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Densities and Excess Molar Properties of Dimethyl Carbonate with Alkanes (C_6 to C_{10}) and VLE of Dimethyl Carbonate with Alkanes (C_9 to C_{10}) at 101.3 kPa

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This paper presents densities and excess molar enthalpies of the binary mixtures dimethyl carbonate with alkanes from C_6 to C_{10} at several temperatures, and isobaric vapor−liquid equilibrium (VLE) data at 101.3 kPa for dimethyl carbonate with nonane and decane are shown too. Correlations of the activity coefficients and reduced excess Gibbs energy using Wilson, NRTL, and UNIQUAC equations were good for all the binary mixtures. The ASOG and UNIFAC methods were used to predict the VLE binary mixtures. The best predictive results were yielded by ASOG for the binary dimethyl carbonate with nonane and by UNIFAC for dimethyl carbonate with decane.

1. Introduction

This work aims to better define the thermodynamic properties of mixtures of dialkyl carbonates with other components. There is a high interest in the dimethyl carbonate application[1] to storage batteries, based on intercalation of solutions of carbonates with lithium and bromine in graphite. Such batteries can be recharged thermally at relatively low temperatures. In this paper, we have continued our earlier work on the determination of thermodynamic properties of dialkyl carbonate with alkane binary mixtures[2,3] and the application of the calculated interaction parameters[2] to predict VLE data.

Densities of dimethyl carbonate with hexane, heptane, octane, nonane, and decane have been measured from (293.15 to 318.15) K, except for the binary dimethyl carbonate with decane that was measured from (298.15 to 318.15) K, due to this binary presenting immiscibility at 293.15 K. The results were used to calculate excess molar volumes over the entire mole fraction range for the mixtures. Excess molar enthalpies were determined at 318.15 K for the above binary mixtures. Excess values were correlated by Redlich−Kister polynomials.[4] The root-mean-square deviations between experimental and calculated values are shown.

The experimental VLE results have been compared with those correlated through the Wilson,[5] NRTL,[6] and UNIQUAC[7] equations. The interaction parameters of the functional group (−OCOO−) with (CH_3−) in the ASOG[8] and UNIFAC[9] methods have been determined previously[2] using the VLE data of the binary mixtures dialkyl carbonate with alkanes from C_6 to C_8. These interaction parameters in ASOG and UNIFAC group contribution methods have been employed to predict the experimental VLE binary data.

Table 1. Comparison of Boiling Point T_{bp} and Density ρ with Literature Data for Pure Components at 298.15 K

	T_{bp}/K		ρ/kg·m^{-3}	
component	expt	lit.	expt	lit.
dimethyl carbonate	363.46	363.50[a]	1063.5	1063.50[b]
hexane	341.93	341.98[c]	654.8	654.93[c] 654.84[d]
heptane	371.18	371.50[e]	679.4	679.40[e]
octane	398.65	398.80[f]	698.5	698.60[g]
nonane	423.66	423.97[g]	713.9	714.10[g] 713.75[c]
decane	446.90	447.30[g]	726.2	726.40[g] 726.35[c]

[a] Daubert and Danner.[10] [b] García de la Fuente et al.[11] [c] Dominguez et al.[12] [d] Riddick et al.[13] [e] Blanco et al.[14] [f] Hiaki et al.[15] [g] Aminabhavi et al.[16]

Comparison between experimental and literature data has been made for the density at 298.15 K for the binary mixtures DMC with heptane, octane, and decane. The rest of the experimental values are new.

2. Experimental Section

Chemicals. DMC, hexane, heptane, octane, nonane, and decane were supplied by Fluka. Their mass fraction purities were >99.0 mass % for the pure components. Before use, the components were degassed ultrasonically and dried over molecular sieves (supplied by Aldrich) Type 3 Å to remove any traces of moisture. Finally the purities specified by the manufacturer were checked with an HP6890 GC, and the obtained values complied with purchaser specifications. Some physical properties of the pure components used were determined experimentally as a test of component quality. The experimental boiling temperature and density at 298.15 K were compared with recently published values in Table 1.

Apparatus and Procedure. The experimental system used to measure the isobaric VLE data was a small-

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Table 2. Densities ρ and Excess Molar Volumes V^E for Dimethyl Carbonate (1) + Hexane (2) at Several Temperatures

T = 293.15 K			T = 298.15 K			T = 303.15 K			T = 313.15 K			T = 318.15 K		
	ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E
x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}
0	659.3	0	0	654.8	0	0	650.4	0	0	641.1	0	0	636.4	0
0.0722	677.3	301	0.0820	674.9	401	0.0468	661.4	283	0.0495	652.7	289	0.0773	654.9	389
0.1448	696.6	549	0.1269	686.7	560	0.0991	674.5	520	0.1000	665.2	525	0.1163	664.6	583
0.2286	720.8	720	0.2131	710.9	780	0.1951	700.4	844	0.2092	694.5	901	0.1621	676.6	757
0.3026	744.0	785	0.3197	744.1	878	0.2950	730.4	998	0.3093	724.6	1048	0.2689	706.8	1040
0.4102	780.8	794	0.3787	764.0	887	0.3832	759.5	1037	0.4043	756.1	1083	0.3288	725.3	1125
0.5062	817.0	738	0.4712	797.6	845	0.4865	797.1	977	0.4941	788.8	1033	0.4097	752.4	1138
0.6026	857.1	614	0.5121	813.4	817	0.5899	838.7	862	0.6052	833.6	893	0.4753	776.0	1097
0.7052	904.0	471	0.6067	852.6	703	0.6960	886.3	675	0.7063	879.2	696	0.5256	795.2	1043
0.7974	950.5	327	0.6987	894.5	555	0.7947	935.5	474	0.8046	928.6	456	0.5452	803.1	1001
0.9010	1008.3	163	0.8420	967.9	318	0.8939	990.5	251	0.9014	982.5	218	0.5879	820.6	931
0.9506	1038.5	70	0.9248	1015.9	152	0.9436	1020.3	145	0.9497	1011.6	102	0.6449	845.2	823
1	1070.0	0	0.9615	1038.7	72	1	1056.5	0	1	1043.4	0	0.6976	869.3	716
			1	1063.5	0							0.7615	900.4	554
												0.8039	922.2	462
												0.8422	942.9	345
												0.8808	964.3	269
												0.9311	993.8	149
												0.9657	1015.1	69
												1	1036.9	0

