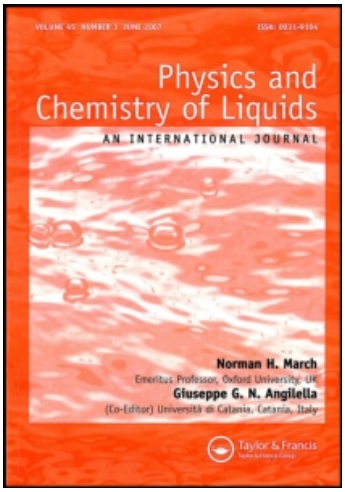

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Excess Molar Volumes and Partial Molar Volumes of Binary Mixtures Containing Diethylcarbonate with Benzene and Substituted Benzenes at 293.15 K

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EXCESS MOLAR VOLUMES AND PARTIAL MOLAR VOLUMES OF BINARY MIXTURES CONTAINING DIETHYLCARBONATE WITH BENZENE AND SUBSTITUTED BENZENES AT 293.15 K

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Densities of the binary mixtures of diethylcarbonate with benzene and substituted benzenes, namely toluene, bromobenzene, chlorobenzene and nitrobenzene have been measured as a function of the composition, at 293.15 K and atmospheric pressure using a bicapillary pycnometer with an accuracy of 4 parts in 10^4. The calculated excess molar volumes, V^E were correlated with Redlich–Kister equation. The excess molar volumes are negative over the entire range of composition for the systems diethylcarbonate with benzene, toluene, bromobenzene and nitrobenzene. An inversion of the sign of V^E is observed over some concentration for mixtures of diethylcarbonate with chlorobenzene. Partial molar volumes, $\bar{V}_i$ are also evaluated and their values have been extrapolated to zero concentration to obtain the limiting value at infinite dilution, $\bar{V}_i^\circ$. The numerical values of the excess molar volumes for binary mixtures decrease in the order: chlorobenzene > benzene > bromobenzene ≈ toluene > nitrobenzene. The results are explained in terms of dissociation of the self-associated solute molecules and the formation of aggregates between unlike molecules.

Keywords: Excess molar volumes; Diethylcarbonate; Benzene; Substituted benzenes; Self-associated Redlich–Kister equation

1. INTRODUCTION

Excess molar volumes, V^E and partial molar volumes, $\bar{V}_i$ of mixing are complex properties that depend not only on solute–solute, solvent–solvent, and solute–solvent interactions, but also on the packing of the solute and solvent molecules. Our experimental study of the thermodynamic properties of the nonelectrolyte solutions demonstrated that specific interactions between unlike molecules can occur [1–5]. In this article, we present excess molar volumes, V^E and partial molar volumes, $\bar{V}_i$ of diethylcarbonate with the benzene and substituted benzenes at 293.15 K. By extrapolation of partial molar volumes to infinite dilution, limiting partial molar volumes, $\bar{V}_i^\circ$ are also obtained. These values are interesting from a theoretical point of view, since, at infinite dilution, the only interactions present are solute–solvent interaction.

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TABLE I Source, purity grades, densities ρ and refractive indices n_D of the pure components at 293.15 K

Component	*Source*	*Purity* (mass %)	ρ (g cm^{-3})		n_D	
			Expt.	*Lit.*[a]	*Expt.*	*Lit.*[a]
Diethylcarbonate	Merk	99	0.9762	0.9764[b]	1.3841	1.3843[b]
Benzene	Merk	99.8	0.87913	0.87901	1.5008	1.50112
Chlorobenzene	Merk	99.5	1.1060	1.1063	1.5251	1.52481
Toluene	Merk	99	0.86691	0.86696	1.4966	1.49693
Bromobenzene	Merk	99	1.4950	1.4952[b]	1.5585	1.5580[b]
Nitrobenzene	Fluka	99	1.20320	1.20329	1.5496	1.54997[c]

[a][7]; [b][8]; [c]At 298.15 K.

