

# Excess Molar Enthalpies and Excess Molar Volumes of Binary Mixtures Containing Dialkyl Carbonates + Anisole or Phenetole at (288.15 and 313.15) K

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Excess molar enthalpies,  $H_m^E$ , and excess molar volumes,  $V_m^E$ , of binary mixtures containing dimethyl carbonate or diethyl carbonate + anisole or + phenetole have been determined at (298.15 and 313.15) K and at atmospheric pressure. Standard deviations have been calculated from correlation of data by the Redlich–Kister polynomial. The calculated quantities have been qualitatively discussed in terms of thermodynamic interactions between the mixing components. Only a slight influence of temperature on the excess properties has been observed.

## Introduction

Continuing our ongoing research program concerning the thermodynamic interactions of binary mixtures containing dialkyl carbonates (Francesconi and Comelli, 1999; Comelli et al., 1999; Francesconi et al., in press) we now present data on densities,  $\rho$ , and excess molar enthalpies,  $H_m^E$ , of dimethyl carbonate or diethyl carbonate + anisole or + phenetole at (298.15 or 313.15) K and at atmospheric pressure. The aim of the present study is to make a qualitative investigation on the effects of molecular structures of dialkyl carbonates on the excess molar enthalpies,  $H_m^E$ , and excess molar volumes,  $V_m^E$ . Excess enthalpies and densities are important properties for mixtures with developing thermodynamic models and engineering applications. Dialkyl carbonates are used as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals, and in agricultural chemistry (Annesini et al., 1984; Martindale, 1989; *Merck Index*, 1989). To our knowledge, no density and enthalpic data are available for these mixtures in the literature.

## Experimental Section

**Chemicals.** All chemicals were from Aldrich Chemical Co. with stated purities >99 mol % from the purchasers. Liquids have been fractionally distilled over sodium in a Vigreux 20-plated column, and the reagent-grade chemicals obtained have been further double-distilled before use. The analyses of the products have been performed on a Hewlett-Packard gas chromatograph model 5890 by using an HP (cross-linked 5% ME siloxane) capillary column. The obtained purities were >99.8 mol % for all compounds. The measured densities,  $\rho$ , and the refractive indices,  $n(D)$ , (298.15 K), have been compared with the literature values and are given in Table 1. Densities and refractive indices have been determined using a digital density meter (model DMA 60/602, Anton Paar, Graz, Austria) and an Abbe

**Table 1. Physical Properties of Pure Compounds Measured at 298.15 K and at Atmospheric Pressure and Comparison with Literature Data**

compound	$\rho/(\text{g}\cdot\text{cm}^{-3})$		$n(D)$	
	this work	lit.	this work	lit.
dimethyl carbonate	1.063 34	1.063 06 <sup>a</sup> 1.063 50 <sup>b</sup>	1.3666	1.3667 <sup>b</sup>
diethyl carbonate	0.969 40	0.969 26 <sup>c</sup> 0.969 40 <sup>d</sup>	1.3826	1.3828 <sup>c</sup> 1.3824 <sup>d</sup>
anisole	0.989 19	0.989 32 <sup>c</sup>	1.5143	1.5143 <sup>c</sup>
phenetole	0.960 18	0.960 49 <sup>c</sup>	1.5050	1.50485 <sup>c</sup>

<sup>a</sup> Negadi et al. (1993). <sup>b</sup> Garcia de la Fuente et al. (1992). <sup>c</sup> Riddick et al. (1986). <sup>d</sup> Cocero et al. (1989).

refractometer (Carl Zeiss, Jena, Switzerland) with accuracies of  $1 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$  and  $1 \times 10^{-4}$ , respectively.

Before measurements, the pure liquids were degassed by ultrasound (ultrasonic bath, type 400, Hellma, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets).