Table 3. Densities ρ and Excess Molar Volumes V^E for Dimethyl Carbonate (1) + Heptane (2) at Several Temperatures

T = 293.15 K			T = 298.15 K			T = 303.15 K			T = 313.15 K			T = 318.15 K		
	ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E
x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}
0	683.6	0	0	679.4	0	0	675.3	0	0	666.6	0	0	661.5	0
0.0500	694.0	194	0.0594	691.6	258	0.0586	687.2	266	0.0649	679.3	375	0.0693	675.1	380
0.0940	703.5	366	0.1204	704.9	495	0.0873	693.2	404	0.1157	690.1	587	0.1044	682.5	532
0.2039	729.2	725	0.2132	726.7	816	0.1996	718.7	827	0.3432	746.6	1200	0.1947	702.6	909
0.3240	761.2	964	0.3135	753.1	036	0.2990	744.2	1068	0.4378	775.1	1253	0.2734	722.0	1133
0.4062	785.9	1032	0.4018	779.0	1149	0.4009	773.6	1204	0.5458	812.0	1202	0.3512	743.2	1253
0.5059	819.4	1022	0.4716	801.6	1170	0.5081	808.9	1205	0.6259	842.9	1091	0.4190	763.3	1300
0.6099	859.2	911	0.6051	851.0	1054	0.6069	846.2	1080	0.7191	883.2	905	0.4889	785.9	1300
0.6987	897.8	745	0.6946	889.3	893	0.6979	885.2	886	0.8128	929.3	661	0.5518	808.1	1249
0.8086	952.7	457	0.8031	943.0	574	0.8051	938.0	573	0.8798	966.5	437	0.6100	830.3	1167
0.9029	1006.6	220	0.9020	999.5	263	0.9069	995.8	267	0.9536	1012.0	174	0.6632	852.0	1099
0.9504	1036.6	102	0.9477	1028.2	139	0.9638	1031.6	94	0.9822	1031.1	66	0.7142	874.6	968
1	1070.0	0	1	1063.5	0	1	1056.5	0	1	1043.4	0	0.7620	897.1	842
												0.8077	920.1	711
												0.8514	943.8	566
												0.8883	965.0	429
												0.9289	989.7	277
												0.9640	1012.4	135
												1	1036.9	0

Table 4. Densities ρ and Excess Molar Volumes V^E for Dimethyl Carbonate (1) + Octane (2) at Several Temperatures

T = 293.15 K			T = 298.15 K			T = 303.15 K			T = 313.15 K			T = 318.15 K		
	ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E		ρ	10^9V^E
x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}
0	702.5	0	0	698.5	0	0	694.5	0	0	686.3	0	0	682.1	0
0.0513	711.1	314	0.0558	707.8	346	0.0519	702.9	362	0.0512	694.5	357	0.0823	695.4	561
0.0997	719.8	565	0.0960	715.0	552	0.0827	708.3	527	0.1005	703.0	643	0.1827	714.2	1018
0.2027	740.5	940	0.1488	725.1	775	0.1947	729.9	1004	0.1860	719.2	1039	0.2965	738.7	1366
0.3063	764.5	1156	0.2289	741.8	1047	0.2829	749.4	1244	0.3010	744.5	1340	0.3626	754.9	1473
0.3994	789.1	1251	0.2947	756.9	1212	0.3948	778.1	1349	0.4072	771.6	1476	0.4360	774.6	1543
0.5123	823.6	1243	0.4216	790.4	1341	0.4942	807.5	1351	0.5002	799.1	1461	0.5156	798.6	1530
0.6078	857.4	1166	0.4883	810.6	1331	0.5964	842.4	1269	0.6042	834.5	1360	0.5606	813.4	1510
0.7137	901.2	990	0.4968	813.3	1329	0.6983	883.1	1093	0.7090	876.3	1169	0.6305	838.7	1392
0.8055	945.8	769	0.5931	846.6	1230	0.7886	925.2	872	0.7993	918.8	906	0.6756	856.4	1305
0.9061	1004.0	429	0.6867	884.1	1047	0.8946	984.3	491	0.8465	944.0	720	0.7428	885.6	1129
0.9516	1034.3	240	0.7879	931.6	770	0.9545	1023.4	227	0.9524	1009.1	259	0.7845	905.6	975
1	1070.0	0	0.8873	987.1	428	1	1056.5	0	1	1043.4	0	0.8233	925.5	832
			0.9502	1027.7	195							0.8711	951.7	657
			1	1063.5	0							0.9071	973.5	471
												0.9640	1010.8	197
												0.9761	1019.5	117
												1	1036.9	0

Table 5. Densities ρ and Excess Molar Volumes V^E for Dimethyl Carbonate (1) + Nonane (2) at Several Temperatures

