Thermophysical Properties of the Binary Mixtures Diethyl Carbonate + (*n*-Dodecane or *n*-Tetradecane) at Several Temperatures

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The density and the speed of sound at (288.15, 293.15, 298.15, and 308.15) K and the isobaric molar heat capacity at (288.15, 298.15, and 308.15) K of binary mixtures of diethyl carbonate with *n*-dodecane or *n*-tetradecane were measured at atmospheric pressure, over the entire composition range. These results are used to calculate molar volumes, isentropic and isothermal compressibilities, isobaric thermal expansivities, and isobaric and isochoric molar heat capacities as well as the corresponding excess quantities. Positive values and a parabolic composition dependence were found for all excess quantities except for the excess molar heat capacities, which take negative values and are W-shaped. Excess molar volumes increase with both alkyl chain length of the *n*-alkane and temperature. Excess isobaric molar heat capacities decrease as the size of the *n*-alkane increases and exhibit different temperature dependences with mole fraction. All other properties, with the exception of the excess isochoric molar heat capacity, show similar behavior for both mixtures.

Introduction

The physical properties and the thermodynamic behavior of polar + nonpolar mixtures have been studied for many reasons, one of the most important of which is that these properties provide information about molecular interactions. An example of this type of mixtures is the diethyl carbonate (polar) + *n*-alkane (nonpolar) systems. In previous studies, excess molar volumes,[1,2] excess molar enthalpies,[3] and excess molar Gibbs free energies[4] of diethyl carbonate + *n*-alkane mixtures were determined, usually at the temperature 298.15 K. To elaborate a detailed study of the interactions of this type of mixtures, it is necessary to know the behavior of a comprehensive set of thermodynamic properties, especially at different temperatures. Taking into account the scarcity of experimental data for some properties, we studied the excess molar volumes V_m^E and the excess isobaric molar heat capacities $C_{p,m}^E$ of dimethyl or diethyl carbonate + *n*-heptane mixtures at several temperatures, as well as the partial derivatives of the excess molar volume with temperature $(\partial V_m^E/\partial T)_p$ at the temperature 298.15 K in a previous work.[5] In this work, we report experimental values for the density ρ and the speed of sound u at (288.15, 293.15, 298.15, and 308.15) K and the isobaric molar heat capacity $C_{p,m}$ at (288.15, 298.15, and 308.15) K for diethyl carbonate + (*n*-dodecane or *n*-tetradecane) mixtures. Magnitudes were measured at atmospheric pressure over the whole composition range. These data were used to calculate the molar volumes V_m, compressibilities (isentropic κ_S and isothermal κ_T), isobaric thermal expansivities α_p, and isochoric molar heat capacities $C_{v,m}$. The excess quantities V_m^E, $C_{p,m}^E$, κ_S^E, κ_T^E, α_p^E, and $C_{v,m}^E$ were calculated from the Benson and Kiyohara criterion.[6] Results are discussed in terms of well-known effects in this type of mixtures.

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Experimental Section

Materials. All the chemicals used were supplied from Aldrich (>99% mol). The purity of the chemicals was checked by gas chromatographic analysis (GC); all were degassed and dried by passage through Fluka 0.4 nm molecular sieves prior to use.

Apparatus and Procedure. The density and the speed of sound were obtained using a densimeter and sound analyzer Anton-Paar DSA-48 equipped with temperature regulation to within 0.005 K via the Peltier effect. This instrument uses a cell to measure the density and another, serially connected to the previous one, to measure the speed of sound. Calibration was done by using pure water (Milli-Q) and *n*-heptane (>99.8% mol) from Fluka as density standards and the former as the speed of sound standard. The densities of pure water at several temperatures were obtained from Riddick et al.,[7] and those of *n*-heptane were obtained in a previous work;[8] the latter were obtained using two density standards supplied by the Deutscher Kalibrierdienst-Physikalisch Technische Bundesanstalt. The speeds of sound of pure water were obtained from the work of Bilaniuk et al.[9,10] The instrument is precise to within $\pm 3 \times 10^{-5}$ g·cm^{-3} for density and ± 0.04 m·s^{-1} for speed of sound.

