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Excess Molar Volumes of Binary Mixtures Containing Dimethyl Carbonate + Linear and Cyclic Ethers

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Densities and excess molar volumes of the six systems containing dimethyl carbonate + two linear and four cyclic ethers have been determined at atmospheric pressure and 298.15 K using an Anton Paar density meter. The results were correlated by a polynomial function. The results are discussed in terms of molecular interactions between dimethyl carbonate and the ring size of the ethers.

Introduction

In continuation of our studies of the thermodynamic properties of binary liquids containing linear or cyclic ethers (*1*–*6*), we report in this paper some volumetric measurements at atmospheric pressure and at 298.15 K of dimethyl carbonate (component 1) + two linear and four cyclic ethers (component 2), namely, dimethoxymethane, 1,2-dimethoxyethane, oxolane, oxane, 1,3-dioxolane, or 1,4-dioxane. The results are interpretated in terms of molecular interactions between the components in such mixtures.

We are not aware of any volumetric data in the literature for the systems presented in this study.

Experimental Section

Materials. Dimethyl carbonate, an Aldrich product, purity 99+ mol %, was used as received. Linear and cyclic ethers are the same as those considered in ref 6. The purities of the cyclic ethers were 99 mol % with the exception of 2,2-dimethoxypropane (analytical grade 98+ mol %) which was fractionally distilled with lithium aluminum hydride.

Before measurements, all liquids were carefully dried with molecular sieves (Union Carbide Type 4A, 1/16-in. pellets) and stored in dark bottles.

Volumetric Measurements. Densities, ρ, of pure components and binary mixtures were determined by an Anton Paar density meter (model DMA 60/602), with a resolution of 2×10^{-6} g cm^{-3} achieved by determining the period of oscillation T of the sample in a U-tube (T = 10 000 period select switch).

Double-distilled and degassed water and dry air were used to calibrate the apparatus, and before measurements the apparatus was checked with benzene + cyclohexane for which densities are accurately known from the literature (*7*) (our value of V^E at 0.5 mole fraction was 0.652 cm^3 mol^{-1} (lit. value 0.6516)).

The temperature of the density meter was measured with a digital thermometer (Anton Paar DT-25), and the temperature of the water bath containing the U-tube was kept constant to within ±0.005 K with a Hetotherm bath circulator (type 01 DBT 623).

The precision of the density measurements is estimated to be on the order of $\pm 3 \times 10^{-6}$ g cm^{-3}. Mixtures were prepared by mass in small air-tight stoppered vessels of about 15 cm^3, using a Mettler balance (model A 160) with a precision of 1×10^{-4} g.

Table 1. Experimental Measurements of Densities ρ for Pure Liquids

		ρ/(g cm^{-3})	
component	T/K	this work	lit.
dimethyl carbonate	298.15	1.063 35	1.063 50 (*10*)
dimethoxymethane	288.15	0.866 48	0.866 45 (*11*)
1,2-dimethoxyethane	298.15	0.863 60	0.863 70 (*11*)
oxolane	298.15	0.882 43	0.882 30 (*12*)
oxane	298.15	0.879 11	0.879 1 (*13*)
1,3-dioxolane	298.15	1.058 64	1.058 65 (*11*)
1,4-dioxane	298.15	1.028 07	1.027 97 (*12*)

All weighings were corrected for buoyancy and for evaporation of components so that the excess molar volume V^E is estimated to be accurate to be ±0.002 cm^3 mol^{-1} at the maximum value.

The performance, the operating procedure of the apparatus, and the procedure of preparing samples are described in ref 8.

Results and Discussion

Densities, ρ, of pure components are reported in Table 1 in comparison with literature data, while densities and the derived excess molar volumes, V^E, for dimethyl carbonate mixtures are listed in Table 2 as a function of the composition of component 1 and graphically represented in Figure 1.

