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Densities, Excess Molar Volumes, Isothermal Compressibilities, and Isobaric Expansivities of Dimethyl Carbonate + Cyclohexane Systems at Temperatures from (293.15 to 313.15) K and Pressures from (0.1 to 40) MPa

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The densities of dimethyl carbonate, cyclohexane, and their mixtures were measured for nine compositions at five different temperatures varying from (293.15 to 313.15) K and over the pressure range of (0.1 to 40) MPa. The densities of pure substances and their mixtures at atmospheric pressure were measured with a vibrating-tube densimeter. The densities at elevated pressures were measured with a high-pressure apparatus and a precise analytical balance. The molar volumes V_m, excess molar volumes V_m^E, isothermal compressibilities κ, and isobaric expansivities α were derived from the experimental densities.

Introduction

Dimethyl carbonate, sometimes regarded as a cornerstone of organic synthesis and a green chemical, is one of the most important chemicals in the chemical industry because of its negligible ecotoxicity, low environmental persistence, and high reaction activity.[1,2] It is a possible replacement for methyl *tert*-butyl ether (MTBE).

The densities and excess volumes of the liquids investigated and their mixtures are required, for instance, for relating the excess enthalpy and excess Gibbs function.[3−7] The relations among excess molar volumes V_m^E, excess molar enthalpy H_m^E, and excess molar Gibbs function G_m^E are exactly the same as those between the total functions: $H_m^E = U_m^E + pV_m^E$ and $G_m^E = H_m^E - TS_m^E$. The partial derivatives of extensive excess functions are analogous to those of the total functions, for example, $(\partial G_m^E/\partial p)_{T,x} = V_m^E$. Excess functions may be positive or negative. When the excess molar volume of a solution is greater than zero, that is, $(\partial G_m^E/\partial p)_{T,x} > 0$, the solution is said to exhibit positive deviations from ideality, whereas if V_m^E is less than zero, the deviation from ideality is said to be negative.[8,9] Therefore, V_m^E is an important parameter for the thermodynamics of solution. From a practical point of view, the data are useful for the design of mixing, storage, and process equipment. Last but not least, the data measured reflect interactions between the molecules of the mixtures studied and can serve for testing the theories of the liquid state.

Densities of dimethyl carbonate, cyclohexane, and their mixtures were determined in this work. The measurements were carried out from (293.15 to 313.15) K and at pressures up to 40 MPa. The molar volumes V_m, excess molar volumes V_m^E, isothermal compressibilities κ, and isobaric expansivities α were derived from the experimental densities.

Experimental Section

Materials. Dimethyl carbonate and cyclohexane (all mass fraction purity stated 0.995) were obtained from the Kewei Pure Chemical Company. They were dried over 4 Å molecular sieves for 48 h and degassed in an ultrasonic bath (model: KQ3200DB, China) for 4 h before measurements. The liquid mixtures were prepared by weight using a precise analytical balance (model: FA2014, SPSIC, China) with an accuracy of $1 \cdot 10^{-4}$ g.

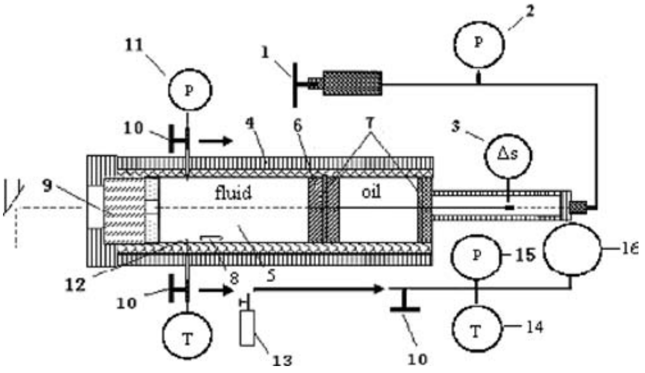

Figure 1. Schematic diagram of the high-pressure apparatus. 1, screw-driven pump; 2, pressure meter; 3, Hall probe; 4, heat jacket; 5, autoclave; 6, piston; 7, O-ring; 8, stirrer; 9, quartz window; 10, sampling valves; 11, pressure sensor; 12, thermocouple; 13, small steel vessel; 14, thermometer; 15, vacuum meter; 16, steel bulb.

Experimental Apparatus and Procedures. The densities of pure substances and mixtures at normal pressure were measured with a vibrating-tube densimeter (model: DA-505, KEM, Japan). The densities at high pressures were measured with a variable-volume autoclave and a precise analytical balance. The high-pressure apparatus is similar to the equipment used earlier to determine high-pressure phase equilibria.[10] A schematic is shown in Figure 1. The cylindrical high pressure autoclave (outer diameter 50 mm, inner diameter 20 mm) was built from a special alloy (austentitic manganese steel). A movable piston separated the content of autoclave from the pressure-transmitting medium, which moved the piston to generate the pressure inside the autoclave. The sapphire window allows the observation of the contents of the autoclave. The homogenization of temperatures was achieved by a magnetic stirring. The temperature of the sample was measured with a calibrated Cr−Al thermocouple (with an uncertainty of ± 0.1 K). On the outside of the autoclave, there were three independent heating jackets and three thermocouple sensors. Temperature inhomogeneities were minimized by adjusting the voltage of different heating jackets.

