

# Isothermal Vapor-Liquid Equilibria, Densities, Refractive Indices, Excess Molar Volumes, and Excess Molar Enthalpies of Dimethyl Carbonate + 1,2-Dichloroethane and + 1,1,1-Trichloroethane

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Isothermal vapor-liquid equilibrium (VLE) data, excess molar volumes  $V_m^E$ , and excess molar enthalpies  $H_m^E$  have been determined for dimethyl carbonate + 1,2-dichloroethane or + 1,1,1-trichloroethane.  $V_m^E$  and  $H_m^E$  were measured at 298.15 and 313.15 K. VLE measurements were also made at 333.15 K. The excess Gibbs free energy for the two systems has been derived at the three temperatures.

## Introduction

This paper reports the excess functions  $G_m^E$ ,  $V_m^E$ , or  $H_m^E$  for the binary mixtures of dimethyl carbonate + 1,2-dichloroethane or + 1,1,1-trichloroethane. Values of  $G_m^E$  were obtained from vapor-liquid equilibrium (VLE) measurements. To the best of our knowledge, we are not aware of any measurements on the excess properties of these systems.

## Experimental Section

**Materials.** Dimethyl carbonate, 1,2-dichloroethane, and 1,1,1-trichloroethane were supplied from Aldrich and used without further purification. Purities of 99+ % mass % for dimethyl carbonate and 1,1,1-trichloroethane and 99.8 % mass % for 1,2-dichloroethane were determined by gas chromatography analysis and excluded any significant impurities.

Prior to each measurement, all liquids were stored in dark bottles over molecular sieves (Union Carbide type 4A, from Fluka) and carefully degassed. The experimental properties of the pure compounds are given in Table 1 and are compared with literature data (1-6).

**Apparatus and Procedure.** The VLE measurements were made in an equilibrium still manufactured by Fritz GmbH (Normag) Hofheim (Germany), the same as that used in previous papers (7-9): the details of the still and its operating procedure were described elsewhere (10).

Temperature,  $T$ , and pressure,  $P$ , were measured by digital instruments both from Otto Fritz GmbH (Normag), Germany. The accuracies of the temperature and pressure were  $\pm 0.05$  K and  $\pm 0.05$  kPa, respectively. The vapor pressures of the pure compounds were measured in the recirculating still and compared with literature values in Table 1.

The liquid and the condensate vapor compositions were determined by refractometry (Abbe refractometer, Carl Zeiss-Jena, precision 0.0001) at  $298.15 \pm 0.1$  K. A previous refractometer check was carried out with standard liquids, supplied with the instrument, with known index values. The refractive indices of solutions of known mole fractions are given in Table 2. Solutions were prepared by mass. Mole fractions are accurate to  $\pm 0.0001$  g. The mole fractions of the liquid and vapor samples taken from the still have accuracies not exceeding  $1.5 \times 10^{-3}$ .

The excess molar volumes,  $V_m^E$ , were determined from density measurements of the liquids with an Anton Paar vibrating density meter (model DMA 60/602, resolution  $1 \times$

**Table 1. Densities,  $\rho$ , Refractive Indices,  $n(D)$ , and Vapor Pressure  $P$  of the Pure Components at 298.15 K**

compound	$\rho/(g \cdot cm^{-3})$		$n(D)$		$P/kPa$	
	exptl	lit.	exptl	lit.	exptl	lit.
dimethyl carbonate	1.063 28	1.063 50 (1)	1.3671	1.3670 (2)	7.3	7.19 (3)
1,2-dichloroethane	1.245 67	1.245 79 (4)	1.4421	1.4421 (5)	10.6	10.7 <sup>a</sup> (6)
1,1,1-trichloroethane	1.329 78	1.329 9 (5)	1.4357	1.4359 (5)	16.5	16.4 (6)

<sup>a</sup> Calculated from the vapor pressure equation.