The isobaric heat capacities per unit volume C_pV^{-1} were measured with a Setaram micro DSC II differential scanning calorimeter, using the stepwise method. To obtain the isobaric molar heat capacity, it is necessary to combine C_pV^{-1} with the density ρ and the molar mass M data using the relation $C_{p,m} = (C_pV^{-1})M\rho^{-1}$. Vacuum and *n*-heptane were used as heat capacity standards; the $C_{p,m}$ values of the latter were taken from literature.[11] The experimental details are available elsewhere.[12] The precision in $C_{p,m}$ was estimated to be ± 0.04 J mol^{-1} K^{-1}. Mixtures were prepared by weighing using a Mettler AE-240 balance with a precision of ± 0.00001 g.

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Table 1. Densities of *x* Diethyl Carbonate + (1 − *x*) (*n*-Dodecane or *n*-Tetradecane) at the Temperature *T*

	ρ/g·cm^{-3}			
x	*T* = 288.15 K	*T* = 293.15 K	*T* = 298.15 K	*T* = 308.15 K
	x Diethyl Carbonate + (1 − *x*) *n*-Dodecane			
0.054 51	0.758 46	0.754 69	0.751 04	0.743 62
0.102 11	0.763 92	0.760 19	0.756 51	0.748 87
0.205 09	0.777 25	0.773 28	0.769 43	0.761 61
0.305 70	0.791 89	0.787 83	0.783 88	0.775 68
0.403 81	0.808 15	0.803 89	0.799 75	0.791 29
0.501 24	0.826 59	0.822 22	0.817 92	0.809 04
0.591 98	0.846 15	0.841 54	0.837 05	0.827 89
0.710 65	0.876 11	0.871 30	0.866 57	0.856 80
0.797 97	0.901 99	0.896 96	0.892 04	0.881 81
0.899 63	0.937 63	0.932 24	0.927 02	0.916 31
0.950 36	0.958 12	0.952 64	0.947 27	0.936 18
	x Diethyl Carbonate + (1 − *x*) *n*-Tetradecane			
0.055 89	0.771 49	0.767 86	0.764 18	0.757 12
0.103 62	0.776 07	0.772 46	0.768 75	0.761 48
0.202 04	0.786 48	0.782 69	0.778 84	0.771 44
0.302 53	0.798 79	0.794 94	0.790 98	0.783 19
0.406 49	0.813 65	0.809 54	0.805 44	0.797 41
0.504 21	0.830 03	0.825 84	0.821 55	0.813 10
0.604 08	0.849 67	0.845 22	0.840 71	0.831 93
0.701 85	0.872 54	0.867 92	0.863 18	0.853 87
0.799 26	0.900 18	0.895 25	0.890 24	0.880 47
0.900 88	0.935 90	0.930 70	0.925 39	0.914 89
0.950 93	0.956 84	0.951 39	0.945 87	0.935 10

Table 2. Speeds of Sound *u* of *x* Diethyl Carbonate + (1 − *x*) (*n*-Dodecane or *n*-Tetradecane) at the Temperature *T*

	u/m·s^{-1}			
x	*T* = 288.15 K	*T* = 293.15 K	*T* = 298.15 K	*T* = 308.15 K
	x Diethyl Carbonate + (1 − *x*) *n*-Dodecane			
0.054 51	1309.44	1289.72	1270.41	1231.96
0.102 11	1302.38	1282.70	1263.25	1224.76
0.205 09	1287.92	1267.96	1248.39	1209.76
0.305 70	1274.69	1254.74	1235.16	1196.31
0.403 81	1262.67	1242.42	1222.64	1183.39
0.501 24	1251.00	1230.84	1210.88	1171.40
0.591 98	1241.10	1220.66	1200.72	1161.06
0.710 65	1229.59	1209.17	1189.04	1149.03
0.797 97	1222.77	1202.20	1181.99	1141.80
0.899 63	1217.59	1196.87	1176.58	1136.12
0.950 36	1217.15	1196.27	1175.79	1135.12
	x Diethyl Carbonate + (1 − *x*) *n*-Tetradecane			
0.055 89	1341.69	1322.79	1303.66	1266.01
0.103 62	1334.43	1315.50	1296.47	1258.52
0.202 04	1319.57	1300.40	1281.25	1243.29
0.302 53	1304.77	1285.70	1266.35	1228.00
0.406 49	1289.59	1270.05	1250.70	1212.10
0.504 21	1275.32	1255.83	1236.28	1197.33
0.604 08	1260.85	1241.25	1221.39	1182.16
0.701 85	1247.42	1227.66	1207.61	1168.11
0.799 26	1234.63	1214.57	1194.40	1154.56
0.900 88	1223.51	1203.43	1183.01	1142.69
0.950 93	1219.69	1199.14	1178.76	1138.27

