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Density, Viscosity, and Speed of Sound of Dialkyl Carbonates with Cyclopentane and Methyl Cyclohexane at Several Temperatures

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Densities, speeds of sound, and viscosities have been measured for the binary mixtures dimethyl carbonate + cyclopentane and diethyl carbonate + cyclopentane or methylcyclohexane at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K and atmospheric pressure. Excess molar volumes, viscosity deviations, and deviations in isentropic compressibility for the above systems have been derived. Derived quantities have been fit to a polynomial equation as a function of mole fraction and temperature. The obtained fitting parameters are listed. Correlated equations have been proposed, and the results in terms of root-mean-square deviations are shown. The UNIFAC−VISCO group contribution method has been used to predict the dynamic viscosities at the above temperatures for the binary mixtures.

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1. Introduction

This work is a continuation of the thermodynamic and transport properties studies of the dialkyl carbonates with alkanes and alcohols[1−4] with the aim to calculate the interaction parameters of the carbonate group with the rest of groups in terms of predictive dynamic viscosity and VLE data. In this case, no data corresponding to these interesting mixtures are available in the literature, although they are widely applied in different industrial processes; for example, dimethyl carbonate[5] is considered an option for increasing the oxygenation specifications of gasoline and as a means of converting natural gas to liquid transportation.

In this paper, densities, viscosities, and speeds of sound of the binary mixtures dimethyl carbonate with cyclopentane and diethyl carbonate with cyclopentane and methylcyclohexane from T = (293.15 to 313.15) K and atmospheric pressure have been measured experimentally. The derived quantities were calculated and fit to a polynomial equation[6] as a function of mole fraction and temperature. Viscosity correlation equations[7−9] have been applied to the binary mixtures at every temperature. The root-mean-square deviations between experimental and correlated values are shown.

Dynamic viscosities for the aforementioned binary mixtures at the cited temperature interval have been obtained by the UNIFAC−VISCO[10] group contribution method, requiring only pure component data and the interaction parameters.

2. Experimental Section

The liquids used were from Merck and were of Lichrosolv quality. The pure components were degassed ultrasonically, dried over freshly activated molecular sieves (types 3 and 4 Å, supplied by Aldrich) for several weeks before use, and kept in an inert argon atmosphere as soon as the bottles were opened. Chromatographic (GLC) tests of the solvents showed purities that fulfilled purchaser specifications. Their mass fraction purities were more than 99.0 for dimethyl carbonate, cyclopentane, and methylcyclohexane and more than 99.5 for diethyl carbonate with maximum water contents of 7×10^{-4} mass % for cyclopentane and 1.1×10^{-3} mass % for methylcyclohexane and inappreciable quantities for carbonates. These quantities were determined using a Metrohm 737 KF coulometer. We have compared the measured densities and viscosities at different temperatures with literature values, and the data are listed in Table 1.

Table 1. Comparison of the Physical Properties of Pure Components with Literature Data at Several Temperatures

		ρ/g·cm^{-3}		η/mPa·s	
component	T/K	exptl	lit	exptl	lit
dimethyl carbonate	293.15	1.06990	1.06969[a]	0.623	0.623[a]
	298.15	1.06333	1.0635[b] 1.0632[d]	0.584	0.585[c]
	303.15	1.05671	1.05635[a]	0.549	0.548[a]
	308.15	1.05007	1.05004[e]	0.517	0.520[f]
	313.15	1.04339	1.0431[a]	0.488	0.486[a]
diethyl carbonate	293.15	0.97480	0.97457[g]	0.809	0.810[h]
	298.15	0.96921	0.96926[i] 0.96924[j]	0.750	0.749[f]
	303.15	0.96358	0.9636[g]	0.702	0.710[h]
	308.15	0.95793	0.9577[f]	0.658	0.658[f]
	313.15	0.95226	0.95243[k]	0.618	0.625[h]
cyclopentane	293.15	0.74443	0.74490[l]	0.438	0.4405[l]
	298.15	0.73947	0.73969[m]	0.415	0.4169[m]
	303.15	0.73447	0.73551[n]	0.394	0.387[o]
	308.15	0.72942		0.374	
	313.15	0.72432	0.72455[m]	0.355	0.3545[m]
methylcyclohexane	293.15	0.76930	0.7692[p]	0.729	0.736[p]
	298.15	0.76496	0.76506[q] 0.7651[r]	0.681	0.685[q]
	303.15	0.76065	0.76060[s]	0.637	0.6387[t]
	308.15	0.75629		0.598	
	313.15	0.75193	0.7517[p]	0.562	0.568[p]

[a] Romano et al.[11] [b] García de la Fuente et al.[12] [c] Rodríguez et al.[3] [d] Pal et al.[13] [e] Lopez et al.[14] [f] Pal and Dass.[15] [g] Rivas et al.[16] [h] Comunas et al.[17] [i] Das et al.[18] [j] Francesconi and Comelli.[19] [k] Ottani et al.[20] [l] Harris et al.[21] [m] Guzman et al.[22] [n] Takagi et al.[23] [o] Oswal et al.[24] [p] Zeberg-Mikkelsen et al.[25] [q] Riddick et al.[26] [r] Garcia et al.[27] [s] Oswal et al.[28] [t] Baylaucq et al.[29]

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Table 2. Density ρ, Viscosity η, Excess Molar Volume V^E, Viscosity Deviations $\Delta\eta$, Speed of Sound u, Isentropic Compressibility κ_s, and Deviation in Isentropic Compressibility $\Delta\kappa_s$ of the Binary Mixture Dimethyl Carbonate (1) + Cyclopentane (2) at Several Temperatures