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Table 1. Comparison of Experimental Densities (ρ) of Pure Components with the Literature Values at Different Temperatures and Pressures[a]

	$\rho/(\mathrm{g \cdot cm^{-3}})$ at T/K									
p	293.15		298.15		303.15		308.15		313.15	
MPa	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
					Dimethyl Carbonate					
0.1	1.0698	1.06969[11] 1.06954[12] 1.06949[13]	1.0632	1.06331[14] 1.06295[12] 1.06284[13]	1.0565	1.05635[12] 1.0565[15] 1.05624[13]	1.0498	1.050011[16] 1.04962[13] 1.05004[14]	1.0430	1.04301[12] 1.04310[11] 1.0434[15]
5	1.0744	1.07422[17] 1.07466[18]	1.0680	1.06770[17]	1.0613	1.06117[17] 1.06165[18]	1.0546	1.05459[17]	1.0481	1.04794[17] 1.04872[18]
10	1.0786	1.07858[17] 1.07901[18]	1.0724	1.07221[17]	1.0660	1.06582[17] 1.06629[18]	1.0594	1.05939[17]	1.0530	1.05291[17] 1.05371[18]
20	1.0869	1.08683[17] 1.08726[18]	1.0808	1.08070[17]	1.0747	1.07459[17] 1.07511[18]	1.0685	1.06843[17]	1.0623	1.06222[17] 1.06305[18]
30	1.0945	1.09450[17] 1.0943[19]	1.0887	1.08862[17]	1.0829	1.08275[17] 1.0827[19]	1.0770	1.07680[17]	1.0710	1.07082[17] 1.0710[19]
40	1.1019	1.10174[17] 1.1015[19]	1.0962	1.09604[17]	1.0904	1.09035[17] 1.0903[19]	1.0848	1.08463[17]	1.0790	1.07887[17] 1.0791[19]
					Cyclohexane					
0.1	0.7788	0.77870[20] 0.77851[21]	0.7739	0.77371[21] 0.7739[22]	0.7693	0.76920[20] 0.7691[22]	0.7645	0.7640[23] 0.7644[24]	0.7597	0.75965[20] 0.7595[22]
5	0.7828	0.78261[25]	0.7783	0.77851[26]	0.7736	0.77358[25]	0.7690		0.7645	0.76444[26]
10	0.7866	0.78647[25]	0.7823	0.7820[3]	0.7778	0.77772[25]	0.7734	0.7731[3]	0.7689	0.76861[26]
20	0.7939		0.7898	0.7894[3]	0.7857		0.7815	0.7810[3]	0.7774	0.77717[26]
30	0.8010		0.7967	0.7961[3]	0.7928		0.7888	0.7883[3]	0.7848	0.7844[27]
40	0.8078		0.8029	0.8017[3]	0.7992		0.7955	0.7943[3]	0.7918	0.7911[27]

[a] The densities at lower temperatures T/K = (293.15, 298.15, and 303.15) are in the supercooled region.

A strain gauge precision transducer was used to measure the pressure. The pressure was manually generated by a screw-driven pump. The position of the piston and hence the volume of the samples were detected magnetically. A Hall-effect probe detected the position of the magnet which was fixed onto the end of the piston inside the autoclave. The Hall-effected probe was fixed on an electronic caliper (which made the position of the piston measurable with an uncertainty of ± 0.1 mm) outside the autoclave.

The relationship between the effective volume of the autoclave and the position of the piston was calibrated by means of weighing water at different temperatures and pressures. The pressure−volume dependence, $(dV/dp)_T/V$, was $2.060 \cdot 10^{-5}$ $\mathrm{MPa^{-1}}$. The temperature−volume dependence, $(dV/dT)_p/V$, was $4.050 \cdot 10^{-5}$ $\mathrm{K^{-1}}$. The uncertainties in temperature and pressure were ± 0.1 K and ± 0.05 MPa, respectively.

The equilibrium, indicated by reaching a constant pressure and temperature, was achieved typically 2 h after terminating stirring. The samples were then removed from the lower sampling valve. The volume of sample was determined by the moved distance of piston. The mass of the samples was weighed using an electronic balance with an accuracy of $1 \cdot 10^{-4}$ g. The densities of the samples were determined using the ratio of the weight to the volume of the sample.

The overall experimental uncertainty in the mole fraction composition is about $\pm 1 \cdot 10^{-4}$, in density is approximately $\pm 1 \cdot 10^{-4}$ $\mathrm{g \cdot cm^{-3}}$, in V_m^E is estimated to be about $\pm 2 \cdot 10^{-3}$ $\mathrm{cm^3 \cdot mol^{-1}}$, in κ is $\pm 3 \cdot 10^{-5}$ $\mathrm{MPa^{-1}}$, and in α is $\pm 2 \cdot 10^{-4}$ $\mathrm{K^{-1}}$.

Results and Discussion

The densities of pure substances (dimethyl carbonate and cyclohexane) were measured at temperatures T/K = (293.15, 298.15, 303.15, 308.15, and 313.15) and under pressures p/MPa = (0.1, 5.0, 10.0, 20.0, 30.0, and 40.0).

