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EXCESS HEAT CAPACITIES AND EXCESS VOLUMES OF BINARY LIQUID MIXTURES OF 1,1,1-TRICHLOROETHANE WITH CYCLIC ETHERS AT 298.15 K

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ABSTRACT

Measurements of volumetric heat capacities at constant pressure, C_p/V (V being the molar volume), at 298.15 K, of the binary liquid mixtures 1,1,1-trichloroethane + oxolane, +1,3-dioxolane, +oxane, +1,3-dioxane, and +1,4-dioxane were carried out in a Picker-type flow microcalorimeter. Molar heat capacities at constant pressure, C_p, and molar excess heat capacities, C_p^E, were calculated from these results as a function of the mole fraction. C_p^E values for these systems are positive and the magnitude depends on the size of the cycle and on the relative position of the oxygen atoms in the cyclic diethers. The precision and accuracy for C_p^E are estimated as better than 2%. Molar excess volumes, V^E, for the same systems, at 298.15 K, have been determined from density measurements with a high-precision digital flow densimeter. The experimental results of V^E and C_p^E, are interpreted in terms of molecular interactions.

INTRODUCTION

This work is a continuation of our investigation on organic solvent mixtures containing cyclic mono- and diethers in order to characterize the behaviour of the "ether" group with respect to the main functional groups of organic chemistry. In fact, we recently studied the type and magnitude of molecular interactions in mixtures of cyclic mono- and diethers with *n*-alkanes [1], cycloalkanes [2], benzene and tetrachloromethane [3], and chloroform [4].

In this work we have determined molar excess heat capacities, C_p^E, and molar excess volumes, V^E, at 298.15 K, of mixtures formed by oxolane (C_4H_8O, tetrahydrofuran), 1,3-dioxolane (1,3-$C_3H_6O_2$), oxane ($C_5H_{10}O$, tetrahydropyran), 1,3-dioxane (1,3-$C_4H_8O_2$), and 1,4-dioxane (1,4-$C_4H_8O_2$), each with 1,1,1-trichloroethane (CH_3CCl_3).

The main purpose of this paper is to characterize the type and magnitude of molecular interactions in these mixtures. The secondary aspect is to study the effect of structural factors and mutual influence of the two oxygen atoms in cyclic diethers on excess thermodynamic properties of these mixtures.

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EXPERIMENTAL

Molar heat capacities at constant pressure, C_p, of pure liquids and their mixtures were determined with a Picker-type flow microcalorimeter [5,6]. Essentially the calorimeter is a thermal balance which directly measures the variation of volumetric heat capacity, C_p/V, of the liquid in the working cell relative to that of the liquid in the reference cell. The two cells, of identical construction, are both equipped with a Zener diode acting as a heater and a thermal detector (thermistor).

Before entering the two cells, the liquids are thermostated to ±0.5 mK and while passing through them, at a flow rate of ca. 0.5 cm^3 min^{-1}, they are heated by a heating power, W, of ca. 20 mW, so as to have an equal increase of temperature of about 1 K. In these conditions any difference in the heat capacity of the liquids in the two cells alters the final thermal balance. Temperature increase of the liquid in the measuring cell depends on initial power supplied, W, the volumetric flow rate, ϕ_v, the specific heat capacity, c_p, and density, d, of the liquid

$$\Delta T = \frac{W}{\phi_v c_p d} \tag{1}$$

Temperature increase of the liquid in the reference cell can be determined in the same way.

When the same liquid flows through both the cells, with the same flow rate and initial power input, the final temperature in the two parts of the calorimeter is the same. On the other hand, when the two cells are crossed by liquids of different heat capacities, a difference in temperature, δT, will appear between the final equilibrium temperatures of the two cells. This difference, δT, is sensed by two thermistors which form two adjacent arms of a bridge; the signal arising from the bridge is used to change the initial power supplied to the working cell, by ΔW, to keep the temperature gradients equal in both cells. Under these conditions the ratio between specific heat of the liquid under consideration and the reference liquid (^{0}) is related to the ratio of the power input to the working and reference cells by the relation

$$c_p/c_p^0 = \left(\frac{W + \Delta W}{W}\right)(d^0/d) \tag{2}$$

The value of c_p in eqn. (2) is the average value for the temperature increment (ca. 1 K) produced by heating. This coincides with the specific heat capacity at the mean temperature in the case in which c_p is a linear function of the temperature over the interval.

The calorimeter was used in the stepwise mode [7,8]: each mixture, after measurement, was used as reference liquid for the following mixture. The molar heat capacities of all the pure liquids were determined using cyclohexane (Fluka puriss. ⩾ 99.5 mole%) as reference liquid; for its molar heat capacity we adopted the value of Fortier et al. [6]: 156.075 J K^{-1} mole^{-1}. The precision of excess molar heat capacities is estimated as ±0.04 J K^{-1} mole^{-1}.

Molar excess volumes of all the binary systems were calculated from experimental values of density of the pure liquids and their solutions by means of the equation

$$V^{E} = x_1 M_1\left(\frac{1}{d}-\frac{1}{d_1}\right) + x_2 M_2\left(\frac{1}{d}-\frac{1}{d_2}\right) \tag{3}$$

where x, M and d are the mole fraction, molar mass, and density, respectively, of the pure components "1 or 2" and of the mixture. The densities were determined with a vibrating tube densimeter [9] (from Sodev, Inc., Sherbrooke, Canada) operating under flow conditions. The vibration period, τ, of the tube is related to the liquid density by the equation

$$d = A + B\tau^2 \tag{4}$$

where A and B are constants of the particular oscillator. The vibration period of the tube was measured with a high-resolution digital frequency meter (Schneider CF 700) and the constants A and B were determined by calibrating the instrument with two fluids of known densities; dry nitrogen at atmospheric pressure and degassed bidistilled water were used.