The Redlich–Kister polynomial

$$V^E/x_1x_2 = \sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (1)$$

was fitted to the results for each mixture by the method of least squares (detailed in ref 9). The values of the coefficients a_k are given in Table 3, along with the standard deviation $\sigma(V^E)$. These coefficients were used to calculate the solid curves in Figure 1.

A qualitative interpretation of the curves in Figure 1 may be achieved in terms of molecular interactions between molecules. In fact, owing to the C=O group, the ester molecule may be conceived to be partially associated in the pure liquid. During mixing with an ether, dissociation of the ester and interaction with negative O atoms of ethers will occur, which contribute to a volume increase and decrease, respectively. The trends of Figure 1 seem to indicate the prevalence of ester dissociation in mixtures with cyclic ethers and relatively small ester–ether interactions. The larger

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Table 2. Densities ρ and Experimental Excess Molar Volumes V^E at 298.15 K

x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})	x_1	ρ/(g cm^{-3})	V^E/(cm^3 mol^{-1})
Dimethyl Carbonate (1) + Dimethoxymethane (2)					
0.0165	0.860 27	−0.009	0.4698	0.952 51	−0.094
0.0996	0.877 08	−0.046	0.5011	0.958 94	−0.091
0.1676	0.890 85	−0.065	0.5614	0.971 34	−0.083
0.2326	0.904 09	−0.083	0.6402	0.987 64	−0.071
0.2915	0.916 09	−0.093	0.7266	1.00 58	−0.054
0.3434	0.926 64	−0.095	0.7976	1.020 43	−0.039
0.4013	0.938 48	−0.097	0.8348	1.028 25	−0.031
0.4346	0.945 30	−0.095	0.9228	1.046 87	−0.014
0.4448	0.947 39	−0.095	0.9841	1.059 94	−0.003
Dimethyl Carbonate (1) + Dimethoxyethane (2)					
0.0870	0.876 46	−0.007	0.5244	0.956 79	0.020
0.2114	0.897 97	−0.008	0.5509	0.962 11	0.024
0.2677	0.908 02	−0.003	0.5889	0.969 89	0.025
0.3292	0.919 24	0.002	0.6579	0.984 33	0.028
0.3780	0.928 86	0.006	0.7347	1.000 10	0.030
0.3792	0.928 58	0.007	0.8064	1.016 99	0.028
0.4013	0.932 76	0.009	0.8606	1.029 51	0.024
0.4328	0.938 81	0.011	0.9243	1.044 66	0.016
0.4950	0.950 95	0.016	0.9843	1.059 40	0.005
0.5065	0.953 25	0.016			
Dimethyl Carbonate (1) + Oxolane (2)					
0.0118	0.884 51	0.011	0.4377	0.960 35	0.248
0.1237	0.904 32	0.109	0.4702	0.966 22	0.250
0.1349	0.906 82	0.117	0.4929	0.970 31	0.250
0.1659	0.911 81	0.139	0.5480	0.980 25	0.250
0.2361	0.924 81	0.180	0.7095	1.009 57	0.211
0.3011	0.935 86	0.213	0.7429	1.015 70	0.196
0.3218	0.939 60	0.218	0.8261	1.031 00	0.150
0.3502	0.944 66	0.230	0.9003	1.044 72	0.093
0.4333	0.959 57	0.247	0.9697	1.057 66	0.031
Dimethyl Carbonate (1) + Oxane (2)					
0.0187	0.881 77	0.036	0.5952	0.977 69	0.418
0.0848	0.891 41	0.148	0.5968	0.977 96	0.421
0.1845	0.906 59	0.280	0.6618	0.990 59	0.389
0.2583	0.918 33	0.353	0.7460	1.007 63	0.328
0.3154	0.927 70	0.394	0.8006	1.018 93	0.275
0.4147	0.944 66	0.434	0.8812	1.036 32	0.181
0.4446	0.949 93	0.439	0.9072	1.042 07	0.147
0.4730	0.955 02	0.441	0.9854	1.059 91	0.027
0.4953	0.959 04	0.442	0.9872	1.060 3	0.023
0.5346	0.966 27	0.436			
Dimethyl Carbonate (1) + 1,3-Dioxolane (2)					
0.0396	1.058 86	0.001	0.4601	1.060 82	0.015
0.0656	1.058 99	0.002	0.5048	1.061 03	0.015
0.1136	1.059 23	0.003	0.5236	1.061 11	0.015
0.1891	1.059 60	0.006	0.5820	1.061 37	0.016
0.2516	1.059 89	0.008	0.6563	1.061 70	0.017
0.2875	1.060 05	0.009	0.7058	1.061 92	0.016
0.3347	1.060 26	0.011	0.8082	1.062 39	0.014
0.3646	1.060 40	0.012	0.8669	1.062 68	0.010
0.3996	1.060 56	0.013	0.9815	1.063 24	0.002
0.4190	1.060 64	0.014			
Dimethyl Carbonate (1) + 1,4-Dioxane (2)					
0.0173	1.028 57	0.011	0.5098	1.044 09	0.154
0.0889	1.030 52	0.056	0.5500	1.045 52	0.152
0.1766	1.033 08	0.098	0.6417	1.048 93	0.138
0.2388	1.034 98	0.121	0.7240	1.052 08	0.118
0.2770	1.036 19	0.131	0.7668	1.053 75	0.105
0.3372	1.038 15	0.144	0.8499	1.057 08	0.074
0.3783	1.039 52	0.149	0.8544	1.057 26	0.072
0.4211	1.040 97	0.153	0.9108	1.059 58	0.047
0.4669	1.042 57	0.154	0.9832	1.062 63	0.009
0.4758	1.042 88	0.154			

