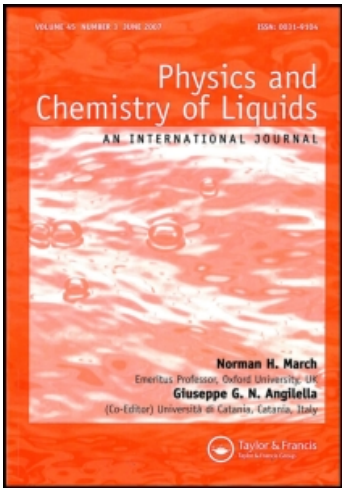

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Volumetric properties of dimethylcarbonate with chloroethanes or chloroethenes at 298.15 K

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Volumetric properties of dimethylcarbonate with chloroethanes or chloroethenes at 298.15 K

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Densities, ρ, of the binary mixtures of dimethylcarbonate with chloroethanes, namely, 1,2-dichloroethane, 1,1,1-trichloroethane, and 1,1,2,2-tetrachloroethane or chlororethenes, namely, trichloroethylene, and tetrachloroethylene have been measured as a function of the composition of dimethylcarbonate at 298.15 K and atmospheric pressure, using an Anton Parr model DMA 4500 oscillating U-tube densitometer. From the experimental results, excess molar volumes V_m^E and partial molar volumes $\overline{V}_i$, were calculated. Limiting partial molar volumes $\overline{V}_i^\circ$, are also calculated by extrapolation of partial molar volumes to infinite dilution. The excess molar volumes are positive for tetrachloroethylene, 1,2-dichloroethane, trichloroethylene, and 1,1,1-trichloroethane and negative for 1,1,2,2-tetrachloroethane in the entire composition range of dimethylcarbonate. For all mixtures, these results were satisfactorily correlated by the Redlich–Kister polynomial. The results are explained in terms of dissociation of the self-associated chloroethanes or chloroethene molecules and the formation of aggregates between unlike molecules.

Keywords: Partial molar volumes; Dimethylcarbonate; Chloroethanes; Chloroethenes

1. Introduction

This article is related to the study of thermodynamic properties of binary mixtures [1–5]. In recent years, measurements of volumetric properties have been adequately employed in understanding the nature of molecular systems and physico-chemical behaviour in liquid mixtures. The nonrectilinear behaviour of volumetric properties of liquid mixtures with changing mole fractions is attributed to the difference in size of the molecules and strength of interactions. Dimethylcarbonate–chloroethanes or chloroethene systems make particularly interesting systems for study because their substituents have a marked effect on the association behaviour. A survey of the

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literature has shown that no excess molar volume measurement for a mixture of dimethylcarbonate with the studied chloroethanes or chloroethenes exists.

We report in this article the densities, ρ, the excess molar volumes, V_m^E, and partial molar volumes $\overline{V}_i$, of binary mixtures containing dimethylcarbonate with chloroethanes or chloroethenes at 298.15 K and atmospheric pressure. The chloroethanes or chloroethenes used are 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, and trichloroethylene and tetrachloroethylene.

2. Experimental

2.1. *Materials*

The materials used in this study, their suppliers, and their purities are listed in table 1. Dimethylcarbonate was purified by the standard method [6]. Chloroethanes and chloroethenes were purified by the standard method described by Perrin and Armarego [7] and stored in a glove box prior to use. The purity of each compound was further ascertained by comparing the densities at 298.15 K. Table 1 also gives the density measurements, which agree with the values obtained from the literature [8].

2.2. *Apparatus and procedure*

The density of the samples was measured with an Anton Paar DMA 4500 oscillating U-tube densitometer, provided with automatic viscosity correction. The temperature in the cell was regulated to ±0.01 K with solid state thermostat. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Air-tight stoppered bottles were used for the preparation of the mixtures. The mass of the dry bottle was first determined. The less volatile component of the mixture was introduced in the bottle and the total mass was recorded. Subsequently, the other component was introduced and the mass of the bottle along with the two components was determined. Each mixture was immediately used after it was mixed well by shaking. All the weightings were performed on an electronic balance (AB 204-N Mettler) accurate to 0.1 mg. The uncertainty in the mole fraction is estimated to be lower than $\pm 2 \times 10^{-4}$.

Table 1. Source, purity grades, and density ρ of the pure component at 298.15 K.