The comparison between the experimental densities in this work and the literature values[11−27] is shown in Table 1. The results show that our experimental data were in good agreement with the literature data. A comparison with the literature data for dimethyl carbonate and cyclohexane results in an absolute mean difference of $7.8 \cdot 10^{-6}$ $\mathrm{g \cdot cm^{-3}}$ and $3.0 \cdot 10^{-4}$ $\mathrm{g \cdot cm^{-3}}$, respectively.

Densities of the mixtures of nine different mole fractions of dimethyl carbonate (x_1 = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9) were measured at temperatures T/K = (293.15, 298.15, 303.15, 308.15, and 313.15) and under pressures p/MPa = (0.1, 5.0, 10.0, 20.0, 30.0, and 40.0). The results are presented in Table 2.

The isothermal experimental densities at a given composition were correlated by the Tait equation[28]

$$(\rho - \rho_0)/\rho = C \ln[(B + p)/(B + p_0)] \tag{1}$$

where B and C are adjustable parameters and ρ_0 is the density at a reference pressure p_0 (p_0 = 0.1 MPa in this work).

The fitted parameters of the above equation and the standard deviations $\sigma(\rho)$ are reported in Table 3.

The excess molar volumes were calculated from the experimental data according to the following equation

$$V_m^E = [x_1 M_1 + x_2 M_2]/\rho - [x_1 M_1/\rho_1 + x_2 M_2/\rho_2] \tag{2}$$

where ρ is density of the mixtures; x_1 and x_2 are the mole fractions; M_1 and M_2 are molar masses; and ρ_1 and ρ_2 are the densities of dimethyl carbonate and cyclohexane, respectively. The excess molar volumes V_m^E are presented in Table 4.

It has been reported[29] that the V_m^E values of the binary mixture result from the chemical, physical, and structural characteristics of the liquids. The excess molar volumes V_m^E are positive over the whole composition, temperature, and pressure range. This indicates that positive contributions (such as destruction of dipole−dipole interactions during the mixing process) overcome the negative contributions (e.g., free volume), resulting in the positive V_m^E values. The pressure dependence of V_m^E is illustrated in Figure 2 for the temperature of 298.15 K. At a fixed temperature and mole fraction composition, the experimental

Table 2. Experimental Densities (ρ) for the Binary Mixture of Dimethyl Carbonate (1) + Cyclohexane (2) at Different Temperatures and Pressures

	$\rho/(\mathrm{g \cdot cm^{-3}})$ at p/MPa					
x_1	0.1	5	10	20	30	40
			T/K = 293.15			
0.1010	0.7979	0.8022	0.8062	0.8139	0.8213	0.8285
0.1993	0.8183	0.8227	0.8270	0.8350	0.8427	0.8502
0.3026	0.8423	0.8469	0.8512	0.8596	0.8675	0.8752
0.3999	0.8660	0.8707	0.8753	0.8839	0.8920	0.8998
0.5001	0.8937	0.8985	0.9031	0.9118	0.9200	0.9280
0.5996	0.9236	0.9284	0.9330	0.9418	0.9500	0.9580
0.7039	0.9575	0.9623	0.9669	0.9757	0.9838	0.9918
0.8005	0.9910	0.9958	1.0003	1.0090	1.0171	1.0250
0.9028	1.0304	1.0351	1.0395	1.0480	1.0558	1.0635
			T/K = 298.15			
0.1010	0.7923	0.7969	0.8012	0.8092	0.8165	0.8232
0.1993	0.8125	0.8173	0.8218	0.8302	0.8378	0.8448
0.3026	0.8363	0.8413	0.8460	0.8546	0.8625	0.8698
0.3999	0.8600	0.8651	0.8700	0.8788	0.8870	0.8945
0.5001	0.8874	0.8926	0.8975	0.9065	0.9148	0.9225
0.5996	0.9170	0.9222	0.9271	0.9361	0.9445	0.9523
0.7039	0.9508	0.9560	0.9608	0.9698	0.9782	0.9861
0.8005	0.9842	0.9894	0.9942	1.0031	1.0114	1.0193
0.9028	1.0232	1.0282	1.0328	1.0415	1.0497	1.0574
			T/K = 303.15			
0.1010	0.7869	0.7914	0.7960	0.8045	0.8121	0.8190
0.1993	0.8069	0.8117	0.8165	0.8253	0.8334	0.8407
0.3026	0.8304	0.8354	0.8404	0.8495	0.8579	0.8654
0.3999	0.8541	0.8592	0.8644	0.8738	0.8823	0.8901
0.5001	0.8812	0.8864	0.8916	0.9012	0.9099	0.9178
0.5996	0.9101	0.9154	0.9206	0.9303	0.9391	0.9472
0.7039	0.9441	0.9493	0.9545	0.9641	0.9728	0.9809
0.8005	0.9774	0.9826	0.9877	0.9971	1.0058	1.0138
0.9028	1.0158	1.0209	1.0258	1.0350	1.0436	1.0514
			T/K = 308.15			
0.1010	0.7812	0.7861	0.7908	0.7995	0.8074	0.8146
0.1993	0.8014	0.8065	0.8114	0.8205	0.8287	0.8363
0.3026	0.8244	0.8297	0.8348	0.8442	0.8528	0.8606
0.3999	0.8479	0.8534	0.8586	0.8683	0.8771	0.8852
0.5001	0.8748	0.8803	0.8856	0.8955	0.9044	0.9127
0.5996	0.9034	0.9089	0.9142	0.9242	0.9333	0.9417
0.7039	0.9369	0.9423	0.9477	0.9576	0.9667	0.9750
0.8005	0.9697	0.9751	0.9804	0.9902	0.9993	1.0076
0.9028	1.0086	1.0137	1.0188	1.0284	1.0373	1.0454
			T/K = 313.15			
0.1010	0.7756	0.7808	0.7856	0.7948	0.8029	0.8105
0.1993	0.7958	0.8013	0.8062	0.8158	0.8242	0.8321
0.3026	0.8185	0.8241	0.8293	0.8392	0.8480	0.8562
0.3999	0.8419	0.8477	0.8530	0.8632	0.8722	0.8807
0.5001	0.8686	0.8744	0.8798	0.8902	0.8994	0.9080
0.5996	0.8967	0.9026	0.9081	0.9185	0.9279	0.9367
0.7039	0.9297	0.9355	0.9410	0.9514	0.9608	0.9695
0.8005	0.9623	0.9680	0.9735	0.9838	0.9931	1.0019
0.9028	1.0011	1.0066	1.0119	1.0218	1.0309	1.0394