2. EXPERIMENTAL SECTION

Materials

The material used in the study, suppliers, and their purities are listed in Table I. Diethylcarbonate was purified by the standard method described by Perrin and Armarego [6]. Benzene and substituted benzenes used were purified by distillation using a 1 m fractionation column [7]. The purified compounds were stored in brown glass bottles and fractionally distilled immediately before use. Purity of each compounds was ascertained by the constancy of the boiling point and also from the density and refractive index. Densities were measured at 293.15 K using a bicapillary pycnometer with an accuracy of 4 parts in 10^4. Refractive indexes were measured at 293.15 K with an Abbe' refractometer. Water was circulated to the refractometer from a constant-temperature bath at 293.15 K. The accuracy of the refractive index measured is on the order of ± 0.0002. Table I also gives the density and refractive index measurements, which agree with values obtained from the literature [8].

3. RESULTS AND DISCUSSION

At least 15 density measurements were performed (with repetition) for each binary system, in the full concentration range ($0 \leq x \leq 1$). The excess molar volumes, V^E of the solutions of molar composition x were calculated from the densities of the pure liquids and their mixtures according to the following equation:

$$V^E = [xM_1 + (1-x)M_2]/\rho - [xM_1/\rho_1 + (1-x)(1-x)M_2/\rho_2] \quad (1)$$

where ρ, ρ_1 and ρ_2 are the densities of the solution and pure components 1 and 2, respectively, and M_1 and M_2 the molar masses of the pure components. The corresponding values of ρ and V^E of binary mixtures of [x diethylcarbonate + $(1-x)$ benzene and substituted benzenes] at 293.15 K are reported in Table II and Fig. 1.

Each set of results were fitted using a Redlich–Kister polynomial [9] which, for binary mixtures, is

$$V^E/(\text{cm}^3\,\text{mol}^{-1}) = x(1-x)\sum_{k=1} A_k(1-2x)^{k-1} \quad (2)$$

TABLE II Densities ρ[a], excess molar volumes $V^{E,b}$, partial molar volumes $\bar{V}_i$[b], for binary mixtures of x diethylcarbonate with $(1-x)$ benzene and substituted benzenes at 293.15 K

