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EXCESS MOLAR VOLUME OF DIMETHYL CARBONATE +*p*-XYLENE + *n*-DECANE AT 288.15 AND 298.15 K

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Abstract

Densities for dimethyl carbonate + *p*-xylene + *n*-decane ternary system, at 288.15 and 298.15 K and at atmospheric pressure, were measured. The corresponding excess molar volumes were calculated from the experimental data and were fitted by means of Cibulka equation.

Keywords: excess molar volumes, dimethyl carbonate, *n*-decane, *p*-xylene

Introduction

One of the problems of fridge industry to replace CFCs by new refrigerants, HFCs, is to find the idoneous lubricants for different kind of compressors. In the last few years, molecules including an alkyl group, an alkyl benzene part, and a carbonate group (O–CO–O) were proposed because of their thermal stability, miscibility with HFCs, and lubricity [1]. In this work, new experimental data of excess molar volume for the ternary mixture at 288.15 and 298.15 K, and atmospheric pressure are reported for a better knowledge of the physical properties of these mixtures.

Experimental

Dimethyl carbonate and *p*-xylene were supplied by Fluka, and *n*-decane by Sigma. The substances were kept in argon (N-55) atmosphere, degassed and stored over molecular sieves (Sigma, type 0.4 nm). The mole fraction of water in each of the liquids were determined by Karl Fischer titration to be <0.01 mole%. All compounds were checked by GLC tests, showing purities better than 99% mass percent. Densities were measured with an Anton–Paar DSA 48 densimeter. The temperature was controlled with a solid-state thermostat working via Peltier effect with a precision of $\pm 5 \cdot 10^{-3}$ K. Further information about the experimental technique was described in a previous work [2]. The instrument is precise to within $\pm 3 \cdot 10^{-5}$ g cm^{-3} for the density.

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Data correlation

From density values, excess molar volumes V_m^E were calculated using the following equation

$$V_m^E = V_m - \sum_{i=1}^{n} x_i M_i / \rho_i \quad (1)$$

where ρ_i, x_i, and M_i, denote the density, mole fraction, and molar mass of component *i* in the binary or ternary mixture, respectively. The densities at 288.15 and 298.15 K are reported in Table 1 for the binary mixtures and in Table 2 for the ternary ones.

Table 1 Densities ρ for the binary mixtures involved at the temperature *T*

x_1	*T* = 288.15 K			x_1	*T* = 298.15 K		
	ρ/g cm^{-3}	x_1	ρ/g cm^{-3}		ρ/g cm^{-3}	x_1	ρ/g cm^{-3}
			x_1 dimethyl carbonate + (1–x_1) *p*-xylene				
0.00000	0.86520	0.53681	0.95518	0.00000	0.85665	0.53681	0.94456
0.04522	0.87147	0.59273	0.96709	0.04522	0.86269	0.59273	0.95621
0.09627	0.87887	0.63325	0.97603	0.09687	0.86989	0.63325	0.96498
0.14999	0.88668	0.69831	0.99127	0.14999	0.87759	0.69831	0.97988
0.19948	0.89432	0.79627	1.01592	0.19948	0.88501	0.79627	1.00403
0.25771	0.90369	0.85308	1.03141	0.25771	0.89419	0.85308	1.01919
0.31356	0.91301	0.90003	1.04501	0.31356	0.90337	0.90003	1.03251
0.41254	0.93072	0.94967	1.06005	0.41254	0.92064	0.94967	1.04726
0.49465	0.94659	1.00000	1.07642	0.49465	0.93615	1.00000	1.06330
			x_1 *p*-xylene + (1–x_1) *n*-decane				
0.00000	0.73356	0.59950	0.79676	0.00000	0.72609	0.54382	0.78135
0.10920	0.74278	0.72933	0.81568	0.06870	0.73172	0.59950	0.7887
0.19840	0.75098	0.78293	0.82432	0.08414	0.73304	0.72933	0.80747
0.31050	0.76221	0.89935	0.84493	0.10920	0.73523	0.78293	0.81603
0.34270	0.76562	0.94994	0.85478	0.19840	0.74331	0.89935	0.83647
0.49190	0.78279	1.00000	0.86520	0.31050	0.75443	0.94994	0.84625
0.54382	0.78935			0.34270	0.75783	1.00000	0.85665
				0.49190	0.77485		