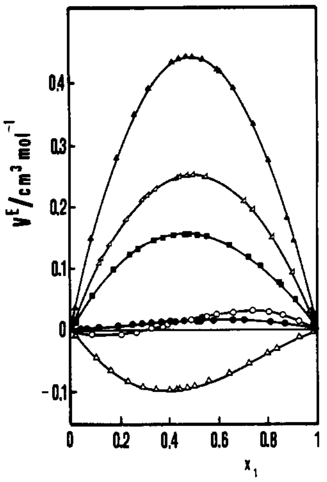

Figure 1. Excess molar volumes at 298.15 K and atmospheric pressure for dimethyl carbonate + dimethoxymethane (△), + 1,2-dimethoxyethane (○), + oxolane (◿), + oxane (▲), + 1,3-dioxolane (■), and + 1,4-dioxane (●). Solid curves calculated from eq 1 using coefficients a_k of Table 3.

Table 3. Coefficients a_k and Standard Deviations $\sigma(V^E)$ of Equation 1

mixture	a_0	a_1	a_2	$\sigma(V^E)$/(cm^3 mol^{-1})
dimethyl carbonate				
+ dimethoxymethane	−0.3614	0.1963		0.0011
+ 1,2-dimethoxyethane	0.0688	0.1829		0.0011
+ oxolane	1.0117	0.0251		0.0015
+ oxane	1.7640	−0.1133	0.0875	0.0011
+ 1,3-dioxolane	0.0612	0.0376		0.0003
+ 1,4-dioxane	0.6185	−0.0698		0.0011

interactions of the ester with diethers, with respect to the ones with monoethers, may explain the lower values of the V^E for the mixtures dimethyl carbonate + diethers, whereas the differences of V^E between oxane and oxolane or dioxane and dioxolane may be due to steric effects, leading to different molecular packing in the mixture.

As to the linear ethers, dimethoxymethane shows a curve similar to that of dioxolane, whereas the smaller molecule of dimethoxymethane exhibits large interactions with the ester and probably the most efficient packing in the mixture with the result of a negative V^E.

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