**Calorimetric Measurements.** Excess molar enthalpies,  $H_m^E$ , have been determined using a microcalorimeter (model 2107, LKB–Producer AB, Bromma, Sweden) operating under constant flow conditions. The details and operating procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986). Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) have been used to pump continuously the required flow of each pure liquid into the mixing cell. The volume of the cylinder was 2.5 cm<sup>3</sup>. Mole fractions have been determined from fluxes, and the flow rates have been selected to cover the entire mole fraction range. The accuracy of the LKB bath temperature was 0.1 K. The experimental uncertainties in the  $H_m^E$ , and mole fraction,  $x_1$ , values of dialkyl carbonates are estimated to be <1% and  $2 \times 10^{-4}$ , respectively. The reliability of the calorimeter and the procedure adopted have been checked by performing  $H_m^E$  measurements on the test system cyclohexane + hexane. Agreement with literature data (Gmehling, 1993) is better than 0.5% at the maximum of the thermal effect.

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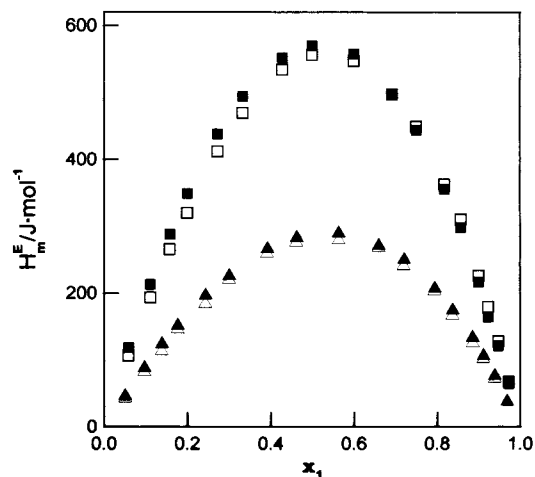
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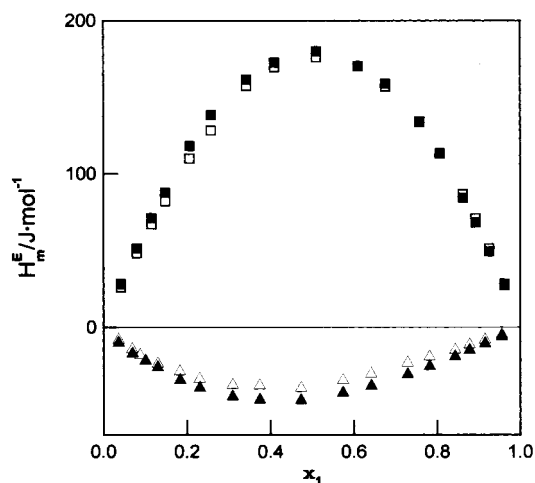
**Table 2. Experimental Excess Enthalpies,  $H_m^E$ , of Dialkyl Carbonates + Anisole or Phenetole at (298.15 and 313.15) K**