x	ρ	V^E	$\bar{V}_1$	$\bar{V}_2$	x	ρ	V^E	$\bar{V}_1$	$\bar{V}_2$
				x diethylcarbonate + (1 − x) benzene					
0.0712	0.8885	−0.029	120.39	88.87	0.5593	0.9444	−0.424	120.57	88.45
0.1251	0.8955	−0.065	120.14	88.90	0.6287	0.9506	−0.418	120.73	88.22
0.1783	0.9024	−0.120	120.00	88.92	0.7123	0.9573	−0.367	120.87	87.92
0.2392	0.9010	−0.190	119.95	88.94	0.7453	0.9597	−0.338	120.92	87.80
0.2987	0.9172	−0.265	119.98	88.92	0.7995	0.9636	−0.277	120.97	87.63
0.3551	0.9236	−0.316	120.07	88.88	0.8436	0.9666	−0.224	120.99	87.51
0.4365	0.9325	−0.382	120.26	88.76	0.8921	0.9697	−0.157	121.00	87.42
0.4935	0.9382	−0.417	120.40	88.63	0.9401	0.9728	−0.087	121.01	87.39
				x diethylcarbonate + (1 − x) chlorobenzene					
0.0851	1.0899	0.331	123.45	101.91	0.5732	1.0304	−0.431	119.82	102.39
0.1372	1.0813	0.415	122.02	102.09	0.6150	1.0256	−0.484	119.10	102.12
0.2191	1.0699	0.385	120.51	102.41	0.6932	1.0165	−0.553	120.34	101.46
0.2965	1.0604	0.253	119.73	102.67	0.7732	1.0068	−0.540	120.65	100.62
0.3624	1.0530	0.099	119.44	102.81	0.8215	1.0006	−0.486	120.79	100.06
0.4103	1.0479	−0.041	119.38	102.85	0.8672	0.9946	−0.402	120.89	99.50
0.4467	1.0439	−0.125	119.42	102.82	0.9232	0.9870	−0.260	120.97	98.82
0.5201	1.0361	−0.319	119.61	102.64					
				x diethylcarbonate + (1 − x) toluene					
0.1183	0.8833	−0.223	119.26	106.27	0.6632	0.9498	−0.874	120.12	105.46
0.1732	0.8906	−0.312	119.34	106.26	0.7269	0.9562	−0.850	120.32	104.10
0.2312	0.8982	−0.409	119.41	106.24	0.7532	0.9588	−0.838	120.41	104.75
0.2896	0.9057	−0.495	119.47	106.22	0.8213	0.9648	−0.733	120.64	103.89
0.3397	0.9120	−0.567	119.52	106.20	0.8736	0.9689	−0.596	120.80	102.99
0.3988	0.9193	−0.645	119.58	106.16	0.9203	0.9721	−0.427	120.92	101.97
0.4793	0.9290	−0.740	119.69	106.07	0.9423	0.9735	−0.328	120.96	101.40
0.5621	0.9387	−0.826	119.85	105.89	0.9821	0.9756	−0.115	120.01	100.22
				x diethylcarbonate + (1 − x) bromobenzene					
0.0629	1.4609	−0.215	117.87	105.01	0.4800	1.2361	−0.752	120.29	104.25
0.1010	1.4402	−0.333	118.26	104.97	0.5325	1.2087	−0.740	120.41	104.13
0.1400	1.4190	−0.435	118.61	104.92	0.5968	1.1757	−0.729	120.53	103.97
0.2045	1.3838	−0.555	119.10	104.82	0.6512	1.1478	−0.681	120.62	103.82
0.2400	1.3645	−0.611	119.33	104.76	0.7192	1.1136	−0.614	120.72	103.60
0.3091	1.3270	−0.680	119.70	104.62	0.7921	1.0774	−0.515	120.82	103.27
0.3588	1.3004	−0.726	119.92	104.51	0.8315	1.0580	−0.447	120.87	103.04
0.4123	1.2718	−0.745	120.10	104.39	0.8972	1.0260	−0.307	120.96	102.55
				x diethylcarbonate + (1 − x) nitrobenzene					
0.1163	1.1748	−0.180	118.85	102.40	0.5830	1.0733	−1.207	119.64	101.35
0.1765	1.1611	−0.337	118.50	102.46	0.6326	1.0623	−1.204	119.91	100.93
0.2190	1.1516	−0.445	118.37	102.49	0.6932	1.0488	−1.168	120.22	100.31
0.2698	1.1406	−0.594	118.34	102.50	0.7825	1.0283	−0.995	120.61	99.23
0.3165	1.1306	−0.725	118.40	102.47	0.8342	1.0162	−0.834	120.77	98.51
0.3758	1.1179	−0.872	118.58	102.38	0.8864	1.0039	−0.626	120.90	97.74
0.4369	1.1048	−1.011	118.84	102.19	0.9232	0.9950	−0.440	120.96	97.17
0.4974	1.0920	−1.125	119.16	101.92	0.9615	0.9857	−0.232	120.10	96.56

[a]Units, g cm^{-3}; [b]Units, cm^3 mol^{-1}.

where x is the mole fraction of diethylcarbonate, A_k is the polynomial coefficient obtained by a linear least-squares fitting procedure. In each case, the optimum number of coefficients was ascertained from an examination of the variation of the standard deviation $\sigma(V^E)$ with

$$\sigma(V^E) = \left[\sum (V^E_{\text{expt.}} - V^E_{\text{calcd.}})^2/(n-p)\right]^{(1/2)} \tag{3}$$

in which n is the number of results and p is the number of parameters retained in Eq. (2).