**Table 2. Indices of Refraction  $n(D)$  of the Binary Mixtures at 298.15 K as a Function of the Mole Fraction  $x_1$**

$x_1$	$n(D)$	$x_1$	$n(D)$
Dimethyl Carbonate (1) + 1,2-Dichloroethane (2)			
0.0000	1.4421	0.5190	1.3994
0.0084	1.4416	0.5732	0.3954
0.0664	1.4365	0.6152	1.3925
0.1312	1.4307	0.6851	1.3876
0.2028	1.4244	0.7624	1.3823
0.2759	1.4184	0.8180	1.3785
0.3499	1.4125	0.9149	1.3721
0.4109	1.4077	0.9860	1.3677
0.4339	1.4059	1.0000	1.3671
0.4925	1.4015		
Dimethyl Carbonate (1) + 1,1,1-Trichloroethane (2)			
0.0000	1.4357	0.5816	1.3968
0.0210	1.4342	0.6227	1.3940
0.0923	1.9843	0.6250	1.3939
0.1611	1.9773	0.7265	1.3867
0.2802	1.4172	0.8169	1.3802
0.3377	1.4135	0.8403	1.3786
0.4082	1.4088	0.8878	1.3750
0.4549	1.4055	0.9306	1.3719
0.5078	1.4020	0.9891	1.3677
0.5383	1.3999	1.0000	1.3671

$10^{-6} g \cdot cm^{-3}$ ). The operating procedures for determining the densities of mixtures are given in ref 11. The temperature was maintained at a constant to within  $\pm 0.005$  K by means of a Hetotherm bath circulator (model 01 DTB 623), and the temperature was measured by two digital thermometers (Anton Paar AT-25 and DT-40), with a precision of  $\pm 0.01$  K.

Densities are estimated to be accurate to  $5 \times 10^{-6} g \cdot cm^{-3}$ . Double-distilled and degassed water ( $\rho(298.15 K) = 0.997 047 g \cdot cm^{-3}$  (12)) and dry air ( $\rho(298.15 K) = 0.001 185 g \cdot cm^{-3}$  (13))

**Table 3. Experimental Vapor-Liquid Equilibrium Data, Pressure  $P$  and Vapor Mole Fraction  $y_1$ , at 298.15, 313.15, and 333.15 K as a Function of Liquid Mole Fraction  $x_1$  and Calculated Activity Coefficients  $\gamma_i$** 