Table 2 Densities ρ for the ternary mixture x_1 dimethyl carbonate + x_2 *p*-xylene + (1–x_1–x_2) *n*-decane at the temperature *T*

x_1	x_2	ρ/g cm^{-3}	x_1	x_2	ρ/g cm^{-3}
		T=288.15 K			
0.05135	0.05173	0.74477	0.22433	0.21947	0.79398
0.04927	0.90008	0.86100	0.27539	0.31001	0.81977
0.10060	0.10293	0.75709	0.22944	0.41097	0.82413
0.09928	0.19719	0.76681	0.28999	0.50629	0.86030
0.09816	0.30654	0.77922	0.30210	0.59791	0.88525
0.09892	0.40318	0.79170	0.39142	0.09980	0.81607
0.10000	0.50141	0.80564	0.40437	0.29554	0.85495
0.10156	0.59074	0.81974	0.40505	0.39477	0.87660
0.09920	0.69832	0.83761	0.40029	0.49523	0.89921
0.10288	0.79357	0.85705	0.48970	0.10129	0.84403
0.19798	0.10029	0.77366	0.49305	0.20275	0.86559
0.19973	0.19899	0.78611	0.52900	0.25128	0.89008
0.19720	0.30448	0.79981	0.49578	0.40299	0.91595
0.19869	0.39377	0.81342	0.60791	0.19484	0.90858
0.19910	0.50285	0.83139	0.59281	0.31208	0.93525
0.19993	0.59510	0.84885	0.68644	0.10542	0.91883
0.20061	0.69926	0.87073	0.70211	0.19539	0.95442
0.29352	0.10022	0.79295	0.79292	0.10133	0.97267
		T=298.15 K			
0.05135	0.05173	0.73711	0.22433	0.21947	0.78552
0.04927	0.90008	0.85232	0.27539	0.31001	0.81094
0.10060	0.10293	0.74921	0.22944	0.41097	0.81537
0.09928	0.19719	0.75885	0.28999	0.50629	0.85109
0.09816	0.30654	0.77112	0.30210	0.59791	0.87581
0.09892	0.40318	0.78350	0.39142	0.09980	0.80701
0.10000	0.50141	0.79733	0.40437	0.29554	0.84553
0.10156	0.59074	0.81128	0.40505	0.39477	0.86698
0.09920	0.69832	0.82901	0.40029	0.49523	0.88941
0.10288	0.79357	0.84830	0.48970	0.10129	0.83444
0.19798	0.10029	0.76545	0.49305	0.20275	0.85582
0.19973	0.19899	0.77777	0.52900	0.25128	0.88003
0.19720	0.30448	0.79134	0.49578	0.40299	0.90578
0.19869	0.39377	0.80482	0.60791	0.19484	0.89813
0.19910	0.50285	0.82264	0.59281	0.31208	0.92465
0.19993	0.59510	0.83994	0.68644	0.10542	0.90805
0.20061	0.69926	0.86164	0.70211	0.19539	0.94334
0.29352	0.10022	0.78433	0.79292	0.10133	0.96114

