Viscosities of Dimethyl Carbonate or Diethyl Carbonate with Alkanes at Four Temperatures. New UNIFAC−VISCO Parameters

A. Rodríguez, J. Canosa, A. Domínguez, and J. Tojo*

Chemical Engineering Department, Vigo University, 36200 Vigo, Spain

Viscosities have been determined for the binary mixtures dimethyl carbonate (DMC) + hexane, + heptane, + octane, and + cyclohexane and diethyl carbonate (DEC) + hexane, + heptane, + octane, and + cyclohexane at (293.15, 298.15, 303.15, and 313.15) K and atmospheric pressure. Viscosity deviations for the binary systems were fitted to the Redlich−Kister equation. From these experimental data, the interaction parameters (CH_3−OCOO), (CH_2−OCOO), and (CH_{2cy}−OCOO) have been determined for their application in the UNIFAC−VISCO method, based on contribution groups, to predict the dynamic viscosities of the binary mixtures. Root-mean-square deviations are also gathered.

1. Introduction

Dialkyl carbonates have been studied because of the possible use of oxygenated volatile organic compounds as fuel additives. This paper continues our work[1−5] on the determination of thermodynamic and transport properties of dialkyl carbonates with alkanes. We present viscosity data for the binary systems DMC + hexane, + heptane, + octane, and + cyclohexane and DEC + hexane, + heptane, + octane, and + cyclohexane at (293.15, 298.15, 303.15, and 313.15) K.

Viscosity deviations for the binary mixtures dimethyl carbonate and diethyl carbonate with four alkanes were correlated using the Redlich−Kister[6] equation.

The predictive UNIFAC−VISCO method[7] can be used to predict viscosities using pure components data and group interaction parameters. As the interaction parameters (CH_3−OCOO), (CH_2−OCOO), and (CH_{2cy}−OCOO) had not been determined, we have used our experimental data to calculate them and incorporate them into the interaction parameter matrix.

2. Experimental Section

Chemicals. The pure components were supplied by Merck except for dimethyl carbonate and diethyl carbonate which were supplied by Fluka. They were degassed by ultrasound and dried over molecular sieves (Aldrich) Type 4 Å and kept in an inert argon atmosphere with a maximum content in water of 2×10^{-6} by mass fraction. Their mass fraction purities, specified by the manufacturer, were >99 mass % for dimethyl carbonate, >99.5 mass % for diethyl carbonate, >99.5 mass % for hexane, >99.5 mass % for heptane, >99 mass % for octane, and more than >99.5 mass % for cyclohexane. The maximum water contents of the liquids were determined using a Metrohm 737 KF coulometer. The corresponding obtained values were negligible quantities for the liquids (<0.04 mass %). The solvents were compared with recent published density and dynamic viscosity values at 298.15 K in Table 1. The densities were measured using an Anton Paar DSA-48 digital vibrating tube densimeter with an uncertainty of ± 0.0001 g·cm^{-3}.

* To whom correspondence should be addressed. E-mail: jtojo@uvigo.es.

Table 1. Comparison of Density ρ and Viscosity η with Literature Data for Pure Components at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s	
component	expt.	literature	expt.	literature
dimethyl carbonate	1.0635	1.0635[a]	0.585	0.589[b]
		1.0632[b]		
diethyl carbonate	0.9691	0.96926[c]	0.749	0.748[c]
		0.96924[d]		0.749[b]
hexane	0.6548	0.65484[c,e]	0.301	0.2968[e]
heptane	0.6794	0.67946[c,e]	0.388	0.3906[e]
octane	0.6985	0.69862[c,e]	0.513	0.5128[e]
cyclohexane	0.7738	0.77389[c]	0.894	0.898[e]

[a] García de la Fuente et al.[10] [b] Pal et al.[11] [c] Riddick et al.[12] [d] Francesconi et al.[13] [e] Das et al.[14]

Apparatus and Procedures. The mixtures were prepared by syringing known masses of the pure liquids into stoppered bottles to prevent preferential evaporation and to reduce possible errors in mole fraction calculations, using a Mettler AT-261 Delta Range balance with a precision of $\pm 10^{-5}$ g.

