Densities and Excess Molar Volumes of Binary Mixtures Containing Propylene Carbonate + 10 Chlorohydrocarbons at 298.15 K and Atmospheric Pressure

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Densities, ϱ, and excess molar volumes, V_m^E, for binary mixtures containing propylene carbonate + 10 chlorohydrocarbons (dichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobuthane, 1,6-dichlorohexane, 1,10-dichlorodecane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, *trans*-1,2-dichloroethene, and trichloroethene) have been measured at 298.15 K and at atmospheric pressure using an Anton Paar digital vibrating tube density meter. The results are fitted to the Redlich–Kister equation. The values of V_m^E for the mixtures containing dichloroalkanes show an increasing trend with the increase of the chain length and vary from a minimum of -0.24 cm^3·mol^{-1} for dichloromethane up to a maximum of $+0.31$ cm^3·mol^{-1} for 1,10-dichlorodecane. The excess molar volumes for the other mixtures are negative over the entire range of composition. Results are qualitatively discussed in terms of molecular interactions.

Introduction

Recently, we have conducted a systematic study of the thermophysical properties of binary mixtures containing esters of carbonic acid which are considered important solvents in industry and in the synthesis of pharmaceuticals. Particularly, propylene carbonate, a dipolar aprotic solvent, dissolves a variety of inorganic or organic substances and is used in organic synthesis and electrochemical studies (Zana et al., 1982; Annesini et al., 1984; Tobishima et al., 1988).

In continuation of this program, we present the densities, ϱ, and excess molar volumes, V_m^E, of binary mixtures containing propylene carbonate with 10 chlorohydrocarbons: namely, dichloromethane, 1,2-dichloroethane, 1,3-dichloropropane, 1,4-dichlorobutane, 1,6-dichlorohexane, 1,10-dichlorodecane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, *trans*-1,2-dichloroethene, and trichloroethene. The mixture formed by propylene carbonate + tetrachloroethene, which would have been of interest to complete the series of chloroalkenes, has not been studied owing to the partial immiscibility of the components.

All measurements were made at (298.15 ± 0.01) K and at atmospheric pressure. To the best of our knowledge, the volumetric properties of the above mentioned mixtures have not been measured previously.

Experimental Section

All chemicals were supplied from Aldrich, with the exception of trichloroethene which was from C. Erba: their purities were ≥99 mol % with the exception of 1,6-dichlorohexane (purity 98 mol %) and *trans*-1,2-dichloroethene (purity 98 mol %) which were purified by fractional distillation over 10% aqueous sodium hydroxide solution using a Widmar 30-plate column. The first and last 20% of the distillate was discarded. Other liquids, with purities varying from 99 up to 99.7 mol %, as in the case of propylene carbonate, were used without further purification. Before use, all liquids were stored in dark bottles over molecular sieves (Union Carbide Type 4A, 1/16-in. pellets) and partially degassed. The purities of the chemicals were verified by the measurements of the densities, ϱ, which are reported in Table 1 and compared with the literature data.

Table 1. Experimental Densities, ϱ, of Pure Compounds at 298.15 K and Atmospheric Pressure with Literature Data

component	ϱ/(g·cm^{-3}) this paper	ϱ/(g·cm^{-3}) lit.
propylene carbonate	1.199 54	1.199 5[a]
		1.199 2[b]
dichloromethane	1.316 13	1.316 3[c]
1,2-dichloroethane	1.245 62	1.245 8[c]
1,3-dichloropropane	1.178 69	1.178 45[d]
1,4-dichlorobutane	1.133 86	1.133 12[e]
1,6-dichlorohexane	1.064 63	1.064 65[f]
1,10-dichlorodecane	0.992 98	0.994 5[g]
1,1,1-trichloroethane	1.329 77	1.329 93[h]
1,1,2,2-tetrachloroethane	1.588 28	1.588 37[k]
		1.587 40[i]
trans-1,2-dichloroethene	1.250 53	1.250 2[l]
trichloroethene	1.455 66	1.455 44[m]

[a] Moumouzias et al. (1991). [b] Wilhelm et al. (1991). [c] Dreisbach (1961). [d] Ortega and Placido (1993). [e] Avedis et al. (1990). [f] Blanco and Ortega (1993). [g] Donhal and Patterson (1992). [h] Riddick et al. (1986). [k] Ortega, (1991). [i] Wilhelm et al. (1989). [l] Beilstein (1973). [m] Smith and Srivastava (1986) (interpolated from the Wagner density equation).