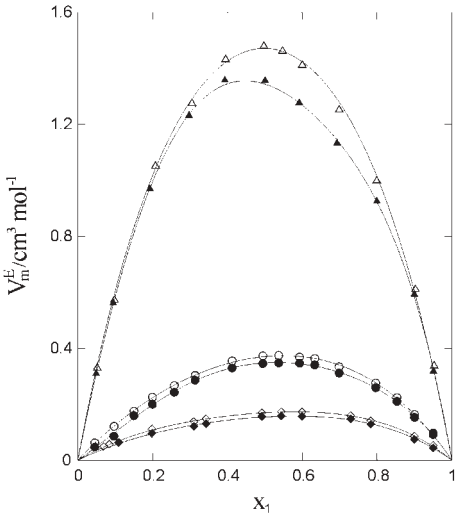

Fig. 1 Excess molar volume V_m^E for x_1 *p*-xylene + (1–x_1) *n*-decane: ◆ – 288.15 K, ◊ – 298.15 K; x_1 dimethyl carbonate + (1–x_1) *p*-xylene: ● – 288.15 K, o – 298.15 K; x_1 dimethyl carbonate + (1–x_1) *n*-decane: ▲ – 288.15 K, Δ – 298.15 K; (—) Eq. 2

Figure 1 shows the excess molar volumes for the binaries (dimethyl carbonate + *p*-xylene), (dimethyl carbonate + *n*-decane), and (*p*-xylene + *n*-decane) at 288.15 and 298.15 K, where the solid lines were calculated by a Redlich-Kister equation [3]

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = x_1(1-x_1)\sum_{p=0}^{m} A_p\,(2x_1-1)^p \qquad (2)$$

In the previous equation, x_1 is the mole fraction of the most volatile compound, dimethyl carbonate for the (dimethyl carbonate + *p*-xylene) and (dimethyl carbonate + *n*-decane) systems, and *p*-xylene for the (*p*-xylene + *n*-decane) one. A_p are the fitting parameters calculated by an unweighed least-squares method and *m* is the degree of the polynomial, optimised by applying the F-test [4] to every new parameter. Ternary excess molar volume V_{123}^E was correlated using the following equation

$$V_{123}^E/\text{cm}^3\ \text{mol}^{-1} = V_{12}^E + V_{13}^E + V_{23}^E + x_1x_2x_3\,(B_0 + B_1x_1 + B_2x_2) \qquad (3)$$

where V_{ij}^E is the binary contribution for each *ij* binary mixture, calculated with equation 2, x_3=1–x_1–x_2, and $x_1x_2x_3(B_0+B_1x_1+B_2x_2)$ is the ternary contribution which was correlated by Cibulka [5] equation. The parameters A_p and B_i of Eqs (2) and (3) and corresponding standard deviations are given in Table 3.

Table 3 Parameters A_p and B_i of equations 2 and 3 respectively, and standard deviations *s*

T/K	A_0	A_1	A_2	A_3	*s*
		x_1 dimethyl carbonate + (1–x_1) *p*-xylene			
288.15	1.392	0.168	0.067	0.355	0.005
298.15	1.483	0.259	0.198		0.004
		x_1 dimethyl carbonate + (1–x_1) *n*-decane*			
288.15	5.376	–0.852	1.711	1.294	0.009
298.15	5.885	–0.025	1.275		0.02
		x_1 *p*-xylene + (1–x_1) *n*-decane			
288.15	0.619	0.153	0.189		0.003
298.15	0.679	0.155	0.256		0.003
T/K	B_0	B_1	B_2		*s*
		x_1 dimethyl carbonate + x_2 *p*-xylene + (1–x_1–x_2) *n*-decane			
288.15	-0.884	4.277	2.641		0.009
298.15	0.470	0.416	1.294		0.008

*Ref. 6

In Fig. 2 experimental values of (dimethyl carbonate + *p*-xylene) and (*p*-xylene + *n*-decane) were compared with literature data.