The source and purity of the cyclic ethers have been given elsewhere [4]. Oxolane, oxane, 1,3-dioxolane, and 1,4-dioxane were further purified by fractional distillation over sodium wires. 1,1,1-Trichloroethane (Fluka, puriss. $\geqslant$99 mole %) and 1,3-dioxane (Fluka, purum $\geqslant$ 99 mole %) were used directly without further purification. All liquids were stored over molecular sieves (Union Carbide type 4A, from Fluka). The mixtures were prepared by weighing the components at ±0.05 mg on an analytical balance; estimated error in the mole fraction is of the order $\pm 1 \times 10^{-4}$.

RESULTS

The molar excess volumes, V^{E}, at 298.15 K, of 1,1,1-trichloroethane + oxolane, + 1,3-dioxolane, + oxane, + 1,3-dioxane, and + 1,4-dioxane calculated by means of eqn. (3) are reported in Table 1.

Table 2 contains the experimental molar excess heat capacities, C_p^E, evaluated from the equation

$$C_p^E = C_p - (x_1 C_{p_1} + x_2 C_{p_2}) \tag{5}$$

were x_i, C_{p_i}, and C_p are the mole fraction, and molar heat capacity of components "1 or 2", and of mixtures. The results for each mixture were fitted by the least-squares method to the equation

$$Y^{E} = x_1 x_2 \sum_{i=0}^{n-1} A_i (x_1 - x_2)^i \tag{6}$$

where Y^E is either V^E or C_p^E.

The choice of the appropriate number of coefficients, A_i, was based on the standard deviation variation

$$\sigma = \left\{\sum_{1}^{n} [Y^{E}_{(\mathrm{exp.})} - Y^{E}_{(\mathrm{calc.})}]^2/(n-m)\right\}^{1/2}$$

TABLE 1

Molar excess volumes, V^E, partial molar volumes, $\overline{V}_i$, and partial molar excess volumes, $\overline{V}_i^E$, at 298.15 K of 1,1,1-trichloroethane + cyclic ether mixtures (x_1 is the mole fraction of 1,1,1-trichloroethane)

x_1	V^E (cm^3 mole^{-1})	$\overline{V}_1$ (cm^3 mole^{-1})	$\overline{V}_2$ (cm^3 mole^{-1})	$\overline{V}_1^E$ (cm^3 mole^{-1})	$\overline{V}_2^E$ (cm^3 mole^{-1})
x_1 CH_3CCl_3 + $(1 - x_1)$ C_4H_8O					
0.0703	−0.119	99.274	81.645	−1.532	−0.012
0.1185	−0.189	99.490	81.619	−1.316	−0.038
0.1789	−0.267	99.702	81.573	−1.104	−0.084
0.2213	−0.287	99.850	81.560	−0.956	−0.097
0.2971	−0.355	100.027	81.480	−0.779	−0.177
0.4117	−0.400	100.264	81.357	−0.542	−0.300
0.5091	−0.411	100.429	81.212	−0.377	−0.445
0.6148	−0.386	100.582	81.013	−0.224	−0.644
0.6735	−0.353	100.655	80.888	−0.151	−0.769
0.7292	−0.311	100.712	80.760	−0.094	−0.897
0.8035	−0.244	100.764	80.584	−0.042	−1.073
0.8872	−0.152	100.794	80.405	−0.012	−1.252
x_1 CH_3CCl_3 + $(1 - x_1)$ $C_5H_{10}O$					
0.0791	−0.111	99.284	98.019	−1.302	−0.009
0.1533	−0.198	99.493	97.992	−1.093	−0.036
0.2362	−0.277	99.702	97.939	−0.884	−0.089
0.3735	−0.355	100.001	97.810	−0.585	−0.218
0.4849	−0.378	100.194	97.664	−0.392	−0.364
0.6068	−0.361	100.359	97.462	−0.227	−0.566
0.7142	−0.305	100.469	97.256	−0.117	−0.772
0.8036	−0.235	100.531	97.058	−0.055	−0.970
0.8631	−0.176	100.560	96.915	−0.026	−1.113
x_1 CH_3CCl_3 + $(1 - x_1)$ 1,3-$C_3H_6O_2$					
0.0071	−0.010	99.660	69.822	−1.019	−0.003
0.0131	−0.016	99.675	69.821	−1.004	−0.004
0.0246	−0.031	99.697	69.818	−0.982	−0.007
0.0336	−0.036	99.721	69.821	−0.958	−0.004
0.0359	−0.038	99.726	69.821	−0.953	−0.004
0.0524	−0.053	99.760	69.820	−0.919	−0.005
0.0607	−0.060	99.776	69.819	−0.903	−0.006
0.0787	−0.074	99.811	69.818	−0.868	−0.007
0.1204	−0.113	99.879	69.806	−0.800	−0.019
0.1438	−0.129	99.918	69.802	−0.761	−0.023
0.1885	−0.156	99.992	69.792	−0.687	−0.033
0.2095	−0.175	100.019	69.779	−0.660	−0.046
0.2222	−0.183	100.038	69.773	−0.641	−0.052
0.2915	−0.217	100.146	69.738	−0.533	−0.087
0.3957	−0.248	100.306	69.659	−0.373	−0.166
0.4074	−0.254	100.320	69.644	−0.359	−0.181
0.4499	−0.258	100.380	69.600	−0.299	−0.225
0.4584	−0.260	100.389	69.589	−0.290	−0.236
0.4814	−0.260	100.420	69.564	−0.259	−0.261
0.5522	−0.252	100.504	69.479	−0.175	−0.346
0.6107	−0.242	100.555	69.399	−0.124	−0.426
0.6141	−0.238	100.560	69.397	−0.119	−0.428
0.7231	−0.193	100.629	69.261	−0.050	−0.564
0.8268	−0.132	100.661	69.149	−0.018	−0.676
0.9245	−0.063	100.675	69.048	−0.004	−0.777