	ρ	η	u	V^E_m	$\Delta\eta$	κ_s	$\Delta\kappa_s$		ρ	η	u	V^E_m	$\Delta\eta$	κ_s	$\Delta\kappa_s$
x_1	$g\cdot cm^{-3}$	mPa·s	$m\cdot s^{-1}$	$cm^3\cdot mol^{-1}$	mPa·s	$T\cdot Pa^{-1}$	$T\cdot Pa^{-1}$	x_1	$g\cdot cm^{-3}$	mPa·s	$m\cdot s^{-1}$	$cm^3\cdot mol^{-1}$	mPa·s	$T\cdot Pa^{-1}$	$T\cdot Pa^{-1}$
$T = 293.15$ K															
0	0.74443	0.438	1232	0	0	886	0	0.5988	0.92084	0.472	1174	0.919	−0.077	788	57
0.0453	0.75575	0.429	1219	0.237	−0.018	891	17	0.6963	0.95464	0.497	1180	0.777	−0.07	753	47
0.0871	0.76647	0.419	1209	0.429	−0.035	893	29	0.8033	0.99339	0.531	1190	0.565	−0.055	711	32
0.1847	0.79272	0.417	1192	0.757	−0.056	887	49	0.9028	1.03140	0.573	1204	0.289	−0.032	669	16
0.2915	0.82338	0.421	1180	0.947	−0.071	872	62	0.9532	1.05109	0.601	1212	0.15	−0.013	648	8
0.3937	0.85433	0.432	1174	1.015	−0.079	850	66	1	1.06990	0.623	1220	0	0	628	0
0.4904	0.88496	0.449	1172	1.004	−0.08	823	64								
$T = 298.15$ K															
0	0.73947	0.415	1206	0	0	930	0	0.5988	0.91470	0.444	1151	0.952	−0.073	825	60
0.0453	0.75069	0.406	1193	0.245	−0.016	935	18	0.6963	0.94841	0.468	1157	0.801	−0.065	788	50
0.0871	0.76131	0.397	1184	0.443	−0.033	937	31	0.8033	0.98701	0.500	1168	0.583	−0.051	743	34
0.1847	0.78729	0.396	1168	0.789	−0.05	932	53	0.9028	1.02485	0.538	1182	0.304	−0.03	698	17
0.2915	0.81776	0.398	1156	0.982	−0.067	915	65	0.9532	1.04457	0.565	1190	0.154	−0.011	676	8
0.3937	0.84847	0.408	1150	1.057	−0.074	891	70	1	1.06333	0.584	1198	0	0	655	0
0.4904	0.87898	0.422	1148	1.041	−0.075	863	68								
$T = 303.15$ K															
0	0.73447	0.394	1180	0	0	977	0	0.5988	0.90854	0.419	1127	0.984	−0.067	866	64
0.0453	0.74558	0.385	1168	0.253	−0.015	983	19	0.6963	0.94213	0.441	1134	0.826	−0.06	826	53
0.0871	0.75609	0.377	1158	0.459	−0.03	986	34	0.8033	0.98064	0.472	1145	0.596	−0.047	777	36
0.1847	0.78198	0.374	1143	0.801	−0.048	980	56	0.9028	1.01817	0.507	1160	0.327	−0.027	730	18
0.2915	0.81207	0.377	1131	1.02	−0.062	963	71	0.9532	1.03801	0.528	1168	0.157	−0.013	706	9
0.3937	0.84265	0.386	1125	1.093	−0.068	937	75	1	1.05671	0.549	1177	0	0	683	0
0.4904	0.87296	0.400	1124	1.079	−0.069	906	73								
$T = 308.15$ K															
0	0.72942	0.374	1154	0	0	1029	0	0.5988	0.90234	0.397	1105	1.016	−0.062	908	68
0.0453	0.74041	0.366	1142	0.262	−0.014	1035	20	0.6963	0.93582	0.418	1111	0.851	−0.056	865	56
0.0871	0.75083	0.358	1133	0.475	−0.028	1037	36	0.8033	0.97420	0.446	1123	0.614	−0.043	814	38
0.1847	0.77638	0.355	1118	0.843	−0.045	1031	60	0.9028	1.01188	0.478	1138	0.314	−0.024	763	19
0.2915	0.80636	0.357	1107	1.057	−0.058	1012	75	0.9532	1.03141	0.501	1146	0.161	−0.009	738	9
0.3937	0.83673	0.366	1102	1.134	−0.064	984	79	1	1.05007	0.517	1155	0	0	714	0
0.4904	0.86691	0.379	1101	1.116	−0.065	952	77								
$T = 313.15$ K															
0	0.72432	0.355	1129	0	0	1083	0	0.5988	0.89610	0.377	1082	1.05	−0.058	954	73
0.0453	0.73520	0.348	1117	0.271	−0.013	1090	22	0.6963	0.92945	0.397	1089	0.878	−0.051	908	59
0.0871	0.74551	0.341	1108	0.492	−0.026	1092	39	0.8033	0.96770	0.424	1101	0.634	−0.037	852	40
0.1847	0.77082	0.338	1093	0.876	−0.042	1086	65	0.9028	1.00528	0.454	1116	0.324	−0.021	798	20
0.2915	0.80054	0.338	1083	1.102	−0.056	1066	81	0.9532	1.02479	0.472	1125	0.165	−0.009	771	10
0.3937	0.83073	0.346	1078	1.181	−0.061	1036	86	1	1.04339	0.488	1134	0	0	746	0
0.4904	0.86070	0.358	1078	1.167	−0.062	1000	83								

The mixtures were prepared by transferring known masses of the pure liquids via syringe into stoppered bottles to prevent preferential evaporation, using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. The estimated uncertainty in the mole fraction was ±0.0001.

