Excess Molar Volumes of Binary Mixtures Containing Diethyl Carbonate + Linear and Cyclic Ethers at 298.15 K

Romolo Francesconi*

Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy

Densitites and excess molar volumes for the eight binary mixtures diethyl carbonate + diethoxymethane, + 1,2-diethoxyethane, + dimethoxymethane, + 1,2-dimethoxyethane, + 1,3-dioxolane, + oxolane, + 1,4-dioxane, or + oxane have been determined at 298.15 K and atmospheric pressure by means of a digital density meter. Excess molar volumes are negative over the entire range of composition for the four mixtures containing linear ethers and positive in the cases of cyclic ethers with the exception of the diethyl carbonate + 1,3-dioxolane mixture, which presents a sign inversion. The results were correlated by the Redlich–Kister equation.

Introduction

Esters of carbonic acid are used as solvents for many synthetic and natural resins and in the synthesis of pharmaceuticals and agricultural chemicals.

In continuation of our research program involved in the accumulation of thermodynamic properties of binary mixtures containing esters of carbonic acid, we now present some new experimental data on densities, ϱ, and excess molar volumes, V_m^E, for the mixtures diethyl carbonate (common component, component 1) plus four linear and four cyclic ethers (noncommon component, component 2), namely diethoxymethane, 1,2-diethoxyethane, dimethoxymethane, 1,2-dimethoxyethane, 1,3-dioxolane, oxolane, 1,4-dioxane, and oxane, respectively.

The aim of this paper is to check the capability of the predictive expression developed by Redlich–Kister (*1*) and to investigate the relative influence of the ether group on molecular interactions of these mixtures.

In previous works (*2*, *3*), we have determined the excess molar volumes of dimethyl carbonate and the excess molar enthalpies of dimethyl and diethyl carbonate plus linear and cyclic ethers.

No volumetric literature data have been reported previously for the mixtures studied in this paper.

Experimental Section

Chemicals. Aldrich chemical reactives were used in the measurements. Liquids were purity grade ≥99 mol % with the exception of 1,2-diethoxyethane, the purity of which was 98 mol % and which was purified by fractionation over a sodium wire.

The other chemicals were used without further purification.

All liquids were stored in dark bottles and dried over molecular sieves (Union Carbide, type 4A, $^1/_{16}$-in. pellets).

The purities of the compounds were checked by measuring their densities ϱ at (298.15 ± 0.01) K, which are reported in Table 1 with their corresponding literature values.

* Author to whom correspondence should be addressed.

Table 1. Densities, ϱ, of Pure Components in Comparison with Literature Data at 298.15 K

component	ϱ/(g·cm^{-3}) exptl	lit.
diethyl carbonate	0.96922	0.96926 (*4*)
diethoxymethane	0.82414	0.82412 (*5*)
1,2-diethoxyethane	0.83598	0.83610 (*5*)
dimethoxymethane	0.85699	0.85654 (*6*)
1,2-dimethoxyethane	0.86214	0.86190 (*7*)
1,3-dioxolane	1.05882	1.05865 (*4*)
oxolane	0.88174	0.88200 (*8*)
1,4-dioxane	1.02803	1.02797 (*4*)
oxane	0.87906	0.8791 (*9*)

Apparatus and Procedure. The apparatus used in this paper was a digital vibrating-tube density meter (Anton Paar DMA 60/602, Graz, Austria) with a resolution of 1×10^{-6} g·cm^{-3} and equipped with a temperature sensor (Anton Paar DT 100-25) which could keep the temperature within ±0.01 K. An external Hetotherm bath circulator (type 01 DBT 623) was used with a temperature control interval of ±0.005 K.

The characteristics of the density meter and the operating procedure have been well described previously (*10*).

Mixtures were prepared by mass by using a Mettler balance (Model AE 160) with airtight stoppered bottles and an accuracy of 0.0001 g.

To minimize the error in composition, which arise from evaporation during the solution preparation, we charged the less volatile component first.

All measurements were corrected for buoyancy and for evaporation of components. This correction leads to a variation of 0.0003 in mole fraction, at the worst.

The density meter technique requires two density standards. We used dry air and freshly bidistilled water for calibrating the apparatus before each series of measurements.

Furthermore, the apparatus was checked with the benzene + cyclohexane mixture, the density of which is accurately known from the literature (*11*): our value for V_m^E at 0.5 mole fraction is 0.652 cm^3·mol^{-1} (lit. value, 0.6514 cm^3·mol^{-1}).