Table 3. Coefficients B and C of Tait Equation Fitted to the Experimental Densities and Standard Deviations $\sigma(\rho)$

x	B/MPa	C	$10^5\,\sigma(\rho)/\mathrm{g \cdot cm^{-3}}$
	T/K = 293.15		
0.0000	126.9	0.1312	7.4
0.1010	119.1	0.1275	7.0
0.1993	113.8	0.1246	6.7
0.3026	110.2	0.1214	6.2
0.3999	106.7	0.1181	5.9
0.5001	104.7	0.1142	5.6
0.5996	103.1	0.1097	5.3
0.7039	101.9	0.1045	5.0
0.8005	100.9	0.0994	4.7
0.9028	100.6	0.0930	4.7
1.0000	99.1	0.0861	4.6
	T/K = 298.15		
0.0000	62.8	0.0736	3.2
0.1010	63.5	0.0770	3.3
0.1993	64.0	0.0791	3.3
0.3026	65.3	0.0807	4.1
0.3999	66.8	0.0824	4.8
0.5001	68.4	0.0828	5.2
0.5996	70.6	0.0829	5.7
0.7039	73.6	0.0826	6.6
0.8005	77.4	0.0825	7.1
0.9028	83.0	0.0823	8.0
1.0000	90.2	0.0822	8.7
	T/K = 303.15		
0.0000	68.7	0.0819	4.4
0.1010	69.7	0.0870	6.1
0.1993	69.4	0.0887	5.2
0.3026	69.9	0.0897	5.1
0.3999	70.4	0.0904	4.2
0.5001	71.3	0.0900	3.7
0.5996	73.0	0.0899	2.8
0.7039	75.6	0.0886	2.4
0.8005	78.4	0.0875	1.7
0.9028	82.6	0.0859	1.2
1.0000	89.3	0.0843	0.7
	T/K = 308.15		
0.0000	63.2	0.0799	0.4
0.1010	63.5	0.0844	0.3
0.1993	64.4	0.0866	0.5
0.3026	65.6	0.0887	0.6
0.3999	66.9	0.0900	0.6
0.5001	68.9	0.0908	1.0
0.5996	71.2	0.0915	1.2
0.7039	74.7	0.0915	1.7
0.8005	79.1	0.0921	2.2
0.9028	85.5	0.0922	2.8
1.0000	96.0	0.0930	3.8
	T/K = 313.15		
0.0000	61.1	0.0808	6.6
0.1010	60.2	0.0847	8.3
0.1993	61.2	0.0870	7.9
0.3026	62.2	0.0891	6.9
0.3999	63.3	0.0901	6.4
0.5001	65.2	0.0910	5.3
0.5996	66.9	0.0913	4.4
0.7039	70.0	0.0912	3.3
0.8005	73.1	0.0907	2.3
0.9028	78.7	0.0900	1.0
1.0000	87.9	0.0893	0.8

excess molar volumes were found to decrease with pressure. The temperature dependence of V_m^E and comparison with the literature values[30] are demonstrated in Figure 3 under the pressure of 0.1 MPa. As can be seen, the excess molar volumes increased with the increasing of temperature at a fixed pressure and mixture composition. The discrepancies between our work and the literature data are maybe mainly due to the difference in material purity.

The V_m^E data were fitted to the following Redlich−Kister polynomial equation[31]

$$V_m^E = x_1(1 - x_1)[\sum_{i=0}^{n} A_i(2x_1 - 1)^i] \quad (3)$$

where A_i are adjustable parameters and x_1 is the mole fraction of dimethyl carbonate.