TABLE 1 (continued)

x_1	V^E (cm^3 mole^{-1})	$\overline{V}_1$ (cm^3 mole^{-1})	$\overline{V}_2$ (cm^3 mole^{-1})	$\overline{V}_1^E$ (cm^3 mole^{-1})	$\overline{V}_2^E$ (cm^3 mole^{-1})
x_1 CH_3CCl_3 + $(1-x_1)$ 1,3-$C_4H_8O_2$					
0.1394	−0.125	99.787	85.553	−0.799	−0.016
0.2353	−0.194	99.926	85.519	−0.660	−0.050
0.4431	−0.274	100.207	85.379	−0.379	−0.190
0.5865	−0.281	100.362	85.206	−0.224	−0.363
0.7148	−0.243	100.474	84.997	−0.112	−0.572
0.8408	−0.162	100.551	84.736	−0.035	−0.833
x_1 CH_3CCl_3 + $(1-x_1)$ 1,4-$C_4H_8O_2$					
0.0815	−0.051	100.185	85.742	−0.621	−0.001
0.1558	−0.097	100.229	85.734	−0.577	−0.008
0.2392	−0.139	100.306	85.716	−0.500	−0.026
0.3355	−0.176	100.408	85.678	−0.398	−0.064
0.4218	−0.203	100.490	85.621	−0.316	−0.121
0.5048	−0.212	100.568	85.556	−0.238	−0.186
0.5819	−0.211	100.630	85.483	−0.176	−0.259
0.6965	−0.187	100.708	85.351	−0.098	−0.391
0.7880	−0.155	100.751	85.213	−0.055	−0.529
0.8542	−0.117	100.780	85.096	−0.026	−0.646
0.9176	−0.075	100.795	84.955	−0.011	−0.787

where n is the number of points and m is the number of parameters. The values of A_i and σ obtained from this analysis are given in Table 3.

Experimental results for V^E and C_p^E are plotted against the mole fraction of 1,1,1-trichloroethane in Figs. 1—4; the solid curves were calculated by

TABLE 2

Molar excess heat capacities, C_p^E, partial molar heat capacities, $\overline{C}_{pi}$, and partial molar excess heat capacities, $\overline{C}_{pi}^E$, of 1,1,1-trichloroethane + cyclic ether mixtures at T = 298.15 K (x_1 is the mole fraction of 1,1,1-trichloroethane)

x_1	C_p^E (J K^{-1} mole^{-1})	$\overline{C}_{p1}$ (J K^{-1} mole^{-1})	$\overline{C}_{p2}$ (J K^{-1} mole^{-1})	$\overline{C}_{p1}^E$ (J K^{-1} mole^{-1})	$\overline{C}_{p2}^E$ (J K^{-1} mole^{-1})
x_1 CH_3CCl_3 + $(1-x_1)$ C_4H_8O					
0.0703	0.643	154.111	122.879	8.347	0.060
0.1185	1.019	153.115	122.987	7.351	0.168
0.1789	1.407	152.024	123.170	6.260	0.351
0.2213	1.654	151.350	123.356	5.586	0.537
0.2971	1.963	150.209	123.733	4.445	0.914
0.4117	2.244	148.734	124.554	2.970	1.735
0.5091	2.272	147.702	125.437	1.938	2.618
0.6148	2.089	146.849	126.511	1.085	3.692
0.6735	1.918	146.516	127.141	0.752	4.322
0.7292	1.687	146.259	127.718	0.495	4.899
0.8035	1.323	146.023	128.492	0.259	5.673
0.8872	0.827	145.858	129.412	0.094	6.593

TABLE 2 (continued)