Results and Discussion

Results for the density, speed of sound, and isobaric heat capacity are given in Tables 1−3. These data were fitted as a function of mole fraction and temperature to the expression

$$Y = \sum_{i=1}^{n} A_i x^{i-1} \tag{1}$$

$$A_i = \sum_{j=1}^{3} A_{ij} 10^{1-j} (T/\mathrm{K} - T_0/\mathrm{K})^{j-1} \tag{2}$$

where *x* is the mole fraction of diethyl carbonate, *T* is the absolute temperature, T_0 = 288.15 K, and *Y* can be the density ρ/g·cm^{-3}, the speed of sound *u*/m·s^{-1}, or the isobaric molar heat capacity $C_{p,m}$/J·mol^{-1}·K^{-1}. The fitting coefficients A_{ij} were obtained using Marquardt's optimization method,[13] and they are given in Table 4 together with their respective standard deviations *s*.

Table 3. Isobaric Molar Heat Capacities $C_{p,m}$ of *x* Diethyl Carbonate + (1 − *x*) (*n*-Dodecane or *n*-Tetradecane) at the Temperature *T*

	$C_{p,m}$/J·mol^{-1}·K^{-1}		
x	*T* = 288.15 K	*T* = 298.15 K	*T* = 308.15 K
	x Diethyl Carbonate + (1 − *x*) *n*-Dodecane		
0.053 80	362.72	366.97	372.19
0.105 48	354.31	358.57	363.61
0.154 22	346.71	350.82	355.74
0.203 10	339.08	343.08	347.78
0.305 19	323.59	327.40	331.93
0.355 62	316.03	319.65	323.96
0.404 52	308.68	312.31	316.26
0.456 79	300.81	304.26	308.22
0.504 79	293.57	296.89	300.81
0.556 33	285.84	288.99	292.69
0.607 87	277.99	281.10	284.71
0.650 77	271.44	274.45	277.98
0.700 62	263.75	266.62	270.11
0.798 14	248.56	251.28	254.66
0.849 89	240.48	243.23	246.40
0.899 35	232.84	235.53	238.68
0.949 43	225.22	227.84	230.78
	x Diethyl Carbonate + (1 − *x*) *n*-Tetradecane		
0.056 19	421.04	425.27	430.75
0.105 40	409.74	413.91	419.28
0.156 94	398.24	402.28	407.54
0.205 33	387.47	391.57	396.58
0.307 23	365.41	369.21	374.03
0.408 78	344.02	347.69	
0.457 47			341.32
0.559 43		315.52	
0.560 58	312.01		319.13
0.609 55	301.64	304.73	308.47
0.647 71	293.52		300.11
0.703 16	281.49	284.49	288.06
0.798 94	260.74	263.59	266.92
0.847 56	250.05	252.90	256.19
0.901 10			244.41
0.948 75	228.30	230.92	233.98

The isentropic compressibility κ_S was calculated from the density ρ and the speed of sound *u* using the Laplace equation:

$$\kappa_S = 1/(\rho u^2) \tag{3}$$

The isobaric thermal expansivity α_p was obtained from analytical differentiation of the density fitting equation. The procedure used to calculate α_p was previously validated[12] and allows the obtainment of data at an intermediate temperature of the working range (298.15 K in our case). The isothermal compressibility κ_T and the isochoric molar heat capacity $C_{v,m}$ were obtained from

$$\kappa_T = \kappa_S + \frac{T V_m \alpha_p^2}{C_{p,m}} \tag{4}$$

$$C_{v,m} = C_{p,m} \frac{\kappa_S}{\kappa_T} \tag{5}$$

Experimental and calculated properties for the pure components are shown in Table 5 compared with literature data. As can be observed, the results of this work agree with the literature data. The agreement is best for the