The density and speed of sound of the pure liquids and mixtures were measured with an Anton Paar DSA-5000 digital vibrating tube densimeter. The repeatability and the uncertainty in our measured densities and the speed of sound have been found to be lower than $\pm 1.0 \times 10^{-6}$ and $\pm 2.0 \times 10^{-6}$ $g\cdot cm^{-3}$ for the density and ±0.01 and ±0.1 $m\cdot s^{-1}$ for the speed of sound. Kinematic viscosities were determined using an automatic viscometer Lauda PVS1 with two Ubbelhode capillary microviscometers of $(0.4 \times 10^{-3}$ and $0.53 \times 10^{-3})$ m diameter. Gravity fall is the principle of measurement on which this viscometer is based. The capillary is maintained in a D20KP LAUDA thermostat with a resolution of 0.01 K. The capillaries are calibrated and credited by the supplier company. The uncertainty of the capillary diameter is ±0.005 mm. The uncertainty in the viscometer has been found to be ±0.01 mPa·s. The equipment has a control unit PVS1 (processor viscosity system) that is a PC-controlled instrument for the precise measurement of liquid viscosity using standardized glass capillaries with an uncertainty of 0.01 s.

The kinematic viscosity is determined from the following relationship:

$$\nu = k(t - y) \qquad (1)$$

where y is the Hagenbach correction, t is the flow time, and k is the Ubbelhode capillary microviscometer constant that is supplied by the company.

3. Results and Discussion

The experimental density, dynamic viscosities, speed of sound, excess molar volume, viscosity deviation, isentropic compressibility (determined by means of the Laplace equation, $\kappa_S = \rho^{-1}\cdot u^{-2}$), and deviation in isentropic compressibility of the binary mixtures dimethyl carbonate + cyclopentane and diethyl carbonate + cyclopentane at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K are given in Tables 2 and 3. The dynamic viscosities, viscosity deviations, speeds of sound, isentropic compressibilities, and deviations in isentropic compressibility of the binary mixture diethyl carbonate + methylcyclohexane from T = (293.15 to 303.15) K are reported in Table 4. The experimental densities of these binary mixtures at the above temperatures have been published previously.[6] Excess molar volumes, viscosity deviations, and deviations in

Table 3. Density ρ, Viscosity η, Excess Molar Volume V^E, Viscosity Deviations $\Delta\eta$, Speed of Sound u, Isentropic Compressibility κ_s, and Deviation in Isentropic Compressibility $\Delta\kappa_s$ of the Binary Mixture Diethyl Carbonate (1) + Cyclopentane (2) at Several Temperatures

x_1	ρ g·cm^{-3}	η mPa·s	u m·s^{-1}	V^E_m cm^3·mol^{-1}	$\Delta\eta$ mPa·s	κ_s T·Pa^{-1}	$\Delta\kappa_s$ T·Pa^{-1}	x_1	ρ g·cm^{-3}	η mPa·s	u m·s^{-1}	V^E_m cm^3·mol^{-1}	$\Delta\eta$ mPa·s	κ_s T·Pa^{-1}	$\Delta\kappa_s$ T·Pa^{-1}
T = 293.15 K															
0	0.74443	0.438	1232	0	0	886	0	0.6023	0.89192	0.601	1179	0.586	−0.060	807	24
0.0491	0.75721	0.440	1219	0.197	−0.017	888	11	0.7021	0.91390	0.646	1181	0.465	−0.053	784	18
0.0999	0.77043	0.445	1209	0.349	−0.031	888	19	0.8053	0.93569	0.696	1186	0.329	−0.041	760	11
0.1898	0.79345	0.462	1196	0.541	−0.046	881	28	0.9032	0.95562	0.748	1191	0.181	−0.025	737	6
0.2872	0.81788	0.486	1186	0.645	−0.059	869	32	0.9520	0.96536	0.778	1194	0.092	−0.013	726	3
0.3894	0.84277	0.518	1180	0.679	−0.064	852	32	1	0.97480	0.809	1197	0	0	715	0
0.5009	0.86892	0.559	1178	0.659	−0.065	829	29								
T = 298.15 K															
0	0.73947	0.415	1206	0	0	930	0	0.6023	0.88643	0.564	1157	0.601	−0.052	843	25
0.0491	0.75218	0.416	1194	0.202	−0.016	932	11	0.7021	0.90838	0.606	1160	0.476	−0.044	818	18
0.0999	0.76534	0.421	1184	0.358	−0.028	932	20	0.8053	0.93014	0.654	1165	0.337	−0.031	792	11
0.1898	0.78824	0.437	1172	0.556	−0.042	924	29	0.9032	0.95004	0.699	1170	0.185	−0.018	768	6
0.2872	0.81258	0.459	1163	0.665	−0.052	911	34	0.9520	0.95978	0.726	1174	0.095	−0.008	756	3
0.3894	0.83737	0.489	1157	0.701	−0.057	892	34	1	0.96921	0.750	1177	0	0	745	0
0.5009	0.86347	0.527	1156	0.678	−0.056	867	30								
T = 303.15 K															
0	0.73447	0.394	1180	0	0	977	0	0.6023	0.88091	0.532	1135	0.616	−0.048	882	25
0.0491	0.74711	0.396	1169	0.208	−0.013	980	12	0.7021	0.90282	0.570	1138	0.488	−0.040	855	19
0.0999	0.76019	0.399	1159	0.368	−0.025	979	21	0.8053	0.92456	0.615	1144	0.344	−0.027	827	11
0.1898	0.78299	0.414	1147	0.572	−0.038	970	31	0.9032	0.94444	0.655	1150	0.189	−0.017	801	6
0.2872	0.80723	0.435	1139	0.684	−0.047	955	35	0.9520	0.95416	0.680	1153	0.097	−0.007	788	3
0.3894	0.83195	0.461	1134	0.721	−0.053	934	35	1	0.96358	0.702	1156	0	0	776	0
0.5009	0.85797	0.496	1133	0.699	−0.052	908	31								
T = 308.15 K															
0	0.72942	0.374	1154	0	0	1029	0	0.6023	0.87535	0.502	1113	0.632	−0.043	922	26
0.0491	0.74199	0.375	1144	0.213	−0.013	1031	13	0.7021	0.89723	0.537	1117	0.500	−0.036	893	19
0.0999	0.75500	0.379	1134	0.378	−0.023	1029	22	0.8053	0.91894	0.578	1123	0.353	−0.024	863	12
0.1898	0.77770	0.393	1123	0.588	−0.035	1019	32	0.9032	0.93880	0.616	1129	0.194	−0.015	836	6
0.2872	0.80184	0.412	1115	0.703	−0.043	1002	37	0.9520	0.94852	0.638	1133	0.098	−0.006	822	3
0.3894	0.82649	0.436	1112	0.741	−0.048	979	36	1	0.95793	0.658	1136	0	0	809	0
0.5009	0.85245	0.470	1111	0.717	−0.046	951	32								
T = 313.15 K															
0	0.72432	0.355	1129	0	0	1083	0	0.6023	0.86975	0.475	1091	0.648	−0.039	965	27
0.0491	0.73682	0.356	1119	0.219	−0.012	1085	14	0.7021	0.89161	0.508	1096	0.512	−0.032	934	19
0.0999	0.74976	0.360	1110	0.389	−0.022	1083	24	0.8053	0.91329	0.545	1102	0.361	−0.022	902	12
0.1898	0.77235	0.373	1099	0.605	−0.032	1072	34	0.9032	0.93314	0.580	1109	0.198	−0.013	872	6
0.2872	0.79639	0.391	1092	0.726	−0.040	1053	39	0.9520	0.94285	0.600	1112	0.101	−0.006	857	3
0.3894	0.82095	0.414	1089	0.766	−0.044	1027	38	1	0.95226	0.618	1116	0	0	843	0
0.5009	0.84690	0.444	1089	0.735	−0.043	996	33								

