Densities and Excess Molar Volumes of Dimethyl Carbonate + Six Methyl *n*-Alkyl Ketones at 298.15 K and Atmospheric Pressure

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Densities and excess molar volumes of dimethyl carbonate + six methyl *n*-alkyl ketones, namely, 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-octanone, and 2-undecanone, have been determined at 298.15 K and atmospheric pressure using an Anton Paar density meter. The results have been correlated by means of the Redlich-Kister equation, and the adjustable parameters have been determined by the least-squares method. All excess volumes are positive with the exception of dimethyl carbonate + 2-propanone. $V^E_m(x_1=0.5)$ increases as the chain length of the ketones increases.

Introduction

Recently, the systematic study of excess properties of some methyl *n*-alkyl ketones has been the subject of our research program. Up to now we have measured excess molar enthalpies (*1-4*) or excess molar volumes (*5*, *6*) of methyl alkyl ketones with aliphatic or aromatic compounds, and as a continuation of our work, we report in this paper the volumetric behavior of dimethyl carbonate (1) + six methyl *n*-alkyl ketones (2), namely, 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-octanone, or 2-undecanone.

The purpose of this work is to investigate the influence of the chain length of the ketones on the excess volumes. As far as we know, no excess volume data have been reported previously for these mixtures.

Experimental Section

Materials. Methyl *n*-alkyl ketones, with the exception of 2-hexanone, are the same as used in ref 5, and their purifications are there described.

2-Hexanone and dimethyl carbonate, two Aldrich products, both with a purity of +99 mol %, were used as received. Before measurements, all liquids were carefully dried with molecular sieves (Union Carbide type 4 A, 1/16-in. pellets) and stored in dark bottles. Values of their densities at 298.15 K and atmospheric pressure are listed in Table 1 along with those of literature data.

Density Measurements. Densities, ρ, of the pure components and binary mixtures were measured with an Anton Paar digital density meter (model DMA 60/602), with a resolution of 2×10^{-6} g cm^{-3}, by determining the period of oscillation T of the sample (T = 10 K period select switch) in a U tube. For each experimental set of measurements, the apparatus was calibrated with doubly distilled and degassed water (ρ at 298.15 = 0.997 047 g/cm^{-3} (*7*)) and dry air at atmospheric pressure (ρ at 298.15 K = 0.001 185 g cm^{-3} (*8*)). The temperature of the water bath containing the oscillator tube was kept constant to within ±0.005 K with a Hetotherm bath circulator (type 01 DBT 623), and temperature was detected with a digital precision thermometer (Anton Paar DT 100-25). The overall precision of the density measurement is estimated to be better than 3×10^{-6} g cm^{-3}.

Table 1. Experimental Densities, ρ, at 298.15 K and Comparison with Literature Data

component	ρ/(g cm^{-3}) this paper	ρ/(g cm^{-3}) kit.
dimethyl carbonate	1.063 35	1.063 50 (*10*)
2-propanone	0.784 37	0.784 40 (*11*)
2-butanone	0.799 71	0.799 70 (*11*)
2-pentanone	0.801 52	0.801 5 (*11*)
2-hexanone	0.806 74	0.806 7 (*11*)
2-octanone	0.814 84	0.814 8 (*11*)
2-undecanone	0.822 31	0.822 16[a] (*12*)

[a] Calculated from the density equation.

The following equation was used to evaluate the V^E_m values from density measurements:

$$V^E_m = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

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

Binary mixtures were prepared by weighing samples in small vessels of about 15 cm^3, using a Mettler balance (model A 160) with a precision of 1×10^{-4} g.

Correction for vapor space was performed but had only a small influence on the final mole fraction for which uncertainties of 1×10^{-4} were estimated. Thus, the excess molar volume is accurate to 0.003 cm^3 mol^{-1} at the maximum value.

The mixtures were pressed into the density meter without losses by evaporation or contact with air. Before the measurements, the apparatus was checked with benzene + cyclohexane for which the densities are accurately known from the literature (*9*) (our value of V^E_m at 0.5 mole fraction is 0.652 cm^3 mol^{-1} (lit. value 0.6516)).