Table 4. Smoothing Coefficients A_{ij} and Standard Deviations s of Eqs 1 and 2

		i						
	j	1	2	3	4	5	6	7
		x Diethyl Carbonate + (1 − *x*) *n*-Dodecane						
ρ/g·cm^{-3}	1	0.75253	0.10319	0.09127	−0.07528	0.21340	−0.18679	0.08199
	2	−0.00721	−0.00271	0.00363	−0.02224	0.04582	−0.04223	0.01371
	3	−0.00004	0.00046	−0.00432	0.01736	−0.03315	0.02889	−0.00922
(s = 0.00005)								
u/m·s^{-1}	1	1317.88	−157.20	51.48	27.86	−117.90	95.94	
	2	−39.40	−0.25	−14.15	30.09	−22.60	4.28	
	3	0.33	0.27	2.05	−9.27	11.16	−4.15	
(s = 0.12)								
$C_{p,m}$/J·mol^{-1}·K^{-1}	1	371.74	−171.66	78.59	−154.84	197.29	−165.50	62.08
	2	3.98	−1.80	−3.30	34.44	−103.25	118.14	−45.81
	3	0.44	−0.26	2.70	−25.53	69.09	−72.74	26.45
(s = 0.05)								
		x Diethyl Carbonate + (1 − *x*) *n*-Tetradecane						
ρ/g·cm^{-3}	1	0.76657	0.08467	0.06747	−0.01373	0.13616	−0.15082	0.09003
	2	−0.00716	−0.00344	0.01350	−0.05503	0.09477	−0.07874	0.02479
	3	0.00006	0.00039	−0.00515	0.02130	−0.04015	0.03543	−0.01185
(s = 0.00006)								
u/m·s^{-1}	1	1350.59	−163.58	100.30	−352.11	690.23	−685.72	278.02
	2	−38.48	11.64	−99.66	322.48	−527.40	420.39	−130.32
	3	0.19	−2.99	23.74	−82.09	138.27	−111.64	34.72
(s = 0.14)								
$C_{p,m}$/J·mol^{-1}·K^{-1}	1	434.33	−237.97	46.65	23.36	−114.25	65.56	
	2	3.57	−0.81	8.72	−37.13	47.84	−19.84	
	3	0.60	1.09	−12.03	28.55	−27.10	9.05	
(s = 0.06)								

Table 5. Properties of the Pure Liquids at the Temperature T

		diethyl carbonate		*n*-dodecane		*n*-tetradecane	
property	T/K	this work	lit.	this work	lit.	this work	lit.
ρ/g·cm^{-3}	288.15	0.980 31	0.980 27[14]	0.752 54		0.766 56	
	293.15	0.974 68		0.748 87	0.748 75[7]	0.763 04	
	298.15	0.969 04	0.969 16[14]	0.745 31	0.745 18[7]	0.759 45	0.759 22[1]
	308.15	0.957 74	0.957 90[14]	0.737 92		0.752 48	
u/m·s^{-1}	288.15	1217.93		1317.94		1350.51	
	293.15	1197.20		1298.25		1331.54	
	298.15	1176.53		1278.86		1312.15	
	308.15	1135.72		1240.41		1274.37	
$C_{p,m}$/J·mol^{-1}·K^{-1}	288.15	217.69		371.74		434.36	
	298.15	220.24	212.4[7]	376.18	375.97[7]	438.51	438.66[15]
	308.15	223.09		381.47		443.87	
κ_S/TPa^{-1}	288.15	687.67		765.03		715.25	
	293.15	715.81		715.81		739.17	
	298.15	745.50		820.38		764.78	
	308.15	809.47		880.77		818.30	
α_p/10^{-3}K^{-1}	298.15	1.165	1.157[14]	0.979	0.974[14]	0.929	0.925[16]
κ_T/TPa^{-1}	298.15	970.04		994.00	988[7]	918.07	910[17]
$C_{v,m}$/J·mol^{-1}·K^{-1}	298.15	169.39		310.48		365.29	

density data. It is relevant to note the scarcity of literature data for κ_S, κ_T, α_p, $C_{p,m}$, and $C_{v,m}$ of diethyl carbonate.