$T = 293.15$ K			$T = 298.15$ K			$T = 303.15$ K			$T = 313.15$ K			$T = 318.15$ K		
x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$
0	717.7	0	0	713.9	0	0	710.1	0	0	702.2	0	0	698.1	0
0.0444	724.2	257	0.0247	717.5	127	0.0444	716.3	305	0.0444	708.3	321	0.0409	703.8	236
0.0909	731.4	508	0.0830	726.1	484	0.0909	723.3	572	0.0909	715.1	604	0.0763	709.0	442
0.1838	747.3	912	0.1221	732.4	680	0.1838	738.9	999	0.1838	730.4	1044	0.1089	714.0	616
0.2800	766.3	1172	0.1812	742.6	931	0.2800	757.5	1279	0.2800	748.7	1343	0.1249	716.6	703
0.3783	789.0	1298	0.2278	751.4	1081	0.3783	779.7	1423	0.3783	770.5	1510	0.1452	719.9	790
0.4778	815.8	1312	0.3170	770.0	1277	0.4778	805.9	1452	0.4778	796.0	1573	0.1957	728.5	1016
0.5789	847.5	1265	0.3986	789.4	1381	0.5789	837.0	1407	0.5789	826.7	1516	0.2309	735.0	1144
0.6816	885.9	1107	0.4701	808.5	1412	0.6816	874.8	1247	0.6816	864.0	1316	0.3153	751.7	1413
0.7851	932.5	881	0.5281	825.7	1385	0.7851	920.7	992	0.7851	909.4	1039	0.3894	768.3	1576
0.8921	991.9	563	0.6010	849.8	1322	0.8921	979.7	605	0.8921	967.3	647	0.4732	789.6	1652
0.9461	1028.3	309	0.6553	869.8	1249	0.9461	1015.6	329	0.9461	1002.8	350	0.5442	810.1	1649
1	1070.0	0	0.7064	890.4	1163	1	1056.6	0	1	1043.4	0	0.6088	831.2	1569
			0.7517	910.5	1056							0.6356	840.8	1511
			0.7982	933.0	927							0.7110	870.1	1347
			0.8404	955.5	787							0.7610	891.8	1222
			0.8725	973.9	673							0.7870	904.0	1136
			0.9073	995.7	507							0.8304	926.0	962
			0.9371	1015.5	374							0.8802	954.1	729
			0.9711	1040.4	179							0.9335	987.7	456
			1	1063.5	0							0.9414	993.1	410
												0.9720	1015.0	216
												1	1036.9	0

Table 6. Densities ρ and Excess Molar Volumes V^E for Dimethyl Carbonate (1) + Decane (2) at Several Temperatures

$T = 298.15$ K			$T = 303.15$ K			$T = 313.15$ K			$T = 318.15$ K		
x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$	x_1	ρ kg·m^{-3}	10^9V^E $\text{m}^3\text{·mol}^{-1}$
0	726.2	0	0	722.3	0	0	714.7	0	0	710.9	0
0.0043	726.8	28	0.0489	728.4	331	0.0489	720.6	349	0.0902	722.1	601
0.0235	729.1	169	0.0996	735.2	622	0.0996	727.2	655	0.1142	725.4	735
0.0888	737.6	556	0.1998	750.3	1084	0.1998	742.0	1144	0.1922	736.9	1100
0.1363	744.6	764	0.2990	768.1	1356	0.2990	759.4	1445	0.3283	760.8	1527
0.1922	753.4	999	0.3991	789.2	1493	0.3991	780.1	1599	0.4184	780.0	1666
0.2402	761.6	1139	0.4992	814.3	1525	0.4992	804.7	1636	0.4855	796.3	1709
0.3348	779.8	1360	0.6023	845.3	1433	0.6023	835.2	1541	0.4962	799.1	1708
0.4201	798.8	1460	0.7013	881.5	1258	0.7013	870.6	1361	0.5666	818.8	1677
0.4876	816.0	1475	0.8008	925.9	1009	0.8008	914.4	1089	0.6142	833.9	1606
0.5607	837.1	1430	0.9012	982.6	626	0.9012	970.3	669	0.6732	854.3	1525
0.6214	856.8	1381	0.9505	1016.6	366	0.9505	1003.6	407	0.7280	875.8	1379
0.6754	876.5	1298	1	1056.6	0	1	1043.4	0	0.7735	895.6	1250
0.7219	895.2	1196							0.8087	912.6	1102
0.7702	916.6	1089							0.8503	934.4	933
0.8104	936.3	979							0.8944	960.1	724
0.8421	953.4	860							0.9252	980.0	553
0.8849	978.5	678							0.9473	995.6	396
0.9135	997.0	541							0.9768	1017.9	183
0.9424	1017.3	382							1	1036.9	0
0.9709	1039.0	206									
1	1063.5	0									

capacity equilibrium still in which the two phases were refluxed, and concentrations were obtained by means of density measurements in an Anton-Paar model DMA-48 densimeter with an uncertainty of ±0.1 kg·m^{-3}, A diagram of the ebulliometer was presented in ref 17. The temperature was measured using a Comarks Electronic model 6800 digital thermometer equipped with PT100 sensors, which were periodically calibrated according to the ITS-90 standard using a ASL-F25 thermometer/calibrator. The uncertainty of the measurement was ±10 mK. Pressure was measured and regulated using a new model PPC2 system from Desgranges et Huot, with an uncertainty better than ±0.02 kPa.

Once equilibrium between the phases, which was observed in practice by a constant pressure and temperature, had been attained, the density of the vapor and liquid phases of the mixtures was measured. The concentrations of the liquid and vapor phases at equilibrium were determined on the basis of density−composition curves obtained previously for each of the binary mixtures. The root-mean-square deviation in the mole fraction of the mixtures at equilibrium was ±0.002.

Excess enthalpies were determined at 318.15 K in a Calvet calorimeter model MS80D, which was periodically calibrated electrically. As verified by measurements using standard mixtures of cyclohexane + hexane and benzene + heptadecane, the uncertainty in the experimental results was estimated to be less than 0.01 of the experimental values.