$x_1$	$H_m^E$ J·mol <sup>-1</sup>		$x_1$	$H_m^E$ J·mol <sup>-1</sup>		$x_1$	$H_m^E$ J·mol <sup>-1</sup>	
Dimethyl Carbonate (1) + Anisole (2)								
TK = 298.15								
0.0510	50	0.3922	269	0.8377	177			
0.0971	91	0.4624	286	0.8856	136			
0.1389	127	0.5635	292	0.9117	109			
0.1770	154	0.6595	274	0.9393	76			
0.2439	200	0.7207	253	0.9687	40			
0.3008	228	0.7947	210					
TK = 313.15								
0.0508	45	0.3911	262	0.8371	169			
0.0967	86	0.4612	279	0.8852	128			
0.1383	116	0.5630	282	0.9113	104			
0.1763	149	0.6591	271	0.9391	75			
0.2431	187	0.7198	244	0.9686	40			
0.2998	223	0.7940	206					
Dimethyl Carbonate (1) + Phenetole (2)								
TK = 298.15								
0.0588	118	0.4286	552	0.8573	297			
0.1111	213	0.5003	565	0.9001	216			
0.1579	287	0.6004	558	0.9232	164			
0.2000	349	0.6927	498	0.9474	121			
0.2727	438	0.7502	443	0.9730	64			
0.3333	495	0.8184	355					
TK = 313.15								
0.0586	106	0.4278	534	0.8568	310			
0.1108	193	0.4991	556	0.8997	226			
0.1575	266	0.5993	547	0.9229	179			
0.1995	320	0.6917	497	0.9472	128			
0.2721	412	0.7494	449	0.9729	67			
0.3327	469	0.8177	362					
Diethyl Carbonate (1) + Anisole (2)								
TK = 298.15								
0.0360	-9	0.3090	-44	0.7820	-24			
0.0695	-16	0.3741	-46	0.8433	-18			
0.1008	-20	0.4728	-46	0.8777	-14			
0.1300	-25	0.5737	-42	0.9150	-10			
0.1832	-33	0.6421	-37	0.9556	-5			
0.2302	-38	0.7291	-29					
TK = 313.15								
0.0359	-7	0.3089	-37	0.7815	-18			
0.0693	-13	0.3733	-37	0.8429	-14			
0.0874	-17	0.4727	-39	0.8777	-10			
0.1297	-23	0.5736	-34	0.9147	-7			
0.1827	-28	0.6413	-29	0.9555	-4			
0.2296	-32	0.7285	-22					
Diethyl Carbonate (1) + Phenetole (2)								
TK = 298.15								
0.0416	28	0.3427	162	0.8068	113			
0.0799	51	0.4100	173	0.8623	84			
0.1153	71	0.5107	180	0.8931	68			
0.1480	88	0.6104	170	0.9261	49			
0.2068	118	0.6761	159	0.9616	27			
0.2579	139	0.7580	134					
TK = 313.15								
0.0416	26	0.3423	158	0.8063	113			
0.0798	48	0.4096	170	0.8620	87			
0.1151	67	0.5100	176	0.8928	71			
0.1478	83	0.6097	170	0.9259	51			
0.2065	110	0.6755	157	0.9615	28			
0.2576	128	0.7574	134					

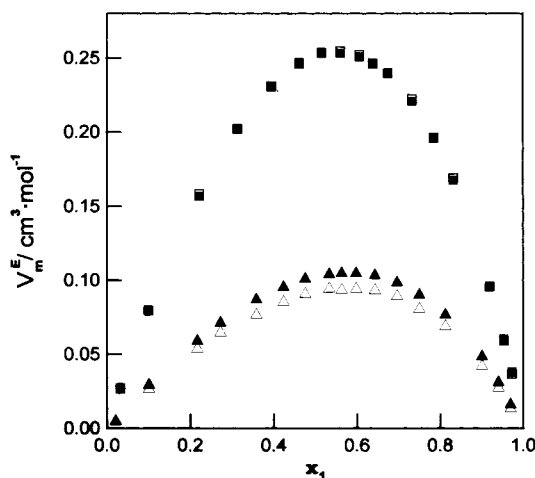
**Volumetric Measurements.** Binary mixtures have been prepared by mass in specially designed stoppered bottles, using an electronic balance (model AE 160, Mettler, Switzerland), resolution  $\pm 1 \times 10^{-4}$  g, following the method well described by Fermiglia and Lapasin (1988). The error in preparing mole fractions of dialkyl carbonates was estimated to be of the order of  $\pm 1 \times 10^{-4}$ . The temperature of the measuring cell of the digital density meter has been controlled to  $\pm 0.005$  K by circulation of thermostated water



**Figure 1.** Experimental excess molar enthalpies,  $H_m^E$ , for dimethyl carbonate (1) + anisole (2) ( $\blacktriangle$ ,  $\triangle$ ) and + phenetole (2) ( $\blacksquare$ ,  $\square$ ). Closed and open points, at (298.15 or 313.15) K, respectively.