x_1	C_p^E (J K^{-1} mole^{-1})	$\bar{C}_{p1}$ (J K^{-1} mole^{-1})	$\bar{C}_{p2}$ (J K^{-1} mole^{-1})	$\bar{C}_{p1}^E$ (J K^{-1} mole^{-1})	$\bar{C}_{p2}^E$ (J K^{-1} mole^{-1})
x_1 CH_3CCl_3 + $(1-x_1)$ $C_5H_{10}O$					
0.0791	0.673	153.176	149.275	7.775	0.062
0.1533	1.187	151.769	149.462	6.368	0.249
0.2362	1.611	150.121	149.863	4.720	0.650
0.3735	1.987	148.411	150.590	3.010	1.377
0.4849	2.064	147.229	151.500	1.828	2.287
0.6068	1.832	145.991	152.963	0.590	3.750
0.7142	1.425	145.616	153.660	0.215	4.447
0.8036	1.032	145.530	153.931	0.129	4.718
0.8631	0.735	145.379	154.724	0.022	5.511
x_1 CH_3CCl_3 + $(1-x_1)$ 1,3-$C_3H_6O_2$					
0.0787	0.401	149.284	120.544	4.486	0.052
0.1438	0.692	149.187	120.563	4.389	0.071
0.2095	0.947	148.885	120.607	4.087	0.115
0.2915	1.263	148.151	120.895	3.353	0.403
0.4074	1.485	147.073	121.433	2.275	0.941
0.4584	1.542	146.758	121.680	1.960	1.188
0.5522	1.582	146.301	122.172	1.503	1.680
0.6141	1.561	145.973	122.616	1.175	2.124
0.7231	1.336	145.374	123.814	0.576	3.322
0.8268	0.976	145.025	125.042	0.227	4.550
0.9245	0.496	144.883	126.016	0.085	5.524
x_1 CH_3CCl_3 + $(1-x_1)$ 1,3-$C_4H_8O_2$					
0.1394	0.726	150.335	146.203	5.183	0.004
0.2553	1.182	149.572	146.385	4.420	0.186
0.4431	1.809	147.984	147.194	2.832	0.995
0.5865	1.944	147.044	148.217	1.892	2.018
0.7148	1.766	146.135	149.928	0.983	3.729
0.8408	1.219	145.414	152.476	0.262	6.277
x_1 CH_3CCl_3 + $(1-x_1)$ 1,4-$C_4H_8O_2$					
0.0815	0.352	149.387	150.108	3.765	0.049
0.1558	0.611	149.196	150.124	3.574	0.065
0.2392	0.913	149.174	150.141	3.552	0.082
0.3355	1.227	148.862	150.269	3.240	0.210
0.4218	1.440	148.320	150.581	2.698	0.522
0.5048	1.602	147.749	151.126	2.127	1.067
0.5819	1.623	147.190	151.759	1.568	1.700
0.6965	1.492	146.478	153.009	0.856	2.950
0.7880	1.237	146.046	154.321	0.424	4.262
0.8542	0.928	145.798	155.396	0.176	5.337
0.9176	0.565	145.665	156.437	0.043	6.378

eqn. (6) using the values of the coefficients reported in Table 3.

The partial molar volumes, $\bar{V}_i$, and partial molar heat capacities, $\bar{C}_{p_i}$, were calculated at each composition, x_i, using the method of the intercepts on the ordinates at $x_1 = 0$ and $x_1 = 1$ of the tangent to the curve $Y_m = f(x_1)$ (Y_m being the molar volume or the molar heat capacity) at x_i. The results ob-

TABLE 3

Values of the least-squares parameters, A_i, in eqn. (6) and standard deviation σ of the molar excess heat capacities and of the molar excess volumes in 1,1,1-trichloroethane + cyclic ether mixtures at 298.15 K

System	Function	A_0	A_1	A_2	A_3	σ
1,1,1-Trichloroethane	C_p^E	9.08	−0.99	−0.21		0.007
+ oxolane	V^E	−1.64	0.08	−0.02	0.20	0.005
1,1,1-Trichloroethane	C_p^E	8.12	−2.05	−0.92		0.02
+ oxane	V^E	−1.514	0.031	0.013		0.001
1,1,1-Trichloroethane	C_p^E	6.33	0.85	−0.11		0.02
+ 1,3-dioxolane	V^E	−1.033	0.077	0.103	0.048	0.002
1,1,1-Trichloroethane	C_p^E	7.63	2.20	0.13		0.01
+ 1,3-dioxane	V^E	−1.133	−0.123	−0.007		0.002
1,1,1-Trichloroethane	C_p^E	6.31	2.41	−0.49	−0.92	0.01
+ 1,4-dioxane	V^E	−0.845	−0.12	0.02	−0.08	0.002

tained in this way, together with partial molar excess volumes $\overline{V}_i^E$ (= $\overline{V}_i - V_i$) and partial molar excess heat capacities $\overline{C}_{p_i}^E$ (= $\overline{C}_{p_i} - C_{p_i}$) are given in Tables 1 and 2.

Figures 5—8 report $\overline{V}_i^E$ and $\overline{C}_{p_i}^E$ as a function of mole fraction of 1,1,1-trichloroethane. These curves have not been extrapolated in order to obtain limit values $\overline{V}_1^E(x_1 = 0)$, $\overline{V}_2^E(x_1 = 1)$, $\overline{C}_{p_1}^E(x_1 = 0)$ and $\overline{C}_{p_2}^E(x_1 = 1)$ because we have few experimental points in the dilute regions.

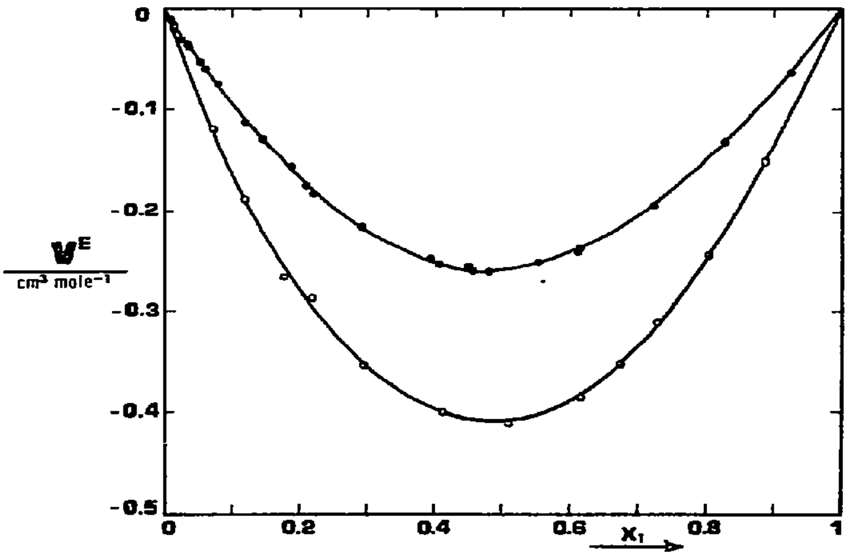

Fig. 1. Molar excess volumes, V^E, of 1,1,1-trichloroethane + cyclic ether mixtures plotted against mole fraction, x_1, of 1,1,1-trichloroethane at 298.15 K. ○, 1,1,1-Trichloroethane + oxolane; ●, 1,1,1-trichloroethane + 1,3-dioxolane.