3. Results and Discussion

Excess Properties. Tables 2−6 present the densities ρ and the excess molar volumes V^E for the binary mixtures of dimethyl carbonate with hexane, heptane, octane, nonane,

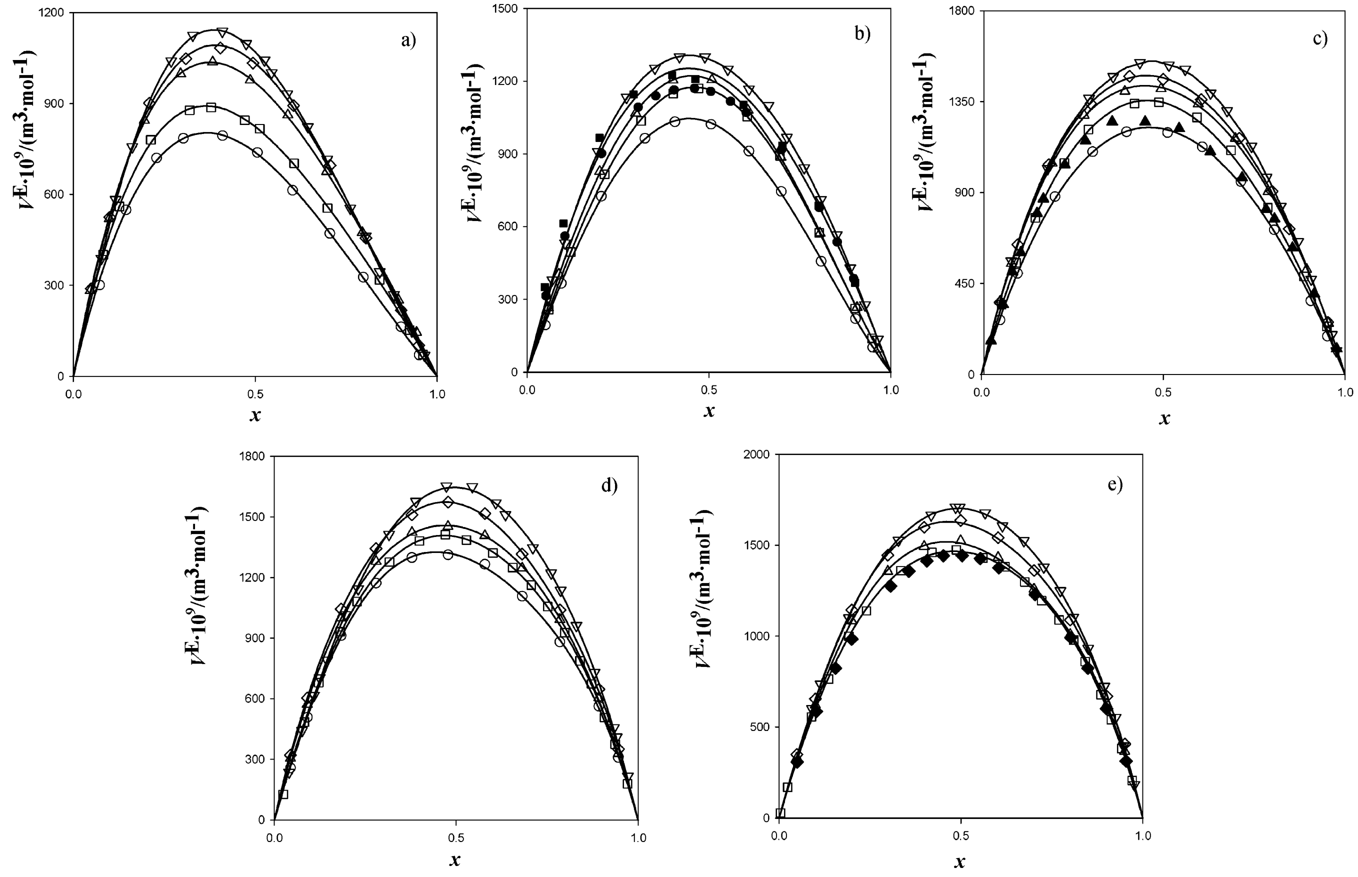

Figure 1. Experimental curves of excess molar volumes, V^E, for (x_1)dimethyl carbonate + $(1 - x_1)$alkanes, obtained from eq 1, and comparison made with the literature data for the binary mixtures of dimethyl carbonate with (○) hexane, (□) heptane, (●) heptane,[11] (■) heptane,[19] (△) octane, (▲) octane,[20] (◇) nonane, (▽) decane, and (◆) decane[11] at (a) 293.15 K, (b) 298.15 K, (c) 303.15 K, (d) 313.15 K, and (e) 318.15 K.

Table 7. Excess Molar Enthalpies H^E for Binary Systems at 318.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Dimethyl Carbonate (1) + Hexane (2)											
0	0	0.5162	2071	0.8660	1096	0.3259	1808	0.7263	1763	1	0
0.0880	716	0.5554	2060	0.9005	852	0.4027	1973	0.7728	1594		
0.1762	1223	0.6261	1994	0.9393	545	0.4703	2049	0.8189	1351		
0.2418	1544	0.6776	1904	0.9822	197						
Dimethyl Carbonate (1) + Heptane (2)											
0	0	0.5205	2143	0.7582	1696	0.3677	1984	0.6326	2061	0.9290	656
0.0950	798	0.5497	2138	0.8053	1493	0.4442	2103	0.6740	1982	0.9663	328
0.1875	1326	0.5542	2133	0.8488	1250	0.5016	2144	0.7188	1853	1	0
0.2819	1726	0.5906	2114	0.8920	962						
Dimethyl Carbonate (1) + Octane (2)											
0	0	0.5544	2208	0.8562	1286	0.3463	1989	0.7224	1930	1	0
0.0844	687	0.6104	2160	0.8987	995	0.4232	2150	0.7671	1755		
0.1746	1252	0.6455	2109	0.9358	697	0.4922	2211	0.8115	1540		
0.2622	1687	0.6830	2042	0.9713	349						
Dimethyl Carbonate (1) + Nonane (2)											
0	0	0.6270	2230	0.8663	1321	0.4426	2252	0.7480	1904	1	0
0.1291	1004	0.6622	2155	0.9069	1044	0.5099	2299	0.7814	1786		
0.2483	1658	0.6743	2131	0.9415	754	0.5730	2300	0.8236	1583		
0.3498	2047	0.7043	2052	0.9752	410						
Dimethyl Carbonate (1) + Decane (2)											
0	0	0.5556	2397	0.7914	1862	0.3757	2193	0.6748	2255	0.9429	726
0.0948	796	0.5944	2376	0.8294	1646	0.4516	2347	0.7141	2167	0.9788	310
0.1964	1425	0.6291	2343	0.8725	1382	0.5089	2395	0.7558	2025	1	0
0.2900	1896	0.6358	2328	0.9085	1067						

and decane from 293.15 K to 318.15 K, except at 293.15 K for the binary DMC with decane, because the binary mixture at this temperature presents inmiscibility. Table 7 shows the excess molar enthalpies H^E for the above mixtures at 318.15 K.