Results

Densities, ρ, and excess molar volumes, V^E_m, for the six binary systems are listed in Table 2. The excess volumes of the same mixtures as a function of the mole fraction of dimethyl carbonate are graphically represented in Figure 1. The following Redlich-Kister polynomial was used to express

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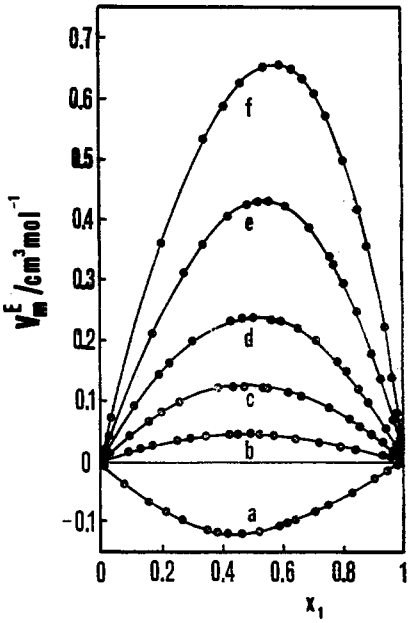

Figure 1. Excess molar volumes V^E_m at 298.15 K and atmospheric pressure for the binary mixtures containing dimethyl carbonate (1) + 2-propanone (2) (a), + 2-butanone (2) (b), + 2-pentanone (2) (c), + 2-hexanone (2) (d), + 2-octanone (2) (e), and + 2-undecanone (2) (f).

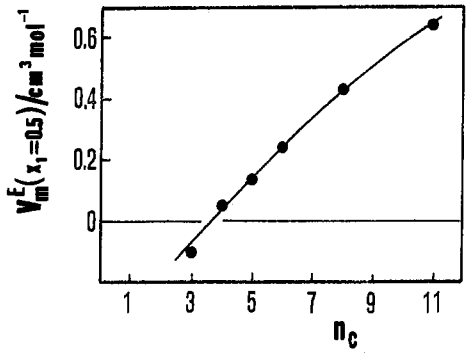

Figure 2. Values of equimolar volumes $V^E_m(x_1=0.5)$ at 298.15 K and atmospheric pressure as a function of the number of carbon atoms of the ketones, n_c, for the binary mixtures of dimethyl carbonate + methyl *n*-alkyl ketones.

the dependence of the excess volumes on composition:

$$V^E_m/x_1x_2 = \sum_{k\geq 0} A_k(x_1 - x_2)^k \qquad (2)$$

The values of adjustable parameters A_k, determined by the least-squares method, are included in Table 3 along with the standard deviations $\sigma(V^E_m)$ defined as

$$\sigma(V^E_m) = |\phi_{min}/(N-n)|^{0.5} \qquad (3)$$

where ϕ_{min} is the minimum of the objective function ϕ:

$$\phi = \sum_{k=1}^{N} \eta_k^2 \qquad (4)$$

N is the number of experimental points, $\eta_k = V^E_{m,calc} - V^E_m$ with $V^E_{m,calc}$ determined from the right-hand side of eq 2, and n is the number of the adjustable parameters.

Figure 2 shows equimolar values of $V^E_m(x_1=0.5)$, plotted against the number n_c of carbon atoms of methyl *n*-alkyl ketones.

Table 2. Experimental Densities, ρ, and Excess Molar Volumes, V^E_m, for Binary Mixtures Containing Dimethyl Carbonate (1) + Methyl *n*-Alkyl Ketones (2) at 298.15 K

