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Excess Molar Volumes for Dimethyl Carbonate + Heptane, Decane, 2,2,4-Trimethylpentane, Cyclohexane, Benzene, Toluene, or Tetrachloromethane†

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Excess molar volumes V^E at atmospheric pressure and at 298.15 K for dimethyl carbonate + heptane, decane, 2,2,4-trimethylpentane, cyclohexane, benzene, toluene, or tetrachloromethane have been calculated from densities measured with a vibrating-tube densimeter. The V^E are positive for all the systems over the whole mole-fraction range. These results, together with previously published excess molar enthalpies H^E, suggest interactions between carbonate and hydrocarbons which are stronger with aromatic hydrocarbons than with aliphatic ones.

Introduction

We are engaged in a systematic study of the thermodynamic properties of mixtures of dialkyl carbonates with various solvents. Up to now we have measured excess molar enthalpies (*1*), isothermal vapor–liquid equilibria and excess molar Gibbs energies (*2, 3*), and liquid–liquid equilibria (*4*) for binary mixtures of dimethyl carbonate with some aliphatic or aromatic hydrocarbons and with tetrachloromethane; we have presented a quantitative treatment in terms of DISQUAC (*5*), an extended quasi-chemical group contribution method, of these results (*6, 7*). In this paper we report experimental excess molar volumes, V^E, at 298.15 K and atmospheric pressure for the same systems. The aim of this work is to measure the properties of mixtures of dialkyl carbonate compounds with selected solvents to obtain a better understanding of the thermodynamic properties of these mixtures.

Experimental Section

Density Measurement. The measurement of densities ρ was carried out with an Anton-Paar DMA 602 vibrating-tube densimeter operating under static conditions. The temperature of the sample contained in the oscillator tube was kept constant with a Grant W38 thermostat bath. The temperature of the circulating water was continuously monitored at the nearest position to the densimeter with a calibrated quartz thermometer (Hewlett-Packard 2804 A) and was stable within ±2 mK.

The oscillation period τ (of about 3 ms) was measured with a Philips PM 6669 frequency meter. This was counted with eight digits which were integrated and renewed every 10 s. Each value of τ was obtained from an average of 80 measurements, and for each pure liquid or mixture three runs were developed. Protection against the generation of static electricity around the instrument and temperature stability were effective in maintaining an overall stable indication of $\Delta\tau = \pm 5$ ns, and hence $|\Delta\tau/\tau| = 1.5 \times 10^{-6}$. This gives a resolution in density of $|\Delta\rho/\rho| = 6 \times 10^{-6}$, where the errors due to the calibration and the density of the reference liquid are not taken into account. All measuring operations and calculations were computer controlled.

Table I. Physical Properties of Pure Compounds at 298.15 K

	refractive index		$\rho/(\text{kg m}^{-3})$	
compound	this study	lit.	this study	lit.
dimethyl carbonate	1.3667	1.366 7[a] 1.366 5[b]	1063.50	1063.6[a] 1063.4[b]
heptane	1.3851	1.385 11	679.51	679.46
decane	1.4097	1.409 67	726.28	726.35
2,2,4-trimethylpentane	1.3890	1.388 98	687.82	687.81
cyclohexane	1.4235	1.423 54	773.85	773.89
benzene	1.4979	1.497 92	873.62	873.60
toluene	1.4941	1.494 13	862.32	862.19
tetrachloromethane	1.4574	1.457 39	1584.34	1584.36

[a] Reference 1. [b] Reference 4.

Before each series of measurements the instrument was calibrated with doubly distilled and degassed water and "vacuum". The accuracy in the determination of ρ is believed to be less than $\pm 2 \times 10^{-2}$ kg m^{-3}. Hexane and acetone or ethanol were used for rinsing the cell tube between measurements.

Materials. All the chemicals used were from Fluka. Dimethyl carbonate and decane (purum, >99 mol %) and heptane, 2,2,4-trimethyl pentane, cyclohexane, benzene, toluene, and tetrachloromethane (puriss pa, >99.5 mol %) were used as received. Prior to measurements, they were carefully dried with molecular sieves (Union Carbide Type 4A, beads, from Fluka) added to the liquids, and then partially degassed. The results of the measurements of their densities and refractive indices at 298.15 K and atmospheric pressure are listed in Table I; they are in good agreement with published values (*8*), since the greatest deviation found is smaller than 0.02%.

