	−0.065	−0.075	−0.077	−0.082
0.459 82	−0.295	−0.339	−0.388	−0.449	0.974 99	−0.023	−0.023	−0.016	
				xDibutyl Ether + (1 − x)Ethyl Acetate					
0.022 55	0.062	0.065	0.066	0.063	0.496 82	0.442	0.479	0.516	0.549
0.061 27	0.120	0.130	0.137	0.143	0.543 04	0.436	0.467	0.511	0.551
0.101 29	0.166	0.183	0.201	0.216	0.591 21	0.412	0.447	0.495	0.532
0.130 28	0.235	0.257	0.275	0.297	0.641 88	0.400	0.425	0.467	0.495
0.158 85	0.273	0.285	0.310	0.334	0.687 49	0.374	0.402	0.441	0.466
0.205 34	0.311	0.331	0.357	0.383	0.727 34	0.330	0.360	0.399	0.424
0.247 19	0.359	0.395	0.425	0.457	0.781 62	0.286	0.298	0.333	0.347
0.259 86	0.375	0.403	0.437	0.458	0.829 89	0.234	0.254	0.291	0.307
0.296 33	0.376	0.405	0.442	0.474	0.877 62	0.201	0.196	0.219	0.230
0.355 75	0.412	0.444	0.479	0.514	0.926 89	0.124	0.137	0.157	0.151
0.404 42	0.424	0.457	0.502	0.541	0.966 32	0.066	0.067	0.085	0.090
0.454 68	0.435	0.470	0.517	0.554					

n = 3, triglyme; n = 4, tetraglyme] and dibutyl ether [$(CH_3CH_2CH_2CH_2)_2O$]. Following these results, isobaric thermal expansivities α at 298.15 K and atmospheric pressure are reported. Also, excess molar isobaric heat capacities C_p^E at 298.15 K were obtained for ethyl acetate with diglyme, tetraglyme, and dibutyl ether.

Experimental Section

Materials. Diglyme (puriss, >99.5 mol %) and ethyl acetate (puriss, >99.5 mol %) were supplied from Fluka, monoglyme (puriss, >99 mol %) and triglyme (puriss, >99 mol %) from Aldrich, and tetraglyme (puriss, >98 mol %) and dibutyl ether (puriss, >99 mol %) from Merck. The chemicals were all partially degassed and dried over Fluka type 4 nm molecular sieves.

Apparatus and Procedure. Densities of the pure components and binary mixtures were obtained with a Kyoto Electronics DA-210 vibrating-tube densimeter. The temperature of the tube was controlled to ±0.005 K using a Hetotherm PFCBIIe thermostat. The estimated uncertainties are about $\pm 2 \times 10^{-5}$ for x, $\pm 5 \times 10^{-5}$ g·cm^{-3} for ρ, and ±0.03 cm^3·mol^{-1} for V^E.

Experimental heat capacities C_p were obtained from volumetric isobaric heat capacity measurements C_p/v and density data, which yield the molar volume v; C_p/v were determined with a programmable differential temperature scanning calorimeter (micro DSCII from SETARAM, Caluire Cedex, France); this apparatus and the experimental technique have been described previously (Tovar *et al.*, 1997a). The temperature of the calorimeter was controlled within a deviation of ±0.001 K. The estimated uncertainties are about $\pm 2 \times 10^{-5}$ for x and ±0.05 J·mol^{-1}·K^{-1} for C_p^E.

Results and Discussion

Table 1 gives the experimental densities ρ, isobaric thermal expansivities α, and isobaric heat capacities C_p of this work for the pure liquids, and they are compared to values found in the literature. Densities of the pure compounds along with those of the binary mixtures were