Viscosities were measured with an automated AMV 200 Anton Paar microviscometer. This apparatus was based on the rolling ball principle. A gold-covered steel ball rolls down the inside of inclined, sample-filled glass capillary. The apparatus is equipped with an automatic timer (±0.01 s) so the time taken for the ball to roll a fixed distance between two magnetic sensor allows one to evaluate the viscosity of the fluid mixture. The time measuring range is from (12 to 250) s, and the accuracy and the precision in this one are ±0.01 s and ±0.1 s, respectively. The capillary was placed in a block, thermostated with a PolyScience controller bath model 9010 with a temperature stability of $\pm 10^{-2}$ K. Apparatus calibration was made periodically, using three fluids of known viscosity, Millipore quality water and degassed and dried Fluka quality octane, and 1-pentanol as reference liquids. These reference fluids have mass fraction purities >99.5 mass %. The uncertainty in the viscosity and the mole fraction were estimated as better than 2×10^{-2} mPa·s and 5×10^{-5}, respectively.

3. Results and Discussion

The experimental viscosities of the binary mixtures DMC + hexane, + heptane, + octane, and + cyclohexane and

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Table 2. Viscosities (η) and Viscosity Deviations ($\Delta\eta$) of the Binary Mixtures DMC with Alkanes at Four Temperatures