$P/\text{kPa}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$	$P/\text{kPa}$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
Dimethyl Carbonate (1) + 1,2-Dichloroethane (2)									
$T = 298.15 \text{ K}$									
10.6	0.000	0.000			8.0	0.682	0.608	1.00	0.94
10.5	0.021	0.012	0.83	1.00	7.8	0.764	0.706	1.00	0.93
10.3	0.068	0.043	0.88	1.00	7.7	0.826	0.778	1.00	0.93
10.1	0.136	0.090	0.91	0.99	7.6	0.884	0.851	1.00	0.93
9.7	0.231	0.161	0.94	0.99	7.6	0.928	0.904	1.00	0.93
9.3	0.328	0.243	0.95	0.98	7.5	0.953	0.938	1.00	0.92
8.8	0.400	0.312	0.96	0.97	7.4	0.974	0.996	1.00	0.92
8.4	0.486	0.398	0.97	0.96	7.3	1.000	1.000		
8.3	0.579	0.494	0.99	0.95					
$T = 313.15 \text{ K}$									
20.7	0.000	0.000			17.0	0.664	0.602	1.00	0.95
20.5	0.070	0.049	0.94	1.00	16.6	0.744	0.692	1.00	0.95
20.2	0.138	0.098	0.93	1.00	16.2	0.802	0.750	1.00	0.96
19.8	0.200	0.145	0.94	1.00	15.9	0.885	0.853	1.00	0.96
19.2	0.287	0.215	0.95	1.00	15.7	0.926	0.906	1.00	0.96
18.6	0.385	0.312	0.97	0.99	15.6	0.957	0.942	1.00	0.95
18.1	0.464	0.389	0.98	0.97	15.5	0.970	0.962	1.00	0.94
17.7	0.539	0.465	0.99	0.96	15.3	1.000	1.000		
17.3	0.600	0.530	1.00	0.96					
$T = 333.15 \text{ K}$									
46.2	0.000	0.000			38.8	0.638	0.588	1.01	0.96
46.0	0.057	0.042	0.95	1.00	38.2	0.704	0.662	1.01	0.94
45.0	0.130	0.098	0.95	1.00	37.7	0.765	0.733	1.01	0.94
43.6	0.229	0.176	0.96	1.00	37.2	0.850	0.818	1.01	0.95
43.0	0.280	0.224	0.96	1.00	36.7	0.890	0.863	1.01	0.97
42.2	0.352	0.294	0.97	0.99	36.5	0.926	0.907	1.00	1.00
40.4	0.488	0.422	0.98	0.98	36.2	0.957	0.940	1.00	1.04
39.8	0.540	0.475	0.99	0.97	35.2	1.000	1.000		
39.4	0.575	0.513	1.00	0.97					
Dimethyl Carbonate (1) + 1,1,1-Trichloroethane (2)									
$T = 298.5 \text{ K}$									
16.5	0.000	0.000			11.2	0.737	0.503	1.03	1.29
16.2	0.051	0.036	1.56	1.00	10.4	0.807	0.528	1.01	1.37
15.7	0.152	0.096	1.37	1.00	9.5	0.878	0.688	1.00	1.45
15.4	0.212	0.131	1.30	1.03	8.7	0.923	0.780	1.00	1.46
14.8	0.310	0.191	1.21	1.05	8.2	0.952	0.859	1.00	1.45
14.1	0.426	0.260	1.15	1.08	7.8	0.973	0.920	1.00	1.43
13.1	0.552	0.339	1.10	1.13	7.3	1.000	1.000		
12.2	0.642	0.419	1.06	1.19					
$T = 313.15 \text{ K}$									
30.9	0.000	0.000			21.5	0.771	0.562	1.02	1.32
30.5	0.110	0.077	1.42	1.01	19.8	0.842	0.660	1.01	1.38
29.8	0.204	0.138	1.31	1.02	18.6	0.890	0.740	1.00	1.42
28.7	0.295	0.198	1.24	1.04	17.6	0.930	0.811	1.00	1.44
27.6	0.382	0.250	1.19	1.07	16.9	0.954	0.872	1.00	1.45
26.3	0.479	0.314	1.13	1.10	16.3	0.968	0.915	1.00	1.45
25.0	0.565	0.374	1.09	1.15	15.2	1.00	1.000		
23.2	0.682	0.464	1.04	1.24					
$T = 333.15 \text{ K}$									
63.8	0.000	0.000			49.8	0.711	0.530	1.04	1.25
62.7	0.145	0.095	1.38	1.02	46.7	0.789	0.618	1.03	1.03
60.8	0.300	0.218	1.24	1.05	43.9	0.853	0.706	1.02	1.37
59.3	0.380	0.274	1.19	1.07	41.7	0.902	0.778	1.01	1.45
57.1	0.468	0.329	1.14	1.11	39.7	0.938	0.846	1.00	1.56
54.7	0.556	0.395	1.09	1.16	38.0	0.965	0.900	1.00	1.68
52.4	0.632	0.456	1.06	1.20	35.2	1.000	1.000		

at atmospheric pressure have been used to calibrate the density meter which was checked with the benzene + cyclohexane mixture for which values are accurately known from the literature (14) (our value of  $V_m^E$  at 0.5 mole fraction is  $0.652 \text{ cm}^3 \cdot \text{mol}^{-1}$ , lit. (14)  $0.6514 \text{ cm}^3 \cdot \text{mol}^{-1}$ ).