The binary values were fitted to a Redlich−Kister type equation:

$$\Delta Q = x_1(1 - x_1)\sum_{p=0}^{M} B_p(x_1 - x_2)^p \qquad (1)$$

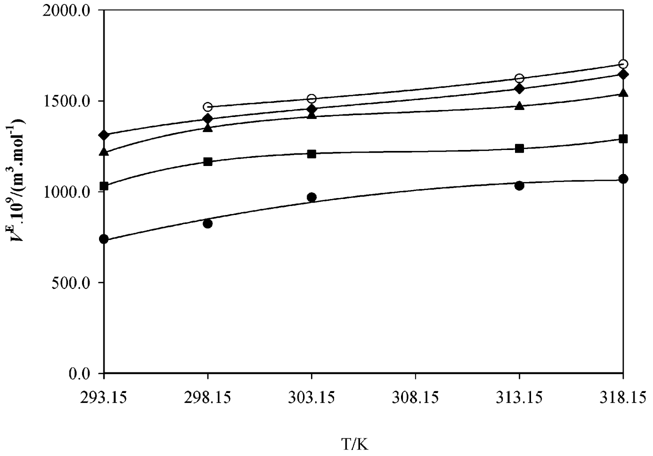

Figure 2. Variation of calculated equimolar excess volumes, for (x_1)dimethyl carbonate + $(1 - x_1)$alkanes, with the alkanes' chain length at several temperatures for the binary mixtures dimethyl carbonate with (●) hexane, (■) heptane, (▲) octane, (◆) nonane, and (○) decane.

where ΔQ is the excess of the properties, x_1 is the mole fraction, B_p is the fitting parameter, and M is the degree of the polynomic expansion. Applying the F-test,[18] the degree of the polynomial expression was optimized.

In Figure 1 excess molar volumes and their comparison with literature data[11,19,20] are shown for the binary mixtures from 293.15 K to 318.15 K, except at 293.15 K for dimethyl carbonate with decane, versus the mole fraction over the whole composition range. Excess molar volumes are positive in the entire composition range. Figure 2 shows the variation of equimolar excess molar volumes of dimethyl carbonate with alkane chain length at several temperatures. In this case, the excess molar volumes increase when chain length increases, at the studied temperatures, giving positive coefficients: $(\partial V^E/\partial T)_{P,x} > 0$.

Figure 3 shows the excess molar enthalpies as a function of carbonate concentration and the variation of the excess molar enthalpies with the length of alkanes. In the internal figure we can observe how the excess quantities increase when the alkane chain length increases, at equimolar composition. In all cases the binary mixtures are endothermic: $(\partial H^E/\partial T)_{P,x} > 0$.

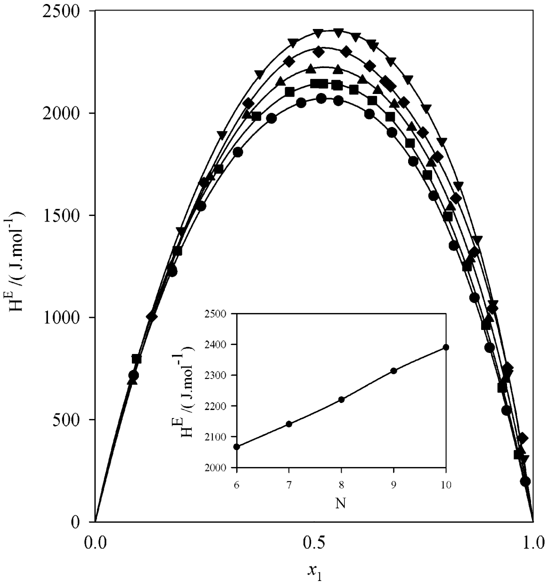

Figure 3. Experimental curves of excess molar enthalpies, H^E, for the binary mixtures at 318.15 K of dimethyl carbonate with (●) hexane, (■) heptane, (▲) octane, (◆) nonane, and (▼) decane. Internal figure: variation of equimolar excess volumes with the alkanes' chain length.

Table 8 presents the correlation parameters and the root-mean-square deviations obtained for each of the mixtures by applying eq 1. This deviation is calculated by applying the following expression:

$$\sigma = \left(\sum_i^{n_{DAT}} (z_{exp} - z_{calc})^2/(n_{DAT} - n_p)\right)^{1/2} \tag{2}$$

where experimental and calculated property values, the number of experimental data, and the number of fitting parameters are represented by z_{exp}, z_{calc}, n_{DAT}, and n_p, respectively.

Vapor Pressures. Experimental vapor pressure values for the pure components have already been published.[2,21,22] Table 9 presents the Antoine parameters for dimethyl carbonate, nonane, and decane over the admissible range

Table 8. Fitting Parameters and Root-Mean-Square Deviations σ for Binary Mixtures DMC with Alkanes To Correlate the Excess Molar Volumes V^E and Excess Molar Enthalpies H_m^E at Several Temperatures