			ρ (g cm^{-3})	
Component	Source	Purity (mass %)	Experimental	Literature[a]
Dimethylcarbonate	Merck	99.0	1.06330	1.0642
1,2-Dichloroethane	Merck	99.0	1.24554	1.2458
1,1,1-Trichloroethane	Merck	98.0	1.32712	1.32096[b]
1,1,2,2-Tetrachloroethane	Fluka	98.0	1.57921	1.5786
Trichloroethylene	Merck	99.5	1.45557	1.4514[b]
Tetrachloroethylene	Merck	99.0	1.60404	1.6064[b]

[a][8].
[b]At 303.15 K.
[c]At 298.15 K.

3. Results and discussion

The experimental results of the excess molar volumes V_m^E, partial molar volumes $\overline{V}_i$ and densities ρ of binary mixtures of dimethylcarbonate with chloroethanes or chloroethenes at atmospheric pressure at 298.15 K are listed in table 2 as a function of the mole fraction x of dimethylcarbonate and are graphically represented in figure 1.

Table 2. Densities, ρ in g cm^{-3}, excess molar volumes, V_m^E in cm^3 mol^{-1}, and partial molar volumes $\overline{V}_i$ in cm^3 mol^{-1}, for binary mixtures of x dimethylcarbonate with $(1-x)$ chloroethanes or chloroethenes at 298.15 K.

x	ρ	V_m^E	$\overline{V}_1$	$\overline{V}_2$	x	ρ	V_m^E	$\overline{V}_1$	$\overline{V}_2$
				x dimethylcarbonate + $(1-x)$ 1,2-dichloroethane					
0.0359	1.23776	0.054	84.72	79.46	0.5067	1.14556	0.335	84.84	79.84
0.0399	1.23696	0.054	84.72	79.46	0.5626	1.13577	0.313	84.81	79.94
0.0998	1.22434	0.127	84.73	79.48	0.6257	1.12483	0.289	84.78	80.04
0.1690	1.21024	0.186	84.76	79.50	0.6916	1.11354	0.258	84.76	80.13
0.2346	1.19701	0.244	84.79	79.53	0.7511	1.10353	0.221	84.75	80.20
0.2976	1.18462	0.287	84.82	79.57	0.8403	1.08876	0.158	84.74	80.27
0.3582	1.17303	0.312	84.84	79.63	0.8694	1.08411	0.128	84.73	80.31
0.4197	1.16157	0.322	84.85	79.71	0.9229	1.07543	0.082	84.72	80.40
0.5063	1.14568	0.332	84.84	79.84					
				x dimethylcarbonate + $(1-x)$ 1,1,1-trichloroethane					
0.0423	1.30790	0.012	85.14	101.27	0.5121	1.17659	0.182	84.91	101.46
0.0979	1.29547	0.039	85.25	101.27	0.5885	1.16112	0.181	84.85	101.54
0.1593	1.28141	0.074	85.27	101.26	0.6480	1.14263	0.164	84.82	101.60
0.2212	1.26706	0.101	85.23	101.27	0.7172	1.12137	0.151	84.78	101.67
0.2961	1.24936	0.130	85.15	101.30	0.7959	1.10327	0.115	84.75	101.77
0.3683	1.23212	0.156	85.06	101.34	0.8608	1.08436	0.091	84.73	101.86
0.4396	1.21433	0.174	84.98	101.40	0.8275	1.06333	0.051	84.72	101.97
0.5046	1.19802	0.180	84.82	101.46					
				x dimethylcarbonate + $(1-x)$ 1,1,2,2-tetrachloroethane					
0.0998	1.54383	−0.034	84.36	105.83	0.6054	1.29893	−0.077	84.71	105.65
0.1508	1.52171	−0.057	84.40	105.83	0.6727	1.26166	−0.059	84.72	105.62
0.2120	1.49431	−0.070	84.45	105.81	0.7497	1.21767	−0.041	84.73	105.60
0.2578	1.47337	−0.079	84.50	105.80	0.8078	1.17338	−0.028	84.73	105.60
0.3238	1.44232	−0.083	84.55	105.78	0.8773	1.14116	−0.011	84.73	105.64
0.4136	1.39868	−0.093	84.62	105.74	0.9478	1.09692	−0.001	84.72	105.74
0.5379	1.33506	−0.088	84.69	105.68					
				x dimethylcarbonate + $(1-x)$ trichloroethylene					
0.0664	1.43024	0.047	85.24	90.28	0.5623	1.23734	0.266	84.89	90.64
0.1022	1.41633	0.088	85.21	90.30	0.6005	1.22237	0.258	84.85	90.70
0.1557	1.39552	0.137	85.19	90.33	0.6515	1.20225	0.247	84.80	90.80
0.2299	1.36695	0.178	85.18	90.38	0.6558	1.20073	0.249	84.80	90.81
0.3133	1.33422	0.224	85.11	90.43	0.7022	1.18229	0.224	84.76	90.92
0.3730	1.31112	0.261	85.07	90.47	0.7776	1.15222	0.201	84.72	91.13
0.4249	1.29092	0.272	85.03	90.50	0.8516	1.12266	0.157	84.70	91.38
0.5078	1.25841	0.281	84.95	90.58	0.9390	1.08764	0.081	84.71	91.68
0.5083	1.25844	0.277	84.95	90.58					
				x dimethylcarbonate + $(1-x)$ tetrachloroethylene					
0.0443	1.59310	0.063	86.39	102.71	0.5485	1.33162	0.484	85.05	103.37
0.1002	1.56518	0.184	86.48	102.70	0.6070	1.29923	0.452	84.97	103.47
0.1739	1.52848	0.286	86.27	102.74	0.6550	1.26955	0.426	84.92	103.57
0.2272	1.50138	0.356	86.04	102.80	0.7144	1.23771	0.396	84.86	103.69
0.3013	1.46337	0.428	85.70	102.92	0.7949	1.19051	0.303	84.79	103.92
0.3717	1.42642	0.485	85.43	103.05	0.8717	1.14408	0.199	84.74	104.17
0.4301	1.39581	0.492	85.27	103.16	0.9428	1.09973	0.099	84.71	104.38
0.5017	1.35717	0.494	85.12	103.29					