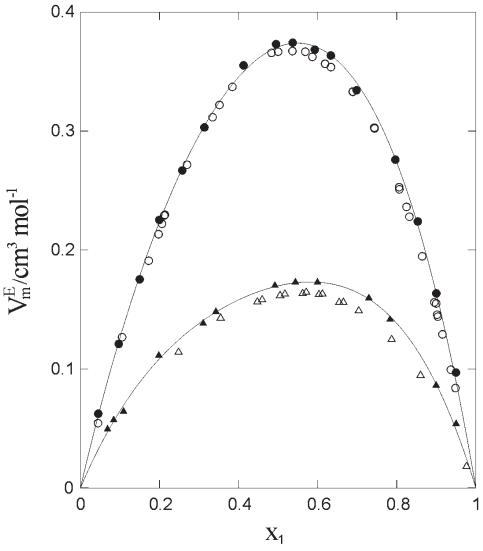

Fig. 2 Excess molar volume V_m^E at 298.15 K for x_1 dimethyl carbonate + (1–x_1) *p*-xylene: ● – experimental points, ○ – Moreiras [7]; x_1 *p*-xylene + (1–x_1) *n*-decane: ▲ – experimental points, △ – Cáceres Alonso *et al.* [8]

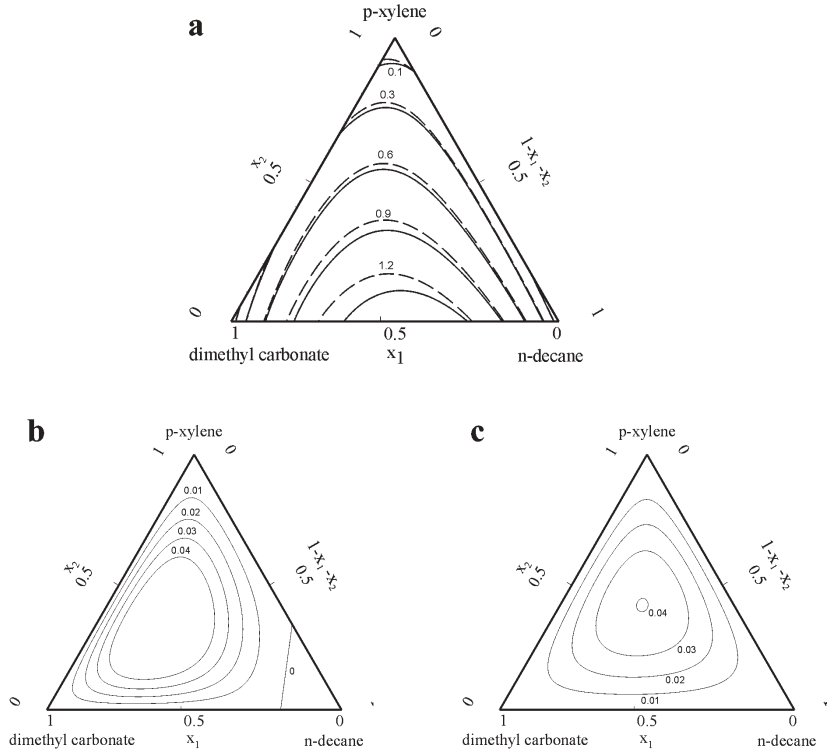

Fig. 3 Isolines of (a) V_m^E/cm^3 mol^{-1}: —— T=288.15 K, ----, T=298.15 K. Ternary contribution in cm^3 mol^{-1}: (b) 288.15 K, (c) 298.15 K, for ternary mixture x_1 dimethyl carbonate + x_2 *p*-xylene + (1–x_1–x_2) *n*-decane

Isolines of the excess molar volume at 288.15 and 298.15 K, and the ternary contributions to this magnitude, have been plotted in Fig. 3. As can be seen, V_m^E is positive in all composition range, showing maximum values shifted to high carbonate concentration on the dimethyl carbonate + *n*-decane binary system. The ternary contribution is always less than 3 per cent, so the three-body effects in the mixture are not relevant (Figs 3b and 3c). Thus, the excess molar volume in the ternary mixture can be probably ascribed to the effects that occur in the binary ones. The maximum value of excess molar volume is due to the contribution of the binary system dimethyl carbonate+ *n*-decane, where the predominant effect is the destruction of the dipolar order of the dimethyl carbonate during mixing.

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