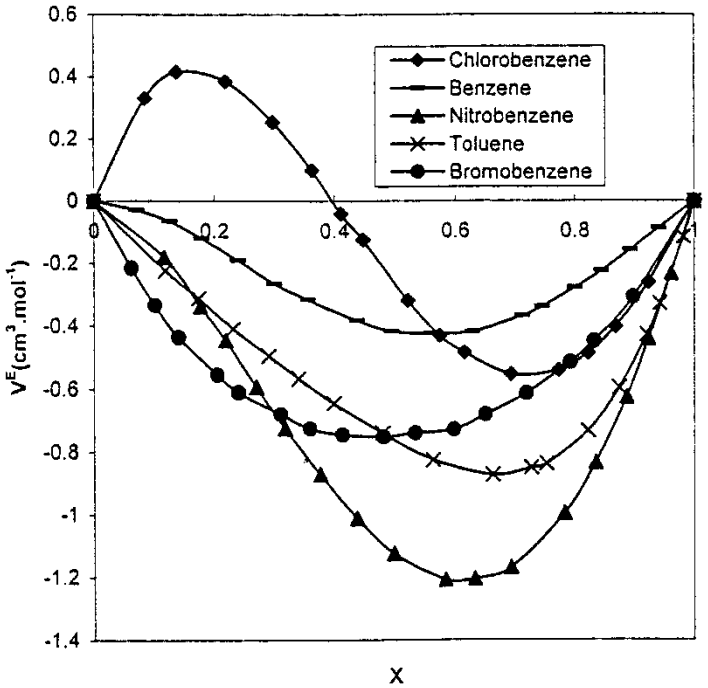

FIGURE 1 Excess molar volume for the binary mixture of {x diethylcarbonate + $(1-x)$ benzene and substituted benzene} at 293.15 K.

TABLE III Values of adjustable coefficients, A_k in Eq. (2) and standard deviation, $\sigma(V_m^E)$ in Eq. (3) for x diethylcarbonate + $(1-x)$ benzene and substituted benzenes at 293.15 K

System	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$ (cm^3 mol^{-1})
x diethylcarbonate + $(1-x)$benzene	−1.6625	0.7037	0.9234	−0.0389	0.003
x diethylcarbonate + $(1-x)$chlorobenzene	−1.0671	4.8055	2.0145	−0.0480	0.005
x diethylcarbonate + $(1-x)$toluene	−3.0673	2.0620	−1.2817	0.2559	0.003
x diethylcarbonate + $(1-x)$bromobenzene	−3.0095	−0.3107	−0.7479	0.2043	0.004
x diethylcarbonate + $(1-x)$nitrobenzene	−4.5115	2.8475	0.9560	−0.0152	0.005

The values adopted for the coefficients, A_k and the standard deviation, $\sigma(V^E)$ are summarized in Table III.

Comparison of V^E for different systems recorded in Fig. 1 reveals several interesting features. It is observed that V^E for the binary mixtures of diethylcarbonate with all the studied mixtures is negative, while those with chlorobenzene an inversion of the sign of V^E is observed. The numerical values of the excess molar volumes for binary mixtures decrease in the order:

$$\text{chlorobenzene} > \text{benzene} > \text{bromobenzene} \approx \text{toluene} > \text{nitrobenzene}.$$

Existence of strong hydrogen bonding and specific interaction between unlike molecules and the association between solvent–solute is stronger, which, therefore, cause a volume contraction $V^E < 0$. For the mixture of chlorobenzene attraction interactions between

unlike species decrease and repulsive interactions predominate, leading to positive excess molar volumes and some composition of diethylcarbonate.

The partial molar volumes of components, $\bar{V}_i$ in binary mixture can be determined from excess molar volumes, V^E data as follows:

$$\bar{V}_1 = V_1^0 + (1-x)(\partial V^E/\partial x) \tag{4}$$

$$\bar{V}_2 = V_2^0 - x(\partial V^E/\partial x) \tag{5}$$

in which $\bar{V}_1$ and $\bar{V}_2$ are partial molar volume of diethylcarbonate and (benzene and substituted benzenes), respectively, where x and $(1-x)$ are the mole fraction of diethylcarbonate and (benzene and substituted benzenes), respectively.