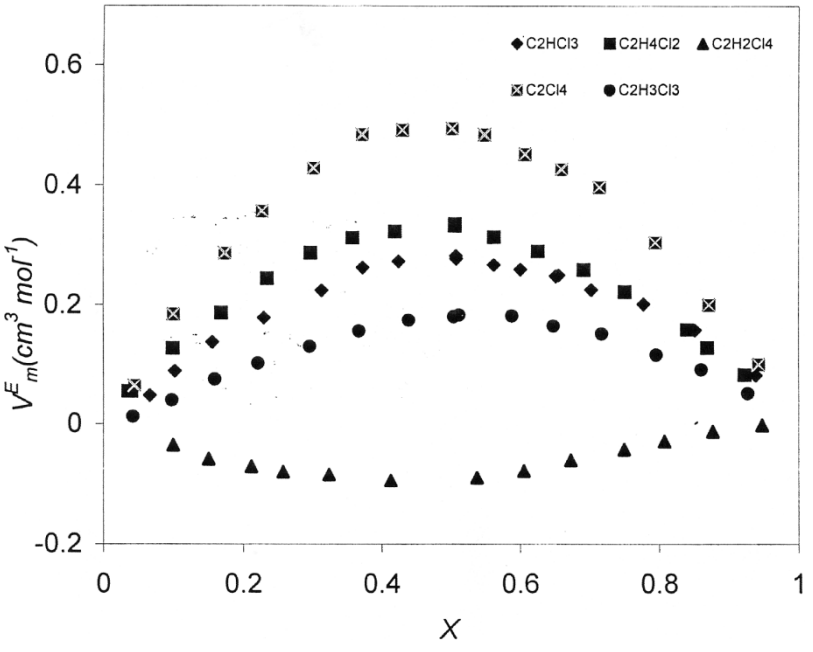

Figure 1. Excess volume of (x) dimethylcarbonate with ($1-x$) chloroethanes or chloroethenes at 298.15 K.

The values of densities ρ, (see table 2) have been used to calculate the excess molar volumes $V^{\mathrm{E}}_{\mathrm{m}}$, with the following equation

$$V^{\mathrm{E}}_{\mathrm{m}} = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{1}$$

where x_i, M_i, and ρ_i ($i=1, 2$) are the mole fractions, molecular weights, and densities of pure components 1 and 2, respectively and ρ is density of the mixtures.

In all cases, it was possible to represent the dependence of $V^{\mathrm{E}}_{\mathrm{m}}$ on mole fraction using the Redlich–Kister [9] polynomial equation

$$V^{\mathrm{E}}_{\mathrm{m}} = x(1-x)\sum_{k=1}^{n} A_k (1-2x)^{k-1} \tag{2}$$

The Redlich–Kister coefficients A_k, with the standard deviation $\sigma(V^{\mathrm{E}}_{\mathrm{m}})$, obtained by unweighted least squares associated with the use of equations (2) and (3), respectively, are summarized in table 3. $\sigma(V^{\mathrm{E}}_{\mathrm{m}})$ is evaluated from the equation

$$\sigma(V^{\mathrm{E}}_{\mathrm{m}}) = \left[\sum_{k=1}^{n} \left(V^{\mathrm{E}}_{\mathrm{m,\,expt.}} - V^{\mathrm{E}}_{\mathrm{m,\,calc.}}\right)^2 / (n-p)\right]^{1/2} \tag{3}$$

where n is the number of results and p is the number of parameters retained in equation (2).