Procedure. Binary mixtures were prepared by mass in small vessels of about 10 cm^3. Caution was taken to prevent evaporation, and for this dimethyl carbonate was usually loaded first into the flask. The probable error in the mole-fraction x is estimated to be less than 0.0001. Conversion to molar quantities was based on the relative atomic mass table of 1985 issued by IUPAC (*9*).

The excess molar volumes were calculated from the densities of the pure liquids and their mixtures. As in order to obtain reliable results for V^E the absolute values of ρ are less important compared to the relative certainty in ρ (*10*), the accuracy in V^E is believed to be less than $\pm|0.01 V^E_{\max} + 0.005|$ cm^3 mol^{-1}, where $V^E_{\max}$ denotes the maximum experimental value of the excess molar volume with respect to x. The experimental technique was checked by determining the

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† Thermodynamics of binary mixtures containing organic carbonates. 8. Part 7: see ref 7.

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Table II. Excess Molar Volume V^E for Dimethyl Carbonate (1) + Solvent (2) at 298.15 K and Atmospheric Pressure

x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$	x_1	$V^E/(cm^3\ mol^{-1})$
			Heptane				
0.0520	0.314	0.3536	1.139	0.5593	1.116	0.8526	0.536
0.1039	0.561	0.4042	1.164	0.6025	1.070	0.8980	0.386
0.2046	0.901	0.4599	1.170	0.7001	0.918		
0.3055	1.092	0.5052	1.157	0.8036	0.678		
			Decane				
0.0501	0.308	0.3070	1.275	0.5035	1.443	0.8016	0.992
0.1027	0.586	0.3572	1.357	0.5533	1.427	0.8489	0.824
0.1553	0.824	0.4062	1.414	0.6041	1.376	0.9004	0.601
0.1998	0.984	0.4515	1.442	0.7039	1.229	0.9540	0.313
			2,2,4-Trimethylpentane				
0.0530	0.265	0.3076	0.880	0.5009	0.899	0.8030	0.477
0.0997	0.449	0.3591	0.915	0.5596	0.854	0.9013	0.246
0.1572	0.625	0.4069	0.925	0.6068	0.804		
0.2301	0.784	0.4572	0.921	0.7067	0.664		
			Cyclohexane				
0.0538	0.417	0.3053	1.356	0.5035	1.450	0.7061	1.151
0.1081	0.740	0.3565	1.424	0.5515	1.416	0.8056	0.858
0.2046	1.132	0.4050	1.452	0.6081	1.345	0.9046	0.463
0.2958	1.342	0.4541	1.466	0.6515	1.276		
			Benzene				
0.0530	0.061	0.3567	0.290	0.5600	0.323	0.8046	0.216
0.1009	0.110	0.4071	0.310	0.6004	0.315	0.9048	0.123
0.2041	0.200	0.4563	0.320	0.6510	0.300	0.9566	0.062
0.3011	0.265	0.5022	0.325	0.7014	0.282		
			Toluene				
0.0500	0.046	0.3554	0.243	0.5604	0.281	0.8060	0.193
0.1153	0.101	0.4032	0.258	0.6044	0.277	0.8977	0.118
0.2033	0.164	0.4546	0.271	0.6480	0.269	0.9479	0.065
0.3031	0.219	0.5052	0.278	0.7025	0.251		
			Tetrachloromethane				
0.0532	0.086	0.3575	0.329	0.5602	0.338	0.8045	0.219
0.1026	0.150	0.4051	0.341	0.6047	0.326	0.9030	0.124
0.1998	0.245	0.4512	0.346	0.6516	0.311	0.9523	0.067
0.3090	0.311	0.5080	0.345	0.7109	0.282		

Table III. Coefficients A_i in Equation 1 and Standard Deviations $\sigma(V^E)$, Equation 2, at 298.15 K and Atmospheric Pressure for Dimethyl Carbonate (1) + Solvent (2)

solvent	A_0	A_1	A_2	A_3	$\sigma(V^E)/(cm^3\ mol^{-1})$
heptane	4.632	−0.933	0.810	−0.332	0.0015
decane	5.770	−0.253	1.187	0.752	0.004
2,2,4-trimethylpentane	3.603	−1.138	0.474	−0.378	0.002
cyclohexane	5.808	−0.942	1.171	−0.852	0.002
benzene	1.299	0.113			0.0018
toluene	1.113	0.196	0.033		0.0009
tetrachloromethane	1.382	−0.121	0.228		0.0009

excess molar volumes of the standard mixtures at 298.15 K (*11*).