Although typical data reported in the literature justify no more than two or at most three parameters, very accurate and extensive data are needed to warrant the use of four or more empirical coefficients.[32] Therefore, $n = 5$ is selected in this work to obtain better fitting results. The coefficients A_i and the standard deviations σ (V_m^E) are summarized in Table 5.

Isothermal compressibilities κ and isobaric expansivities α were derived from the experimental densities. The calculated isothermal compressibilities κ and isobaric expansivities α at

Table 4. Excess Molar Volumes (V_m^E) for the Binary Mixture of Dimethyl Carbonate (1) + Cyclohexane (2) at Different Temperatures and Pressures

	V_m^E/(cm^3·mol^{-1}) at p/MPa					
x_1	0.1	5	10	20	30	40
			T/K = 293.15			
0.1010	0.573	0.536	0.512	0.466	0.430	0.385
0.1993	0.981	0.937	0.879	0.805	0.738	0.663
0.3026	1.200	1.140	1.089	0.981	0.900	0.812
0.3999	1.395	1.331	1.251	1.134	1.039	0.950
0.5001	1.352	1.288	1.217	1.107	1.013	0.915
0.5996	1.208	1.155	1.093	0.991	0.908	0.823
0.7039	0.980	0.937	0.884	0.800	0.738	0.665
0.8005	0.743	0.710	0.673	0.614	0.560	0.505
0.9028	0.342	0.327	0.306	0.279	0.259	0.230
			T/K = 298.15			
0.1010	0.655	0.629	0.590	0.529	0.483	0.429
0.1993	1.074	1.025	0.965	0.862	0.789	0.711
0.3026	1.297	1.230	1.153	1.041	0.946	0.850
0.3999	1.472	1.400	1.307	1.185	1.071	0.969
0.5001	1.441	1.367	1.283	1.157	1.049	0.945
0.5996	1.305	1.240	1.166	1.057	0.956	0.861
0.7039	1.059	1.004	0.950	0.859	0.776	0.692
0.8005	0.808	0.761	0.715	0.648	0.589	0.523
0.9028	0.415	0.393	0.371	0.336	0.301	0.270
			T/K = 303.15			
0.1010	0.751	0.724	0.671	0.593	0.534	0.476
0.1993	1.175	1.113	1.040	0.933	0.822	0.728
0.3026	1.411	1.333	1.243	1.114	0.984	0.882
0.3999	1.562	1.480	1.376	1.226	1.101	0.981
0.5001	1.538	1.455	1.362	1.207	1.080	0.967
0.5996	1.447	1.364	1.282	1.135	1.016	0.901
0.7039	1.148	1.087	1.017	0.899	0.811	0.716
0.8005	0.877	0.826	0.775	0.691	0.620	0.550
0.9028	0.504	0.471	0.447	0.395	0.348	0.311
			T/K = 308.15			
0.1010	0.864	0.806	0.764	0.685	0.611	0.552
0.1993	1.242	1.162	1.099	0.980	0.881	0.785
0.3026	1.521	1.422	1.341	1.200	1.070	0.965
0.3999	1.673	1.558	1.472	1.313	1.177	1.054
0.5001	1.646	1.541	1.453	1.292	1.165	1.039
0.5996	1.561	1.465	1.387	1.235	1.107	0.990
0.7039	1.280	1.206	1.128	1.009	0.904	0.815
0.8005	1.026	0.960	0.901	0.808	0.722	0.650
0.9028	0.575	0.544	0.511	0.455	0.406	0.367
			T/K = 313.15			
0.1010	0.966	0.906	0.849	0.752	0.663	0.589
0.1993	1.323	1.228	1.164	1.026	0.915	0.815
0.3026	1.618	1.517	1.423	1.262	1.119	0.998
0.3999	1.759	1.641	1.545	1.364	1.218	1.079
0.5001	1.729	1.622	1.525	1.341	1.195	1.063
0.5996	1.672	1.563	1.467	1.301	1.156	1.021
0.7039	1.411	1.323	1.240	1.095	0.974	0.869
0.8005	1.145	1.076	1.003	0.885	0.794	0.696
0.9028	0.667	0.625	0.582	0.517	0.465	0.410

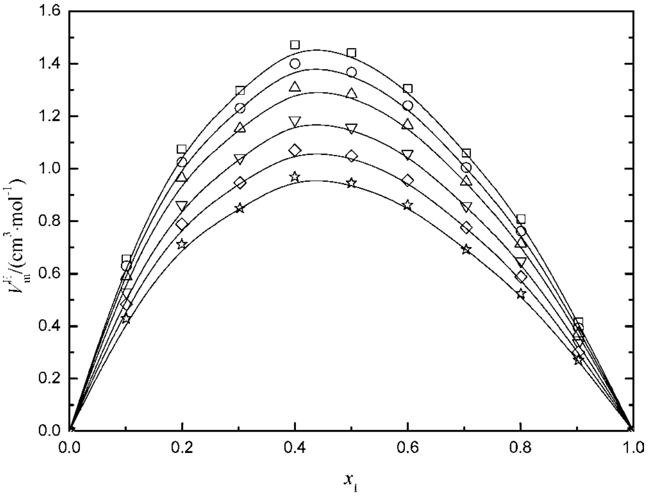

Figure 2. Excess molar volumes V_m^E against mole fraction x_1 for dimethyl carbonate (1) + cyclohexane (2) at constant temperature T/K = 298.15 and pressure p: □, 0.1 MPa; ○, 5 MPa; △, 10 MPa; ▽, 20 MPa; ◇, 30 MPa; ☆, 40 MPa. The symbols represent experimental values, and the solid lines are calculated with the Redlich−Kister equation.