**Figure 2.** Experimental excess molar enthalpies,  $H_m^E$ , for diethyl carbonate (1) + anisole (2) ( $\blacktriangle$ ,  $\triangle$ ) and + phenetole (2) ( $\blacksquare$ ,  $\square$ ). Closed and open points, at (298.15 or 313.15) K, respectively.



**Figure 3.** Experimental excess molar volumes,  $V_m^E$ , for dimethyl carbonate (1) + anisole (2) ( $\blacktriangle$ ,  $\triangle$ ) and + phenetole (2) ( $\blacksquare$ ,  $\square$ ). Closed and open points, at (298.15 or 313.15) K, respectively.

using an external bath (model 01 DBT 623, Heto, Birkerød, Denmark) and two precision digital thermometers (DT 100-25 and DT 100-40, Anton Paar, Graz, Austria) with a thermistor probe used to read the cell temperature to an accuracy of  $\pm 0.01$  K. The oscillation period,  $\tau$ , of the

**Table 3. Densities,  $\delta$ , and Experimental Excess Volumes,  $V_m^E$ , of Dialkyl Carbonates + Anisole or Phenetole at (298.15 and 313.15) K**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ g·cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ g·cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$x_1$	$\rho$ g·cm <sup>-3</sup>	$V_m^E$ cm <sup>3</sup> ·mol <sup>-1</sup>
Dimethyl Carbonate (1) + Anisole (2)						Diethyl Carbonate (1) + Anisole (2)					
TK = 298.15						TK = 298.15					
0.0209	0.990 34	0.006	0.5977	1.027 72	0.106	0.0208	0.988 87	-0.016	0.5121	0.980 18	-0.195
0.1004	0.994 81	0.030	0.6430	1.031 23	0.104	0.0724	0.988 07	-0.052	0.5535	0.979 34	-0.193
0.2164	1.001 68	0.060	0.6967	1.033 55	0.099	0.1259	0.987 22	-0.086	0.6172	0.978 02	-0.184
0.2726	1.005 16	0.072	0.7498	1.039 97	0.092	0.2292	0.985 48	-0.139	0.6654	0.976 99	-0.172
0.3579	1.010 67	0.088	0.8126	1.045 42	0.078	0.2803	0.984 58	-0.158	0.7700	0.974 71	-0.136
0.4233	1.015 09	0.096	0.9011	1.053 54	0.050	0.3366	0.983 56	-0.175	0.8696	0.972 46	-0.087
0.4756	1.018 72	0.102	0.9400	1.057 30	0.032	0.3846	0.982 67	-0.186	0.9042	0.971 65	-0.065
0.5331	1.022 88	0.105	0.9699	1.060 27	0.017	0.4346	0.981 71	-0.192	0.9577	0.970 41	-0.030
0.5634	1.025 13	0.106				0.4770	0.980 88	-0.195			
TK = 313.15						TK = 313.15					
0.0209	0.976 11	0.006	0.5977	1.010 72	0.095	0.0208	0.974 65	-0.015	0.5121	0.964 59	-0.213
0.1004	0.980 26	0.028	0.6430	1.013 95	0.094	0.0724	0.973 70	-0.054	0.5535	0.963 63	-0.210
0.2164	0.986 64	0.055	0.6967	1.017 92	0.090	0.1259	0.972 69	-0.091	0.6172	0.962 15	-0.202
0.2725	0.989 86	0.066	0.7498	1.022 00	0.082	0.2292	0.970 68	-0.149	0.6654	0.961 00	-0.191
0.3579	0.994 98	0.078	0.8126	1.027 01	0.070	0.2803	0.969 64	-0.171	0.7700	0.958 46	-0.157