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Table 2. Experimental Densities, ϱ, and Excess Molar Volumes, V_m^E, for Diethyl Carbonate + Linear or Cyclic Ethers at 298.15 K and Atmospheric Pressure

x_1	ϱ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	x_1	ϱ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	x_1	ϱ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	x_1	ϱ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})
Diethyl Carbonate (1) + Diethoxymethane (2)											
0.0200	0.82702	−0.012	0.3779	0.87886	−0.159	0.5893	0.90957	−0.165	0.8771	0.95133	−0.068
0.0858	0.83651	−0.050	0.4192	0.88487	−0.169	0.5949	0.91038	−0.164	0.9369	0.96001	−0.034
0.1723	0.84901	−0.092	0.4670	0.89181	−0.170	0.6526	0.91876	−0.153	0.9868	0.96728	−0.008
0.2118	0.85476	−0.112	0.5030	0.89703	−0.171	0.7125	0.92746	−0.138			
0.3128	0.86942	−0.146	0.5100	0.89805	−0.171	0.7803	0.93729	−0.114			
Diethyl Carbonate (1) + 1,2-Diethoxyethane (2)											
0.0234	0.83875	−0.012	0.3891	0.88405	−0.128	0.6201	0.91479	−0.130	0.9388	0.96007	−0.030
0.0757	0.84499	−0.037	0.4594	0.89323	−0.137	0.6640	0.92081	−0.122	0.9894	0.96762	−0.005
0.18076	0.85778	−0.081	0.4932	0.89770	−0.137	0.7340	0.93055	−0.106			
0.2785	0.86994	−0.110	0.5427	0.90431	−0.137	0.7984	0.93967	−0.085			
0.3149	0.87454	−0.116	0.5689	0.90783	−0.134	0.8877	0.95256	−0.052			
Diethyl Carbonate (1) + Dimethoxymethane (2)											
0.0197	0.86006	−0.006	0.2961	0.89855	−0.053	0.5090	0.92337	−0.053	0.9054	0.96131	−0.004
0.0774	0.86877	−0.021	0.3347	0.90333	−0.056	0.5481	0.92754	−0.051	0.9744	0.96711	−0.003
0.1297	0.87636	−0.032	0.3777	0.90850	−0.056	0.6336	0.93631	−0.041			
0.2132	0.88784	−0.045	0.4235	0.91385	−0.057	0.7198	0.94467	−0.030			
0.2458	0.89213	−0.049	0.4577	0.91777	−0.057	0.8422	0.95584	−0.012			
Diethyl Carbonate (1) + 1,2-Dimethoxyethane (2)											
0.0160	0.86413	−0.001	0.32532	0.90074	−0.008	0.5540	0.92552	−0.005	0.9163	0.96140	−0.000
0.0659	0.87031	−0.003	0.3715	0.90590	−0.008	0.5889	0.92916	−0.005	0.9852	0.96786	−0.000
0.1461	0.87999	−0.005	0.4237	0.91162	−0.007	0.6561	0.93604	−0.003			
0.1836	0.88444	−0.007	0.4909	0.91886	−0.007	0.7630	0.94671	−0.001			
0.2768	0.89524	−0.008	0.5033	0.92019	−0.006	0.8474	0.95490	−0.000			
Diethyl Carbonate (1) + 1,3-Dioxolane (2)											
0.0097	1.05733	−0.001	0.2484	1.02610	−0.002	0.4418	1.00683	0.005	0.8683	0.97630	0.008
0.0597	1.04994	−0.003	0.2937	1.02118	−0.001	0.4886	1.00278	0.006	0.9856	0.06995	0.001
0.0979	1.04461	−0.003	0.3263	1.01781	0.001	0.5774	0.99564	0.008			
0.1360	1.03958	−0.004	0.3702	1.01345	0.002	0.6612	0.98948	0.010			
0.1962	1.03211	−0.002	0.4036	1.01031	0.002	0.8135	0.97954	0.010			
Diethyl Carbonate (1) + Oxolane (2)											
0.0108	0.88309	0.005	0.2799	0.91306	0.078	0.4920	0.93257	0.093	0.8139	0.95714	0.052
0.0568	0.88869	0.025	0.3261	0.91756	0.086	0.5344	0.93612	0.091	0.9166	0.96396	0.027
0.1163	0.89562	0.045	0.3488	0.91973	0.088	0.6127	0.94241	0.085	0.9748	0.96765	0.008
0.1606	0.90055	0.058	0.3996	0.92443	0.091	0.6930	0.94853	0.074			
0.2269	0.90764	0.082	0.4332	0.92746	0.093	0.7137	0.95005	0.071			
Diethyl Carbonate (1) + 2,4-Dioxane (2)											
0.0139	1.02672	0.013	0.2739	1.00603	0.139	0.4956	0.99228	0.153	0.9036	0.97294	0.046
0.0632	1.02231	0.049	0.3437	1.00138	0.151	0.5531	0.98913	0.148	0.9741	0.97018	0.014
0.1236	1.01724	0.084	0.3627	1.00017	0.154	0.6181	0.98576	0.138			
0.1632	1.01411	0.103	0.4091	0.99730	0.157	0.7290	0.98043	0.110			
0.2363	1.00867	0.130	0.4514	0.99478	0.157	0.8191	0.97643	0.080			
Diethyl Carbonate (1) + Oxane (2)											
0.0079	0.87986	0.010	0.3202	0.91049	0.218	0.5286	0.92972	0.219	0.9245	0.96323	0.052
0.0623	0.88531	0.071	0.3710	0.91528	0.226	0.5839	0.93464	0.207	0.9826	0.96784	0.014
0.1144	0.89049	0.120	0.3997	0.91796	0.228	0.6607	0.94135	0.183			
0.2009	0.89900	0.175	0.4457	0.92219	0.230	0.7286	0.94715	0.157			
0.2535	0.90411	0.198	0.4812	0.92545	0.225	0.8512	0.95733	0.095			

The average error in densities is estimated to be $\leq 3 \times 10^{-6}$ g·cm^{-3}, while that in V_m^E is 0.002 cm^3·mol^{-1}, at the worst.