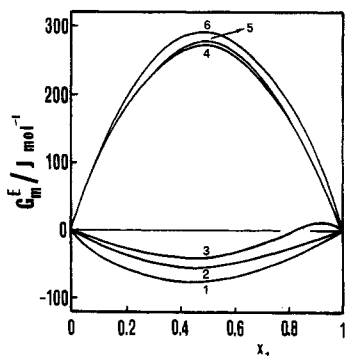
The following equation was used to evaluate  $V_m^E$  values from density measurements:

$$V_m^E = (x_1 M_1 + x_2 M_2) / \rho - x_1 M_1 / \rho_1 - x_2 M_2 / \rho_2 \quad (1)$$

where  $\rho$  and  $\rho_i$  are the densities of the mixture and of the pure compound  $i$ . Mixtures were prepared from the degassed

samples by mass using air-tight screw-capped flasks (capacity  $20 \text{ cm}^3$ ). Corrections for buoyancy and for evaporation of components were made. The accuracy in  $x_1$  is  $1 \times 10^{-4}$  (in the worse cases).  $V_m^E$  is accurate to  $\pm 0.002 \text{ cm}^3 \cdot \text{mol}^{-1}$  at about equimolar composition.

Excess molar enthalpies,  $H_m^E$ , were measured in an LKB flow microcalorimeter (model 2107, LKB Bromma, Sweden) as described elsewhere (15). Two identical automatic burets (ABU-Radiometer, Copenhagen, Denmark) were employed to pump liquids through the mixing cell of the calorimeter; details of the apparatus and experimental procedure are given in ref 16. The temperature inside the equilibrium cell was



**Figure 1.** Excess molar Gibbs energy  $G_m^E$  for dimethyl carbonate + two chlorohydrocarbons as a function of the mole fraction  $x_1$  of dimethyl carbonate: (1, 2, 3) 1,2-dichloroethane at 298.15, 313.15, and 333.15 K; (4, 5, 6) 1,1,1-trichloroethane at 298.15, 313.15, and 333.15 K, respectively.

**Table 4.** Densities  $\rho$  and Excess Molar Volumes  $V_m^E$  of Binary Mixtures as a Function of the Mole Fraction  $x_1$  at 298.15 K or 313.15 K and at Atmospheric Pressure

$x_1$	$\rho/(g \cdot cm^{-3})$	$V_m^E/(cm^3 \cdot mol^{-1})$	$x_1$	$\rho/(g \cdot cm^{-3})$	$V_m^E/(cm^3 \cdot mol^{-1})$
Dimethyl Carbonate (1) + 1,2-Dichloroethane (2)					
$T = 298.15$ K					
0.084	1.243 77	0.017	0.5191	1.14 53	0.326
0.0665	1.231 31	0.096	0.5734	1.133 91	0.315
0.1313	1.217 76	0.171	0.6154	1.126 59	0.300
0.2029	1.203 22	0.235	0.6852	1.114 58	0.269
0.2760	1.188 00	0.283	0.7625	1.101 61	0.220
0.3500	1.174 62	0.313	0.8181	1.092 44	0.177
0.4111	1.163 17	0.328	0.9150	1.076 76	0.090
0.4341	1.158 95	0.329	0.9858	1.065 55	0.013
0.4926	1.148 30	0.328			
$T = 313.15$ K					
0.0084	1.221 79	0.014	0.5191	1.122 80	0.321
0.0665	1.209 51	0.091	0.5734	1.113 28	0.310
0.1313	1.196 15	0.165	0.6154	1.106 05	0.295
0.2030	1.181 80	0.228	0.6853	1.094 15	0.266
0.2760	1.167 56	0.276	0.763	1.081 30	0.218
0.3500	1.153 55	0.306	0.8181	1.072 24	0.175
0.4111	1.142 23	0.321	0.9150	1.056 71	0.089
0.4341	1.138 06	0.322	0.9858	1.045 60	0.014
0.4926	1.127 51	0.323			
Dimethyl Carbonate (1) + 1,1,1-Trichloroethane (2)					
$T = 298.15$ K					
0.0211	1.324 80	0.017	0.5813	1.183 90	0.158
0.0924	1.307 76	0.070	0.6229	1.172 62	0.149
0.1613	1.291 10	0.109	0.6252	1.172 00	0.149
0.2804	1.261 82	0.151	0.7267	1.143 84	0.121
0.3379	1.247 89	0.162	0.8170	1.118 06	0.084
0.4084	1.229 40	0.171	0.8405	1.111 23	0.076
0.4551	1.217 82	0.172	0.8880	1.097 25	0.054
0.5080	1.203 43	0.170	0.9307	1.084 49	0.031
0.5385	1.195 35	0.166	0.9891	1.066 67	0.003
$T = 313.15$ K					
0.0211	1.299 55	0.019	0.5813	1.161 37	0.174
0.0924	1.282 80	0.077	0.6229	1.150 32	0.165
0.1613	1.266 47	0.118	0.6252	1.149 73	0.163
0.2804	1.237 73	0.165	0.7267	1.122 15	0.134
0.3379	1.223 58	0.178	0.8170	1.096 91	0.095
0.4084	1.205 93	0.188	0.8405	1.090 25	0.084
0.4551	1.194 14	0.186	0.8880	1.076 55	0.061
0.5080	1.180 52	0.186	0.9307	1.064 07	0.036
0.5385	1.172 60	0.181	0.9891	1.046 64	0.005