x_1	ρ/(g cm^{-3})	V^E_m/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V^E_m/(cm^3 mol^{-1})
Dimethyl Carbonate + 2-Propanone					
0.0142	0.788 90	−0.001	0.5993	0.961 74	−0.108
0.0796	0.809 86	−0.036	0.6170	0.966 48	−0.105
0.1593	0.834 80	−0.067	0.6405	0.972 76	−0.103
0.2132	0.851 32	−0.083	0.7028	0.989 10	−0.087
0.2704	0.868 53	−0.097	0.7524	1.001 94	−0.075
0.3382	0.888 55	−0.110	0.8331	1.022 37	−0.048
0.3786	0.900 26	−0.114	0.9094	1.041 36	−0.029
0.4157	0.910 92	−0.117	0.9477	1.050 68	−0.015
0.4674	0.925 54	−0.120	0.9773	1.057 87	−0.006
0.5255	0.941 66	−0.117			
Dimethyl Carbonate + 2-Butanone					
0.0130	0.803 01	0.002	0.5286	0.934 58	0.041
0.0925	0.822 71	0.015	0.5781	0.947 71	0.040
0.1293	0.831 91	0.020	0.65p14	0.967 27	0.039
0.1725	0.842 69	0.024	0.7276	0.987 91	0.031
0.2550	0.863 63	0.034	0.7958	1.006 50	0.028
0.2997	0.875 02	0.037	0.8421	1.019 25	0.022
0.3522	0.888 54	0.038	0.9338	1.044 76	0.010
0.4328	0.909 41	0.043	0.9610	1.052 38	0.006
0.4529	0.914 67	0.043	0.9833	1.058 65	0.003
0.5047	0.928 28	0.042			
Dimethyl Carbonate + 2-Pentanone					
0.0292	0.807 47	0.014	0.6216	0.948 08	0.116
0.0974	0.821 71	0.044	0.6693	0.961 34	0.108
0.1539	0.833 84	0.062	0.7600	0.987 48	0.088
0.2018	0.844 37	0.081	0.8191	1.005 23	0.071
0.2595	0.853 73	0.097	0.8333	1.009 57	0.067
0.3900	0.888 18	0.119	0.8950	1.028 88	0.045
0.4392	0.900 32	0.124	0.9329	1.041 10	0.030
0.4693	0.907 87	0.126	0.9763	1.055 39	0.011
0.5419	0.926 66	0.122	0.9830	1.057 60	0.009
0.5535	0.929 74	0.121			
Dimethyl Carbonate + 2-Hexanone					
0.0243	0.812 59	0.021	0.6525	0.949 61	0.220
0.1165	0.828 91	0.090	0.7136	0.967 07	0.199
0.1964	0.843 92	0.143	0.7832	0.988 14	0.166
0.2329	0.851 07	0.162	0.8123	0.997 33	0.150
0.3092	0.866 66	0.196	0.8572	1.012 06	0.120
0.4359	0.894 64	0.231	0.8854	1.021 63	0.101
0.4694	0.902 51	0.237	0.9458	1.043 05	0.049
0.5075	0.911 72	0.238	0.9707	1.052 23	0.027
0.5691	0.927 29	0.234	0.9899	1.059 47	0.010
0.5939	0.933 77	0.231			
Dimethyl Carbonate + 2-Octanone					
0.0303	0.818 94	0.043	0.6923	0.947 62	0.391
0.1724	0.838 87	0.214	0.7597	0.968 23	0.342
0.2789	0.855 91	0.314	0.7763	0.973 63	0.328
0.3412	0.866 87	0.359	0.8109	0.985 37	0.294
0.4322	0.884 38	0.407	0.8475	0.998 55	0.250
0.4975	0.898 25	0.426	0.9006	1.019 18	0.177
0.5233	0.904 06	0.429	0.9232	1.028 51	0.140
0.5603	0.912 76	0.428	0.9654	1.047 02	0.070
0.6195	0.927 59	0.420	0.9889	1.058 03	0.022
0.6541	0.936 85	0.409			
Dimethyl Carbonate + 2-Undecanone					
0.0357	0.826 47	0.073	0.7517	0.951 39	0.573
0.2096	0.845 02	0.363	0.8067	0.970 21	0.501
0.3587	0.865 07	0.540	0.8431	0.984 16	0.440
0.4176	0.874 38	0.591	0.8529	0.988 12	0.420
0.4741	0.884 23	0.625	0.8822	1.000 68	0.357
0.5467	0.898 40	0.652	0.9335	1.025 81	0.223
0.6052	0.911 31	0.655	0.9597	1.039 29	0.146
0.6332	0.918 03	0.649	0.9769	1.049 15	0.087
0.6708	0.927 71	0.635	0.9901	1.057 15	0.039
0.712	0.939 18	0.611			

Discussion

Figures 1 and 2 show a regular increase of V^E_m with the increased chain length of the methyl *n*-alkyl ketones in mixtures with dimethyl carbonate.

Table 3. Values of the Adjustable Parameters A According to Equation 2 and Standard Deviations $\sigma(V^E_m)$ for Mixtures Containing Dimethyl Carbonate + Methyl *n*-Alkyl Ketones at 298.15 K

mixture	A_0	A_1	A_2	$\sigma(V^E_m)$/ (cm^3 mol^{-1})
dimethyl carbonate				
+ 2-propane	−0.4737	0.0966	0.1076	0.0018
+ 2-butanone	0.1700	−0.0109		0.0009
+ 2-pentanone	0.4946	−0.0141		0.0013
+ 2-hexanone	0.9459	0.0650		0.0012
+2-octanone	1.7049	0.3304		0.0011
+2-undecanone	2.5469	0.8393	0.4145	0.0016

Only the mixture dimethyl carbonate + 2-propanone has negative values of V^E_m, and all plots of V^E_m against x_1 are nearly symmetric.

The behavior of dimethyl carbonate in mixtures with the ketones in Figure 1 may be qualitatively accounted for if we consider that, during mixing, the ketone associates will be partially destroyed with a consequent volume increase, whereas interactions between the C=O groups of dissimilar molecules contribute to a reduction of volume.

The regular increase of V^E_m as a function of the chain length of the ketones seems to suggest the prevailence of the former effect with the increase of the number of carbon atoms of the ketones.

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