Results and Discussion

The density values, ϱ, and the excess molar volumes, V_m^E, are given in Table 2. V_m^E values are also plotted in Figures 1 and 2.

The results were fitted to the Redlich–Kister equation

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \qquad (1)$$

where x_1 and x_2 are the mole fractions of diethyl carbonate and linear or cyclic ethers, respectively.

a_k are the adjustable parameters which were evaluated by the least-squares method and are reported, together with the standard deviation $\sigma(V_m^E)$, in Table 3.

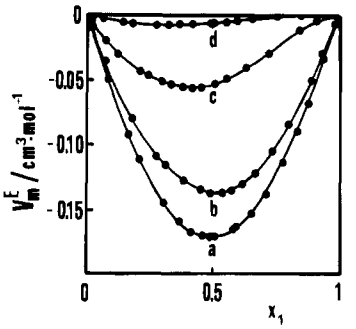

Figure 1. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures containing diethyl carbonate + linear ethers: a–d refer to diethyl carbonate + diethoxymethane, + 1,2-diethoxyethane, + dimethoxymethane, + 1,2-dimethoxyethane, respectively. (●) Experimental points; (solid curves) calculated from eq 1 using the parameters a_k of Table 3.

From Figures 1 and 2, we see that diethyl carbonate + cyclic ethers have positive V_m^E, with the exception of 1,3-

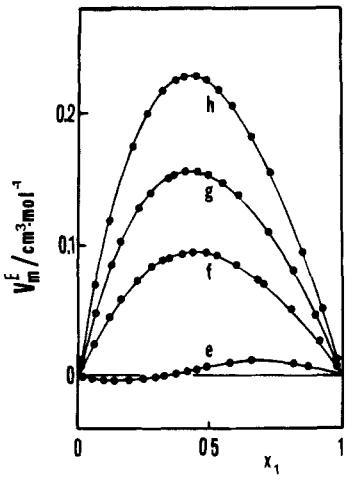

Figure 2. Excess molar volumes, V_m^E, at 298.15 K for the binary mixtures containing diethyl carbonate + cyclic ethers: e–h refer to diethyl carbonate + 1,3-dioxolane, + oxolane, + 1,4-dioxane, + oxane, respectively. (●) Experimental points; (solid curves) calculated from eq 1 using the parameters of a_k of Table 3.

Table 3. Parameters a_k According to Equation 1 and Standard Deviation $\sigma(V_m^E)$ for Diethyl Carbonate + Linear or Cyclic Ethers at 298.15 K

ether	a_0	a_1	a_2	a_3	$\sigma(V_m^E)$/ (cm³·mol⁻¹)
diethoxymethane	−0.6865	0	0.0784		0.0012
1,2-diethoxyethane	−0.5491	0	0.0347		0.0010
dimethoxymethane	−0.2174	0.1188	0.0725	0.0390	0.0004
1,2-dimethoxyethane	−0.0251	0.0326			0.0004
1,3-dioxolane	0.0240	0.0652			0.0005
oxolane	0.3676	−0.0566	0.0347		0.0008
1,4-dioxane	0.6157	−0.1579	0.0715		0.0007
oxane	0.8937	−0.2667	0.1029		0.0010

dioxolane showing a nearly ideal behavior with a sign inversion of V_m^E as a function of composition.

The mixture diethyl carbonate + dimethoxymethane has $V_m^E < 0$, whereas dimethoxyethane presents zero values of V_m^E in the diethyl carbonate reach mixtures, corresponding to experimental points having V_m^E values smaller than the estimated error.

Furthermore, cyclic diethers have values of V_m^E smaller than the corresponding cyclic monoethers, while linear diethers show increasing V_m^E (V_m^E is less negative) in passing from OC_2H_5 to OCH_3 groups and from methane to ethane molecule.

It is interesting that the same trends are offered by cyclic and linear ether mixtures with dimethyl carbonate (*2*), and thus the qualitative considerations which were drawn on the basis of those mixtures are valid for the ones of this paper.

As can be deduced from a comparison between the two sets of data referring to diethyl and dimethyl carbonate, the former set shows $|V_m^E|$ values smaller than the latter one, the ratio being about 1/2. This trend seems to be a constant for the two carbonates, which is confirmed also by the H_m^E data of diethyl and dimethyl carbonate in mixtures with cyclic ethers (*3*) and linear (*12*) and cyclic ketones (*13*).

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