isentropic compressibility were calculated from experimental values as follows:

$$V^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{\circ -1}) \qquad (2)$$

$$\Delta\eta = \eta - \sum_{i=1}^{N} (\eta_i^{\circ} x_i) \qquad (3)$$

$$\Delta\kappa_s = \kappa_s - \sum_{i=1}^{N} x_i \kappa_{s,i} \qquad (4)$$

where, ρ and ρ_i° are the densities of the mixture and of the pure components, respectively, η is the dynamic viscosity of the mixture, η_i° and x_i represent the viscosity and mole fraction of each pure component, respectively, k_s is the isentropic compressibility of the mixture, and $k_{s,i}$ is the isentropic compressibility of the pure components.

The derived quantities were fit to a polynomial equation:

$$\Delta Q_m = x(1 - x)\sum_{i=1}^{2} \sum_{j=1}^{2} A_{ij} x^{i/\alpha} (T - T_o)^{j-1} \qquad (5)$$

where T_o is 298.15 K, x is the mole fraction, and α and A_{ij} are the fitting parameters. The degree of this equation was optimized by applying the F test.[30] The correlation parameters are listed in Table 5, together with the root-mean-square deviations (σ). This deviation is calculated by applying the following expression:

$$\sigma = \left(\frac{\sum_{i}^{n_{DAT}} (z_{exp} - z_{pred})^2}{n_{DAT}} \right)^{1/2} \qquad (6)$$

where the property values and the number of experimental data are represented by z and n_{DAT}, respectively.

Parts a and b of Figure 1show excess molar volumes for the binary mixtures dimethyl carbonate + cyclopentane and diethyl carbonate + cyclopentane, respectively, from T = (293.15 to 313.15) K versus the mole fraction over the whole composition range. In this Figure, we can observe that the excess molar volumes are positive over the entire composition range at all temperatures, and the diethyl carbonate mixtures have higher excess properties than the dimethyl carbonate mixtures. In the insets, we can observe how the excess quantities increase when the temperature increases for both systems at equimolar composition.

Table 4. Viscosity η, Viscosity Deviations $\Delta\eta$, Speed of Sound u, Isentropic Compressibility κ_S, and Deviation in Isentropic Compressibility $\Delta\kappa_S$ of the Binary Mixture Diethyl Carbonate (1) + Methylcyclohexane (2) at Several Temperatures

x_1	η/mPa·s	u/m·s^{-1}	$\Delta\eta$/mPa·s	κ_S/T·Pa^{-1}	$\Delta\kappa_S$/T·Pa^{-1}	x_1	η/mPa·s	u/m·s^{-1}	$\Delta\eta$/mPa·s	κ_S/T·Pa^{-1}	$\Delta\kappa_S$/T·Pa^{-1}
					T = 293.15 K						
0	0.729	1237	0	849	0	0.5999	0.695	1189	−0.082	799	30
0.0473	0.709	1229	−0.024	851	8	0.6985	0.709	1189	−0.076	780	25
0.0978	0.692	1222	−0.045	851	15	0.7988	0.732	1191	−0.061	760	18
0.1985	0.678	1211	−0.068	847	24	0.8996	0.762	1194	−0.039	737	9
0.2968	0.670	1203	−0.083	839	30	0.9509	0.787	1196	−0.018	726	4
0.3924	0.672	1196	−0.089	829	33	1	0.809	1198	0	715	0
0.4993	0.680	1192	−0.089	814	32						
					T = 298.15 K						
0	0.681	1215	0	885	0	0.5999	0.649	1168	−0.073	832	32
0.0473	0.662	1207	−0.022	888	9	0.6985	0.663	1168	−0.066	813	26
0.0978	0.647	1201	−0.040	887	16	0.7988	0.684	1170	−0.052	791	19
0.1985	0.633	1189	−0.062	883	26	0.8996	0.711	1173	−0.032	768	10
0.2968	0.627	1181	−0.074	875	32	0.9509	0.735	1175	−0.012	756	5
0.3924	0.628	1175	−0.080	865	35	1	0.750	1177	0	744	0
0.4993	0.635	1171	−0.080	849	34						
					T = 303.15 K						
0	0.637	1193	0	923	0	0.5999	0.609	1147	−0.067	868	34
0.0473	0.621	1185	−0.020	926	10	0.6985	0.622	1147	−0.061	848	28
0.0978	0.607	1179	−0.037	926	17	0.7988	0.642	1149	−0.048	825	20
0.1985	0.593	1168	−0.057	921	28	0.8996	0.666	1152	−0.030	801	10
0.2968	0.588	1160	−0.068	913	34	0.9509	0.687	1155	−0.012	788	5
0.3924	0.589	1154	−0.074	902	37	1	0.702	1157	0	776	0
0.4993	0.596	1149	−0.073	886	37						
					T = 308.15 K						
0	0.598	1172	0	963	0	0.5999	0.572	1126	−0.062	906	36
0.0473	0.583	1164	−0.018	966	10	0.6985	0.584	1126	−0.056	885	30
0.0978	0.570	1157	−0.034	966	18	0.7988	0.603	1128	−0.043	861	21
0.1985	0.558	1146	−0.052	962	29	0.8996	0.625	1132	−0.027	835	11
0.2968	0.553	1138	−0.063	954	36	0.9509	0.645	1134	−0.010	821	5
0.3924	0.554	1132	−0.068	942	39	1	0.658	1136	0	808	0
0.4993	0.561	1128	−0.066	925	39						
					T = 313.15 K						
0	0.562	1150	0	1006	0	0.5999	0.539	1105	−0.057	946	39
0.0473	0.548	1142	−0.016	1009	11	0.6985	0.550	1106	−0.051	924	32
0.0978	0.537	1136	−0.031	1009	19	0.7988	0.568	1108	−0.039	898	23
0.1985	0.525	1125	−0.048	1005	32	0.8996	0.588	1112	−0.024	871	12
0.2968	0.521	1117	−0.058	996	39	0.9509	0.607	1114	−0.009	856	5
0.3924	0.522	1111	−0.062	984	42	1	0.618	1116	0	843	0
0.4993	0.529	1107	−0.061	966	42						