Binary mixtures were prepared from pure liquids weighed in air-tight bottles with a digital Mettler balance (Switzerland, model AE-160) to an accuracy of ±0.0001 g. The average uncertainty in the mole fraction is estimated to be about $\pm 5 \times 10^{-4}$, obtained from GLC on mixtures of varying mole fractions.

Densities and excess molar volumes were determined with an Anton Paar DMA 60/602 (Graz, Austria) digital vibrating tube density meter. These determinations are based on measuring the oscillation period T of the vibrating U-shaped hollow tube filled with the sample. The esti-

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Table 2. Densities, ρ, and Excess Molar Volumes, V_m^E, for Propylene Carbonate + Chlorohydrocarbons at 298.15 K and Atmospheric Pressure

x_1	ρ/(g·cm^{-3})	V_m^E/(cm^3·mol^{-1})	x_1	ρ/(g·cm^{-3})	V_m^E/(cm^3·mol^{-1})	x_1	ρ/(g·cm^{-3})	V_m^E/(cm^3·mol^{-1})	x_1	ρ/(g·cm^{-3})	V_m^E/(cm^3·mol^{-1})
Propylene Carbonate (1) + Dichloromethane (2)											
0.0744	1.307 20	−0.113	0.3043	1.277 74	−0.237	0.5135	1.251 85	−0.215	0.8469	1.214 78	−0.080
0.1113	1.302 54	−0.151	0.3495	1.272 00	−0.238	0.5178	1.251 34	−0.214	0.9133	1.208 02	−0.046
0.1343	1.299 62	−0.171	0.3887	1.267 08	−0.237	0.5753	1.244 56	−0.195			
0.1826	1.293 41	−0.201	0.4360	1.261 23	−0.231	0.6394	1.237 23	−0.174			
0.2410	1.285 89	−0.226	0.4682	1.257 25	−0.222	0.7189	1.228 38	−0.141			
Propylene Carbonate (1) + 1,2-Dichloroethane (2)											
0.0014	1.245 24	−0.022	0.3479	1.231 48	−0.173	0.5734	1.220 44	−0.136	0.9278	1.203 02	−0.026
0.0085	1.242 98	−0.098	0.4022	1.228 86	−0.169	0.6171	1.218 28	−0.125	0.9783	1.200 58	−0.007
0.1466	1.240 57	−0.137	0.4385	1.227 10	−0.165	0.6936	1.214 49	−0.103			
0.2167	1.237 55	−0.161	0.4808	1.225 00	−0.156	0.7566	1.211 38	−0.083			
0.2859	1.234 40	−0.171	0.5199	1.223 09	−0.149	0.8689	1.205 89	−0.046			
Propylene Carbonate (1) + 1,3-Dichloropropane (2)											
0.0044	1.179 53	−0.002	0.3176	1.184 58	0.015	0.5840	1.189 85	0.030	0.8001	1.194 62	0.024
0.1065	1.180 69	−0.001	0.4018	1.186 16	0.023	0.6486	1.191 22	0.030	0.8406	1.195 58	0.020
0.1876	1.182 18	0.004	0.4792	1.187 71	0.026	0.6977	1.192 29	0.029	0.9078	1.197 20	0.013
0.2535	1.183 39	0.010	0.5263	1.188 66	0.028	0.7056	1.192 47	0.029	0.9803	1.199 01	0.004
Propylene Carbonate (1) + 1,4-Dichlorobutane (2)											
0.0296	1.135 26	0.009	0.4297	1.156 56	0.104	0.6366	1.170 00	0.109	0.9424	1.194 24	0.028
0.1046	1.138 84	0.035	0.4881	1.160 18	0.108	0.6968	1.174 33	0.101	0.9817	1.197 81	0.009
0.2048	1.143 96	0.061	0.5224	1.162 37	0.109	0.7550	1.178 67	0.093			
0.2780	1.147 85	0.080	0.5604	1.164 82	0.112	0.8139	1.183 32	0.076			
0.3599	1.152 44	0.095	0.6025	1.167 66	0.110	0.9101	1.191 37	0.043			