x_1	η/mPa·s	$\Delta\eta$/mPa·s	x_1	η/mPa·s	$\Delta\eta$/mPa·s	x_1	η/mPa·s	$\Delta\eta$/mPa ·s	x_1	η/mPa·s	$\Delta\eta$/mPa ·s
Dimethyl Carbonate (1) + Hexane (2)											
T = 293.15 K						T = 298.15 K					
0	0.313	0	0.6026	0.412	−0.090	0	0.301	0	0.5121	0.37	−0.076
0.0722	0.312	−0.024	0.7052	0.451	−0.083	0.0820	0.306	−0.018	0.6067	0.392	−0.081
0.1448	0.315	−0.043	0.7974	0.494	−0.069	0.1269	0.311	−0.026	0.6987	0.423	−0.076
0.2286	0.325	−0.060	0.9010	0.552	−0.043	0.2131	0.322	−0.040	0.8420	0.487	−0.053
0.3026	0.338	−0.070	0.9506	0.585	−0.026	0.3197	0.336	−0.056	0.9248	0.53	−0.034
0.4102	0.359	−0.082	1	0.626	0	0.3787	0.345	−0.064	0.9615	0.555	−0.019
0.5062	0.384	−0.087				0.4712	0.362	−0.073	1	0.585	0
T = 303.15 K						T = 313.15 K					
0	0.282	0	0.5899	0.363	−0.069	0	0.258	0	0.6052	0.347	−0.054
0.0468	0.287	−0.007	0.6960	0.394	−0.065	0.0495	0.267	−0.003	0.7063	0.379	−0.046
0.0991	0.293	−0.014	0.7947	0.433	−0.051	0.1000	0.274	−0.008	0.8046	0.416	−0.032
0.1951	0.305	−0.027	0.8939	0.478	−0.031	0.2092	0.286	−0.021	0.9014	0.458	−0.013
0.2950	0.314	−0.043	0.9436	0.507	−0.015	0.3093	0.296	−0.035	0.9497	0.477	−0.005
0.3832	0.327	−0.052	1	0.536	0	0.4043	0.306	−0.047	1	0.494	0
0.4865	0.342	−0.064				0.4941	0.321	−0.054			
Dimethyl Carbonate (1) + Heptane (2)											
T = 293.15 K						T = 298.15 K					
0	0.411	0	0.6099	0.462	−0.080	0	0.388	0	0.6051	0.430	−0.077
0.0500	0.407	−0.015	0.6987	0.488	−0.073	0.0594	0.383	−0.017	0.6946	0.452	−0.073
0.0940	0.405	−0.026	0.8086	0.527	−0.058	0.1204	0.384	−0.028	0.8031	0.489	−0.057
0.2039	0.407	−0.048	0.9029	0.567	−0.038	0.2132	0.385	−0.045	0.9020	0.528	−0.038
0.3240	0.413	−0.068	0.9504	0.594	−0.021	0.3135	0.388	−0.062	0.9477	0.554	−0.021
0.4062	0.422	−0.076	1	0.626	0	0.4018	0.397	−0.070	1	0.585	0
0.5059	0.441	−0.079				0.4716	0.406	−0.075			
T = 303.15 K						T = 313.15 K					
0	0.370	0	0.6069	0.426	−0.070	0	0.334	0	0.7191	0.393	−0.056
0.0586	0.370	−0.014	0.6979	0.454	−0.061	0.0649	0.330	−0.014	0.8128	0.416	−0.048
0.0873	0.367	−0.019	0.8051	0.495	−0.051	0.1157	0.328	−0.025	0.8798	0.443	−0.032
0.1996	0.368	−0.040	0.9069	0.518	−0.026	0.3432	0.334	−0.055	0.9536	0.475	−0.012
0.2990	0.375	−0.055	0.9638	0.518	−0.012	0.4378	0.341	−0.063	0.9822	0.485	−0.006
0.4009	0.388	−0.065	1	0.536	0	0.5458	0.355	−0.066	1	0.494	0