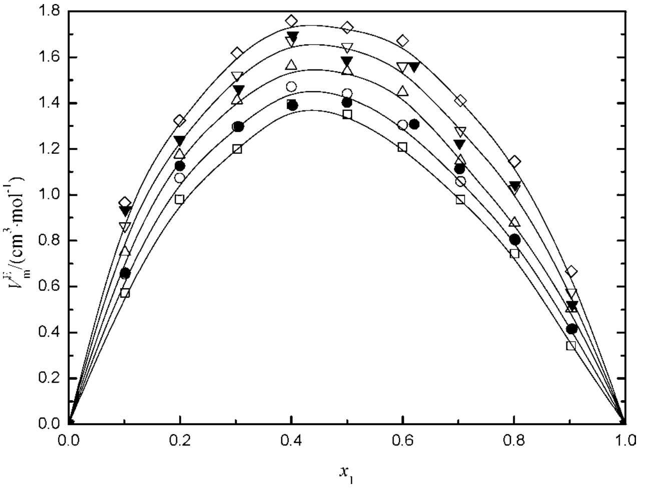

Figure 3. Excess molar volumes V_m^E against mole fraction x_1 for dimethyl carbonate (1) + cyclohexane (2) at constant pressure p/MPa = 0.1 and temperature T: □, 293.15 K; ○, ●, 298.15 K; △, 303.15 K; ▽, ▼, 308.15 K; ◇, 313.15 K. The symbols represent experimental values (unfilled points, this work; solid points, Aminabhavi and Banerjee[30]), and the solid lines are calculated with the Redlich−Kister equation in this work.

different temperatures and pressures for the binary mixtures can be found as the Supporting Information.

The isothermal compressibility κ can be calculated from the following equation by differentiating eq 1

$$\kappa = \{1/[1 - C\ln((D + p)/(D + p_0))]\}[C/(D + p)] \tag{4}$$

with the coefficients from Table 3.

Curves of isothermal compressibility κ for the binary system against mole fraction x_1 of dimethyl carbonate at constant temperature T/K = 298.15 and constant pressure p/MPa = 0.1 are shown in Figures 4 and 5, respectively. Obviously κ increases with temperature and decreases with pressure at a fixed mole fraction.

Isobaric expansivity α can be calculated from $\rho(T, p)$ data from its own definition. To obtain $(\partial\rho/\partial T)_p$, the experimental densities of pure substances were correlated by the following Tait equation

$$\rho(T, p) = \frac{\rho_0(T, p_0)}{1 - A\ln\dfrac{B(T) + p}{B(T) + p_0}} \tag{5}$$

with the reference pressure p_0 equal to 0.1 MPa. The ρ_0 and B parameters were assumed to be dependent on temperature according to the following equations:

$$\rho_0(T, p_0) = \rho_{00} + \rho_{01}(T/\mathrm{K}) + \rho_{02}(T/\mathrm{K})^2 + \rho_{03}(T/\mathrm{K})^3 \tag{6}$$

Table 5. Coefficients A_i of the Redlich−Kister Equation for V_m^E of Dimethyl Carbonate (1) + Cyclohexane (2) and Standard Deviations σ (V_m^E)

p/MPa	A_0	A_1	A_2	A_3	A_4	A_5	$10^2\ \sigma\ (V_m^E)$/$cm^3 \cdot mol^{-1}$
T/K = 293.15							
0.1	5.3854	1.7963	−0.3584	−3.4050	0.1203	4.5894	0.2574
5	5.1278	1.7103	−0.3413	−3.2423	0.1147	4.3702	2.246
10	4.8764	1.6265	−0.3247	−3.0832	0.1093	4.1560	2.108
20	4.4226	1.4751	−0.2945	−2.7964	0.0992	3.7692	1.860
30	4.0301	1.3443	−0.2683	−2.5484	0.0903	3.4348	1.655
40	3.6745	1.2256	−0.2446	−2.3234	0.0822	3.1316	1.467
T/K = 298.15							
0.1	5.7585	1.5888	−0.4501	−1.2754	1.5156	2.0319	0.2074
5	5.4514	1.5041	−0.4261	−1.2079	1.4347	1.9242	1.981
10	5.1571	1.4229	−0.4032	−1.1426	1.3574	1.8203	1.869
20	4.6389	1.2799	−0.3626	−1.0280	1.2210	1.6377	1.667
30	4.1975	1.1582	−0.3281	−0.9304	1.1047	1.4819	1.496
40	3.7944	1.0469	−0.2964	−0.8408	0.9982	1.3394	1.339
T/K = 303.15							
0.1	6.2240	1.2160	−0.7428	1.3696	3.2103	−1.0205	0.1921
5	5.8474	1.1424	−0.6979	1.2868	3.0162	−0.9587	1.805
10	5.5052	1.0756	−0.6569	1.2115	2.8394	−0.9027	1.699
20	4.8890	0.9552	−0.5833	1.0761	2.5214	−0.8019	1.509
30	4.3688	0.8535	−0.5212	0.9615	2.2532	−0.7164	1.348
40	3.8896	0.7599	−0.4640	0.8558	2.0059	−0.6375	1.200
T/K = 308.15							
0.1	6.6405	1.3353	−0.1743	−1.7498	3.7698	3.8808	0.2105
5	6.2508	1.2569	−0.1640	−1.6467	3.5484	3.6526	1.963
10	5.8965	1.1857	−0.1546	−1.5531	3.3472	3.4451	1.857
20	5.2587	1.0574	−0.1378	−1.3849	2.9851	3.0721	1.670
30	4.7202	0.9491	−0.1237	−1.2429	2.6793	2.7572	1.511
40	4.2241	0.8494	−0.1107	−1.1126	2.3978	2.4678	1.366
T/K = 313.15							
0.1	7.0469	1.2874	0.4525	−2.8209	4.3353	5.9332	0.2390
5	6.6168	1.2089	0.4248	−2.6491	4.0710	5.5715	2.459
10	6.2087	1.134	0.3985	−2.4854	3.8201	5.2276	2.331
20	5.4797	1.0011	0.3518	−2.1933	3.3714	4.6133	2.114
30	4.8747	0.8906	0.3129	−1.9511	2.9993	4.1039	1.926
40	4.3208	0.7894	0.2774	−1.7293	2.6584	3.6373	1.756

