Densities and Excess Molar Volumes of Propylene Carbonate + Linear and Cyclic Ketones at 298.15 K

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Densities, ϱ, and excess molar volumes, V_m^E, have been determined for the binary mixtures propylene carbonate + eight methyl n-alkyl ketones and + three cyclic ketones at 298.15 K and at atmospheric pressure. V_m^E increases with the increase of the chain length of linear ketones and decreases with the increase of the methyl groups of cyclic ketones. Smooth representations of the results are presented.

Introduction

Propylene carbonate is identified as an outstanding dipolar aprotic solvent, widely used in extractions and in electrochemical studies. Some lithium batteries have adopted mixed organic electrolytes containing propylene carbonate (*1–3*) since their molecules have no active hydrogen atoms reacting with lithium, which prevents the evolution of hydrogen into the cell. Furthermore, it was found that mixtures of more electrolytes present improved electrical properties compared with those of a pure solvent so that the studies of the physical properties of mixtures containing propylene carbonate are important. There are relatively few thermodynamic studies on the excess volumes of such mixtures, so we present in this paper new experimental data on densities, ϱ, and excess molar volumes, V_m^E, for the mixtures containing propylene carbonate (component 1) + eight methyl n-alkyl ketones and three cyclic ketones (component 2), namely, 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-octanone, 2-nonanone, 2-decanone, 2-undecanone, cyclohexanone, 2-methylcyclohexanone, and 2,6-dimethylcyclohexanone, respectively.

All measurements were carried out at 298.15 K and atmospheric pressure. To the best of our knowledge, no measurements of these mixtures have been published in the literature. Our previous works (*4–6*) report the excess molar enthalpies of propylene carbonate + linear and cyclic ketones and the excess molar volumes of dialkyl carbonates + linear and cyclic ketones.

Experimental Section

Materials. All compounds used in this study were purchased from Aldrich Chemical Co. with the exception of 2-pentanone which was from Fluka. Liquids were purity grade ≥99 mol % with the exception of 2-octanone, 2-decanone, and 2,6-dimethylcyclohexanone whose purity grades were 98 mol %. These three ones were fractionally distilled following the method of Collerson et al. (*7*) while the other solvents, owing to their high-grade purity, were used without further purification. Before measurements the liquids were stored in dark sealed containers, to prevent contamination from air, and dried over molecular sieves (Union Carbide, type 4A, 1/16-in. pellets).

Table 1. Comparison of Experimental Desities, ϱ, of Pure Components with Literature Data at 298.15 K

component	ϱ/(g·cm^{-3}) exptl	ϱ/(g·cm^{-3}) lit.
propylene carbonate	1.199 18	1.199 3 (*8*)
2-propanone	0.784 88	0.784 65 (*9*)
2-butanone	0.799 74	0.799 70 (*10*)
2-pentanone	0.801 76	0.801 5 (*10*)
2-hexanone	0.807 26	0.806 86[a] (*11*)
2-octanone	0.815 66	0.815 15[a] (*11*)
2-nonanone	0.817 58	0.817 29[a] (*11*)
2-decanone	0.820 09	
2-undecanone	0.822 19	0.822 15[a] (*11*)
cyclohexanone	0.942 46	0.942 21 (*12*)
2-methylcyclohexanone	0.920 85	0.920 48[a] (*11*)
2,6-dimethylcyclohexanone	0.910 37	

[a] Calculated from the density equation.

The purities of the compounds were checked by determining their densities at (298.15 ± 0.01) K and are reported in Table 1 in comparison with literature data (*8–12*).

Apparatus. Mixtures were prepared by mass using a Mettler balance (model AE 160) with air-tight-stoppered bottles with an accuracy of ±0.0001 g, charging the heavier component first to minimize the error in composition. Correction for buoyancy and for evaporation of the components had only a small influence on the final mole fraction, presenting an estimated uncertainty of 1×10^{-4}.

The densities were determined by using a digital density meter (Anton Paar DMA 60, Graz, Austria) equipped with a density measuring cell (DMA 602) with a sensitivity up to 10^{-6} for the measured period T and an estimated uncertainty in ϱ of 1×10^{-5} g·cm^{-3}. For each experimental set of measurements, the apparatus was calibrated with doubly distilled and degassed water (ϱ(298.15 K) = 0.997 047 g·cm^{-3} (*13*)) and dry air at atmospheric pressure (ϱ(298.15 K) = 0.001 185 g·cm^{-3} (*14*)). Details on the operating procedure of the apparatus are reported elsewere (*15*).

The temperature was maintained constant to ±0.005 K by means of a Hetotherm bath circulator (type 01 DBT 623) and checked by a temperature sensor (Anton Paar DT 100-25) inserted into the jacket of the measuring cell which could keep the temperature to within ±0.01 K.