Excess properties were calculated by using the following expression:

$$Y^E = Y - Y^{id} \tag{6}$$

where Y^E is the excess quantity of the property Y, and Y^{id} its ideal value. Y^{id} values were calculated using the criterion of Benson and Kiyohara,[6] from which each of them are defined as follows:

$$V_m^{id} = xV_{m,l}^* + (1-x)V_{m,2} \tag{7}$$

$$C_{p,m}^{id} = xC_{p,m,l}^* + (1-x)C_{p,m,2} \tag{8}$$

$$\alpha_p^{id} = \phi\alpha_{p,l}^* + (1-\phi)\alpha_{p,2}^* \tag{9}$$

$$\kappa_T^{id} = \phi\kappa_{T,l}^* + (1-\phi)\kappa_{T,2}^* \tag{10}$$

$$\kappa_S^{id} = \kappa_T^{id} - \frac{TV_m^{id}(\alpha_p^{id})^2}{C_{p,m}^{id}} \tag{11}$$

$$C_{v,m}^{id} = C_{p,m}^{id}\frac{\kappa_S^{id}}{\kappa_T^{id}} \tag{12}$$

$$\phi = xV_{m,l}^*/V_m^{id} \tag{13}$$

where ϕ and x are the volume and mole fractions, respectively, of component 1 (diethyl carbonate in this work) and superscript * denotes properties of the pure components.

The results thus obtained are shown in Figures 1−5, where solid lines correspond to fitting polynomials of the Redlich−Kister type:

$$Y = x(1-x)\sum_{i=1}^{n} A_i(2x-1)^{i-1} \tag{14}$$

Table 6. Smoothing Coefficients A_i and Standards Deviations s of Eq 14 at the Temperature T

property	T/K	A_1	A_2	A_3	A_4	A_5	s
			x Diethyl Carbonate + $(1-x)$ *n*-Dodecane				
V_m^E/cm^3·mol^{-1}	288.15	4.467	0.128	0.662			0.010
	293.15	4.594	0.123	0.684			0.009
	298.15	4.705	0.102	0.622			0.013
	308.15	4.964	0.282	0.619			0.008
$C_{p,m}^E$/J·mol^{-1}·K^{-1}	288.15	−1.54	6.82	−7.99	−2.52	−3.68	0.03
	298.15	−2.10	5.28	−10.01			0.05
	308.15	−2.96	5.31	−8.10			0.07
κ_S^E/TPa^{-1}	298.15	156.71	50.93	35.32	10.98		0.16
κ_T^E/TPa^{-1}	298.15	205.43	76.08	45.53	14.47		0.17
α_p^E/10^{-3}K^{-1}	298.15	0.11309	0.06406	0.00527	0.00216		0.00004
$C_{v,m}^E$/J·mol^{-1}·K^{-1}	298.15	−4.26	3.49	−7.11	0.47		0.009
			x Diethyl Carbonate + $(1-x)$ *n*-Tetradecane				
V_m^E/cm^3·mol^{-1}	288.15	4.786	0.527	0.852			0.008
	293.15	4.911	0.535	0.889			0.015
	298.15	5.034	0.575	1.016			0.017
	308.15	5.302	0.601	1.013			0.008
$C_{p,m}^E$/J·mol^{-1}·K^{-1}	288.15	−4.76	12.41	−12.66	−7.93		0.06
	298.15	−4.64	10.81	−11.07	−7.08		0.07
	308.15	−4.99	9.27	−7.60	−6.67		0.07
κ_S^E/TPa^{-1}	298.15	147.2	70.2	50.6	30.9		0.3
κ_T^E/TPa^{-1}	298.15	191.8	93.9	82.4	45.4		0.3
α_p^E/10^{-3}K^{-1}	298.15	0.10596	0.06398	0.05507	0.01119	0.00729	0.00005
$C_{v,m}^E$/J·mol^{-1}·K^{-1}	298.15	−6.72	9.64	−11.25	−4.50		0.009