Propylene Carbonate (1) + 1,6-Dichlorohexane (2)											
0.0411	1.067 77	0.021	0.4999	1.112 78	0.165	0.7079	1.142 98	0.154	0.9507	1.187 95	0.043
0.1328	1.075 20	0.065	0.5521	1.119 44	0.167	0.7479	1.148 52	0.144	0.9868	1.196 63	0.013
0.2459	1.085 33	0.108	0.5824	1.123 49	0.168	0.8012	1.157 82	0.127			
0.3279	1.093 37	0.137	0.6253	1.129 49	0.166	0.8539	1.167 70	0.103			
0.4200	1.103 32	0.154	0.6677	1.135 78	0.158	0.9195	1.181 10	0.065			
Propylene Carbonate (1) + 1,10-Dichlorodecane (2)											
0.0603	0.997 79	0.059	0.5852	1.065 16	0.307	0.7783	1.111 07	0.263	0.9322	1.166 17	0.130
0.1559	1.006 45	0.142	0.6443	1.077 26	0.305	0.8014	1.117 97	0.253	0.9539	1.176 06	0.094
0.2820	1.019 69	0.233	0.6641	1.081 70	0.299	0.8373	1.129 57	0.231			
0.4546	1.042 65	0.297	0.7175	1.094 49	0.288	0.8621	1.138 24	0.210			
0.5214	1.053 48	0.307	0.7609	1.106 10	0.271	0.8997	1.152 51	0.172			
Propylene Carbonate (1) + 1,1,1-Trichloroethane (2)											
0.0303	1.327 59	−0.089	0.3848	1.291 93	−0.535	0.6215	1.261 12	−0.516	0.9314	1.211 91	−0.140
0.0904	1.322 52	−0.215	0.4583	1.282 95	−0.553	0.6711	1.253 92	−0.481	0.9921	1.200 98	−0.017
0.1881	1.313 44	−0.376	0.4994	1.277 69	−0.552	0.7313	1.244 91	−0.431			
0.2511	1.306 96	−0.445	0.5366	1.272 82	−0.549	0.8010	1.233 92	−0.348			
0.3396	1.297 21	−0.513	0.5840	1.266 42	−0.536	0.8946	1.218 32	−0.205			
Propylene Carbonate (1) + 1,1,2,2-Tetrachloroethane (2)											
0.0393	1.576 70	−0.074	0.4076	1.454 43	−0.317	0.6436	1.361 64	−0.250	0.9361	1.230 72	−0.054
0.1209	1.552 32	−0.186	0.4694	1.431 19	−0.311	0.6893	1.342 36	−0.227	0.9877	1.205 61	−0.011
0.1976	1.527 73	−0.253	0.5141	1.413 91	−0.301	0.7416	1.319 78	−0.195			
0.2554	1.508 42	−0.286	0.5563	1.397 23	−0.288	0.8062	1.291 11	−0.153			
0.3600	1.471 79	−0.315	0.5882	1.384 39	−0.275	0.8957	1.249 92	−0.087			
Propylene Carbonate (1) + *trans*-1,2-Dichloroethene (2)											
0.0386	1.250 10	−0.107	0.3180	1.242 06	−0.566	0.5331	1.231 05	−0.590	0.7854	1.214 90	−0.359
0.1602	1.247 59	−0.372	0.3667	1.239 92	−0.597	0.6074	1.226 60	−0.548	0.8922	1.207 34	−0.194
0.1790	1.247 01	−0.401	0.4071	1.237 96	−0.610	0.6430	1.224 45	−0.523	0.9720	1.201 56	−0.053
0.2515	1.244 65	−0.502	0.4799	1.234 12	−0.609	0.7041	1.220 45	−0.463			
Propylene Carbonate (1) + Trichloroethene (2)											
0.0176	1.451 80	−0.025	0.3627	1.370 17	−0.255	0.6006	1.309 04	−0.238	0.9274	1.219 94	−0.055
0.0768	1.438 58	−0.095	0.4324	1.352 58	−0.260	0.6385	1.299 03	−0.228	0.9878	1.202 97	−0.009
0.1560	1.420 26	−0.163	0.4751	1.341 67	−0.259	0.7182	1.277 65	−0.193			
0.2577	1.395 97	−0.221	0.5117	1.332 26	−0.256	0.7857	1.259 25	−0.154			
0.3078	1.383 74	−0.240	0.5493	1.322 42	−0.246	0.8845	1.231 97	−0.088			