measured with a precision of  $\pm 0.01$  K by means of an electronic unit. The calorimeter was checked against hexane + cyclohexane at 298.15 K, the agreement with the results of ref 17 being better than 0.5% over the central range of concentration. Values of the mole fraction of the mixtures obtained from the calibrated flow rates and the fluid density are estimated to

**Table 5.** Excess Molar Enthalpies  $H_m^E$  for the Binary Systems as a Function of the Mole Fraction  $x_1$  at 298.15 or 313.15 K and at Atmospheric Pressure

$x_1$	$H_m^E/(J \cdot mol^{-1})$	$x_1$	$H_m^E/(J \cdot mol^{-1})$	$x_1$	$H_m^E/(J \cdot mol^{-1})$
Dimethyl Carbonate (1) + 1,2-Dichloroethane (2)					
$T = 298.15$ K					
0.0376	-16.0	0.3192	-147.3	0.7896	-105.7
0.0725	-32.6	0.3847	-171.0	0.8491	-68.8
0.1049	-48.2	0.4840	-189.7	0.8824	-50.0
0.1352	-64.1	0.5846	-183.5	0.9184	-29.9
0.1899	-90.3	0.6528	-167.6	0.9575	-12.5
0.2382	-112.4	0.7378	-130.0		
$T = 313.15$ K					
0.0376	-22.6	0.3190	-174.1	0.7893	-118.2
0.0724	-43.5	0.3844	-191.7	0.8490	-86.6
0.1048	-65.7	0.4837	-204.2	0.8823	-66.5
0.1350	-85.6	0.5842	-195.7	0.9183	-45.7
0.1819	-116.8	0.6520	-176.6	0.9574	-23.3
0.2379	-141.0	0.7376	-144.6		
Dimethyl Carbonate (1) + 1,1,1-Trichloroethane (2)					
$T = 298.15$ K					
0.0470	53.0	0.3719	270.2	0.8257	143.5
0.0898	95.5	0.4412	284.8	0.8766	103.3
0.1298	131.6	0.5422	285.8	0.9046	80.1
0.1648	163.7	0.6399	254.8	0.9343	53.3
0.2284	209.1	0.7031	229.4	0.9660	24.4
0.2830	238.1	0.7804	178.1		
$T = 313.15$ K					
0.0470	58.2	0.3720	295.3	0.8257	162.6
0.0898	106.5	0.4412	314.0	0.8767	114.8
0.1290	143.2	0.5422	314.5	0.9046	91.6
0.1649	178.7	0.6400	283.3	0.9343	63.0
0.2285	226.7	0.7032	253.4	0.9660	29.2
0.2831	257.9	0.7804	202.9		

be precise to  $1 \times 10^{-4}$ . Excess molar enthalpies,  $H_m^E$ , are estimated to be accurate to 1% at the equimolar composition.