Table 5. Fitting Parameters and Root-Mean-Square Deviations σ for Binary Mixtures to Correlate the Excess Molar Volumes V^E, the Viscosity Deviations $\Delta\eta$, and the Deviations in Isentropic Compressibility $\Delta\kappa_S$

	A_{11}	A_{12}	A_{21}	A_{22}	A_{31}	A_{32}	α	σ
			Dimethyl Carbonate (1) + Cyclopentane (2)					
10^9V^E/m^3·mol^{-1}	18.542	0.0439	−32.766	−0.0313	20.158	0.0314	3	0.005
$\Delta\eta$/mPa·s	−1.9537	0.0414	3.7436	−0.0906	−2.2299	0.05060	2	0.001
$\Delta\kappa_S$/T·Pa^{-1}	1013.4	10.474	−1640.5	−15.626	1055.6	11.584	2	0.60
			Diethyl Carbonate (1) + Cyclopentane (2)					
10^9V^E/m^3·mol^{-1}	17.300	0.1184	−15.434	−0.1097			10	0.005
$\Delta\eta$/mPa·s	−1.8702	0.0555	3.1122	−0.1174	−1.4582	0.0681	5	0.001
$\Delta\kappa_S$/T·Pa^{-1}	1048.7	13.705	−1000.3	−13.942			8	0.16
			Diethyl Carbonate (1) + Methylcyclopentane (2)					
$\Delta\eta$/mPa·s	−2.8645	0.0567	5.4753	−0.1183	−2.9916	0.0696	3	0.002
$\Delta\kappa_S$/T·Pa^{-1}	653.07	9.7109	−545.06	−8.3092			9	0.40

Figures 2 and 3 show viscosity deviations and deviations in isentropic compressibility, respectively, for the binary mixtures dimethyl and diethyl carbonate with cycloalkanes from T = (293.15 to 313.15) K plotted against mole fraction together with the fitted curve obtained from eq 5. The viscosity deviations for these systems at every temperature are negative over the entire composition range, whereas for the deviation in isentropic compressibility the trend is the opposite. Each inset represents viscosity deviations and deviations in isentropic compressibility versus the temperature for each system at equimolar composition, and we can observe how the excess quantities increase with temperature for every system.

On the basis of Eyring's theory of viscosities of pure liquids, many investigators have correlated the viscosities of binary liquid mixtures as follows:

$$\ln(\eta V) = \sum_{i=1}^{n} x_i \ln(\eta_i^\circ V_i^\circ) + \frac{\Delta G^{*E}}{RT} \qquad (7)$$

