Densities and Excess Molar Volumes of Binary Mixtures Containing Diethyl Carbonate + Linear or Cyclic Ketones at 298.15 K

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Excess molar volumes, V_m^E, for binary mixtures containing diethyl carbonate + 2-propanone, + 2-butanone, + 2-pentanone, + 2-hexanone, + 2-octanone, + 2-undecanone, + cyclohexanone, + 2-methylcyclohexanone, or + 2,6-dimethylcyclohexanone have been determined from density measurements at 298.15 K using an Anton Paar DMA 60/602 vibrating density meter. Mixtures of diethyl carbonate with linear ketones show a regular increase of V_m^E with the ketone chain length. Irregular trends and lower values of V_m^E are displayed by the diethyl carbonate + cyclic ketones. Results have been correlated by means of the Redlich–Kister equation.

Introduction

Continuing our research on the thermodynamic properties of binary mixtures containing ketones (*1–6*), we report new experimental results for the densities, ϱ, and excess molar volumes, V_m^E, of nine binary mixtures including diethyl carbonate as the common component (component 1) and nine ketones (six linear and three cyclic) as the noncommon components (component 2). The ketones are 2-propanone, 2-butanone, 2-pentanone, 2-hexanone, 2-octanone, 2-undecanone, cyclohexanone, 2-methylcyclohexanone, and 2,6-dimethylcyclohexanone. The aim of this research is to correlate the experimental results. All measurements were determined at atmospheric pressure and 298.15 K. We are not aware of any measurements on the excess volumes of these systems.

Experimental Section

Materials. All liquids used were from Aldrich: their purities were better than 99 mol % with the exception of 2-octanone and 2,6-dimethylcyclohexanone whose purity was +98 mol %. 2-Octanone was purified following the method of Collerson et al. (*7*) while 2,6-dimethylcyclohexanone, a mixture of isomers, was used as received. No further purification was attempted for the other liquids owing to their high-purity grade.

Refractive Index and Density Measurements. The purity of the solvents was further ascertained by comparing their refractive indices and densities with the corresponding literature values (*8–14*); see Table 1. The refractive indices n_D were obtained by means of a calibrated Abbe refractometer (Carl Zeiss, Jena, precision ±0.0001). The densities ϱ of the pure components and mixtures were determined by means of an Anton Paar DMA 60/602 vibrating density meter (Anton Paar, Graz, Austria) with a resolution of $\pm 1 \times 10^{-6}$ g·cm^{-3}. Details on the apparatus and procedure are described elsewhere (*15*). The composition of each mixture was determined directly by mass, with an uncertainty in the mole fraction of about 2×10^{-4}.

Table 1. Densities, ϱ, and Refractive Indices, n_D, of the Pure Compounds at 298.15 K and Comparison with Literature Values

	ϱ/(g·cm^{-3})		n_D	
component	this paper	lit.	this paper	lit.
diethyl carbonate	0.969 20	0.969 26 (*8*)	1.3827	1.382 87 (*8*)
2-propanone	0.784 80	0.784 70 (*9*)	1.3567	1.355 96 (*8*)
2-butanone	0.799 50	0.799 66 (*10*)	1.3767	1.376 85 (*8*)
2-pentanone	0.801 71	0.801 57 (*11*)	1.3885	1.388 49 (*8*)
2-hexanone	0.807 23	0.806 70 (*8*)	1.3992	1.398 7 (*8*)
2-octanone	0.815 56	0.815 15 (12)	1.4139	1.413 3 (*8*)
2-undecanone	0.823 25	0.823 15 (*12*)	1.4289[a]	1.428 99[a] (*13*)
cyclohexanone	0.942 20	0.942 21 (*14*)	1.4499	1.450 0 (*8*)
2-methylcyclo-hexanone	0.921 54	0.921 48 (*12*)	1.4483[a]	1.448 5[a] (*13*)
2,6-dimethyl-cyclohexanone	0.912 12		1.4470[a]	1.447 0[a] (*13*)

[a] At 291.15 K.