0.4233	0.999 05	0.086	0.9011	1.034 47	0.043	0.3366	0.968 46	-0.190	0.8696	0.955 96	-0.106
0.4756	1.002 41	0.092	0.9400	1.037 88	0.030	0.3846	0.967 43	-0.202	0.9042	0.955 06	-0.083
0.5331	1.006 24	0.095	0.9699	1.040 62	0.014	0.4346	0.966 34	-0.209	0.9577	0.953 63	-0.041
0.5634	1.008 33	0.095				0.4770	0.965 39	-0.213			
Dimethyl Carbonate (1) + Phenetole (2)						Diethyl Carbonate (1) + Phenetole (2)					
TK = 298.15						TK = 298.15 K					
0.0317	0.962 19	0.026	0.6382	1.013 40	0.247	0.0266	0.960 44	-0.003	0.5468	0.965 44	-0.039
0.0992	0.966 61	0.079	0.6740	1.017 46	0.240	0.0922	0.961 09	-0.012	0.5860	0.965 79	-0.038
0.2212	0.975 29	0.157	0.7325	1.024 44	0.221	0.1386	0.961 54	-0.017	0.7179	0.966 98	-0.031
0.3134	0.982 49	0.202	0.7845	1.031 06	0.196	0.2595	0.962 72	-0.029	0.7509	0.967 27	-0.029
0.3941	0.989 29	0.230	0.8322	1.037 46	0.167	0.3106	0.963 21	-0.032	0.7912	0.967 62	-0.025
0.4616	0.995 38	0.247	0.9193	1.050 19	0.095	0.3818	0.963 89	-0.036	0.8660	0.968 26	-0.016
0.5195	1.000 5	0.253	0.9532	1.055 53	0.060	0.4272	0.964 32	-0.038	0.9391	0.968 88	-0.006
0.5604	1.005 08	0.253	0.9732	1.058 77	0.038	0.4691	0.964 72	-0.039	0.9771	0.969 22	-0.002
0.6062	1.009 90	0.251				0.5163	0.965 16	-0.039			
TK = 313.15						TK = 313.15					
0.0317	0.948 01	0.027	0.6382	0.996 36	0.246	0.0266	0.946 31	-0.003	0.5468	0.949 92	-0.053
0.0992	0.952 19	0.080	0.6740	1.000 18	0.240	0.0922	0.946 80	-0.015	0.5860	0.950 17	-0.052
0.2212	0.963 08	0.158	0.7325	1.006 75	0.222	0.1386	0.947 14	-0.022	0.7179	0.950 95	-0.044
0.3134	0.967 19	0.202	0.7845	1.013 00	0.196	0.2595	0.948 01	-0.038	0.7509	0.951 14	-0.040
0.3941	0.973 61	0.231	0.8322	1.019 02	0.169	0.3106	0.948 37	-0.044	0.7912	0.951 37	-0.034
0.4615	0.979 36	0.246	0.9193	1.031 02	0.096	0.3818	0.948 85	-0.049	0.8660	0.951 77	-0.025
0.5150	0.984 18	0.253	0.9532	1.036 06	0.059	0.4272	0.949 15	-0.051	0.9391	0.952 14	-0.012
0.5604	0.988 50	0.255	0.9732	1.039 13	0.037	0.4691	0.949 43	-0.053	0.9771	0.953 23	0.003
0.6062	0.993 04	0.252				0.5163	0.949 73	-0.053			

sample in the vibrating U-tube has been converted to density using the following formula

$$\rho = A(\tau^2 - B) \quad (1)$$

with  $A$  and  $B$  constants of the apparatus, determined from literature density data of twice distilled water (Wagenbreth and Blanke, 1971) and dry air (Kohlrausch, 1968).

Buoyancy corrections have been made for density measurements. The estimated error in  $V_m^E$  was less than  $\pm 3 \times 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1}$ .

## Results and Discussion

The experimental  $H_m^E$  and  $V_m^E$  values are reported in Tables 2 and 3, respectively.