$$B(T) = B_0 + B_1(T/\mathrm{K}) + B_2(T/\mathrm{K})^2 \qquad (7)$$

The number of terms in the above expressions was determined statistically. The fitted parameters and the standard deviations are presented in Table 6.

The mixture densities were correlated by the following six-parameter equation[33]

$$\rho(T,p,x_1) = \frac{M_1x_1 + M_2x_2}{\dfrac{M_1x_1}{\rho_1^0(T,p)} + \dfrac{M_2x_2}{\rho_2^0(T,p)} + \dfrac{a(T,p)x_1x_2}{b(T,p)x_1 + x_2}} \qquad (8)$$

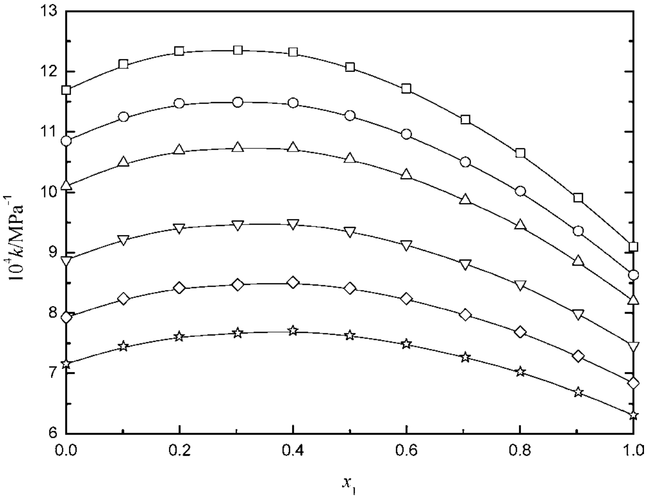

Figure 4. Isothermal compressibility κ against mole fraction x_1 for dimethyl carbonate (1) + cyclohexane (2) at constant temperature T = 298.15 K and pressure p: □, 0.1 MPa; ○, 5 M Pa; △, 10 MPa; ▽, 20 MPa; ◇, 30 MPa; ☆, 40 MPa. Lines for κ are arbitrary ones, only to show tendencies.

where M_i, x_i, and ρ_i^0 present the molecular weight, mole fraction, and density of component i, respectively, and $a(T, p)$ and $b(T, p)$ are the parameters linearly dependent on T and p according to the formulas

$$[a(T,p)/\mathrm{cm^3 \cdot mol^{-1}}] = a_0 + a_1[(p/\mathrm{MPa}) - 0.1] + a_2[(T/\mathrm{K}) - 273.15] \qquad (9)$$

$$b(T,p) = b_0 + b_1[(p/\mathrm{MPa}) - 0.1] + b_2[(T/\mathrm{K}) - 273.15] \qquad (10)$$

It was confirmed statistically that the higher-order terms in the above expansions could be neglected. The correlation equation requires six adjustable parameters (a_0, a_1, a_2, b_0, b_1, b_2) which were adjusted to the experimental densities with the overall standard deviation of 0.000683 $g \cdot cm^{-3}$. These parameters are given in Table 7.

Equations 5 to 10 enable one to calculate the isobaric expansivities of the mixture. The results show that α increases with increasing temperature and decreases with elevated pressure for a fixed mole fraction. Meanwhile, α increases to a maximum as the mole fraction of dimethyl carbonate equal to 0.3 and then decreases.