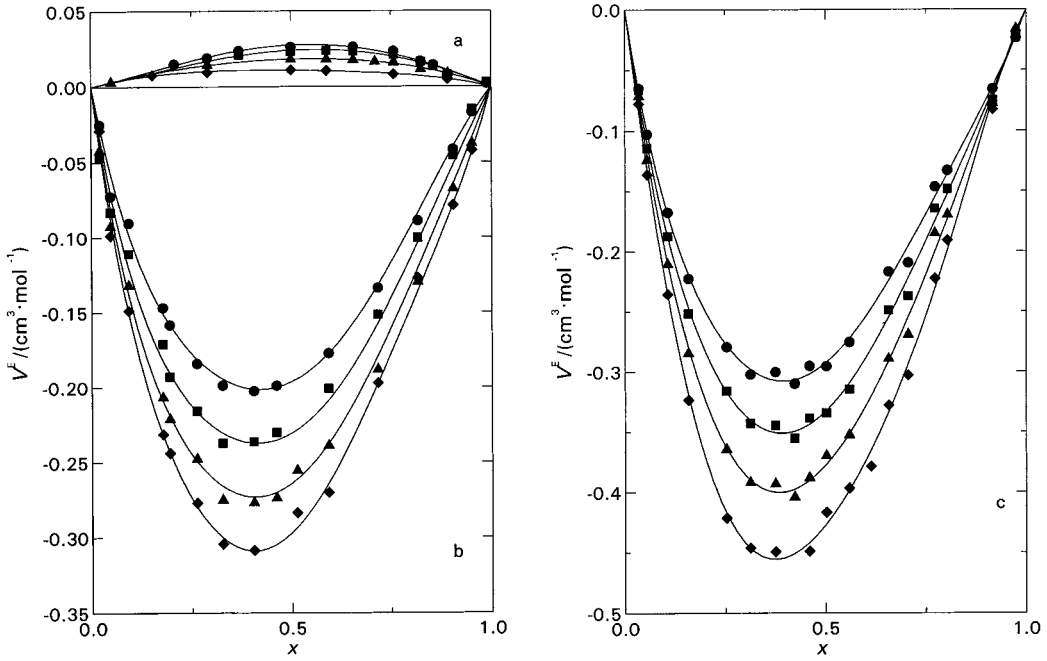

Figure 2. Excess molar volumes V^E for $x CH_3O(CH_2CH_2O)_nCH_3 + (1 - x)$ethyl acetate: (a) $n = 1$, (b) $n = 3$, and (c) $n = 4$; (●) 278.15 K, (■) 288.15 K, (▲) 298.15 K, (◆) 308.15 K; (—) eq 1.

Table 3. Coefficients A_{ij} of Eq 1 and Standard Deviations s

	i				
j	1	2	3	4	5
	xMonoglyme + $(1 - x)$Ethyl Acetate				
	A_{ij} ($s = 0.0013$)				
1	0.1103	0.0253	−0.0249		
2	−0.0100	0.0015	0.0092		
3	−0.0044	−0.0030	0.0050		
	xDiglyme + $(1 - x)$Ethyl Acetate				
	A_{ij} ($s = 0.0028$)				
1	−0.3259	0.0384	−0.0240	0.0868	0.1081
2	−0.0820	0.0233	0.0275	0.0806	−0.1687
3	0.0035	0.0041	−0.0135	−0.0441	0.0487
	xTriglyme + $(1 - x)$Ethyl Acetate				
	A_{ij} ($s = 0.0073$)				
1	−0.7849	0.2616	0.0357	0.2680	−0.1231
2	−0.1381	0.0364	−0.0972	0.0921	−0.0326
3	0.0014	0.0151	0.0337	−0.0529	−0.0257
	xTetraglyme + $(1 - x)$Ethyl Acetate				
	A_{ij} ($s = 0.0072$)				
1	−1.1710	0.5580	0.0275	0.0684	−0.3847
2	−0.1516	0.0921	0.0194	−0.0311	0.0440
3	−0.0092	−0.0002	−0.0586	0.0170	0.0921
	xDibutyl Ether + $(1 - x)$Ethyl Acetate				
	A_{ij} ($s = 0.010$)				
1	1.7476	−0.1985	0.1029	0.0290	0.2568
2	0.1516	−0.0064	−0.0387	0.0094	0.0884
3	0.0017	−0.0014	0.0053	−0.0025	−0.0185

used to calculate the excess molar volumes V^E given in Table 2.

Densities and excess molar volumes were fitted respectively to polynomials of the form

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x(1-x)\sum_{i=1}^{n}\sum_{j=1}^{3}A_{ij}10^{1-j}(2x-1)^{i-1}(T/\text{K} - T_0)^{j-1} \quad (1)$$

where x is the mole fraction of ether, T is the absolute temperature, and $T_0 = 278.15$ K; the coefficients A_{ij} were obtained using the Marquardt algorithm (Marquardt, 1963), and their values as well as the standard deviations s are given in Table 3.

Table 4. Excess Molar Isobaric Heat Capacities, C_p^E for the Mixtures at 298.15 K, Coefficients A_i of Eq 2, and Standard Deviations s