0.5081	0.403	−0.069				0.6259	0.370	−0.064			
Dimethyl Carbonate (1) + Octane (2)											
T = 293.15 K						T = 298.15 K					
0	0.545	0	0.6078	0.512	−0.082	0	0.513	0	0.4883	0.475	−0.073
0.0513	0.532	−0.017	0.7137	0.524	−0.079	0.0558	0.504	−0.013	0.5931	0.479	−0.077
0.0997	0.524	−0.029	0.8055	0.541	−0.069	0.0960	0.498	−0.022	0.6867	0.491	−0.071
0.2027	0.508	−0.053	0.9061	0.575	−0.043	0.1488	0.489	−0.035	0.7879	0.509	−0.061
0.3063	0.506	−0.064	0.9516	0.596	−0.026	0.2289	0.478	−0.051	0.8873	0.541	−0.036
0.3994	0.502	−0.075	1	0.626	0	0.2947	0.477	−0.057	0.9502	0.561	−0.020
0.5123	0.507	−0.079				0.4216	0.474	−0.069	1	0.585	0
T = 303.15 K						T = 313.15 K					
0	0.484	0	0.5964	0.450	−0.065	0	0.434	0	0.6042	0.417	−0.053
0.0519	0.478	−0.009	0.6983	0.460	−0.060	0.0512	0.432	−0.005	0.7090	0.430	−0.047
0.0827	0.474	−0.014	0.7886	0.473	−0.052	0.1005	0.43	−0.010	0.7993	0.446	−0.036
0.1947	0.457	−0.037	0.8946	0.500	−0.031	0.1860	0.419	−0.026	0.8465	0.459	−0.026
0.2829	0.452	−0.047	0.9545	0.520	−0.014	0.3010	0.413	−0.039	0.9524	0.485	−0.006
0.3948	0.450	−0.055	1	0.536	0	0.4072	0.409	−0.049	1	0.494	0
0.4942	0.448	−0.062				0.5002	0.410	−0.054			
Dimethyl Carbonate (1) + Cyclohexane (2)											
T = 293.15 K						T = 298.15 K					
0	0.976	0	0.6002	0.600	−0.166	0	0.894	0	0.5908	0.557	−0.154
0.0495	0.886	−0.073	0.7028	0.593	−0.137	0.0378	0.833	−0.049	0.6864	0.553	−0.129
0.0987	0.814	−0.127	0.7994	0.590	−0.106	0.0808	0.776	−0.093	0.7918	0.555	−0.094
0.2078	0.709	−0.194	0.9017	0.597	−0.063	0.1764	0.681	−0.158	0.8976	0.561	−0.056
0.2961	0.660	−0.212	0.9513	0.609	−0.034	0.2896	0.619	−0.186	0.9503	0.572	−0.028
0.3974	0.626	−0.211	1	0.626	0	0.3880	0.587	−0.187	1	0.585	0
0.5014	0.608	−0.193				0.4938	0.567	−0.174			
T = 303.15 K						T = 313.15 K					
0	0.813	0	0.5958	0.508	−0.140	0	0.697	0	0.6633	0.465	−0.097
0.0391	0.758	−0.044	0.6909	0.504	−0.118	0.1010	0.605	−0.071	0.7699	0.470	−0.071
0.0931	0.703	−0.084	0.7975	0.507	−0.085	0.1482	0.574	−0.093	0.8688	0.479	−0.042
0.1875	0.632	−0.129	0.8912	0.522	−0.044	0.2563	0.524	−0.121	0.9757	0.491	−0.008
0.2908	0.581	−0.151	0.9441	0.528	−0.023	0.3646	0.495	−0.128	0.9935	0.493	−0.002
0.3897	0.545	−0.160	1	0.536	0	0.4661	0.477	−0.125	1	0.494	0
0.4962	0.522	−0.154				0.5720	0.468	−0.113			