Furthermore, the apparatus was checked with benzene + cyclohexane, the densities of which are accurately known

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

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) + 2-Propanone (2)							
0.0238	0.79715	−0.088	0.3224	0.93951	−0.665	0.5645	1.04141	−0.658	0.9012	1.16570	−0.184
0.0679	0.81948	−0.235	0.3992	0.97298	−0.694	0.5946	1.05330	−0.633	0.9464	1.18116	−0.102
0.1316	0.85089	−0.398	0.4201	0.98218	−0.704	0.6622	1.07930	−0.557			
0.2138	0.89002	−0.549	0.4655	1.00111	−0.702	0.7638	1.11717	−0.424			
0.2769	0.91910	−0.629	0.4955	1.01343	−0.688	0.8412	1.14485	−0.295			
				Propylene Carbonate (1) + 2-Butanone (2)							
0.0254	0.80996	−0.071	0.3760	0.95042	−0.541	0.6051	1.04196	−0.506	0.9402	1.17537	−0.105
0.0936	0.83741	−0.233	0.4317	0.97269	−0.555	0.6401	1.05597	−0.485	0.9808	1.19150	−0.034
0.1820	0.87278	−0.378	0.4769	0.99079	−0.555	0.7255	1.09000	−0.404			
0.2215	0.88858	−0.427	0.5196	1.00783	−0.546	0.7713	1.10827	−0.355			
0.3029	0.92117	−0.504	0.5436	1.01741	−0.537	0.8761	1.14991	−0.208			
				Propylene Carbonate (1) + 2-Pentanone (2)							
0.0278	0.81104	−0.064	0.4181	0.95055	−0.476	0.6365	1.03758	−0.434	0.9395	1.17063	−0.098
0.1089	0.83858	−0.215	0.4729	0.97173	−0.482	0.6820	1.05659	−0.403	0.9838	1.19143	−0.025
0.2029	0.87138	−0.343	0.5175	0.98933	−0.482	0.7570	1.08866	−0.339			
0.2692	0.89513	−0.406	0.5555	1.00445	−0.468	0.8122	1.11286	−0.276			
0.3566	0.92729	−0.456	0.5928	1.01961	−0.457	0.8972	1.15113	−0.162			
				Propylene Carbonate (1) + 2-Hexanone (2)							
0.0297	0.81563	−0.047	0.4680	0.95807	−0.353	0.6780	1.04233	−0.306	0.9550	1.17513	−0.059
0.0744	0.82849	−0.108	0.5054	0.97221	−0.353	0.7051	1.05413	−0.292	0.9862	1.19194	−0.016
0.2182	0.87222	−0.255	0.5502	0.98960	−0.349	0.7655	1.08131	−0.249			
0.3045	0.90034	−0.309	0.5890	1.00510	−0.341	0.8385	1.11585	−0.190			
0.3733	0.92388	−0.337	0.6241	1.01953	−0.333	0.9045	1.14878	−0.122			
				Propylene Carbonate (1) + 2-Octanone (2)							
0.0361	0.82339	−0.021	0.5216	0.95895	−0.113	0.7252	1.04230	−0.100	0.9646	1.17503	−0.016
0.1013	0.83799	−0.047	0.5681	0.97615	−0.114	0.7620	1.05986	−0.093	0.9859	1.18936	−0.005
0.2658	0.87908	−0.088	0.5926	0.98564	−0.115	0.8140	1.08618	−0.075			
0.3465	0.90190	−0.102	0.6516	1.00966	−0.111	0.8646	1.11378	−0.056			
0.4391	0.93068	−0.110	0.6842	1.02373	−0.108	0.9315	1.15369	−0.030			
				Propylene Carbonate (1) + 2-Nonanone (2)							
0.0412	0.82551	−0.012	0.5340	0.95504	−0.046	0.7437	1.04177	−0.031	0.9534	1.16464	−0.008
0.1220	0.84204	−0.031	0.6038	0.98095	−0.041	0.7728	1.05626	−0.028	0.9912	1.19243	−0.001
0.2967	0.88316	−0.048	0.63226	0.99227	−0.039	0.8297	1.08668	−0.023			
0.3482	0.89698	−0.048	0.6660	1.00636	−0.038	0.8743	1.11273	−0.018			
0.4680	0.93257	−0.049	0.7132	1.02734	−0.033	0.9418	1.15648	−0.009			
				Propylene Carbonate (1) + 2-Decanone (2)							
0.0559	0.82987	0.000	0.4767	0.92967	0.022	0.7425	1.03337	0.031	0.9145	1.13361	0.016
0.1763	0.85318	0.002	0.5660	0.95955	0.027	0.7472	1.03570	0.030	0.9463	1.15656	0.010
0.3261	0.88745	0.012	0.6420	0.98860	0.029	0.8102	1.06867	0.025	0.9905	1.19148	0.002
0.4130	0.91069	0.019	0.6859	1.00716	0.030	0.8563	1.09564	0.023			
				Propylene Carbonate (1) + 2-Undecanone (2)							
0.1198	0.84302	0.027	0.5854	0.96072	0.096	0.7419	1.02611	0.094	0.8942	1.11454	0.060
0.2783	0.87441	0.055	0.6392	0.98096	0.101	0.7724	1.04145	0.090	0.9356	1.14479	0.042
0.4074	0.90568	0.075	0.6703	0.99371	0.098	0.8139	1.06408	0.083	0.9648	1.16824	0.026
0.50625	0.93420	0.088	0.7071	1.00977	0.097	0.8410	1.08003	0.078	0.9916	1.19154	0.006
				Propylene Carbonate (1) + Cyclohexanone (2)							
0.0195	0.94649	0.009	0.4024	1.03260	0.102	0.6268	1.08998	0.099	0.9379	1.17989	0.023
0.0821	0.95966	0.034	0.4667	1.04846	0.105	0.6863	1.10619	0.090	0.9802	1.19318	0.005
0.1890	0.98292	0.068	0.5007	1.05703	0.106	0.7336	1.11940	0.080			
0.2780	1.00312	0.084	0.5552	1.07105	0.104	0.8086	1.14091	0.064			
0.3469	1.01922	0.098	0.5955	1.08163	0.101	0.8910	1.16548	0.039			
				Propylene Carbonate (1) + 2-Methylcyclohexanone (2)							
0.0288	0.92649	0.000	0.4346	1.01799	0.024	0.6716	1.08442	0.032	0.9514	1.18042	0.010
0.0933	0.93953	0.001	0.5102	1.03793	0.031	0.7152	1.09800	0.031	0.9861	1.19398	0.004
0.23156	0.96926	0.007	0.5499	1.04885	0.031	0.7670	1.11474	0.029			
0.2719	0.97843	0.010	0.5888	1.05988	0.033	0.8267	1.13489	0.025			
0.3931	1.00746	0.023	0.6234	1.06994	0.033	0.9128	1.16580	0.015			
				Propylene Carbonate (1) + 2,6-Dimethylcyclohexanone (2)							
0.0296	0.91574	−0.008	0.4965	1.01941	−0.002	0.6773	1.07310	0.008	0.9319	1.16870	0.005
0.1383	0.93647	−0.024	0.5304	1.02879	−0.001	0.7241	1.08887	0.010	0.9867	1.19329	0.001
0.2653	0.96303	−0.023	0.5623	1.03784	0.003	0.7631	1.10227	0.011			
0.3380	0.97951	−0.017	0.6181	1.05441	0.006	0.8007	1.11596	0.011			
0.3847	0.99067	−0.013	0.6465	1.06322	0.007	0.8912	1.15147	0.007			