For dimethyl carbonate at 293.15 K, we compared the isothermal compressibilities and isobaric expansivities obtained in this work with those obtained by Fernández et al.[18] A comparison with the literature data for isothermal compress-

Table 6. Coefficients of the Tait Equations 5 to 7 Fitted to the Experimental Densities of Dimethyl Carbonate and Cyclohexane and the Root of Mean Squared Deviations σ

	$A \cdot 10^2$	B_i	ρ_{0i}	σ/$g \cdot cm^{-3}$
dimethyl carbonate	7.83524	B_0/MPa = 310.206 B_1/$MPa \cdot K^{-1}$ = −1.3871 B_2/$MPa \cdot K^{-2}$ = $2.1375 \cdot 10^{-3}$	ρ_{00}/$g \cdot cm^{-3}$ = 1.3577 ρ_{01}/$g \cdot cm^{-3} \cdot K^{-1}$ = $-6.4709 \cdot 10^{-4}$ ρ_{02}/$g \cdot cm^{-3} \cdot K^{-2}$ = $-1.1429 \cdot 10^{-6}$ ρ_{03}/$g \cdot cm^{-3} \cdot K^{-3}$ = $1.2423 \cdot 10^{-18}$	0.00028
cyclohexane	8.81027	B_0/MPa = 315.479 B_1/$MPa \cdot K^{-1}$ = −1.8326 B_2/$MPa \cdot K^{-2}$ = $3.5318 \cdot 10^{-3}$	ρ_{00}/$g \cdot cm^{-3}$ = 6.6246 ρ_{01}/$g \cdot cm^{-3} \cdot K^{-1}$ = $-5.6075 \cdot 10^{-2}$ ρ_{02}/$g \cdot cm^{-3} \cdot K^{-2}$ = $1.8189 \cdot 10^{-4}$ ρ_{03}/$g \cdot cm^{-3} \cdot K^{-3}$ = $-2.0000 \cdot 10^{-7}$	0.00034

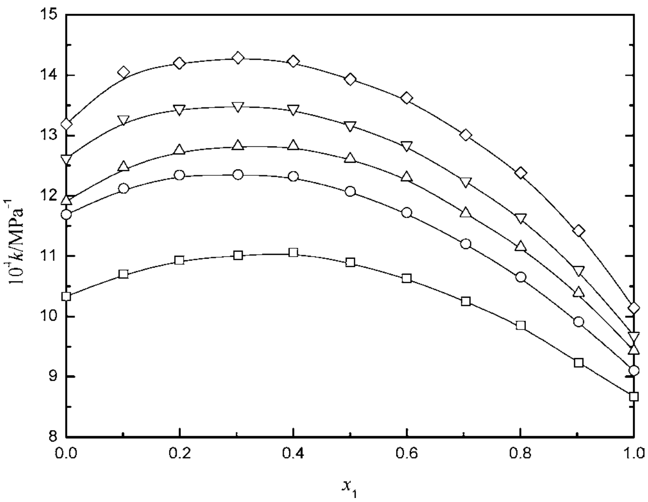

Figure 5. Isothermal compressibility κ against mole fraction x_1 for dimethyl carbonate (1) + cyclohexane (2) at constant pressure $p = 0.1$ MPa and temperature T: □, 293.15 K; ○, 298.15 K; △, 303.15 K; ▽, 308.15 K; ◇, 313.15 K. Lines for κ are arbitrary ones, only to show tendencies.

Table 7. Coefficients of Equations 8 to 10 Fitted to the Experimental Densities of the Dimethyl Carbonate (1) + Cyclohexane (2) Systems as a Function of Molar Fraction, Temperature, and Pressure and the Root of Mean Squared Deviations σ

i	a_i / $\text{cm}^3 \cdot \text{mol}^{-1}$	b_i	σ / $\text{g} \cdot \text{cm}^{-3}$
0	7.2123	4.12432	0.000683
1	$-4.12338 \cdot 10^{-2}$	$7.94739 \cdot 10^{-3}$	
2	$3.11928 \cdot 10^{-2}$	$-1.51031 \cdot 10^{-2}$	

ibility and isobaric expansivity results in an absolute mean difference of $1.36 \cdot 10^{-5}$ MPa^{-1} and $7.3 \cdot 10^{-6}$ K^{-1}, respectively. As for cyclohexane, we compared the isothermal compressibilities at 298.15 K and isobaric expansivities at 303.15 K with those obtained by Morávková et al.[3] and Sun et al.,[25] respectively. The absolute mean deviation in isothermal compressibility is $2.68 \cdot 10^{-5}$ MPa^{-1} and in isobaric expansivity is $7.25 \cdot 10^{-6}$ K^{-1}.

Conclusions

Densities of dimethyl carbonate, cyclohexane, and their mixtures have been determined from (293.15 to 313.15) K and at pressures from (0.1 to 40) MPa. A modified Tait equation was used to fit each experimental density. The molar volumes V_m, excess molar volumes V_m^E, isothermal compressibilities κ, and isobaric expansivities α were derived from the experimental densities. The excess molar volumes V_m^E were correlated using the Redlich−Kister polynomial equation. The excess molar volumes for the binary system were positive over the whole composition, temperature, and pressure range. This indicates a positive deviation from ideal liquid mixtures.

Supporting Information Available:

Calculated molar volumes, isothermal compressibilities, and isobaric expansivities for the binary system studied here. This material is available free of charge via the Internet at http://pubs.acs.org.

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