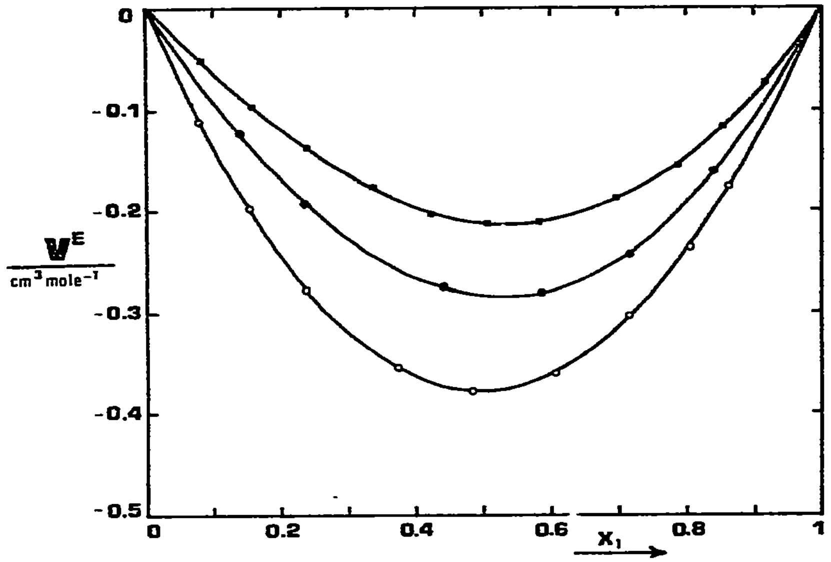

Fig. 2. Molar excess volumes, V^E, of 1,1,1-trichloroethane + cyclic ether mixtures plotted against mole fraction, x_1, of 1,1,1-trichloroethane at 298 15 K. ○, 1,1,1-Trichloroethane + oxane; ●, 1,1,1-trichloroethane + 1,3-dioxane; ■, 1,1, -trichloroethane + 1,4-dioxane.

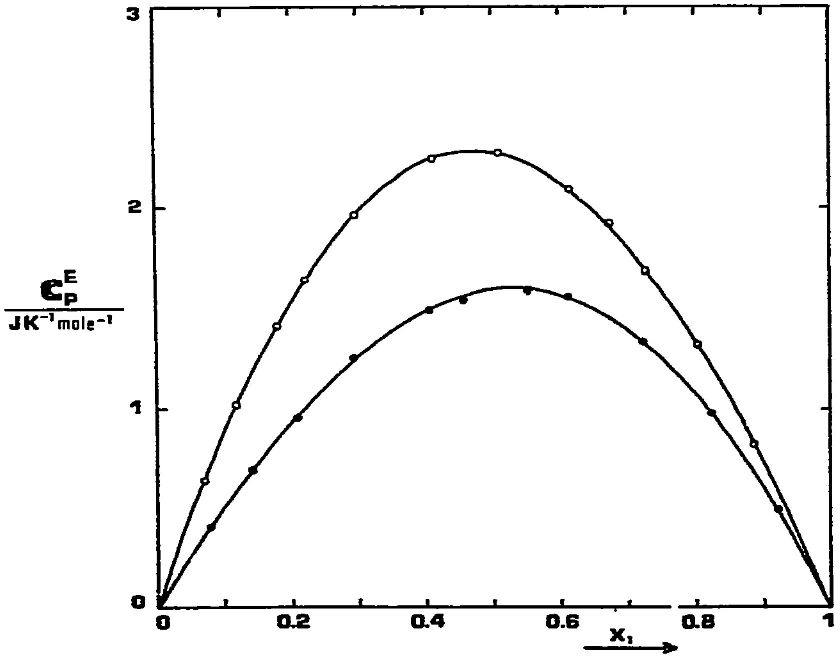

Fig. 3. Molar excess heat capacities, C_p^E, of 1,1,1-trichloroethane + cyclic ether mixtures plotted against mole fraction, x_1, of 1,1,1-trichloroethane at 298.15 K. ○, 1,1-Trichlochloroethane + oxolane; ●, 1,1,1-trichloroethane + 1,3-dioxolane.