mated uncertainty in the density is 1×10^{-5} g·cm^{-3}. This technique requires two density standards; we used freshly boiled, bidistilled, and degassed water and dehumified air (Kohlrausch, 1968; Wagenreth and Blanke, 1971). The temperature was measured with a thermistor thermometer (Anton Paar DT 100-25, Graz, Austria) inserted into a thermowell in the glass densimeter cell with an accuracy of ±0.01 K, while an Hetotherm bath circulator (Heto 01 DBT 623, Birkerød, Denmark) maintained the temperature constant to within ±0.005 K. The description of the apparatus and the measurement procedure are reported elsewere (Fermeglia and Lapasin, 1988).

In an effort to estimate the accuracy of our equipment and experimental technique, the densities of the test system benzene + cyclohexane at 298.15 K were obtained and compared with those of the literature (Wilhelm, 1985). Agreement between our V_m^E data and those of the literature is within 0.5% in the central range of mole fraction. (Our value of V_m^E at $x = 0.5$ is 0.652 cm^3·mol^{-1}, lit. value 0.6514 cm^3·mol^{-1}).

All measurements were corrected for buoyancy and for evaporation of the components, which had only a small influence on the final mole fraction. Uncertainties in V_m^E are in the range $1 \cdot 10^{-3}$ to $3 \cdot 10^{-3}$.

Results and Discussion

Experimentally determined densities and derived excess molar volumes at (298.15 ± 0.01) K and atmospheric

Table 3. Adjustable Parameters, a_k, and Standard Deviations, $\sigma(V_m^E)$ Calculated According to Eq 1 for Propylene Carbonate + Chlorohydrocarbons at 298.15 K

mixture	a_0	a_1	a_2	a_3	$\sigma(V_m^E)/(cm^3 \cdot mol^{-1})$
propylene carbonate +					
dichloromethane	−0.8686	0.4897	−0.3123	0.1857	0.0009
1,2-dichloroethane	−0.6124	0.4045	−0.2544	0.1591	0.0015
1,3-dichloropropane	0.1119	0.0078	−0.0056	0.0057	0.0006
1,4-dichlorobutane	0.4392	0.1067			0.0010
1,6-dichlorohexane	0.6601	0.1563	0.0729	0.0067	0.0012
1,10-dichlorodecane	1.2145	0.2074	0.3867	0.5191	0.0020
1,1,1-trichloroethane	−2.2131	0.1280	−0.2710	0.2259	0.0028
1,1,2,2-tetrachloroethane	−1.2155	0.5041	−0.2095		0.0016
trans-1,2-dichloroethene	−2.4217	0.5146			0.0025
trichloroethene	−1.0302	0.1974	−0.0077	0.1328	0.0016

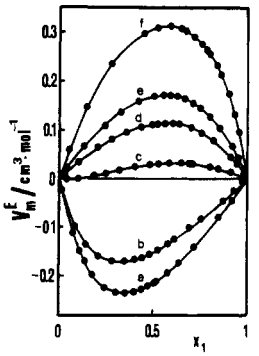

Figure 1. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures propylene carbonate (1) + dichloromethane (2) (a), + 1,2-dichloroethane (2) (b), + 1,3-dichloropropane (2) (c), + 1,4-dichlorobutane (2) (d), + 1,6-dichlorohexane (2) (e), and + 1,10-dichlorodecane (2) (f): (●), experimental points; solid curves, calculated from eq 1 using the parameters a_k of Table 3.