The excess molar volumes,  $V_m^E$ , have been calculated from densities by the following equation

$$V_m^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2 \quad (2)$$

where  $x_i$ ,  $M_i$ , and  $\rho_i$  ( $i = 1, 2$ ) are the mole fractions, molar masses, and densities of the pure compounds, respectively, and  $\rho$  is the density of the mixture.

To each set of experimental values, a Redlich–Kister polynomial of the type

$$Q_m^E = x_1 x_2 \sum_{k=0}^n a_k (x_1 - x_2)^k \quad (3)$$

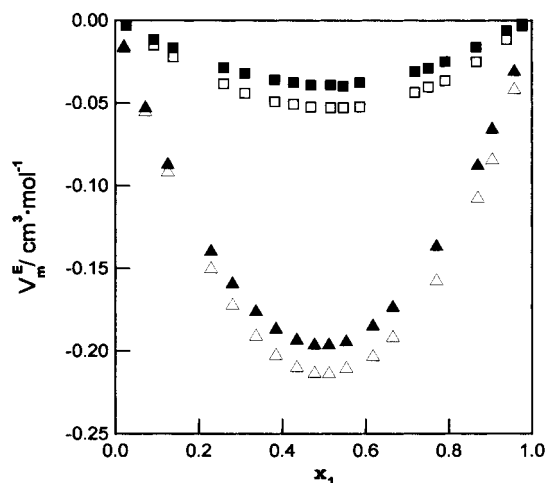
has been fitted by an unweighted least-squares method, where  $Q_m^E = H_m^E / J \cdot \text{mol}^{-1}$  or  $V_m^E / \text{cm}^3 \cdot \text{mol}^{-1}$ ,  $x_1$  and  $x_2$  are the molar fractions of dialkyl carbonates and component 2, and  $a_k$  are the adjustable parameters. The  $a_k$  values are given in Table 4 together with the standard deviation  $\sigma(Q_m^E)$ , defined as

$$\sigma(Q_m^E) = |\phi_{\min} / (N - n)|^{0.5} \quad (4)$$

with  $N$  and  $n$  the numbers of experimental points and of parameters, whereas  $\phi_{\min}$  is the minimum value of the objective function  $\phi$ , defined as

$$\phi = \sum_{k=1}^N \eta_k^2 \quad (5)$$

where  $\eta_k = Q_{m,\text{calcd}}^E - Q_m^E$ ,  $Q_m^E$  is the experimental value, and  $Q_{m,\text{calcd}}^E$  is evaluated through eq 3.



**Figure 4.** Experimental excess molar volumes,  $V_m^E$ , for diethyl carbonate (1) + anisole (2) ( $\blacktriangle$ ,  $\triangle$ ) and + phenetole (2) ( $\blacksquare$ ,  $\square$ ). Closed and open points, at (298.15 or 313.15) K, respectively.

**Table 4.** Least-Squares Parameters,  $a_k$  (Eq 3), and Standard Deviations,  $\sigma(Q_m^E)$  (Eq 4), of Dialkyl Carbonates + Anisole or Phenetole at (298.15 and 313.15) K

function	$a_0$	$a_1$	$a_2$	$a_3$	$\sigma(Q_m^E)$
Dimethyl Carbonate (1) + Anisole (2)					
TK = 298.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	1170.3	187.2			1.9
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	0.4140	0.1302	0.0454		0.0004
TK = 313.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	1132.3	191.3			2.1
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	0.3720	0.1141	0.0413		0.0008
Dimethyl Carbonate (1) + Phenetole (2)					
TK = 298.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	2278.5	164.1			2.8
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	1.0040	0.1968	0.1055	0.0808	0.0010
TK = 313.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	2223.8	338.4			2.7
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	1.0059	0.2025	0.1145	0.0564	0.0008
Diethyl Carbonate (1) + Anisole (2)					
TK = 298.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	-180.1	66.7			0.4
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.7828	0.0153	0.0254		0.0003
TK = 313.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	-145.8	67.9			0.6
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.8500	-0.0060	-0.0055		0.0005
Diethyl Carbonate (1) + Phenetole (2)					
TK = 298.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	718.4	10.0			1.2
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.1565	-0.0030	0.0310		0.0006
TK = 313.15					
$H_m^E$ /(J·mol <sup>-1</sup> )	703.6	47.7			1.2
$V_m^E$ /(cm <sup>3</sup> ·mol <sup>-1</sup> )	-0.2127	-0.0183	0.0251		0.0007