from the literature (*16*) (our value V_m^E (x=0.5) = 0.652 cm^3·mol^{-1}; lit. (*16*) V_m^E (x=0.5) = 0.6514 cm^3·mol^{-1}). The excess molar volume is accurate to 0.004 cm^3·mol^{-1} at the worst and has been obtained through the formula

$$V_m^E = (x_1M_1 + x_2M_2)/\varrho - x_1M_1/\varrho_1 - x_2M_2/\varrho_2 \qquad (1)$$

where ϱ and ϱ_i are the densities of the mixture and of pure compound i.

Results and Discussion

Excess molar volumes, V_m^E, of the binary mixtures are listed in Table 2 and graphically represented in Figures 1

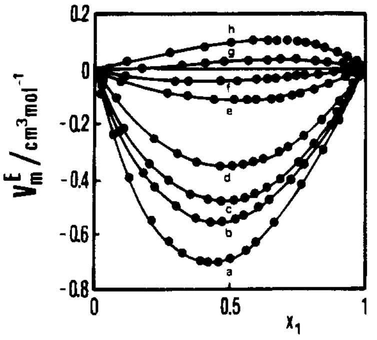

Figure 1. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures containing propylene carbonate + 2-propanone (a), + 2-butanone (b), + 2-pentanone (c), + 2-hexanone (d), + 2-octanone (e), + 2-nonanone (f), + 2-decanone (g), and + 2-undecanone (h): (●), experimental points; (solid curves) calculated from eq 1 using the parameters a_k of Table 3.