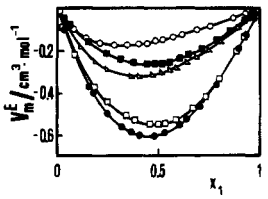

Figure 2. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures propylene carbonate (1) + *trans*-1,2-dichloroethene (2) (●), + 1,1,1-trichloroethane (2) (□), + 1,1,2,2-tetrachloroethane (1) (△), + trichloroethene (2) (■), and + 1,2-dichloroethane (2) (○): solid curves, calculated from eq 1 using the parameters a_k of Table 3.

pressure are given in Table 2 and graphically represented in Figures 1 and 2.

The dependence of excess molar volume as a function of composition may be expressed by the Redlich–Kister equation

$$V_m^E/(cm^3 \cdot mol^{-1}) = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \qquad (1)$$

where a_k are the adjustable parameters, x_1 is the mole fraction of propylene carbonate, and x_2 is the mole fraction of chlorohydrocarbons.

The values of a_k and the standard deviations $\sigma(V_m^E)$, obtained by the least-squares method (Green and Margerison, 1977; Francesconi and Comelli, 1994), are listed in Table 3.

Figure 3 reports the equimolar excess volumes $V_m^E(x = 0.5)$ plotted against n_c, the number of carbon atoms of dichloroalkanes.

Figures 1 and 3 show the regular increase of V_m^E with the increase of the chain length of the dichloroalkanes in mixtures with propylene carbonate. A similar trend is

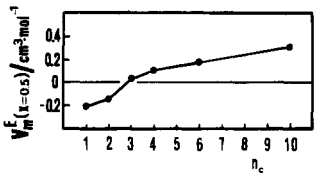

Figure 3. Values of equimolar volumes, $V_m^E(x = 0.5)$ at 298.15 K as a function of the number of carbon atoms n_c of the dichloroalkane molecules for the binary mixtures with propylene carbonate.

observed in the values of H_m^E for mixtures of diethyl carbonate with the same dichloro compounds (Comelli and Francesconi, 1995).

Figure 2 shows a plot of V_m^E against x_1 for the mixtures propylene carbonate (1) + 1,2-dichloroethane (2), + 1,1,1-trichloroethane (2), 1,1,2,2-tetrachloroethane (2), + *trans*-1,2-dichloroethene (2), or + trichloroethene (2).

An increase in the number of Cl atoms has no regular effect on the values of V_m^E, which are all negative. Instead, the V_m^E values for the mixtures dimethyl carbonate + 1,2-dichloroethane or + 1,1,1-trichloroethane are positive (Comelli and Francesconi, 1994), whereas the corresponding values of H_m^E are positive for the dichloro compound and negative for the trichloro compound.

Finally, the mixtures diethyl carbonate (1) + 1,2-dichloroethane (2) or 1,1,1-trichloroethane (2), or + 1,1,2,2-tetrachloroethane (2) have negative values of H_m^E.

A qualitative interpretation of the results may be attempted only for the mixtures of Figure 1, where the regular increase of the chain length of the dichloro compounds will be accompained by a corresponding increase of their dipole moments (Riddick et al., 1986) with an interaction energy between similar molecules stronger than that between dissimilar molecules after mixing and a consequent increase in V_m^E.

More difficult to interpret are the results for the mixtures of Figure 2, where hydrogen bonding chloro compound–propylene carbonate and steric effects of chloroalkenes (influencing packing of molecules in the mixtures) combine with dipole–dipole interactions.

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