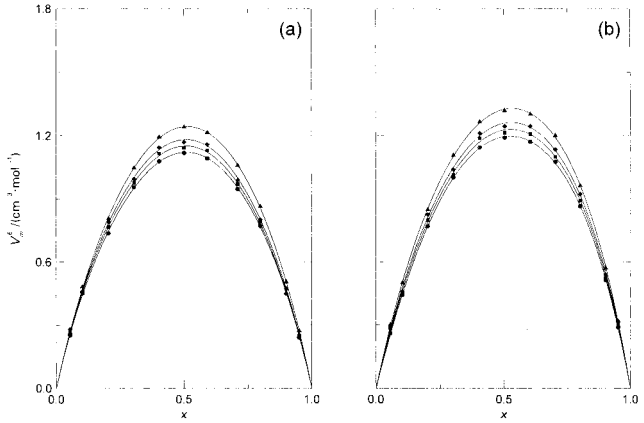

Figure 1. Excess molar volumes V_m^E for (a) x diethyl carbonate + $(1-x)$ *n*-dodecane and for (b) x diethyl carbonate + $(1-x)$ *n*-tetradecane at the temperatures (●) 288.15 K, (■) 293.15 K, (◆) 298.15 K, and (▲) 308.15 K. (—) Calculated values from eq 14.

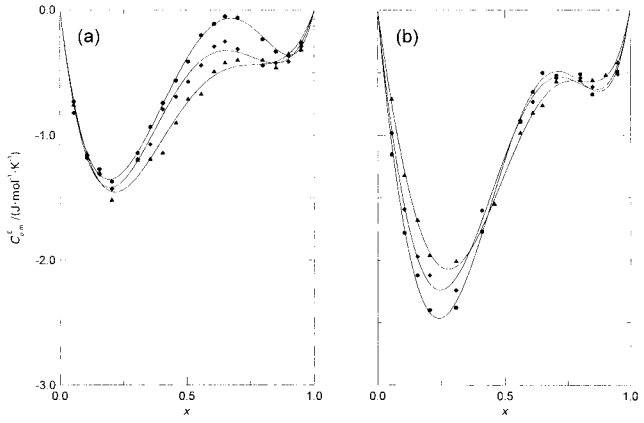

Figure 2. Excess isobaric molar heat capacities $C_{p,m}^E$ for (a) x diethyl carbonate + $(1-x)$ *n*-dodecane and for (b) x diethyl carbonate + $(1-x)$ *n*-tetradecane at the temperatures (●) 288.15 K, (◆) 298.15 K, and (▲) 308.15 K. (—) Calculated values from eq 14.

The least-squares method was used to determine the polynomial coefficients A_i, whose values for V_m^E, $C_{p,m}^E$, $C_{v,m}^E$, κ_S^E, κ_T^E, and α_p^E are given in Table 6 together with their

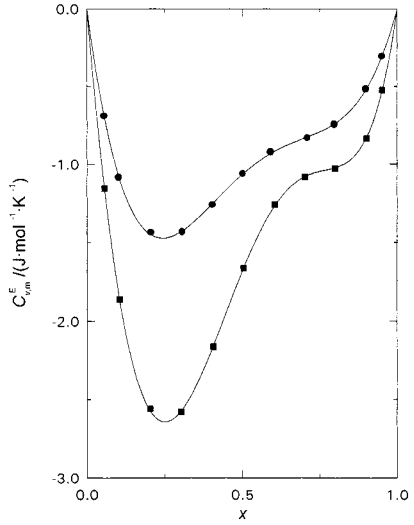

Figure 3. Excess isochoric molar heat capacities $C_{v,m}^E$ at 298.15 K for (●) x diethyl carbonate + $(1-x)$ *n*-dodecane and for (■) x diethyl carbonate + $(1-x)$ *n*-tetradecane. (—) Calculated values from eq 14.

respective standard deviations s. The number of coefficients was determined in each case using an F-test.