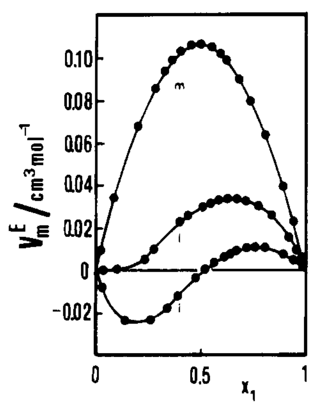

Figure 2. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures containing propylene carbonate + 2,6-dimethylcyclohexanone (i), + 2-methylcyclohexanone (l), and + cyclohexanone (m): (●), experimental points; (solid curves) calculated from eq 1 using parameters a_k of Table 3.

Table 3. Adjustable Parameters, a_k, and Standard Deviations, $\sigma(V_m^E)$, According to Eq 2 for Propylene Carbonate + Ketone Mixtures

mixture	a_0	a_1	a_2	a_3	$\sigma(V_m^E)$/(cm³·mol⁻¹)
propylene carbonate +					
2-propanone	−2.7556	0.7474	−0.1095	0.2950	0.0030
2-butanone	−2.2028	0.4461	−0.1331		0.0030
2-pentanone	−1.9280	0.2502	−0.1034		0.0029
2-hexanone	−1.4180	0.0831	0.0073		0.0018
2-octanone	−0.4582	−0.0944	−0.0704	0.1856	0.0014
2-nonanone	−0.1866	0.0804	−0.0706		0.0006
2-decanone	0.0957	0.1225			0.0007
2-undecanone	0.3498	0.2326	0.1522		0.0013
cyclohexanone	0.4235	−0.0183			0.0012
2-methylcyclohexanone	0.1153	0.1140	−0.0410	0.0010	
2,6-dimethylcyclohexanone	−0.0107	0.1833	−0.1032		0.0008

and 2. The composition dependence of V_m^E has been calculated in accordance with the Redlich–Kister equation

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1 x_2 \sum_{k=0} a_k (x_1 - x_2)^k \qquad (2)$$

where x_1 is the mole fraction of propylene carbonate and x_2 the mole fraction of ketone.

The adjustable parameters a_k, determined by the method of least squares with all points equally weighted, and the standard deviations $\sigma(V_m^E)$ are reported in Table 3. As can be seen, the V_m^E values increase regularly with the increase of the chain length of linear ketones. A similar pattern is shown by the V_m^E values of dimethyl carbonate or diethyl carbonate + the same linear ketones (*4, 5*).

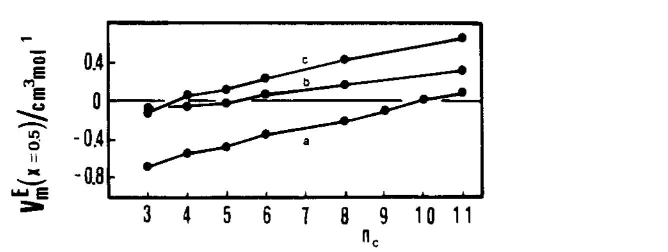

Figure 3. Values of equimolar excess volumes, $V_m^E(x{=}0.5)$ at 298.15 K as a function of the number of carbon atoms, n_c, in the linear ketones: (a) propylene carbonate + methyl *n*-alkyl ketones; (b) diethyl carbonate + methyl *n*-alkyl ketones; or (c) dimethyl carbonate + methyl *n*-alkyl ketones; see refs 3 and 4.

These results are also illustrated by Figure 3, where the equimolar excess volumes $V_m^E(x{=}0.5)$ are plotted against n_c, the number of carbon atoms of methyl *n*-alkyl ketones. The equimolar excess volumes of diethyl carbonate or dimethyl carbonate + methyl *n*-alkyl ketones (*4, 5*) are also represented in this graph.

As for the cyclic ketones, the increasing number of methyl groups in the cyclohexane molecule leads to decreased values of V_m^E; see Figure 2.

The behavior of H_m^E for the binary mixtures of propylene carbonate with the ketones of this paper is contradictory (*6*). In fact, mixtures containing linear ketones display the same regular increase of H_m^E shown by V_m^E, whereas mixtures containing cyclic ketones show a reverse trend for H_m^E and V_m^E, with the increasing size of the ketones.

Dimethyl carbonate in mixtures with the same cyclic ketones (*5*) does not show a regular trend, since the V_m^E values increase in the order 2-methylcyclohexanone < 2,6-dimethylcyclohexanone < cyclohexanone. The complexity in the molecular structure of these mixtures and the contrast among the results from comparable systems make it difficult to make either a theoretical or a qualitative treatment of the results.

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