Table 2 (Continued)

x_1	η/mPa·s	$\Delta\eta$/mPa·s	x_1	η/mPa·s	$\Delta\eta$/mPa·s	x_1	η/mPa·s	$\Delta\eta$/mPa ·s	x_1	η/mPa·s	$\Delta\eta$/mPa ·s
Diethyl Carbonate (1) + Hexane (2)											
T = 293.15 K						T = 298.15 K					
0	0.313	0	0.6357	0.524	−0.095	0	0.301	0	0.5719	0.475	−0.082
0.0576	0.318	−0.023	0.7334	0.588	−0.079	0.0586	0.318	−0.009	0.7051	0.546	−0.071
0.1106	0.326	−0.040	0.7246	0.652	−0.058	0.1024	0.323	−0.024	0.7965	0.605	−0.053
0.2219	0.353	−0.067	0.9171	0.721	−0.034	0.2106	0.347	−0.048	0.8894	0.67	−0.029
0.3358	0.388	−0.087	0.9589	0.757	−0.018	0.3050	0.370	−0.068	0.9095	0.688	−0.020
0.4303	0.422	−0.098	1	0.795	0	0.3592	0.389	−0.073	0.9794	0.737	−0.003
0.5384	0.471	−0.101				0.4259	0.412	−0.080	1	0.749	0
T = 303.15 K						T = 313.15 K					
0	0.282	0	0.6072	0.463	−0.072	0	0.258	0	0.5992	0.410	−0.067
0.0583	0.292	−0.014	0.7059	0.512	−0.064	0.0502	0.264	−0.012	0.7005	0.454	−0.060
0.0941	0.299	−0.022	0.8002	0.568	−0.048	0.1001	0.278	−0.017	0.8096	0.509	−0.044
0.1925	0.324	−0.038	0.8947	0.628	−0.027	0.2001	0.295	−0.036	0.8980	0.558	−0.028
0.2897	0.347	−0.056	0.9532	0.672	−0.007	0.3008	0.318	−0.050	0.9671	0.599	−0.012
0.3927	0.378	−0.068	1	0.699	0	0.4021	0.344	−0.061	1	0.623	0
0.5087	0.420	−0.074				0.4972	0.371	−0.068			
Diethyl Carbonate (1) + Heptane (2)											
T = 293.15 K						T = 298.15 K					
0	0.411	0	0.6010	0.549	−0.093	0	0.388	0	0.5924	0.516	−0.086
0.0490	0.410	−0.020	0.7014	0.594	−0.086	0.0509	0.390	−0.016	0.7096	0.565	−0.079
0.0983	0.413	−0.036	0.8012	0.647	−0.072	0.0977	0.394	−0.029	0.8054	0.612	−0.067
0.1973	0.427	−0.060	0.8985	0.707	−0.049	0.1973	0.410	−0.049	0.9028	0.673	−0.041
0.2970	0.449	−0.076	0.9482	0.744	−0.031	0.3052	0.430	−0.068	0.9495	0.709	−0.022
0.3989	0.477	−0.087	1	0.795	0	0.3949	0.453	−0.078	1	0.749	0
0.4952	0.508	−0.093				0.5028	0.486	−0.084			
T = 303.15 K						T = 313.15 K					
0	0.375	0	0.6133	0.501	−0.073	0	0.334	0	0.5992	0.456	−0.051
0.0506	0.386	−0.005	0.7037	0.539	−0.064	0.0493	0.337	−0.011	0.6990	0.49	−0.046
0.1001	0.389	−0.018	0.8029	0.584	−0.051	0.0986	0.344	−0.019	0.8009	0.528	−0.037
0.1991	0.399	−0.041	0.8988	0.637	−0.029	0.1975	0.362	−0.029	0.8984	0.573	−0.021
0.3010	0.416	−0.057	0.9460	0.667	−0.014	0.2962	0.381	−0.039	0.9508	0.599	−0.010
0.4058	0.438	−0.068	1	0.699	0	0.3992	0.403	−0.046	1	0.623	0
0.5006	0.464	−0.073				0.4943	0.426	−0.051			
Diethyl Carbonate (1) + Octane (2)											
T = 293.15 K						T = 298.15 K					
0	0.545	0	0.6012	0.604	−0.091	0	0.513	0	0.6050	0.578	−0.078
0.0504	0.535	−0.023	0.6971	0.641	−0.078	0.0568	0.514	−0.012	0.7054	0.614	−0.065
0.0990	0.528	−0.042	0.7996	0.684	−0.061	0.1069	0.510	−0.028	0.8042	0.653	−0.050
0.1947	0.529	−0.065	0.8871	0.727	−0.040	0.1985	0.511	−0.049	0.9035	0.698	−0.028
0.2939	0.535	−0.083	0.9502	0.763	−0.020	0.2979	0.515	−0.068	0.9549	0.728	−0.010
0.3911	0.550	−0.093	1	0.795	0	0.3968	0.528	−0.079	1	0.749	0
0.4965	0.574	−0.095				0.5035	0.551	−0.081			
T = 303.15 K						T = 313.15 K					
0	0.484	0	0.6019	0.550	−0.063	0	0.434	0	0.6036	0.508	−0.040
0.0504	0.485	−0.010	0.7055	0.580	−0.056	0.0495	0.436	−0.007	0.6992	0.529	−0.037
0.1002	0.485	−0.021	0.8011	0.613	−0.043	0.0984	0.440	−0.013	0.7994	0.554	−0.031
0.2035	0.486	−0.042	0.8999	0.654	−0.023	0.1957	0.448	−0.023	0.8992	0.586	−0.018
0.2953	0.494	−0.053	0.9498	0.677	−0.011	0.2957	0.459	−0.031	0.9502	0.608	−0.006
0.3942	0.507	−0.062	1	0.699	0	0.3958	0.472	−0.037	1	0.623	0
0.5035	0.525	−0.067				0.4982	0.488	−0.040			
Diethyl Carbonate (1) + Cyclohexane (2)											
T = 293.15 K						T = 298.15 K					
0	0.976	0	0.5984	0.718	−0.150	0	0.894	0	0.6454	0.685	−0.115
0.0501	0.906	−0.061	0.6977	0.728	−0.122	0.0531	0.832	−0.054	0.6801	0.689	−0.106
0.0992	0.850	−0.108	0.8080	0.742	−0.088	0.0940	0.792	−0.088	0.7828	0.701	−0.079
0.1969	0.780	−0.160	0.9037	0.761	−0.051	0.1931	0.725	−0.141	0.8852	0.719	−0.047
0.2923	0.741	−0.182	0.9511	0.776	−0.028	0.2865	0.691	−0.161	0.9177	0.726	−0.035
0.4023	0.720	−0.183	1	0.795	0	0.3821	0.676	−0.163	1	0.749	0
0.5020	0.712	−0.173				0.4802	0.674	−0.150			
T = 303.15 K						T = 313.15 K					
0	0.813	0	0.5943	0.635	−0.110	0	0.697	0	0.5914	0.568	−0.085
0.0497	0.760	−0.047	0.6778	0.643	−0.093	0.0511	0.659	−0.034	0.7001	0.576	−0.069
0.1018	0.717	−0.084	0.7897	0.657	−0.066	0.0983	0.632	−0.058	0.8098	0.589	−0.048
0.1958	0.665	−0.126	0.8649	0.671	−0.043	0.2003	0.594	−0.088	0.9014	0.603	−0.027
0.2930	0.637	−0.143	0.9400	0.684	−0.022	0.3002	0.572	−0.103	0.9494	0.613	−0.014
0.3922	0.628	−0.140	1	0.699	0	0.3963	0.560	−0.108	1	0.623	0
0.4767	0.626	−0.133				0.4953	0.563	−0.097			