	T/K	B_0	B_1	B_2	B_3	B_4	σ		T/K	B_0	B_1	B_2	B_3	B_4	σ
Dimethyl Carbonate (1) + Hexane (2)															
$10^9V^E/m^3\cdot mol^{-1}$	293.15	2954	−1802	348			7	$10^9V^E/m^3\cdot mol^{-1}$	313.15	4133	−2068	104			7
$10^9V^E/m^3\cdot mol^{-1}$	298.15	3294	−1868	698			5	$10^9V^E/m^3\cdot mol^{-1}$	318.15	4300	−2407	−360	669		7
$10^9V^E/m^3\cdot mol^{-1}$	303.15	3877	−2009	646			4	$H^E/J\cdot mol^{-1}$	318.15	8267.1	679.2	1569.9	−336.3	−264.0	8.8
Dimethyl Carbonate (1) + Heptane (2)															
$10^9V^E/m^3\cdot mol^{-1}$	293.15	4124	−1143	−1102			5	$10^9V^E/m^3\cdot mol^{-1}$	313.15	4952	−1105	79			6
$10^9V^E/m^3\cdot mol^{-1}$	298.15	4665	−938	−1209			8	$10^9V^E/m^3\cdot mol^{-1}$	318.15	5196	−1057	−131	164		9
$10^9V^E/m^3\cdot mol^{-1}$	303.15	4832	−1181	−1144			4	$H^E/J\cdot mol^{-1}$	318.15	8562.2	760.8	1463.9	−412.6	129.6	6.8
Dimethyl Carbonate (1) + Octane (2)															
$10^9V^E/m^3\cdot mol^{-1}$	293.15	4864	−720	245			9	$10^9V^E/m^3\cdot mol^{-1}$	313.15	5874	−954	845			6
$10^9V^E/m^3\cdot mol^{-1}$	298.15	5386	−870	332			7	$10^9V^E/m^3\cdot mol^{-1}$	318.15	6162	−671	415	−493		8
$10^9V^E/m^3\cdot mol^{-1}$	303.15	5672	−941	1086			8	$H^E/J\cdot mol^{-1}$	318.15	8881.5	729.2	1172.0	1018.7	662.1	8.3
Dimethyl Carbonate (1) + Nonane (2)															
$10^9V^E/m^3\cdot mol^{-1}$	293.15	5250	−985	1147	1186		7	$10^9V^E/m^3\cdot mol^{-1}$	313.15	6272	−720	306	513	1242	7
$10^9V^E/m^3\cdot mol^{-1}$	298.15	5601	−619	984	740		8	$10^9V^E/m^3\cdot mol^{-1}$	318.15	6584	−115	132			9
$10^9V^E/m^3\cdot mol^{-1}$	303.15	5817	−536	1239			7	$H^E/J\cdot mol^{-1}$	318.15	9254.9	832.2	−46.5	1842.5	3734.9	16.2
Dimethyl Carbonate (1) + Decane (2)															
$10^9V^E/m^3\cdot mol^{-1}$	298.15	5863	−367	1327	681		7	$10^9V^E/m^3\cdot mol^{-1}$	318.15	6808	−174	971	655		8
$10^9V^E/m^3\cdot mol^{-1}$	303.15	6045	−790	1443	1297		8	$H^E/J\cdot mol^{-1}$	318.15	9559.8	1316.0	1619.9	1512.7	863.9	8.1
$10^9V^E/m^3\cdot mol^{-1}$	313.15	6490	−743	1478	1443		8								

Table 9. Antoine Parameters

component	A	B	C
DMC[a]	9.102 96	1200.99	70.03
nonane[b]	8.791 81	1241.80	95.54
decane[c]	8.989 28	1431.54	87.52

[a] Rodriguez et al.[2] [b] Ortega et al.[21] [c] Ortega et al.[22]

Table 10. Vapor−Liquid Equilibrium Data for DMC (1) + Nonane (2) and DMC (1) + Decane (2) Binary Systems at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_2	G^E/RT
		Dimethyl Carbonate (1) + Nonane (2)			
421.70	0.0022	0.0418	4.499	1.005	0.009
421.00	0.0045	0.0593	3.112	1.007	0.012
419.40	0.0059	0.0990	4.090	1.006	0.015
415.94	0.0154	0.1908	3.241	0.999	0.017
415.00	0.0189	0.2131	3.005	1.000	0.020
410.92	0.0353	0.3315	2.718	0.965	0.001
404.23	0.0616	0.4647	2.531	0.960	0.018
401.26	0.0723	0.5129	2.550	0.963	0.033
398.58	0.0878	0.5549	2.419	0.970	0.050
393.72	0.1175	0.6331	2.318	0.960	0.062
392.67	0.1219	0.6437	2.333	0.968	0.074
386.15	0.1674	0.7224	2.248	0.981	0.120
384.17	0.1801	0.7409	2.258	0.993	0.141
380.98	0.2180	0.7753	2.126	1.006	0.169
378.95	0.2415	0.7892	2.065	1.044	0.207
377.32	0.2663	0.8051	1.998	1.056	0.225
375.49	0.2889	0.8190	1.971	1.080	0.251
373.28	0.3257	0.8333	1.894	1.136	0.294
372.21	0.3568	0.8457	1.810	1.146	0.299
370.96	0.3925	0.8559	1.727	1.186	0.318
369.93	0.4257	0.8673	1.662	1.201	0.322
368.85	0.4661	0.8774	1.586	1.243	0.331
367.92	0.5050	0.8857	1.518	1.295	0.339
367.19	0.5255	0.8924	1.503	1.308	0.341
366.92	0.5548	0.8956	1.440	1.366	0.341
366.66	0.5930	0.8964	1.359	1.498	0.346
366.34	0.6298	0.8984	1.295	1.634	0.344
365.93	0.6677	0.9048	1.245	1.733	0.329
365.46	0.6878	0.9111	1.235	1.755	0.321
365.26	0.7141	0.9164	1.204	1.816	0.303
364.92	0.7502	0.9220	1.165	1.966	0.283
364.66	0.7740	0.9264	1.143	2.071	0.268
364.44	0.8035	0.9339	1.117	2.161	0.241
364.16	0.8271	0.9398	1.102	2.259	0.221
364.06	0.8529	0.9469	1.080	2.356	0.191
363.43	0.9147	0.9667	1.048	2.613	0.125
363.05	0.9778	0.9907	1.016	2.856	0.039
		Dimethyl Carbonate (1) + Decane (2)			
440.54	0.0066	0.1436	3.508	1.006	0.015
435.15	0.0130	0.2462	3.367	1.022	0.038
427.18	0.0222	0.3910	3.649	1.031	0.058
418.22	0.0374	0.5345	3.530	1.032	0.077
406.72	0.0617	0.6822	3.495	1.024	0.100
397.71	0.0895	0.7722	3.360	1.014	0.121
391.77	0.1194	0.8210	3.100	1.010	0.143
380.74	0.1834	0.8889	2.913	1.008	0.203
374.62	0.2743	0.9180	2.384	1.058	0.279
372.62	0.3343	0.9280	2.094	1.096	0.308
369.00	0.4381	0.9422	1.803	1.206	0.364
367.55	0.5073	0.9472	1.634	1.335	0.391
366.67	0.5531	0.9497	1.543	1.453	0.407
365.93	0.6216	0.9515	1.406	1.708	0.415
365.58	0.7027	0.9549	1.262	2.051	0.377
365.06	0.7430	0.9582	1.217	2.250	0.354
364.86	0.8091	0.9627	1.129	2.722	0.290
364.58	0.8509	0.9674	1.088	3.088	0.240
363.84	0.8998	0.9774	1.064	3.287	0.175
363.29	0.9521	0.9870	1.032	4.067	0.097
363.09	0.9810	0.9940	1.015	4.762	0.045