where η is the dynamic viscosity of the mixture, V is the

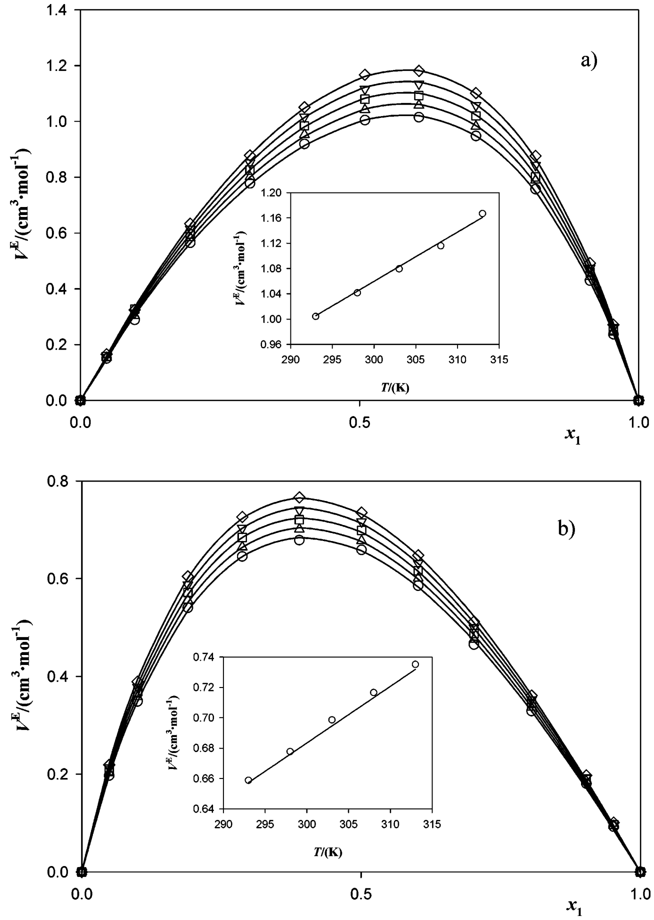

Figure 1. Experimental curves of excess molar volumes, V^E, obtained from eq 5 versus mole fraction for the binary mixtures: (a) dimethyl carbonate + cyclopentane and (b) diethyl carbonate + cyclopentane at ○, $T = 293.15$ K; △, $T = 298.15$ K; □, $T = 303.15$ K; ▽, $T = 308.15$ K; and ◇, $T = 313.15$ K. (Inset) excess molar volumes at equimolar composition versus temperature from $T = 293.15-313.15$ K for (a) dimethyl carbonate + cyclopentane and (b) diethyl carbonate + cyclopentane.

molar volume of the mixture, x_i is the mole fraction of the pure components, V_i° is the molar volume of the pure component, and ΔG^{*E} is the activation energy of the viscous flow.

In this paper, we have considered the energy terms of Noda–Ishida,[7] Wilson,[8] and the UNIQUAC[9] models. The root-mean-square deviations between experimental and correlated values are gathered in Table 6. In the following equation, we represent the energy term of the Noda–Ishida equation. This equation was developed on the basis of viscosity theory instead of the other equations that can be used with VLE data.

$$\frac{\Delta G^{*E}}{RT} = \sum_{j=1}^{n} x_j \sum_{i=1}^{n} \frac{x_i W_{ji}}{\sum_{k=1}^{n} x_k \exp(-W_{ki}/RT)} \tag{8}$$

where W_{ji} and W_{ki} are the adjustable parameters determined from the binary experimental data.

In general terms, low standard deviation values were obtained with the correlated equations. The binary system dimethyl carbonate + cyclopentane shows the best results for the equations because of the low variation of dynamic viscosity values with composition. In view of the results, we can say that the best correlation equation for the binary mixtures is the Wilson equation.

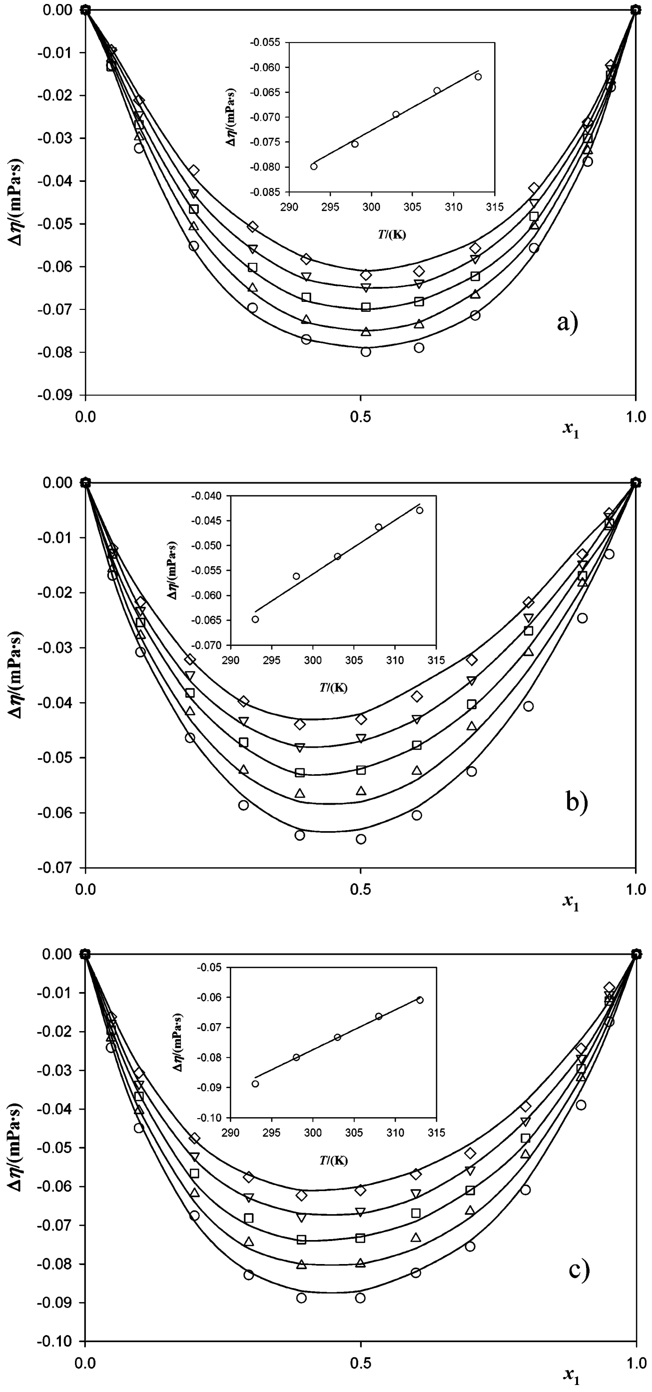

Figure 2. Experimental curves of viscosity deviations, $\Delta\eta$, obtained from eq 5 versus mole fraction for the binary mixtures: (a) dimethyl carbonate + cyclopentane, (b) diethyl carbonate + cyclopentane, and (c) diethyl carbonate + methylcyhexane at ○, $T = 293.15$ K; △, $T = 298.15$ K; □, $T = 303.15$ K; ▽, $T = 308.15$ K; and ◇, $T = 313.15$ K. (Inset) viscosity deviation at equimolar composition versus temperature from $T = 293.15-313.15$ K for (a) dimethyl carbonate + cyclopentane, (b) diethyl carbonate + cyclopentane, and (c) diethyl carbonate + methylcyclohexane.