Table 3. Fitting Parameters and Root-Mean-Square Deviations (σ) for the Binary Systems DMC with Alkanes at Four Temperatures

T/K	B_0	B_1	B_2	B_3	σ
Dimethyl Carbonate (1) + Hexane (2)					
293.15	−0.3495	−0.0790	−0.1034		0.001
298.15	−0.3012	−0.1368	−0.0558		0.001
303.15	−0.2593	−0.1163	0.0390		0.001
313.15	−0.2162	−0.0608	−0.1545		0.002
Dimethyl Carbonate (1) + Heptane (2)					
293.15	−0.3185	0.0628	−0.0640		0.001
298.15	−0.3047	−0.0807	−0.0501		0.001
303.15	−0.2772	−0.0475	−0.0137		0.001
313.15	−0.2608	−0.0475	−0.0181		0.001
Dimethyl Carbonate (1) + Octane (2)					
293.15	−0.3185	−0.0969	−0.1647		0.001
298.15	−0.2990	0.0713	−0.0467		0.001
303.15	−0.2511	−0.0739	−0.0341		0.001
313.15	−0.2183	−0.0432	0.0865		0.001
Dimethyl Carbonate (1) + Cyclohexane (2)					
293.15	−0.7657	0.4473	−0.4606		0.001
298.15	−0.6908	0.3824	−0.3365		0.001
303.15	−0.6134	0.1860	−0.1761	0.2246	0.001
313.15	−0.4886	0.2406	−0.1373		0.001
Diethyl Carbonate (1) + Hexane (2)					
293.15	−0.4008	−0.0163	−0.0128		0.001
298.15	−0.3389	−0.0286	0.1129		0.001
303.15	−0.2971	−0.0319	0.0560		0.002
313.15	−0.2673	−0.0594	0.0233		0.001
Diethyl Carbonate (1) + Heptane (2)					
293.15	−0.3676	−0.0692	−0.1518		0.002
298.15	−0.3364	−0.0831	−0.0889		0.001
303.15	−0.2929	−0.0605	0.0437		0.002
313.15	−0.2018	−0.0325	−0.0206		0.001
Diethyl Carbonate (1) + Octane (2)					
293.15	−0.3791	0.0326	−0.0657		0.001
298.15	−0.3281	−0.0030	0.0507		0.001
303.15	−0.2666	−0.0146	0.0278		0.001
313.15	−0.1613	−0.0326	−0.0096		0.001
Diethyl Carbonate (1) + Cyclohexane (2)					
293.15	−0.6819	0.3718	−0.3091		0.001
298.15	−0.5892	0.3593	−0.2451		0.001
303.15	−0.5127	0.3346	−0.2189		0.001
313.15	−0.3904	0.2086	−0.1274		0.001

DEC + hexane, + heptane, + octane, and + cyclohexane at (293.15, 298.15, 303.15, and 313.15) K and atmospheric pressure are given in Table 2. The experimental densities of these binary mixtures at the above temperatures have been published previously.[4]

The viscosity deviations are calculated from experimental viscosities of the pure components and the mixture by the equation

$$\Delta\eta/mPa{\cdot}s = \eta - \sum_{i=1}^{N}(\eta_i^0{\cdot}x_i) \qquad (1)$$

where η and η_i^0 are the viscosity of the mixture and the pure component, respectively, x_i represents the mole fraction of the pure component, and N is the number of components in the mixture.

The binary viscosity deviations were fitted to a Redlich−Kister[6] type equation

$$\Delta\eta/mPa{\cdot}s = x_i x_j \sum_{p=0}^{M} B_p(x_i - x_j)^p \qquad (2)$$

where x is the mole fraction, B_P is the fitting parameter, and M is the degree of the polynomic expansion, which was optimized using the F-test.[8] The viscosity deviations of the binary mixtures at several temperatures are given in Table 2. The fitting parameters are given in Table 3, together