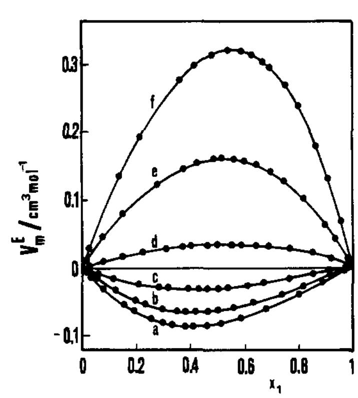

Figure 1. Excess molar volumes at 298.15 K for the binary mixtures containing diethyl carbonate + linear ketones: a–f refer to diethyl carbonate + 2-propanone, + 2-butanone, + 2-pentanone, + 2-hexanone, + 2-octanone, and + 2-undecanone mixtures, respectively.

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Table 2. Mole Fractions, x_1, Densities, ϱ, and Excess Molar Volumes, V^E_m, for Diethyl Carbonate + Linear or Cyclic Ketones 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})	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})
					Diethyl Carbonate (1) + 2-Propanone (2)						
0.0120	0.788 51	−0.008	0.2563	0.852 31	−0.076	0.4630	0.893 79	−0.086	0.8941	0.956 99	−0.021
0.0271	0.793 05	−0.016	0.3015	0.862 18	−0.079	0.5131	0.902 53	−0.081	0.9805	0.967 02	−0.004
0.0759	0.807 09	−0.032	0.3340	0.869 01	−0.083	0.5889	0.914 97	−0.074			
0.1605	0.829 52	−0.055	0.3816	0.878 56	−0.086	0.6806	0.928 85	−0.063			
0.1958	0.838 17	−0.062	0.4104	0.884 10	−0.087	0.8077	0.946 23	−0.038			
					Diethyl Carbonate (1) + 2-Butanone (2)						
0.0184	0.803 76	−0.006	0.2972	0.861 75	−0.061	0.5053	0.898 46	−0.064	0.9183	0.958 81	−0.010
0.0553	0.812 10	−0.017	0.3471	0.871 02	−0.065	0.5595	0.907 24	−0.060	0.9654	0.964 86	−0.005
0.1254	0.827 36	−0.035	0.3834	0.877 56	−0.066	0.6377	0.919 42	−0.053			
0.1982	0.824 43	−0.049	0.4193	0.883 87	−0.065	0.7395	0.934 44	−0.040			
0.2336	0.849 50	−0.055	0.4688	0.892 36	−0.064	0.8163	0.945 12	−0.025			
					Diethyl Carbonate (1) + 2-Pentanone (2)						
0.0153	0.804 64	−0.003	0.3179	0.859 87	−0.030	0.5427	0.898 04	−0.030	0.9121	0.956 10	−0.004
0.0603	0.813 14	−0.009	0.3959	0.873 38	−0.032	0.6103	0.909 09	−0.027	0.9743	0.965 39	−0.002
0.1122	0.822 84	−0.017	0.4316	0.879 46	−0.033	0.6722	0.919 01	−0.021			
0.2056	0.839 90	−0.024	0.4669	0.885 43	−0.032	0.7657	0.933 74	−0.016			
0.2818	0.853 52	−0.029	0.5087	0.892 42	−0.031	0.8580	0.947 93	−0.008			
					Diethyl Carbonate (1) + 2-Hexanone (2)						
0.0274	0.811 57	0.002	0.3686	0.866 03	0.032	0.5876	0.901 45	0.035	0.9227	0.956 36	0.014
0.070	0.818 29	0.008	0.4052	0.871 93	0.032	0.6441	0.910 63	0.034	0.9799	0.965 86	0.004
0.1506	0.831 14	0.016	0.4647	0.881 54	0.6901	0.918 13	0.032				
0.2246	0.842 95	0.023	0.4971	0.886 76	0.7724	0.931 61	0.027				
0.3122	0.856 96	0.029	0.5531	0.895 84	0.034	0.8488	0.944 17	0.021			
					Diethyl Carbonate (1) + 2-Octanone (2)						
0.0206	0.817 97	0.012	0.4253	0.870 63	0.153	0.6448	0.904 36	0.152	0.9375	0.956 71	0.043
0.0777	0.824 75	0.042	0.4910	0.880 29	0.159	0.6963	0.912 91	0.141	0.9823	0.965 58	0.016