Figure 4 shows experimental dynamic viscosities and the correlated lines for the binary mixture dimethyl carbonate + cyclopentane from $T = (293.15$ to $313.15)$ K versus the mole fraction over the whole composition range. The inset represents dynamic viscosity values versus the temperature for this system at equimolar composition, and we can

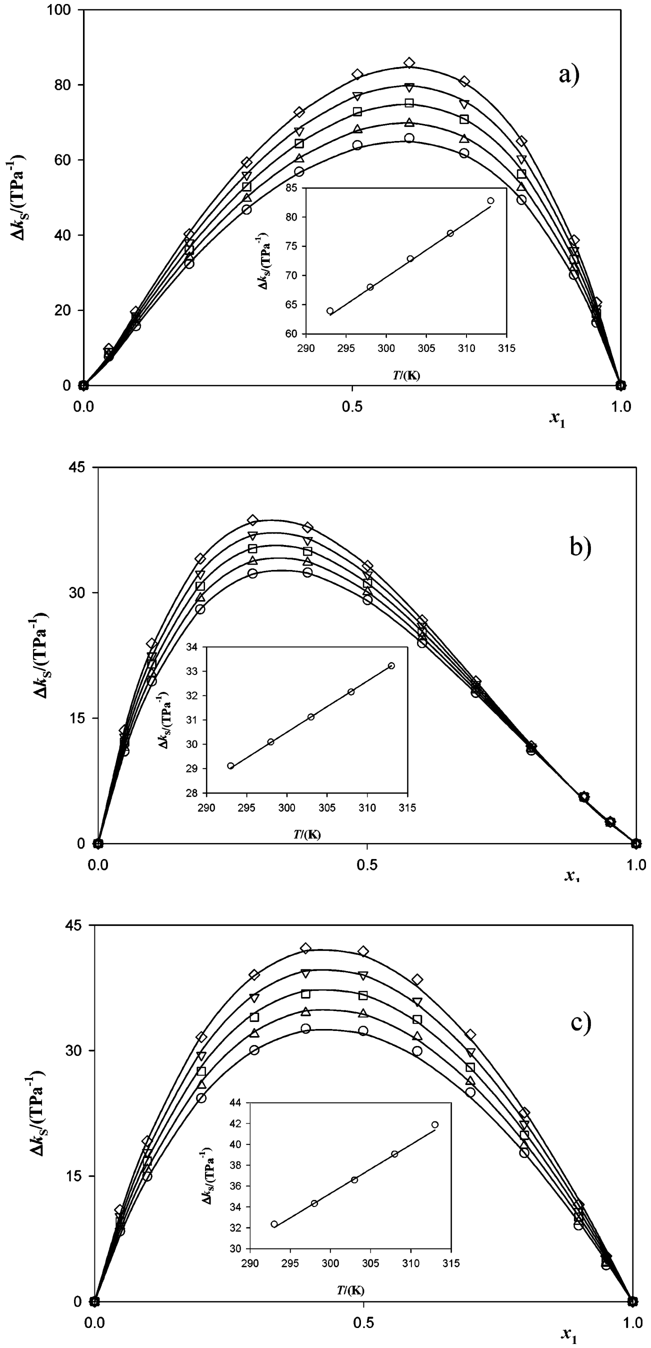

Figure 3. Experimental curves of deviations in isentropic compressibility, $\Delta\kappa_S$, obtained from eq 5 versus mole fraction for the binary mixtures (a) dimethyl carbonate + cyclopentane, (b) diethyl carbonate + cyclopentane, and (c) diethyl carbonate + methylcyhexane at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K; ▽, T = 308.15 K; and ◇, T = 313.15 K. (Inset) deviation in isentropic compressibility at equimolar composition versus temperature from T = 293.15−313.15 K for (a) dimethyl carbonate + cyclopentane, (b) diethyl carbonate + cyclopentane, and (c) diethyl carbonate + methylcyclohexane.

Table 6. Root-Mean-Square Deviations (σ) of the Experimental Results and Estimated Viscosities of Noda-Ishida, Wilson, and UNIQUAC

$\sigma(\eta)$/mPa·s		
Noda-Ishida	Wilson	UNIQUAC
Dimethyl Carbonate (1) + Cyclopentane (2)		
0.0044	0.0017	0.0019
Diethyl Carbonate (1) + Cyclopentane (2)		
0.0059	0.0048	0.0041
Diethyl Carbonate (1) + Methylcyhexane (2)		
0.0053	0.0026	0.0036

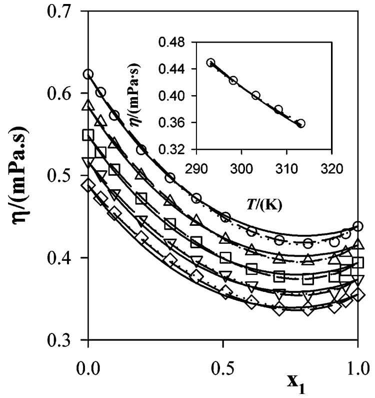

Figure 4. Experimental dynamic viscosities, η, versus mole fraction for the binary mixture dimethyl carbonate + cyclopentane at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K; ▽, T = 308.15 K; and ◇, T = 313.15 K and the estimated values by Noda−Ishida, −; Wilson, ···; and UNIQUAC − −.