To obtain values of the partial molar volumes, $\bar{V}_i$, we start by differentiation of Eq. (2) with respect to x and substitution of the result in Eqs. (4) and (5) leads to the following equations for the partial molar volumes of diethylcarbonate, $\bar{V}_1$ and (benzene and substituted benzenes), $\bar{V}_2$

$$\bar{V}_1 = (1-x)^2 \sum_{k=1} A_k(1-2x)^{k-1} - 2x(1-x)^2 \sum_{k=1} A_k(k-1)(1-2x)^{k-2} + V_1^0 \tag{6}$$

$$\bar{V}_2 = x^2 \sum_{k=1} A_k(1-2x)^{k-1} - 2x^2(1-x) \sum_{k=1} A_k(k-1)(1-2x)^{k-2} + V_2^0 \tag{7}$$

Partial molar volumes of diethylcarbonate, $\bar{V}_1$ and of $\bar{V}_2$ for all compositions can be calculated by using the Redlich–Kister coefficients (Table III) in Eqs. (6) and (7). Results at 293.15 K are also listed in Table II and shown for $\bar{V}_2$ in Fig. 2.

The partial molar volume at infinite dilution $\bar{V}_i^\circ$ appears to be of interest. In the limit of infinite dilution, solute–solute interaction disappear. Thus, the values of the partial molar volumes at infinite dilution provide insight into solute–solvent interactions.

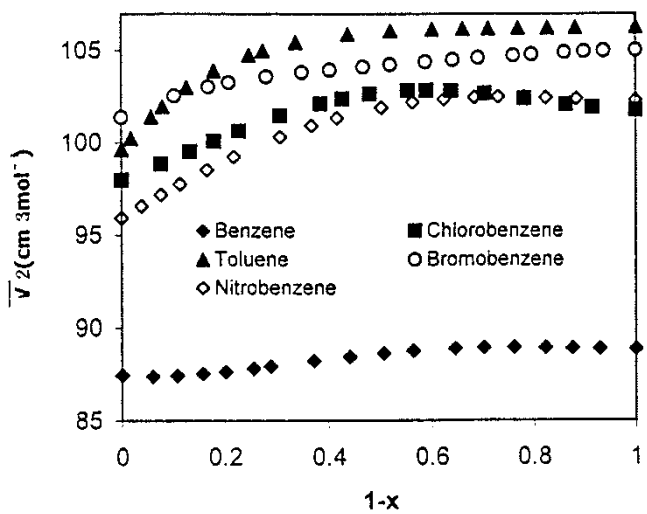

FIGURE 2 Partial molar volume of benzene and substituted benzenes in mixtures of {x diethylcarbonate + $(1-x)$ benzene and substituted benzenes} at 293.15 K.

TABLE IV Partial molar volumes of x diethylcarbonate at infinite dilution in $(1-x)$ benzene and substituted benzenes, $\bar{V}_1^\circ$ and benzene and substituted benzenes at infinite dilution in diethylcarbonate, $\bar{V}_2^\circ$ from Eqs. (8) and (9), for x diethylcarbonate $+(1-x)$ benzene and substituted benzenes at 293.15 K

System	$\bar{V}_1^\circ$	$\bar{V}_2^\circ$
x diethylcarbonate $+(1-x)$benzene	120.93	87.44
x diethylcarbonate $+(1-x)$chlorobenzene	126.71	97.95
x diethylcarbonate $+(1-x)$toluene	118.97	99.61
x diethylcarbonate $+(1-x)$bromobenzene	117.15	101.38
x diethylcarbonate $+(1-x)$nitrobenzene	120.28	95.93

We can consider diethylcarbonate at infinite dilution ($x=0$) in (benzene and substituted benzenes), and of (benzene and substituted benzenes), at infinite dilution ($x=1$) in diethylcarbonate. Setting $x=0$ in Eq. (6) leads to

$$\bar{V}_1^\circ = \sum_{k=1} A_K + V_1^0 \tag{8}$$

Similary, setting $x=1$ in Eq. (7) leads to

$$\bar{V}_2^\circ = \sum_{k=1} A_K(-1)^{k-1} + V_2^0 \tag{9}$$

In Eqs. (8),(9), $\bar{V}_1^\circ$ and $\bar{V}_2^\circ$ represent the partial molar volumes of diethylcarbonate at infinite dilution in (benzene and substituted benzenes), and the partial molar volume of (benzene and substituted benzenes), at infinite dilution in diethylcarbonate, respectively. All partial molar volumes at infinite dilution, $\bar{V}_i^\circ$ were calculated using the Redlich–Kister coefficients (Table III) in Eqs. (8) and (9) and are listed in Table IV.

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