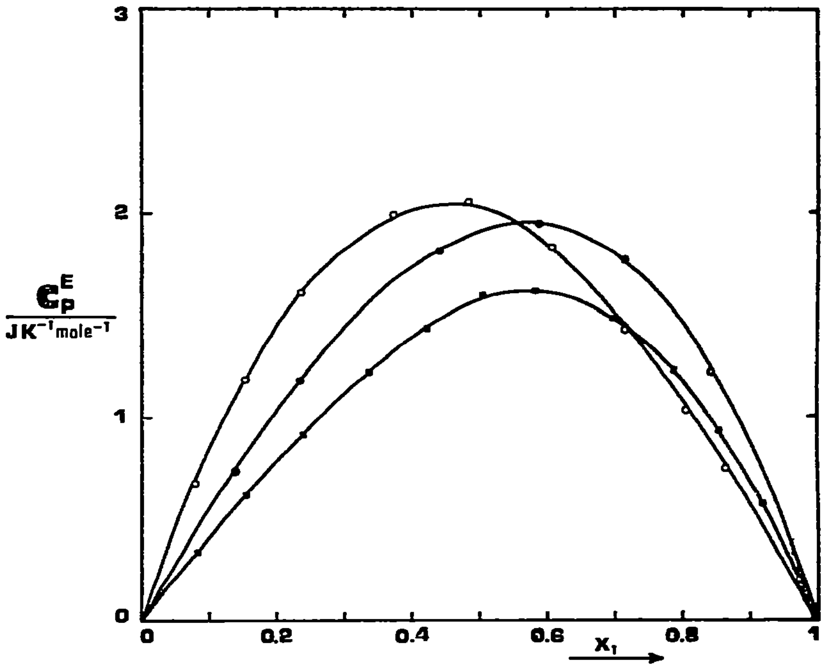

Fig. 4. Molar excess heat capacities, C_p^E, of 1,1,1-trichloroethane + cyclic ether mixtures plotted against mole fraction, x_1, of 1,1,1-trichloroethane at 298.15 K. ○, 1,1,1-Trichloroethane + oxane; ●, 1,1,1-trichloroethane + 1,3-dioxane; ■, 1,1,1-trichloroethane + 1,4-dioxane.

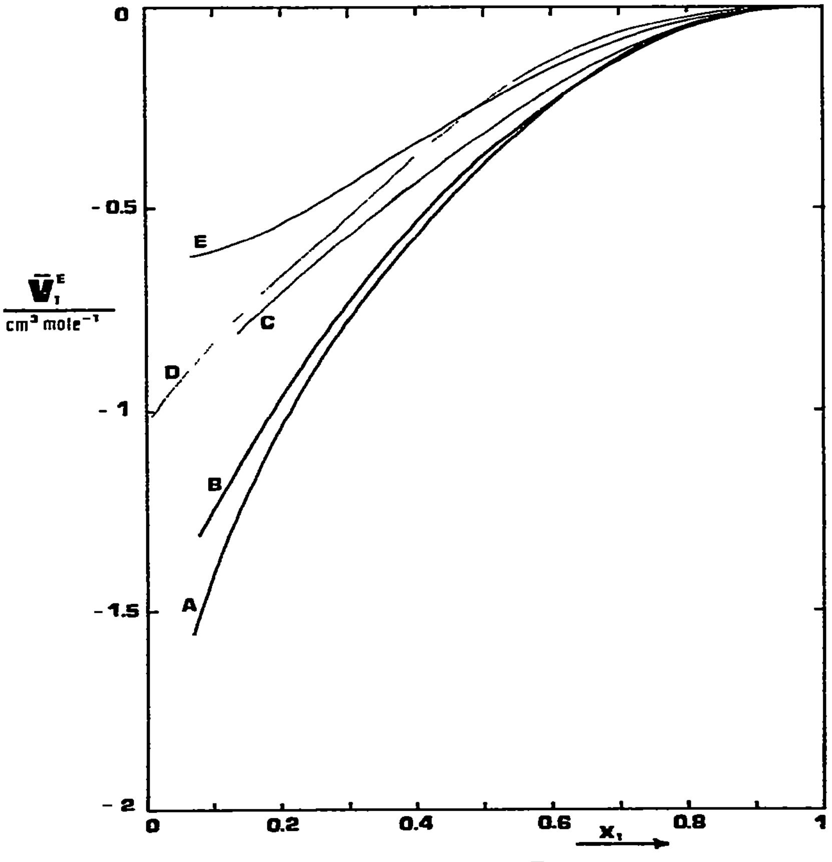

Fig. 5. Partial molar excess volumes, $\overline{V}_1^E$, of 1,1,1-trichloroethane in 1,1,1-trichloroethane(1) + cyclic ether (2) mixtures at 298.15 K. A, 1,1,1-Trichloroethane + oxolane; B, 1,1,1-trichloroethane + oxane; C, 1,1,1-trichloroethane + 1,3-dioxane; D, 1,1,1-trichloroethane + 1,3-dioxolane; E, 1,1,1-trichloroethane + 1,4-dioxane.