Figures 1–4 report the experimental points of binary mixtures at (298.15 and 313.15) K.

Two important features are shown by Figures 1 and 2. First, the temperature dependence of  $H_m^E$  is negligibly small.

Moreover, in going from diethyl carbonate to dimethyl carbonate, both anisole and phenetole have an increase of  $H_m^E$ , about three times for phenetole whereas anisole turns from negative to positive values.

The same behavior is observed for the  $V_m^E$  values, which, however, have a more marked temperature dependence and negative values for the mixtures of both anisole and phenetole in diethyl carbonate.

**Table 5.** Interaction Energies,  $E_{ij}$ , of Dialkyl Carbonates + Anisole and Phenetole at 298.15 K<sup>a</sup>

	anisole (2)	phenetole (2)
	$E_{22} = 46.9$	$E_{22} = 51.1$
dimethyl carbonate (1)	$E_{12} = 41.7$	$E_{12} = 43.7$
	$E_{11} = 36.7$	
diethyl carbonate (2)	$E_{12} = 45.3$	$E_{12} = 47.3$
	$E_{11} = 43.6$	

<sup>a</sup>  $E_{ij}$  in kJ·mol<sup>-1</sup>.

A qualitative interpretation of these results may be obtained by considering the bonds between the oxygen atom of the phenyl alkyl ethers and the C=O group in the esters of carbonic acid as the prevailing molecular interactions in the mixture formation.

In addition, the approximate expression  $H_m^E \propto E_{11} + E_{22} - 2E_{12}$  may be used for a qualitative discussion of thermal data for mixtures, owing to the relatively small values of  $H_m^E$  and the symmetry of the curve  $H_m^E$  versus  $x_1$ .

Table 5 reports values of interaction energies  $E_{ij}$ , between molecules  $i$  and  $j$ , calculated from a modified Prigogine model, following the procedure used in previous works (Francesconi and Comelli, 1995; Francesconi et al., 1996; Francesconi et al., 1999).

As the C<sub>2</sub>H<sub>5</sub> group is more an electron donor than CH<sub>3</sub>, the oxygen atom of phenetole has a negative charge larger than that of anisole and, hence, stronger interactions between phenetole molecules are calculated (first row of Table 5).

The different behavior of C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub> groups is enhanced in the alkyl carbonates, due to the presence of a couple of these groups. Consequently, the carbon atom of the C=O group in alkyl carbonates (component 1) must have a larger positive charge in the ethyl-substituted molecule, diethyl carbonate.

Thus, we see from Table 5 that  $E_{11}$  increases by about 7 kJ·mol<sup>-1</sup> in passing from dimethyl carbonate to diethyl carbonate, which must be compared with a value of about 4 kJ·mol<sup>-1</sup>, which is the increased molecular interaction energy in going from anisole to phenetole molecules.

As to the  $V_m^E$  data, only variations of excess volumes in going from mixtures with a fixed component can be qualitatively explained by Table 5.

For instance, the increase of  $V_m^E$  in going from anisole to phenetole in mixtures with diethyl carbonate may be referred to the increase of  $E_{22} - 2E_{12}$ , that is the relative prevailing of  $E_{22}$  over  $E_{12}$  interactions, which leads to a volume increase.

More difficult is the prediction of the sign of  $V_m^E$ , since excess volume depends on several effects whose contribution cannot be described by simple thermodynamic models.

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