0.1524	0.833 92	0.080	0.6963	0.5164	0.884 12	0.160	0.7477	0.921 72	0.128		
0.2789	0.850 30	0.123	0.5667	0.891 88	0.159	0.8184	0.934 27	0.102			
0.3805	0.864 25	0.146	0.5989	0.896 97	0.156	0.9029	0.949 99	0.064			
					Diethyl Carbonate (1) + 2-Undecanone (2)						
0.0285	0.825 61	0.029	0.4829	0.873 40	0.312	0.6939	0.904 91	0.293	0.9581	0.958 61	0.067
0.1400	0.835 46	0.132	0.5418	0.881 43	0.319	0.7492	0.914 63	0.266	0.9893	0.966 42	0.021
0.2184	0.843 02	0.193	0.5913	0.888 62	0.316	0.7987	0.923 91	0.236			
0.3644	0.858 75	0.276	0.6251	0.893 77	0.312	0.8647	0.937 32	0.179			
0.4157	0.864 88	0.295	0.6679	0.900 59	0.303	0.9079	0.946 82	0.129			
					Diethyl Carbonate (1) + Cyclohexanone (2)						
0.0229	0.942 79	0.015	0.3462	0.951 93	0.069	0.5395	0.957 41	0.048	0.9097	0.967 04	0.006
0.0563	0.943 67	0.033	0.3871	0.953 11	0.066	0.6006	0.959 09	0.039	0.9703	0.968 51	0.001
0.1182	0.945 35	0.057	0.4177	0.953 99	0.063	0.6581	0.960 64	0.031			
0.2152	0.948 13	0.072	0.4580	0.955 13	0.058	0.7557	0.963 20	0.019			
0.3058	0.950 76	0.072	0.5021	0.956 37	0.053	0.8521	0.965 64	0.010			
					Diethyl Carbonate (1) + 2-Methylcyclohexanone (2)						
0.0181	0.922 41	−0.001	0.5823	0.949 28	0.004	0.3583	0.938 63	0.000	0.9315	0.965 93	0.002
0.0763	0.925 19	−0.001	0.6333	0.951 71	0.004	0.4197	0.941 55	0.001	0.9760	0.968 06	0.001
0.1158	0.926 08	−0.001	0.7012	0.954 94	0.005	0.4534	0.943 15	0.002			
0.1805	0.930 16	−0.002	0.7792	0.958 65	0.005	0.5023	0.945 48	0.002			
0.3147	0.936 56	−0.004	0.7962	0.959 46	0.005						
					Diethyl Carbonate (1) + 2,6-Dimethylcyclohexanone (2)						
0.0228	0.913 27	0.001	0.3912	0.932 65	0.015	0.6166	0.945 44	0.019	0.9327	0.964 82	0.008
0.0990	0.917 14	0.003	0.4318	0.934 90	0.016	0.6714	0.952 66	0.019	0.9800	0.967 90	0.002
0.1577	0.920 16	0.006	0.4968	0.938 55	0.018	0.7378	0.952 66	0.018			
0.2645	0.925 79	0.010	0.5377	0.940 87	0.019	0.7912	0.955 92	0.017			
0.3366	0.929 67	0.012	0.5618	0.942 25	0.019	0.8842	0.961 73	0.011			

The apparatus was maintained at constant temperature to within 0.005 K by means of a Hetotherm bath circulator (model 01 DTB 623), and the temperature was measured using a digital thermometer (DT 100−25, Anton Paar, Graz, Austria). The uncertainty in the densities was 1×10^{-6} g·cm^{-3}, which gives an estimated uncertainty in V^E_m not exceeding 2×10^{-3}. Before the measurements, the density meter was checked with the benzene + cyclohexane mixture for which the densities are accurately known from the literature (*16*) (our value of V^E_m at 0.5 mole fraction is 0.652 cm^3·mol^{-1} (lit. value 0.6514)).