of pressures for the glass ebulliometer used in this work. Antoine coefficients were obtained by applying the equation

$$\ln P_i^\circ(\mathrm{Pa}) = A - \frac{B}{T/\mathrm{K} - C} \tag{3}$$

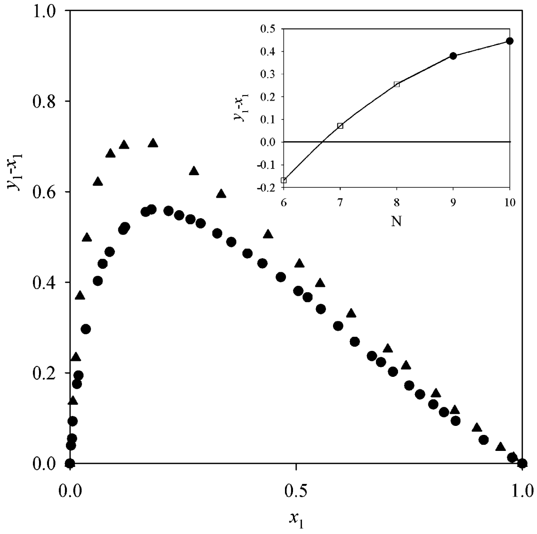

Figure 4. Curves of ($y_1 - x_1$) vs x for the binary mixtures DMC with (●) nonane and (▲) decane. Internal figure: variation ($y_1 - x_1$) with the alkanes' chain length from C_6 to C_{10} [(□) Rodriguez et al.[2] and (●) this work] at equimolar composition.

Table 11. Parameters and Root-Mean-Square Deviations between Experimental and Correlated Values for the Binary Systems at 101.3 kPa

model	parameters[a]				$\sigma(\gamma_i)$
	Dimethyl Carbonate (1) + nonane (2)				
Wilson	$\lambda_{11} - \lambda_{12}$	4754.6	$\lambda_{21} - \lambda_{22}$	−162.6	0.076
NRTL (α = 0.54)	$g_{11} - g_{12}$	2285.5	$g_{21} - g_{22}$	2384.6	0.076
UNIQUAC	$u_{11} - u_{12}$	−902.2	$u_{21} - u_{22}$	2418.2	0.076
	Dimethyl Carbonate (1) + Decane (2)				
Wilson	$\lambda_{11} - \lambda_{12}$	5207.0	$\lambda_{21} - \lambda_{22}$	845.1	0.062
NRTL (α = 0.36)	$g_{11} - g_{12}$	3249.4	$g_{21} - g_{22}$	2312.0	0.062
UNIQUAC	$u_{11} - u_{12}$	−783.3	$u_{21} - u_{22}$	2543.6	0.061

[a] $\lambda_{ij} - \lambda_{ii}$/J·mol^{-1}. $g_{ij} - g_{ii}$/J·mol^{-1}. $u_{ij} - u_{jj}$/J· mol^{-1}.

Experimental VLE Values. The temperature T, the liquid-phase and vapor-phase mole fractions x_i and y_i at equilibrium, the activity coefficients γ_i, and the excess Gibbs energy G^E/RT for the binary systems dimethyl carbonate with nonane and decane at 101.3 kPa are listed in Table 10. The γ_i values were calculated from the equation

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^L)(P - P_i^\circ)}{RT} + \frac{P}{2RT}\sum_{j=1}^{n}\sum_{k=1}^{n} y_i y_k (2\delta_{ji} - \delta_{jk}) \tag{4}$$

where δ_{ji} and δ_{jk} are defined by

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \tag{5}$$

$$\delta_{jk} = 2B_{jk} - B_{jj} - B_{kk} \tag{6}$$

where T and P are the boiling point and the total pressure, respectively, V_i^L is the molar liquid volume of component i, B_{ii} and B_{jj} are the second virial coefficients of the pure gases, P_i° is the saturation pressure, and δ_{ij} is related to the cross second virial coefficient. The molar virial coefficients B_{ii} and B_{ij} were estimated using the empirical correlations proposed by Tsonopoulos.[23] The liquid molar volumes V_i^L at the different temperatures were calculated using the modified Rackett equation by Spencer and