Two replicate measurements were made over the entire composition range at each temperature for the two systems. The agreement between replicate runs was found to be better than 99%.

The mixtures measured in the present paper have viscosities typical of easy-to-mix systems, and hence no correction is needed to account for fluid frictional effects (18, 19).

## Results

Experimental values of  $T$ ,  $P$ ,  $x_1$ ,  $y_1$ , and activity coefficients  $\gamma_1$  and  $\gamma_2$  are reported in Table 3. The activity coefficients were evaluated from

$$\gamma_i = P y_i / P_i x_i \quad (2)$$

where  $P_i$  is the corrected vapor pressure (20) obtained from virial coefficients calculated with the Wohl formula (21) following the procedure described in ref 22.

In order to check the thermodynamic consistency of the isothermal VLE measurements, the area test  $I$  was applied:

$$I = \int_0^1 \left( \ln(\gamma_1/\gamma_2) + \frac{V_m^E}{RT} \frac{dP}{dx_1} \right) dx_1 \quad (3)$$

This integral should be zero, and thus only a comparison of  $I$  with the uncertainty  $\delta I$  may decide the consistency of the data.

A possible consistency criterion is given by compliance of data with the relationship

$$I \leq \delta I \quad (4)$$

Values of  $\delta I$  are evaluated in the present paper following the same procedure outlined in ref 23. The  $(V_m^E/RT)(dP/dx_1)$

Table 6. Least-Squares Parameters  $a_k$  and Standard Deviations  $\sigma$  of the Polynomial Equations for Binary Mixtures

mixture	function	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$\sigma$
$T = 298.15 \text{ K}$							
dimethyl carbonate + 1,2-dichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	-0.123	0.029	0.021	0.034	-0.045	0.014
	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	1.313	-0.209	0.041			0.001
	$H_m^E/(\text{J}\cdot\text{mol}^{-1})$	-761.1	-86.15	204.0			1.2
dimethyl carbonate + 1,1,1-trichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	0.441	0.026	0.082	-0.124	-0.017	0.025
	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	0.677	-0.170				0.001
	$H_m^E/(\text{J}\cdot\text{mol}^{-1})$	1156	-63.49	-168.3	-169.1		2.1
$T = 313.15 \text{ K}$							
dimethyl carbonate + 1,2-dichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	-0.008	0.039	0.073	-0.047	-0.06 $\rho$	0.023
	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	1.294	-0.184				0.001
	$H_m^E/(\text{J}\cdot\text{mol}^{-1})$	-820.3	45.46	247.4			1.7
dimethyl carbonate + 1,1,1-trichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	0.448	0.011	-0.019	-0.090	0.028	0.034
	$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$	0.744	-0.172				0.001
	$H_m^E/(\text{J}\cdot\text{mol}^{-1})$	1269	-31.44	-151.5	-197.5		2.0
$T = 333.15 \text{ K}$							
dimethyl carbonate + 1,2-dichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	-0.068	0.016	0.078	0.077	0.016	0.019
dimethyl carbonate + 1,1,1-trichloroethane	$G_m^E/(\text{J}\cdot\text{mol}^{-1})$	0.469	-0.013	-0.004	-0.003	0.197	0.014