Table 3. Values of adjustable coefficient A_k, in equation (2) and standard deviation $\sigma(V_m^E)$, in equation (3) for x dimethylcarbonate + $(1-x)$ chloroethanes or chloroethenes.

System	A_1	A_2	A_3	A_4	A_5	$\sigma(V_m^E)/cm^3\,mol^{-1}$
x dimethylcarbonate + $(1-x)$ 1,2-dichloroethane	1.3225	0.1814	−0.3436	−0.3780	0.4335	0.001
x dimethylcarbonate + $(1-x)$ 1,1,1-trichloroethane	0.7180	−0.6670	−0.1306	−0.2081	−0.0925	0.004
x dimethylcarbonate + $(1-x)$ 1,1,2,2-tetrachloroethane	−0.3581	−0.1821	0.1273	−0.0264	0.0724	0.003
x dimethylcarbonate + $(1-x)$ trichloroethylene	1.1027	0.1245	0.0716	−0.6211	−0.0797	0.004
x dimethylcarbonate + $(1-x)$ tetrachloroethylene	1.9573	0.0150	0.3702	1.3296	−0.9204	0.008

Comparison of the values of V_m^E for different systems in figure 1 reveals that V_m^E values for the binary mixtures of dimethylcarbonate with 1,1,2,2-tetrachloroethane are negative, while those with 1,2-dichloroethane, 1,1,1-trichloroethane, and trichloroethylene and tetrachloroethylene are positive over the entire composition range studied. The V_m^E *versus* x curves for all the mixtures are almost symmetrical with a minimum or maximum around $x \approx 0.5$. The values of V_m^E at this concentration follow the order:

$$\text{Tetrachloroethylene} > 1,2\text{-dichloroethane} > \text{trichloroethylene} > 1,1,1\text{-trichloroethane} > 1,1,2,2\text{-tetrachloroethane}$$

The observed values of V_m^E in all of the binary mixtures over the entire range of compositions can be attributed to the following factors: (I) interactions between the unlike molecules, dispersion forces, dipole-induced dipole interactions; (II) complex formation between unlike molecules; (III) contributions due to size and shape. The experimental results suggest that the first two factors are dominant in the mixtures of dimethylcarbonate with 1,1,2,2-tetrachloroethane, whereas the last factor is dominant in the mixtures of dimethylcarbonate + 1,1,2,2-tetrachloroethane, +1,2-dichloroethane, +1,1,1-trichloroethane, +trichloroethylene, and +tetrachloroethylene.

The partial molar volumes of components $\overline{V}_i$ in binary mixtures can be determined from the excess molar volumes V_m^E data as follows:

$$\overline{V}_1 = V_1^\circ + (1-x)\left(\frac{\partial V_m^E}{\partial x}\right) \tag{4}$$

$$\overline{V}_2 = V_2^\circ - x\left(\frac{\partial V_m^E}{\partial x}\right) \tag{5}$$

in which $\overline{V}_1$ and $\overline{V}_2$ are partial molar volumes of dimethylcarbonate and chloroethanes or chloroethenes, respectively, where x and $(1-x)$ are the mole fraction of dimethylcarbonate or chloroethanes and chloroethenes, respectively.

To obtain values of the partial molar volumes, $\overline{V}_i$, we start by differentiation of equation (2) with respect to x and substitution of the result in equations (4) and (5)