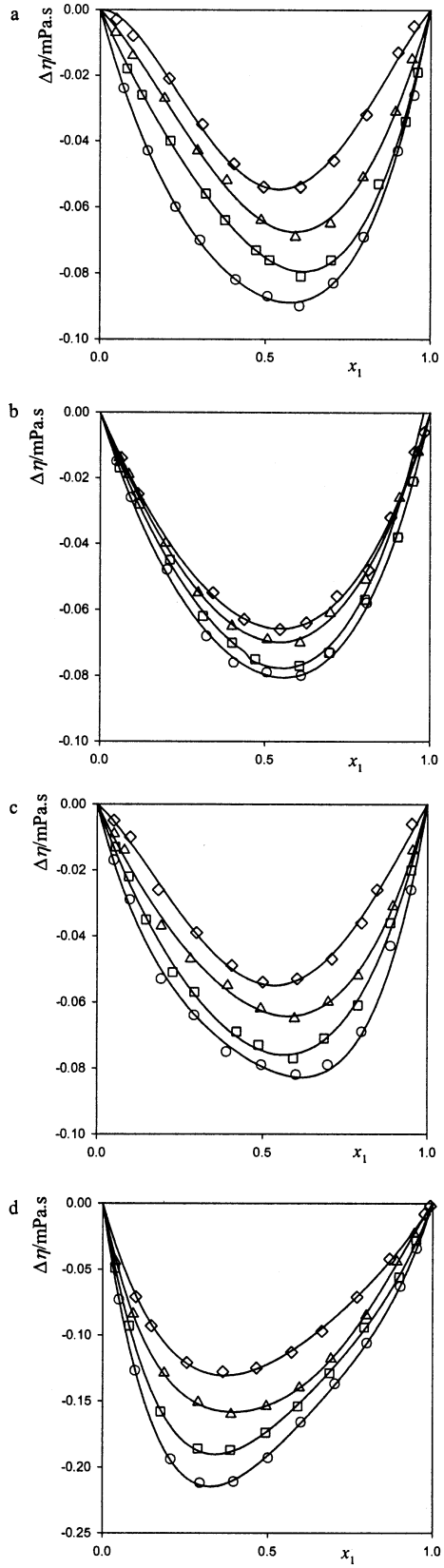

Figure 1. Curves of viscosity deviations ($\Delta\eta$) from the Redlich−Kister equation, eq 2, for the binary mixtures (a) dimethyl carbonate (1) + hexane (2), (b) dimethyl carbonate (1) + heptane (2), (c) dimethyl carbonate (1) + octane (2), and (d) dimethyl carbonate (1) + cyclohexane (2) at ○, 293.15 K; □, 298.15 K; △, 303.15 K; and ◇, 313.15 K.

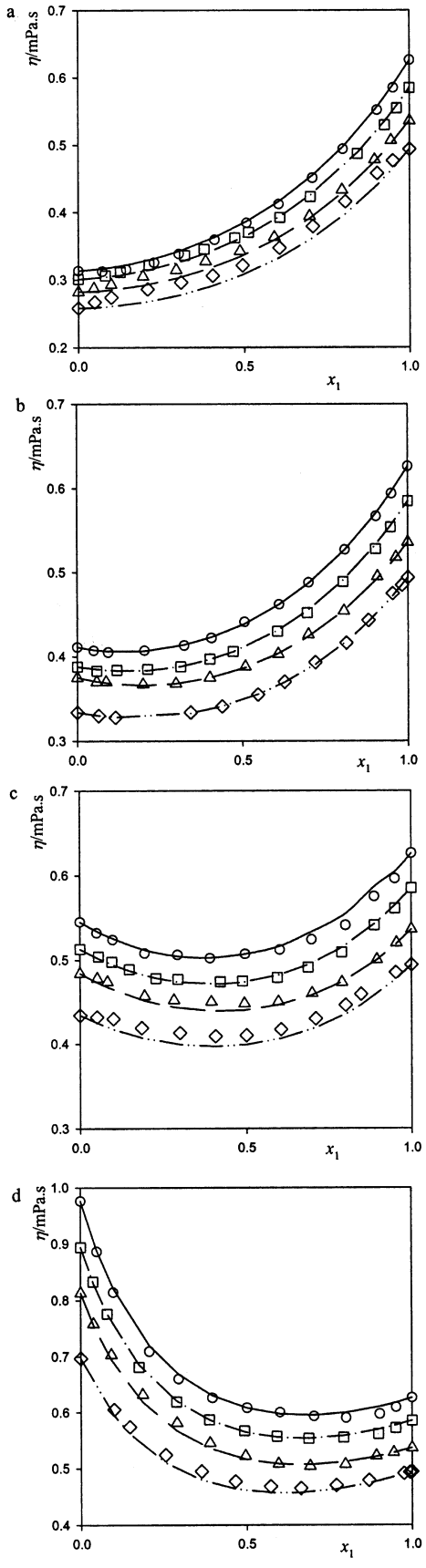

Figure 2. Curves of predictive values of viscosities (η) from UNIFAC−VISCO method, for the binary mixtures (a) dimethyl carbonate (1) + hexane (2), (b) dimethyl carbonate (1) + heptane (2), (c) dimethyl carbonate (1) + octane (2), and (d) dimethyl carbonate (1) + cyclohexane (2) at ○, —, 293.15 K; □, —•—•—, 298.15 K; △, ---, 303.15 K; and ◇, —••—••—, 313.15 K.