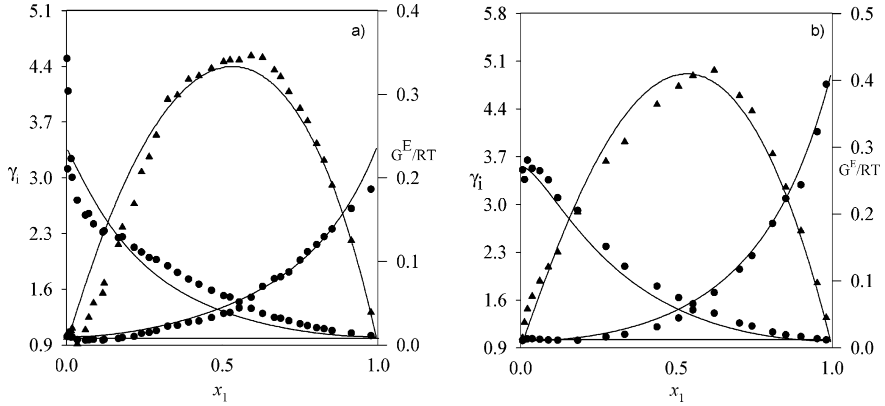

Figure 5. Experimental data and the fitting curves for the correlative model (Wilson) of G^E/RT (●) and γ_i (▲) for the binary mixtures at 101.3 kPa: (a) dimethyl carbonate (1) + nonane (2); (b) dimethyl carbonate (1) + decane (2).

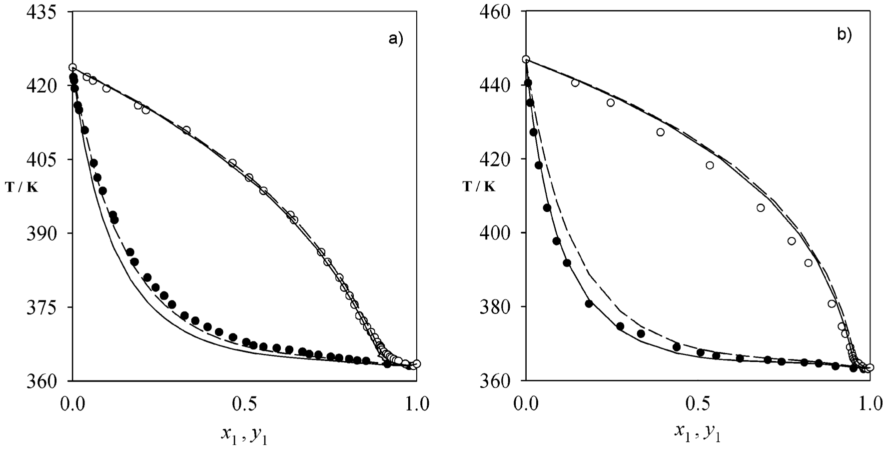

Figure 6. Experimental data of temperature T vs x, y and the corresponding fitting curves using the predictive methods (—) UNIFAC and (- - -) ASOG for the binary systems at 101.3 kPa: (a) dimethyl carbonate (1) + nonane (2); (b) dimethyl carbonate (1) + decane (2).

Danner. Critical properties of all components were taken from TRC.[24] Application of the point-to-point test of Fredeslund et al.[25] based on Van Ness et al.[26] yielded root-mean-square deviations for the set of points for each system (Δy_1) of less than 0.01 and a positive consistency according to that method.

Figure 4 shows the difference of experimental liquid and vapor mole fraction ($y_1 - x_1$) versus liquid mole fraction x for the VLE binary systems, and the inset shows the variation of ($y_1 - x_1$) at equimolar composition versus the alkane chain length for the binary VLE data for DMC with alkanes from C_6 to C_{10}. The experimental VLE data of the binary mixtures DMC with alkanes from C_6 to C_8 were determined previously.[2] In this figure we can observe how the ($y_1 - x_1$) quantities at equimolar mole fraction increase when the alkanes chain length is increased.

Correlation and Prediction. The isobaric VLE data were correlated by Wilson, NRTL, and UNIQUAC equations and were optimized by minimizing the objective function

$$\mathrm{OF} = \sum[(\gamma_1^{\mathrm{calc}} - \gamma_1^{\mathrm{exp}})/\gamma_1^{\mathrm{exp}}]^2 + [(\gamma_2^{\mathrm{calc}} - \gamma_2^{\mathrm{exp}})/\gamma_2^{\mathrm{exp}}]^2 \quad (7)$$

Table 11 gives the correlating parameters and the root-mean-square deviations for the activity coefficients and the reduced excess Gibbs energy. Inspection of the results shows that all the correlative equations obtain similar results. Figure 5 shows γ_i and G^E/RT versus x for the binary mixtures considered in this study, and it shows the correlated line corresponding to the Wilson equation. In this figure it is interesting to note the maximum of the activity coefficient at low concentrations of DMC for the binary mixture DMC + decane which produces an inflection in the curves of G^E/RT. This same behavior has been observed in a previous paper[2] for VLE data of the binary mixtures DMC with alkanes.

Table 12. Root-Mean-Square Deviations of Boiling Points $\sigma(T)$ and Vapor Phase Mole Fraction $\sigma(y)$ Resulting by the Prediction of VLE Using ASOG and UNIFAC Methods

method	$\sigma(y)$	$\sigma(T)$/K
Dimethyl Carbonate (1) + Nonane (2)		
ASOG	0.016	1.09
UNIFAC	0.036	3.14
Dimethyl Carbonate (1) + Decane (2)		
ASOG	0.036	5.40
UNIFAC	0.016	1.25

VLE predictions for the mixtures dimethyl carbonate with nonane and with decane at 101.3 kPa were carried out using the ASOG and UNIFAC methods. The volume R_k and surface area Q_k parameters were obtained from the literature.[24,27] The interaction parameters in the ASOG and UNIFAC methods were taken from the literature.[2]

Figure 6 displays the comparison of the calculated and the experimental temperature versus mole fraction of vapor and liquid phases for the binary systems, with a very good agreement achieved. Table 12 presents the root-mean-square deviation between experimental and predicted values of the boiling points and the vapor-phase mole fractions for the binary systems. According to the results summarized in the table, the root-mean-square deviations of the temperature and the composition of the vapor phase indicate that the ASOG method obtains better results for the binary mixture dimethyl carbonate with nonane. However, the UNIFAC method yielded better predictions for the binary mixture dimethyl carbonate with decane.

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