x	C_p^E/J·mol^{-1}·K^{-1}	x	C_p^E/J·mol^{-1}·K^{-1}	x	C_p^E/J·mol^{-1}·K^{-1}
	xDiglyme + $(1 - x)$Ethyl Acetate				
0.082 62	0.12	0.401 46	0.20	0.750 94	0.32
0.152 20	0.15	0.536 26	0.20	0.805 92	0.33
0.202 30	0.24	0.607 02	0.27	0.855 50	0.19
0.303 82	0.23	0.657 14	0.23		
0.352 09	0.27	0.705 25	0.36		
$A_1 = 0.9506$		$A_2 = 0.4248$	$A_3 = 1.6814$		$s = 0.047$
	xTetraglyme + $(1 - x)$Ethyl Acetate				
0.049 55	−0.10	0.416 64	−0.23	0.804 75	0.03
0.101 18	−0.08	0.500 88	−0.22	0.949 36	0.04
0.200 04	−0.22	0.606 11	−0.10		
0.300 24	−0.29	0.704 29	−0.02		
$A_1 = -0.8143$		$A_2 = 1.3462$	$A_3 = 0.7320$		$s = 0.029$
	xDibutyl Ether + $(1 - x)$Ethyl Acetate				
0.051 34	0.01	0.454 59	−0.10	0.706 39	−0.11
0.151 20	−0.08	0.506 82	−0.16	0.806 58	−0.04
0.200 92	−0.17	0.563 72	−0.24	0.854 75	−0.04
0.302 13	−0.08	0.608 64	−0.23	0.904 02	−0.06
0.399 14	−0.18	0.655 20	−0.10	0.949 52	0.00
	$A_1 = -0.6410$	$A_2 = 0.1247$	$s = 0.051$		

The isobaric thermal expansivities α of the pure products and mixtures were obtained from eq 1; it is noticeable that the results obtained with this procedure agree closely with those found in the literature (Table 1). On the other hand Figure 1 shows the isobaric thermal expansivities of this work for the mixtures investigated in the complete composition range; a diminution of α is observed as the length of the glyme chain increases.

In Figures 2 and 3 the composition dependence of the excess volumes for the mixtures investigated is represented; the V^E values are parabolic for all systems and decrease with increased temperature for the mixtures containing glymes; however, for dibutyl ether + ethyl acetate this tendency is inverted. In Figure 3 it can also be observed how the V^E values vary with the number of oxygen atoms in the ether chain; diglyme and dibutyl ether

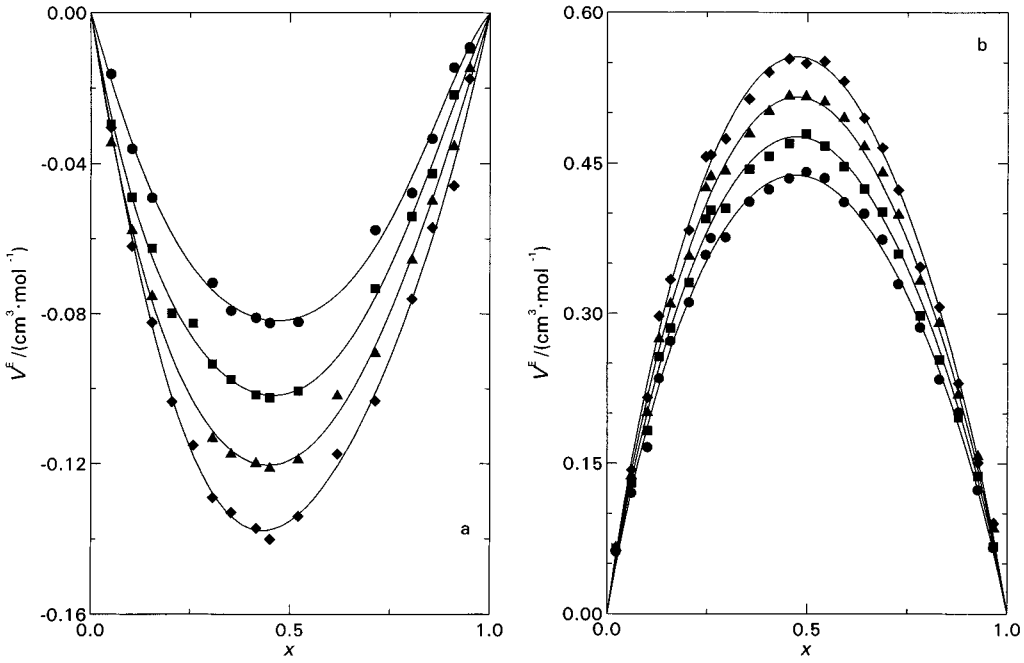

Figure 3. Excess molar volumes V^E for $x CH_3O(CH_2CH_2O)_nCH_3 + (1 - x)$ethyl acetate: (a) $n = 2$, (b) $x$dibutyl ether + $(1 - x)$ethyl acetate; (●) 278.15 K, (■) 288.15 K, (▲) 298.15 K, (◆) 308.15 K; (—) eq 1.