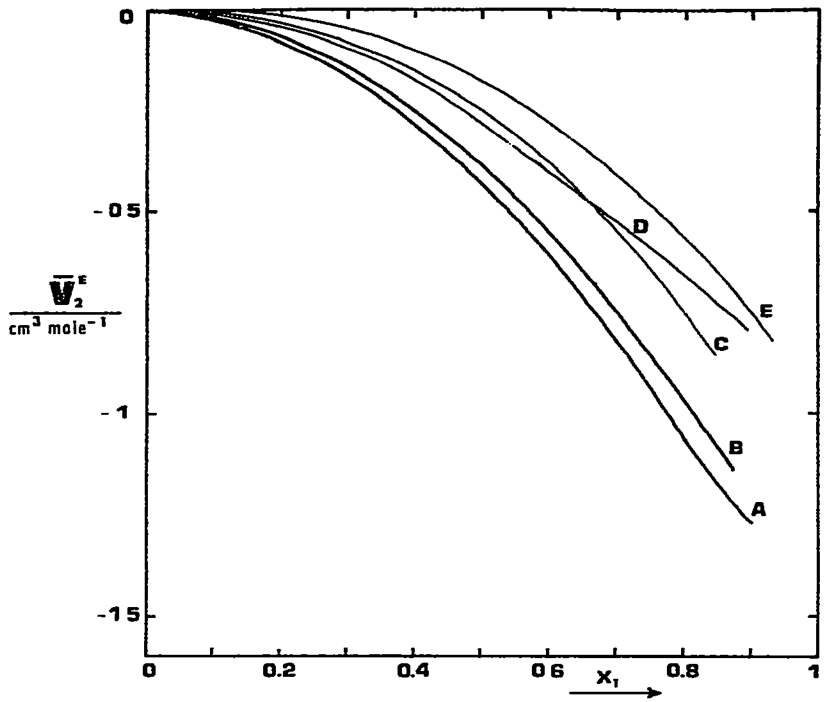

Fig. 6. Partial molar excess volumes, $\overline{V}_2^E$, of cyclic ethers in 1,1,1-trichloroethane (1) + cyclic ether (2) mixtures at 298.15 K. A, Oxolane; B, oxane; C, 1,3-dioxane; D, 1,3-dioxolane; E, 1,4-dioxane.

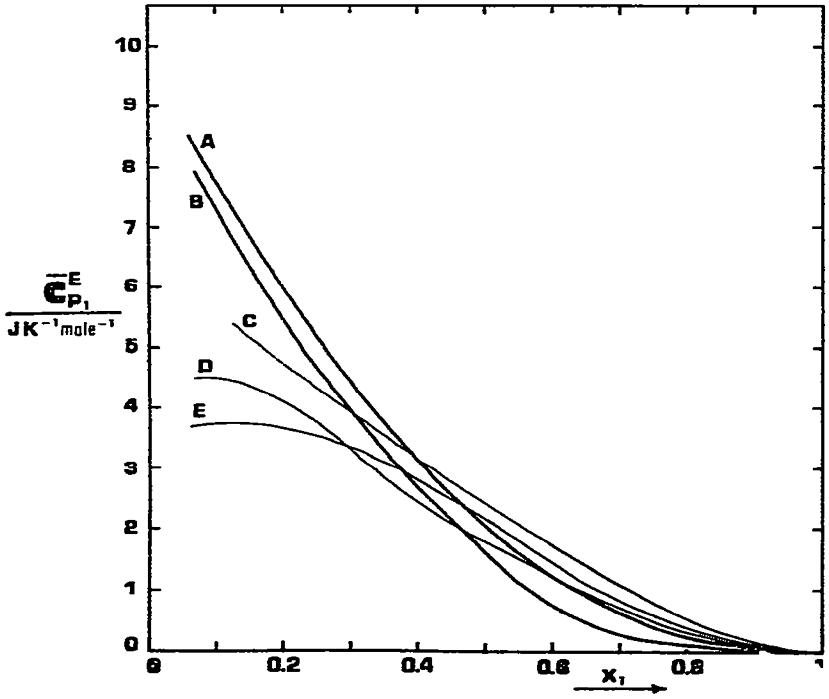

Fig. 7. Partial molar excess heat capacities, $\overline{C}_{p_1}^E$, of 1,1,1-trichloroethane in 1,1,1-trichloroethane (1) + cyclic ether(2) mixtures at 298.15 K. A, 1,1,1-trichloroethane + oxolane; B, 1,1,1-trichloroethane + oxane; C, 1,1,1-trichloroethane + 1,3-dioxane; D, 1,1,1-trichloroethane + 1,3-dioxolane; E, 1,1,1-trichloroethane + 1,4-dioxane.

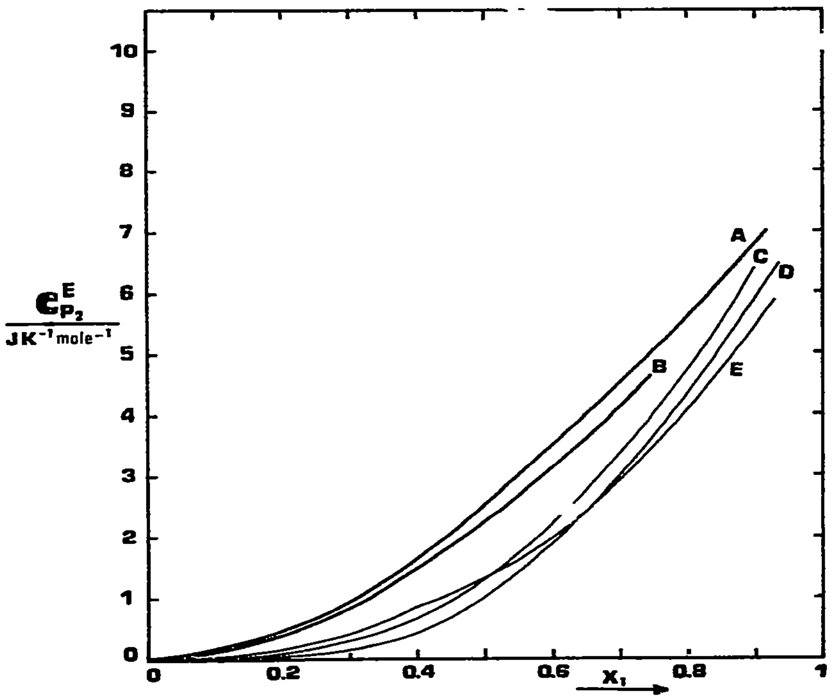

Fig. 8. Partial molar excess heat capacities, $\overline{C}^E_{p_2}$, of cyclic ethers in 1,1,1-trichloroethane (1) + cyclic ether (2) mixtures at 298.15 K. A, Oxolane; B, oxane; C, 1,3-dioxane; D, 1,4-dioxane; E, 1,3-dioxolane.