The values of the excess molar volumes and the fitted curves are presented in Figure 1. The V_m^E values are positive over the whole composition range and take a parabolic shape. The destruction of both the dipolar order of the carbonate and the orientational order of the *n*-alkanes during the mixing process can explain the positive values. In addition, the values of V_m^E are higher for the mixture with *n*-tetradecane because the orientational order increases as the size of the *n*-alkane increases. On the other hand, excess molar volumes increase with temperature.

The plots of $C_{p,m}^E$ and $C_{v,m}^E$ against x are shown in Figures 2 and 3. Both are negative in the entire range of composition, decrease with increasing number of carbon atoms of the *n*-alkane, and are W-shaped. $C_{p,m}^E$, as a liquid order sensible property, has a negative contribution due to the pure liquid order destruction described above, which dominates at the extremes of the range composition, and

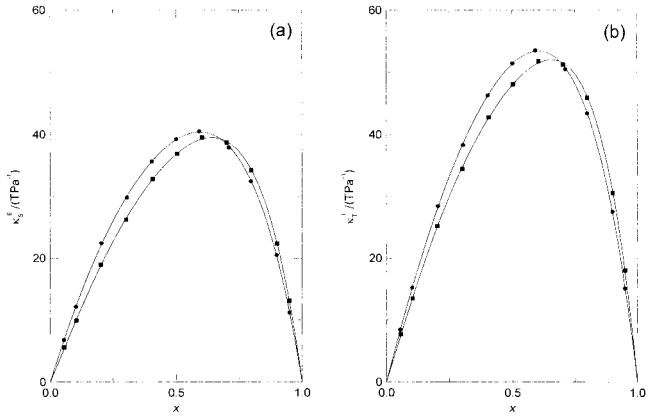

Figure 4. Excess compressibilities, (a) isentropic κ_S^E and (b) isothermal κ_T^E, at 298.15 K for (●) x diethyl carbonate + (1 − x) n-dodecane and for (■) x diethyl carbonate + (1 − x) n-tetradecane. (—) Calculated values from eq 14.

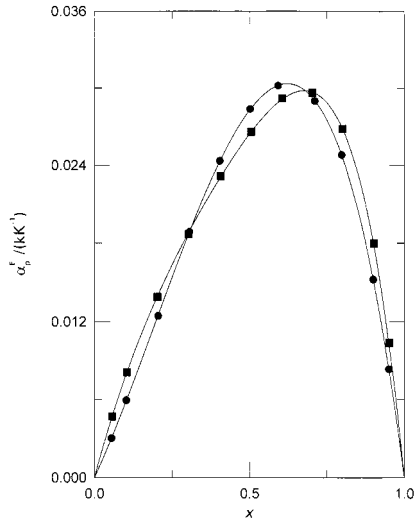

Figure 5. Excess isobaric thermal expansivities α_p^E at 298.15 K for (●) x diethyl carbonate + (1 − x) n-dodecane and for (■) x diethyl carbonate + (1 − x) n-tetradecane. (—) Calculated values from eq 14.

a positive one originated from the nonrandomness in the mixture, which dominates in the central region. The characteristic forms of the curves result from the combination of both contributions. It is worth noting that the temperature dependence of $C_{p,m}^E$ for diethyl carbonate + n-tetradecane presents a nonmonotonic behavior. At the extremes of the composition range, $C_{p,m}^E$ increases with temperature, and in the central region, it decreases with temperature; as a result, two curve crossings are found.

The calculated data of κ_S^E, κ_T^E, and α_p^E are displayed in Figures 4 and 5, with their respective fitted curves. All quantities take positive values over the whole range of composition and parabolic form. In addition, for a given property the maxima occur at different mole fractions for each system. From a quantitative point of view, all these quantities have similar values irrespective of the n-alkane in the mixture.

In future research, we will continue the study of the behavior of the thermodynamic properties of organic carbonates with hydrocarbons.

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