Table 7. UNIFAC−VISCO Interaction Parameters

parameters	α_{mn}/K
$CH_{2cy}-OCOO$	338.064
$OCOO-CH_{2cy}$	−106.309

Table 8. Root-Mean-Square Deviations of Dynamic Viscosity $\sigma(\eta)$ Resulting by Using the UNIFAC−VISCO Model at Several Temperatures for the Binary Mixtures

$\sigma(\eta)$/mPa·s				
293.15 K	298.15 K	303.15 K	308.15 K	313.15 K
Dimethyl Carbonate (1) + Cyclopentane (2)				
0.026	0.024	0.023	0.022	0.021
Diethyl Carbonate (1) + Cyclopentane (2)				
0.039	0.038	0.035	0.033	0.031
Diethyl Carbonate (1) + Methylcyclohexane (2)				
0.039	0.038	0.035	0.033	0.031

observe how the quantities decrease with temperature increases for this system.

To improve the application range of the predictive UNIFAC−VISCO method, based on a group contribution scheme, we have recalculated the interaction parameters corresponding to the carbonate group (−OCOO−) with cycloalkanes ($-CH_{2cy}$). In a previous paper,[3] we calculated this parameter using our experimental data of dimethyl carbonate and diethyl carbonate with cyclohexane, and we have considered that this calculation was based on few systems. Taking into account this fact, we have increased the number of experimental data and the position of the cycloalkane group in these mixtures with the aim of generalizing the database.

The UNIFAC−VISCO parameters have been calculated using the Nelder−Mead[31] equation for minimizing the following objective function:

$$\mathrm{OF} = \frac{1}{N}\sum_{i=1}^{N}\frac{|\nu_{i,\mathrm{exptl}} - \nu_{i,\mathrm{calcd}}|}{\nu_{i,\mathrm{exptl}}} \tag{9}$$

with N being the number of experimental data points and ν_{exptl} and ν_{calcd} being the experimental and calculated kinematic viscosities, respectively.

The carbonate−cycloalkane interaction parameters, obtained from our experimental data, are summarized in Table 7. In Table 8, the root-mean-square deviations

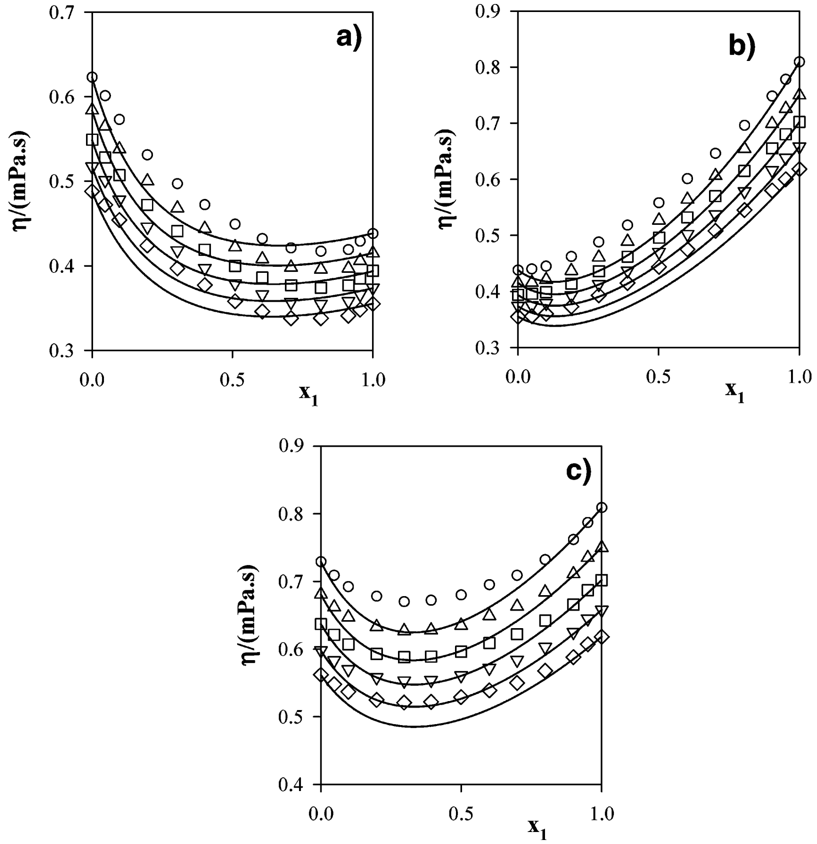

Figure 5. Experimental dynamic viscosities, η, versus mole fraction for the binary mixtures (a) dimethyl carbonate + cyclopentane, (b) diethyl carbonate + cyclopentane, and (c) diethyl carbonate + methylcyhexane at ○, T = 293.15 K; △, T = 298.15 K; □, T = 303.15 K; ▽, T = 308.15 K; and ◇, T = 313.15 K and the calculated values using UNIFAC−VISCO, −.

between experimental and calculated viscosity deviations are shown. In view of the results shown in this Table, we can say that good results are obtained in the prediction of the binary mixtures of dialkyl carbonates with cycloalkanes. Figure 5 shows graphically experimental values of dynamic viscosities for the binary mixtures dimethyl carbonate with cyclopentane and diethyl carbonate with cyclopentane or methylcyclohexane at T = (293.15, 298.15, 303.15, 308.15, and 313.15) K and the corresponding predictive curves obtained by applying the UNIFAC−VISCO method.

4. Conclusions

In this paper, we have determined the experimental density, dynamic viscosity, and speed of sound of the binary mixtures dimethyl carbonate with cyclopentane and diethyl carbonate with cyclopentane or methylcyclohexane from T = (293.15 to 313.15) K. To test the quality of the experimental values, we have calculated the excess molar volumes, viscosity deviations, isentropic compressibilities, and deviations in isentropic compressibility for the above binary mixtures over the temperature interval.

The correlated equations of Noda−Ishida, Wilson, and UNIQUAC have been used to correlate the dynamic viscosities for the temperature interval used, and good results have been reached.

The predictive method UNIFAC−VISCO, based on contribution groups, has been used to predict the dynamic viscosities of the binary mixtures at several temperatures. Because of the poor results achieved using a previous interaction parameter $-OCOO-/CH_{2cy}$, we have recalculated it, and the results in terms of root-mean-square deviations are shown.

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