Results and Discussion

The values of V^E_m for the binary mixtures are reported in Table 2 and graphically represented in Figures 1 and 2. Experimental V^E_m data have been fitted to the polynomial Redlich−Kister expression for each set of data:

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

where x_1 and x_2 denote the mole fractions of components 1

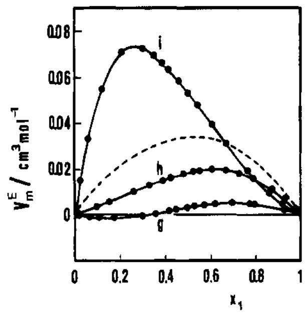

Figure 2. Excess molar volumes at 298.15 K for the binary mixtures containing diethyl carbonate + cyclic ketones: g–i refer to diethyl carbonate + 2-methylcyclohexanone, + 2,6-dimethylcyclohexanone, and + cyclohexanone mixtures, respectively. The dashed line refers to the diethyl carbonate + 2-hexanone mixture, the same reported in Figure 1, and here drawn for comparison.

Table 3. Adjustable Parameters, a_k, and Standard Deviations, $\sigma(V_m^E)$, of the Polynomial Function, Eq 1, for Binary Liquid Mixtures Containing Diethyl Carbonate + Linear or Cyclic Ketones

ketone	a_0	a_1	a_2	a_3	$\sigma(V_m^E)$/ ($cm^3 \cdot mol^{-1}$)
2-propanone	−0.3311	0.1277			0.0015
2-butanone	−0.2564	0.1043	0.0331		0.0009
2-pentanone	−0.1248	0.0598	0.0289		0.0008
2-hexanone	0.1379	0.0222	0.0194		0.0008
2-octanone	0.6371	0.0661	0.0364		0.0011
2-undecanone	1.2581	0.2816	0.1012		0.0015
cyclohexanone	0.2109	−0.2595	0.1517	−0.0866	0.0007
2-methylcyclohexanone	0.0102	0.0345			0.0003
2,6-dimethylcyclohexanone	0.0721	0.0462			0.0004

and 2 and a_k are the adjustable parameters obtained by the least-squares method. Table 3 summarizes the values of parameters a_k together with the standard deviations $\sigma(V_m^E)$. These coefficients were used to calculate the solid curves in Figures 1 and 2. Figure 3 shows V_m^E (x_1 = 0.5), the equimolar volume of V_m^E for diethyl carbonate + linear ketones, plotted against the number n_c of carbon atoms of the ketones. From Figures 1 and 3, the binary mixtures containing linear ketones show a regular increase in V_m^E as a function of the number n_c with almost symmetric curves with respect to x = 0.5. Mixtures of diethyl carbonate with cyclic ketones show, on the contrary, strongly asymmetric curves, which is particularly evident from comparison of the curves referring to cyclohexanone and 2-hexanone. The mixture containing 2-methylcyclohexane, however, has a volumetric behavior very close to ideality.

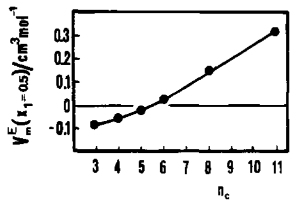

Figure 3. Values of equimolar volumes V_m^E (x = 0.5) at 298.15 K and atmospheric pressure as a function of the number carbon atoms of the ketones, n_c, for the binary mixtures containing diethyl carbonate + linear ketones.

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