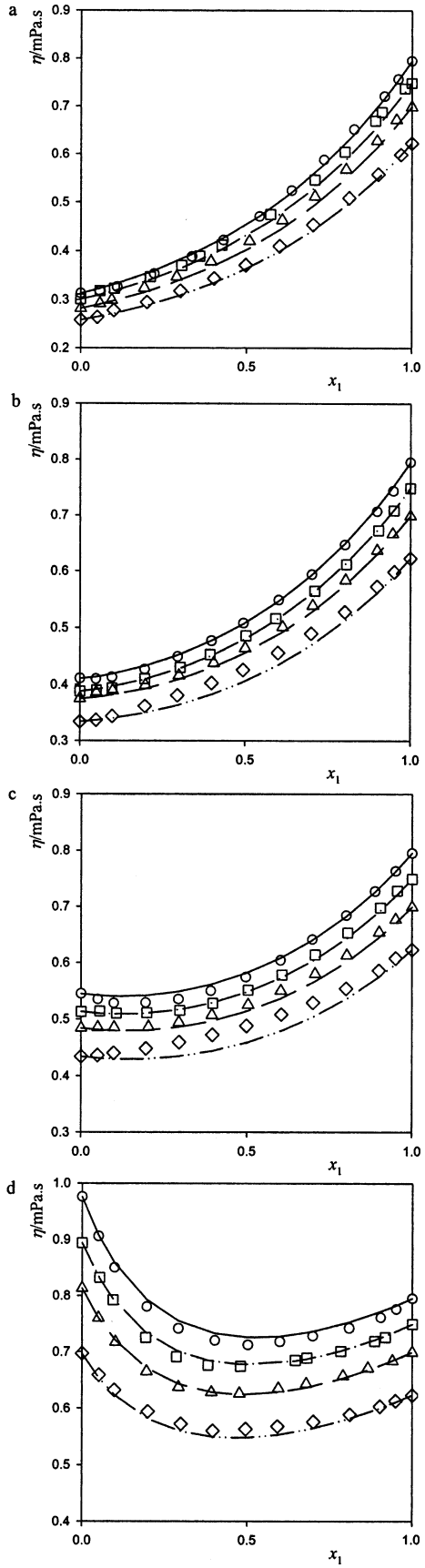

Figure 3. Curves of predictive values of viscosities (η) from UNIFAC−VISCO method, for the binary mixtures (a) diethyl carbonate (1) + hexane (2), (b) diethyl carbonate (1) + heptane (2), (c) diethyl carbonate (1) + octane (2), and (d) diethyl carbonate (1) + cyclohexane (2) at ○, —, 293.15 K; □, —•—•—, 298.15 K; △, ---, 303.15 K; and ◇, —••—••—, 313.15 K.

Table 4. UNIFAC−VISCO Interaction Parameters

α_{mn}	CH_2	CH_3	CH_{2cy}	OCOO
CH_2	0	66.53[a]	1172.0[a]	367.2
CH_3	−709.5[a]	0	−130.7[a]	328.6
CH_{2cy}	−538.1[a]	187.3[a]	0	214.6
OCOO	276.5	−334.4	−1.7	0

[a] Gaston-Bonhomme et al.[7]

with the root-mean-square deviations. These are calculated by applying the values of the property, and the number of experimental data are represented by z_{exp} and n_{DAT}, respectively:

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \quad (3)$$

Figure 1 shows viscosity deviations for the binary mixtures dimethyl carbonate with alkanes at (293.15, 298.15, 303.15, and 313.15) K, respectively, plotted against mole fraction together with the fitted curve, obtained from the Redlich−Kister equation. The viscosity deviations for these systems at these temperatures are negative over the entire composition range.

To increase the application range of the predictive UNIFAC−VISCO method, based on a group contribution sheme, we have determined the interaction parameters corresponding to carbonate (−OCOO−) with alkanes (CH_3−), (−CH_2−), and (−CH_{2cy}−). The UNIFAC−VISCO parameters have been calculated from our experimental values of viscosities using the Nelder and Mead[9] equation for minimizing the following objective function:

$$\text{O.F.} = \frac{1}{N} \sum_{i=1}^{N} \frac{|\nu_{i,exp} - \nu_{i,calc}|}{\nu_{i,exp}} \quad (4)$$

being N the number of experimental data and ν_{exp} and ν_{calc} the experimental and calculated kinematic viscosity, respectively.

The interaction parameters, obtained from our experimental data, are summarized in Table 4. Figures 2 and 3 show graphically the viscosities and the predictive values by applying the UNIFAC−VISCO method for the binary mixtures dimethyl and diethyl carbonate with hexane, heptane, octane, and cyclohexane at (293.15, 298.15, 303.15, and 313.15) K, respectively.

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