Results and Discussion

Table II gives experimental results of V^E as a function of the mole fraction x_1 of dimethyl carbonate. These data were fitted by unweighted least-squares polynomial regression to the equation

$$V^E/(\mathrm{cm^3\ mol^{-1}}) = x_1(1 - x_1)\sum_{i=0}^{k} A_i(2x_1 - 1)^i \qquad (1)$$

The number of coefficients k used in eq 1 for each mixture was determined by applying an F test (*12*) at the 99% confidence level. The parameters A_i obtained in the regression are shown in Table III, along with the standard deviations $\sigma(V^E)$:

$$\sigma(V^E) = [\sum(V^E_{\mathrm{calcd}} - V^E_{\mathrm{exptl}})^2/(N - k)]^{1/2} \qquad (2)$$

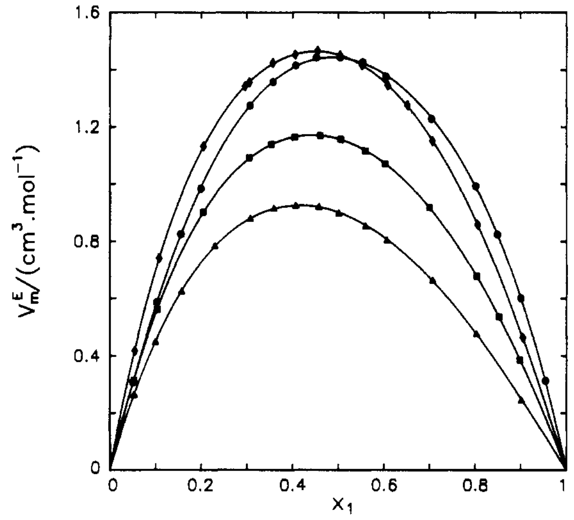

Figure 1. Excess molar volume V^E at 298.15 K for dimethyl carbonate (1) + solvent (2) mixtures versus x_1, the mole fraction of component 1: (■) heptane; (●) decane; (◆) cyclohexane; (▲) 2,2,4-trimethylpentane. Full curves represent smoothing eq 1 with the coefficients of Table III.

where N is the number of direct experimental values. For all the mixtures $\sigma(V^E)/V^E_{\mathrm{max}} < 0.006$, in accord with the precision attainable with the instrument used. A graphical representation of the experimental results together with the smoothing curves appears in Figures 1 and 2. We are not aware of any previous measurements of V^E of these mixtures.

For all the systems studied V^E is positive over the whole mole-fraction range, some even surprisingly large (perhaps a

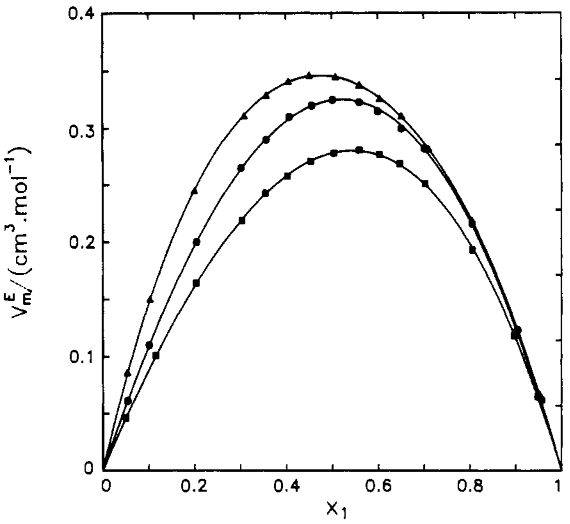

Figure 2. Excess molar volume V^E at 298.15 K for dimethyl carbonate (1) + solvent (2) mixtures versus x_1, the mole fraction of component 1: (●) benzene; (■) toluene; (▲) tetrachloromethane. Full curves represent smoothing eq 1 with the coefficients of Table III.

"size" effect), and interactions with aromatics and tetrachloromethane seem to be stronger than with saturated alkanes, as expected from our previous works (*6*, *7*).

Glossary

A_i	coefficients
x	mole fraction
H	molar enthalpy
V	molar volume
Greek Letters	
Δ	absolute error
ρ	density
σ	standard deviation
τ	oscillation period
Superscript	
E	excess property

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