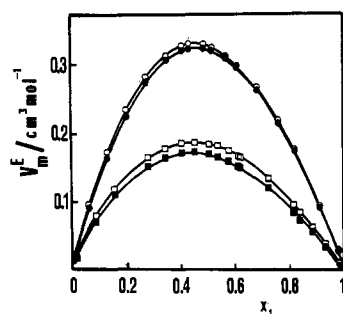


Figure 2. Excess molar volumes,  $V_m^E$ , of binary mixtures containing dimethyl carbonate + two chlorohydrocarbons as a function of the mole fraction  $x_1$  of dimethyl carbonate: (●, ○) experimental points for dimethyl carbonate + 1,2-dichloroethane at 298.15 and 313.15 K; (■, □) experimental points for dimethyl carbonate + 1,1,1-trichloroethane at 298.15 and 313.15 K; (—) calculated curves.

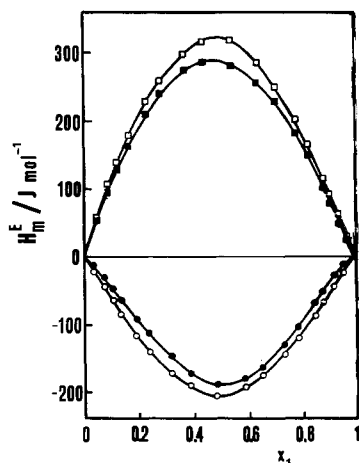


Figure 3. Excess molar enthalpies,  $H_m^E$ , of binary mixtures containing dimethyl carbonate + two chloro compounds. The symbols are the same as those in Figure 2.

term in  $I$  was calculated, but its contribution is negligible. All mixtures verify the criterion of eq 4.

The excess molar Gibbs energy  $G_m^E$  was then calculated from

$$G_m^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \quad (4)$$

and is shown in Figure 1. Tables 4 and 5 report experimental values for  $V_m^E$  and  $H_m^E$  data. Table 6 gives the parameters and the standard deviations of the expressions correlating VLE,  $V_m^E$ , and  $H_m^E$  data through a least-squares method.

The objective function to be minimized was

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

where  $N$  is the number of experimental points. The residual  $\eta$  for the VLE data was

$$\eta = \ln(\gamma_1/\gamma_2)^{\text{exptl}} - \ln(\gamma_1/\gamma_2)^{\text{calcd}} \quad (6)$$

with  $\ln \gamma_i^{\text{calcd}}$  calculated from the five-parameter Redlich-Kister expression (24) and  $\ln \gamma_i^{\text{exptl}}$  evaluated by means of eq 2. The residual  $\eta$  for  $V_m^E$  and  $H_m^E$  data was obtained as the difference between the two sides of the following Redlich-Kister equation:

$$Z_m^E/x_1x_2 = \sum_{k \geq 0} a_k(x_1 - x_2)^k \quad (7)$$

where  $Z_m^E$  is either  $V_m^E/(\text{cm}^3\cdot\text{mol}^{-1})$  or  $H_m^E/(\text{J}\cdot\text{mol}^{-1})$ . The solid curves of Figures 2 and 3 were calculated from eq 7 with the parameters of Table 6.

## Conclusions

Dimethyl carbonate + 1,2-dichloroethane shows activity coefficients only slightly smaller than unity (low negative deviations from the Raoult law), while dimethyl carbonate + 1,1,1-trichloroethane shows large positive deviations (see Table 3 and Figure 1) where a sign inversion of  $G_m^E$  as a function of mole fraction is observed at the highest temperature for dimethyl carbonate + 1,2-dichloroethane. A sign change is also observed for  $H_m^E$  which is positive for 1,2-dichloroethane + dimethyl carbonate and negative for 1,1,1-trichloroethane + dimethyl carbonate. The excess volume  $V_m^E$  is positive for all mixtures.

The influence of temperature on excess functions is interesting:  $G_m^E$  and  $V_m^E$  show a positive temperature dependence whereas  $H_m^E$  shows a positive dependence for dimethyl carbonate + 1,1,1-trichloroethane and a negative temperature dependence for dimethyl carbonate + 1,2-dichloroethane.

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