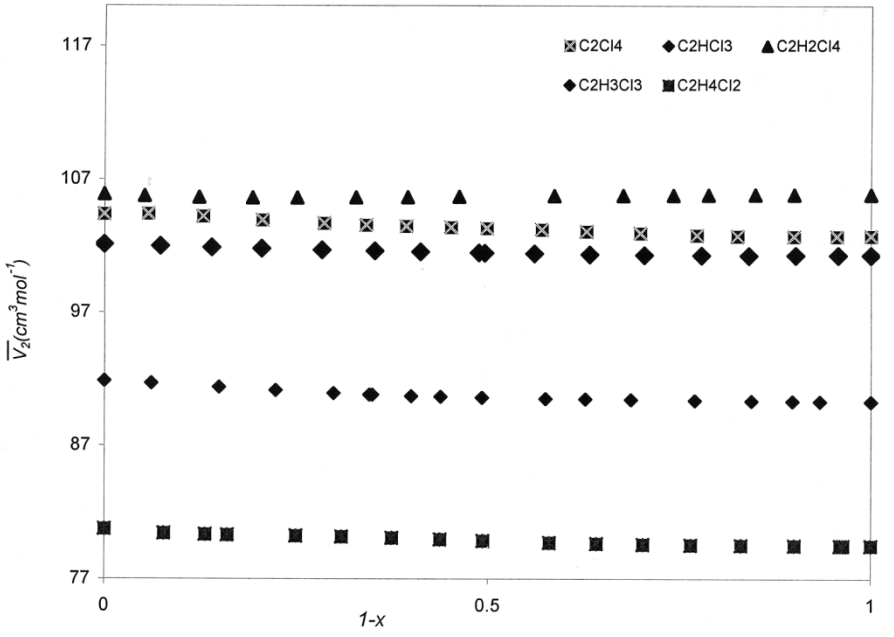

Figure 2. Partial molar volume of chloroethanes or chloroethenes at infinite dilution in dimethylcarbonate at 298.15 K.

leads to the following equations for the partial molar volumes $\overline{V}_1$ of dimethylcarbonate and $\overline{V}_2$ of chloroethanes or chloroethenes,

$$\overline{V}_1 = (1-x)^2 \sum_{k=1} A_k (1-2x)^{k-1} - 2x(1-x)^2 \sum_{k=1} A_k (k-1)(1-2x)^{k-2} + V_1^\circ \quad (6)$$

$$\overline{V}_2 = x^2 \sum_{k=1} A_k (1-2x)^{k-1} - 2x^2(1-x) \sum_{k=1} A_k (k-1)(1-2x)^{k-2} + V_2^\circ \quad (7)$$

Partial molar volumes of dimethylcarbonate, $\overline{V}_1$ and $\overline{V}_2$ for all compositions can be calculated by using the Redlich–Kister coefficients (table 3) in equations (6) and (7). Results at 298.15 K are also listed in table 2 and shown for $\overline{V}_2$ in figure 2.

The partial molar volume at infinite dilution $\overline{V}_i^\circ$ appears to be of interest. In the limit of infinite dilution, solute–solute interactions disappear. Thus, the values of the partial molar volumes at infinite dilution provide insight into the solute–solvent interactions. We can consider dimethylcarbonate at infinite dilution ($x = 0$) in chloroethanes or chloroethenes, and of chloroethanes or chloroethenes at infinite dilution ($x = 1$) in dimethylcarbonate. Setting $x = 0$ in equation (6) leads to

$$\overline{V}_1^\circ = \sum_{k=1} A_k + V_1^\circ \quad (8)$$

Similarly, setting ($x = 1$) in equation (7) leads to

$$\overline{V}_2^\circ = \sum_{k=1} A_k (-1)^{k-1} + V_2^\circ \quad (9)$$

Table 4. Partial molar volumes of x dimethylcarbonate at infinite dilution in $(1-x)$ chloroethanes or chloroethenes, $\overline{V}_1^\circ$ and chloroethanes or chloroethenes at infinite dilution in dimethylcarbonate, $\overline{V}_2^\circ$ from equations (8) and (9), for x dimethylcarbonate + $(1-x)$ chloroethanes or chloroethenes at 298.15 K.

System	$\overline{V}_1^\circ$	$\overline{V}_2^\circ$
x dimethylcarbonate + $(1-x)$ 1,2-dichloroethane	86.27	80.72
x dimethylcarbonate + $(1-x)$ 1,1,1-trichloroethane	84.95	102.05
x dimethylcarbonate + $(1-x)$ 1,1,2,2-tetrachloroethane	85.76	104.37
x dimethylcarbonate + $(1-x)$ trichloroethylene	85.31	91.85
x dimethylcarbonate + $(1-x)$ tetrachloroethylene	85.76	104.37

In equations (8) and (9), $\overline{V}_1^\circ$ and $\overline{V}_2^\circ$ represent the partial molar volumes of dimethylcarbonate at infinite dilution in chloroethanes or chloroethenes, and the partial molar volume of chloroethanes or chloroethenes, at infinite dilution in dimethylcarbonate, respectively. All partial molar volumes at infinite dilution, $\overline{V}_1^\circ$, were calculated using the Redlich–Kister coefficients (table 3) in equations (8) and (9) and are listed in table 4.

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