DISCUSSION

Molar excess volumes, V^E, for the 1,1,1-trichloroethane + cyclic mono- and diether mixtures are all negative, with a minimum a. $x \sim 0.5$. The magnitude of the molar excess volumes for these systems depends on structural factors and on the mutual influence of the two oxygen atoms present in the same molecule. For the mixture containing 1,3-dioxane, V^E at $x = 0.5$ is ~35% more negative than the value obtained for the mixture containing 1,4-dioxane. For cyclic monoethers, V^E curves are almost symmetrical, with a V^E increase of ~10% for the 1,1,1-trichloroethane + oxane system compared to the 1,1,1-trichloroethane + oxolane system. The relative order of the molar excess volumes of 1,1,1-trichloroethane with five- and six-membered cyclic mono- and diether mixtures is analogous to that observed for the mixtures of the same cyclic ethers with chloroform [4] and tetrachloromethane [11]. This order may principally be attributed to the difference in size and shape of the cyclic ethers, the number of oxygen atoms in the cycle, and their relative positions. Moreover, we can see that at $x = 0.5$, V^E values for the mixtures of oxolane, oxane, and 1,4-dioxane, each with CH_3CCl_3, CCl_4, and $CHCl_3$, follow the order: $V^E_{CHCl_3} > V^E_{CH_3CCl_3} > V^E_{CCl_4}$. The increment of V^E for each of these cyclic ethers when changing from CCl_4 to CH_3CCl_3 may be mainly attributed to structural differences of the two solvents because the molecular interactions in these mixtures are of the same kind and also very close in magnitude. The less negative V^E values obtained for the mixtures of these cyclic ethers with $CHCl_3$ compared to those of mixtures with CCl_4 and CH_3CCl_3 may be attributed to structural effects and different molecular interactions (hydrogen bonding) taking place in these mixtures.

For 1,3-dioxolane we only have V^E values for mixtures with $CHCl_3$ and CH_3CCl_3 and in this case the order is reversed compared to the behaviour observed for other cyclic ethers. This anomalous behaviour could be attributed to the particular structure of this molecule and to the mutual influence of the two oxygen atoms which should be particularly important in this kind of molecular structure.

As shown in Figs. 3 and 4 molar excess heat capacities are moderately positive; C_p^E curves for 1,1,1-trichloroethane + cyclic monoether mixtures are moderately skewed towards low mole fractions of CH_3CCl_3 ($x_{CH_3CCl_3} \sim 0.42$), while all the other curves are shifted towards the region rich in CH_3CCl_3 ($x_{CH_3CCl_3} \sim 0.60$). This difference in behaviour between cyclic monoethers and diethers seems to be due to physical and structural modifications deriving from the presence of the second oxygen atom in the ring and their mutual influence.

Molar excess enthalpies [12], H^E, for all the 1,1,1-trichloroethane + cyclic mono- and diether mixtures are exothermic, except 1,3-dioxolane which has very small positive H^E values. It is well known that $C_p^E \neq 0$ values, i.e. an H^E variation with temperature, are found when the molecular interactions due to geometrical and energetic effects have an orientated character. "Centre-symmetric" type dispersion forces lead to weak H^E variations with temperature, i.e. $C_p^E \simeq 0$. In our case, positive C_p^E values and negative H^E and V^E values are characteristic of mixtures where there is predominance of interactions between different molecules in the solution compared to interactions between molecules of the same type in pure liquids.

For our 1,1,1-trichloroethane + cyclic mono- and diether mixtures, the observed results may be mainly attributed to specific n—σ type interactions between oxygen (n-donor) and chloro (σ-acceptor). The same type of interactions were observed for mixtures of the same cyclic mono- and diethers with CCl_4 [3,11—14] and it appears, from comparison of H^E and V^E values, that these interactions are stronger in mixtures with CCl_4.

$\bar{V}_1^E$ vs. x_1 trends show that the partial molar excess volume of 1,1,1-trichloroethane in mixtures with different five- and six-membered cyclic mono- and diethers decreases considerably, especially in the region rich in cyclic ether, when changing from cyclic diethers to cyclic monoethers [$\bar{V}^E_{1(\text{oxolane})} < \bar{V}^E_{1(\text{oxane})} < \bar{V}^E_{1(1,3\text{-dioxolane})} \sim \bar{V}^E_{1(1,3\text{-dioxane})} < \bar{V}^E_{1(1,4\text{-dioxane})}$]. Considerable decrease is observed for cyclic monoethers compared to cyclic diethers for excess partial molar volumes, $\bar{V}_2^E$, as well [$\bar{V}^E_{2(\text{oxolane})} < \bar{V}^E_{2(\text{oxane})} < \bar{V}^E_{2(1,3\text{-dioxane})} < \bar{V}^E_{2(1,3\text{-dioxolane})} < \bar{V}^E_{2(1,4\text{-dioxane})}$].

The partial molar excess heat capacities of 1,1,1-trichloroethane, $\bar{C}^E_{p_1}$, and various cyclic ethers, $\bar{C}^E_{p_2}$, are all positive and lead to the conclusion analogous to that for partial molar excess volumes. We think it is important to emphasize that in this case too, there is a considerable difference between partial molar excess heat capacities of CH_3CCl_3 in mixtures with cyclic monoethers compared with those observed in mixtures with cyclic diethers.

These results confirm conclusions made from analysis of excess molar functions.

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