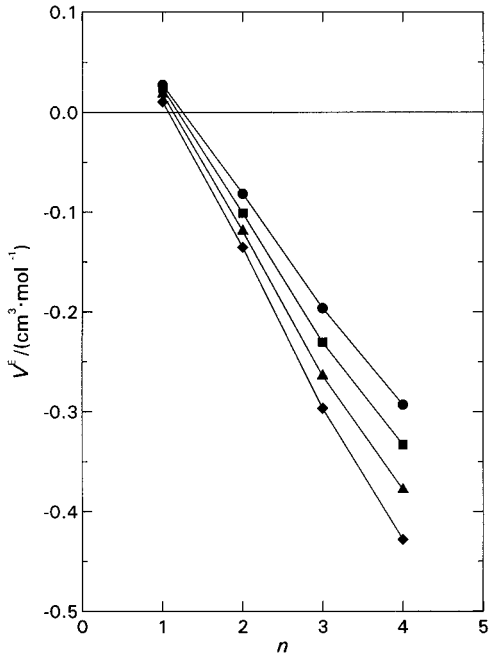

Figure 4. Excess molar volumes V^E for $CH_3O(CH_2CH_2O)_nCH_3$ with ethyl acetate at equimolecular composition: (●) 278.15 K, (■) 288.15 K, (▲) 298.15 K, (◆) 308.15 K.

are molecules of the same chain length, but the V^E values are negative for the former and positive for the latter. Thus, the presence of oxygen atoms in the ether chain lowers the excess volume. This fact can also be noted in Figure 4 where the excess volumes for the equimolar mixtures as a function of the number of diethyleneglycol units [CH_2CH_2O] in the glyme chain n are shown; the V^E values decrease from slightly positive (monoglyme) to negative values (diglyme, triglyme, and tetraglyme), and the temperature dependence is stronger with increased n.

Excess heat capacities C_p^E of Table 4 were fitted by means of the least-squares method to a Redlich−Kister polynomial of the form

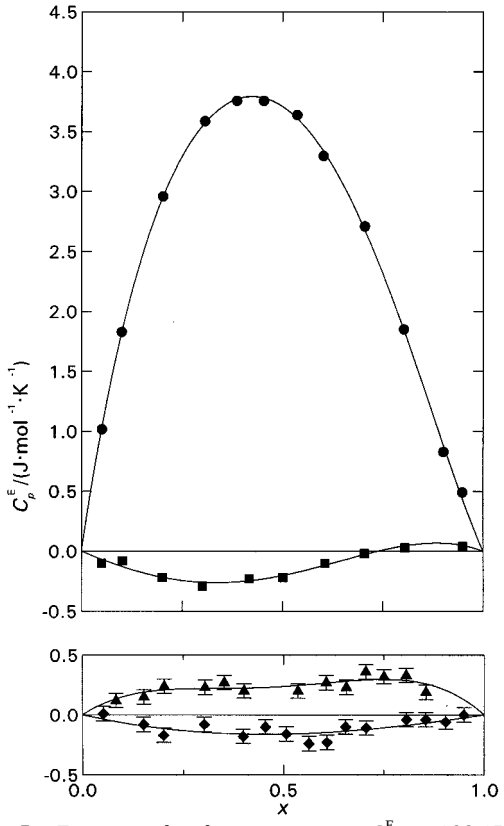

Figure 5. Excess molar heat capacities C_p^E at 298.15 K for $CH_3O(CH_2CH_2O)_nCH_3$ with ethyl acetate: (■) $n = 4$, (▲) $n = 2$, (◆) $x$dibutyl ether + $(1 - x)$ethyl acetate; this work. (●) $x CH_3O(CH_2CH_2O)_3CH_3 + (1 - x)$propyl formate; experimental data from Tovar *et al.* (1997b); (—) eq 2.

$$C_p^E/(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) = x(1-x)\sum_{i=1} A_i(2x-1)^{i-1} \qquad (2)$$

where x is the mole fraction of the ether and the coefficients A_i are contained in Table 4. Figure 5 shows the excess heat capacities of this work compared to literature values of triglyme + propyl formate. C_p^E values of ethyl acetate

with diglyme (slightly positive) and tetraglyme (S-shaped) are surprisingly much lower than those of triglyme with propyl formate (parabolic). Previous studies on the variation of C_p^E in binary mixtures of $C_4H_8O_2$ ester isomers (ethyl acetate, propyl formate, and methyl propanoate) with *n*-alkanes (Baluja *et al.*, 1985) and cycloalkanes (Jiménez *et al.*, 1986, 1994) show that excess heat capacities of mixtures containing ethyl acetate and methyl propanoate are roughly similar, but those of propyl formate are much greater. Finally, comparison between the values for ethyl acetate with dibutyl ether (slightly negative) and with diglyme show that in contrast to v^E, C_p^E increases with the presence of oxygen atoms in the ether chain.

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