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EXCESS HEAT CAPACITIES AND EXCESS VOLUMES OF BINARY LIQUID MIXTURES OF CHLOROFORM WITH CYCLIC ETHERS AT 298.15 K

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ABSTRACT

Molar excess heat capacities at constant pressure, C_p^E, of binary liquid mixtures chloroform + oxolane, chloroform + 1,3-dioxolane, chloroform + oxane, and chloroform + 1,4-dioxane have been determined at 298.15 K from measurements of volumetric heat capacities in a Picker flow microcalorimeter. A precision of ± 0.04 J K^{-1} mole^{-1} was achieved by using the stepwise procedure. Experimental molar excess heat capacities are compared with values derived from H^E results at different temperatures. Excess molar volumes, V^E, for the same systems at 298.15 K have been determined by measuring the density of the pure liquids and solutions with a high-precision digital flow densimeter.

INTRODUCTION

There is sufficient spectroscopic and thermodynamic evidence for the specific interaction O···H—C in the chloroform + cyclic ether mixtures. Searles and Tambres [1] have studied the electron donor ability of a series of saturated cyclic monoethers in hydrogen bonding formation by both calorimetric and spectroscopic methods. Their results show that the extent of hydrogen bonding of the cyclic ethers in mixtures with chloroform varies with the number of atoms in the ring in the following order: trimethylene oxide > oxolane > oxane > propylene oxide > ethylene oxide.

The low electron donor ability of propylene oxide and ethylene oxide [2], compared with other cyclic ethers, has been attributed to an alteration in the electron distribution which renders oxygen more positive than in large-ring ethers. The saturated cyclic diethers (1,4-dioxane, 1,3-dioxolane) have two bonding sites and with chloroform they can form the A_2B complex.

McGlashan and Rastogi [3] have interpreted the free energies and heats of mixing of the chloroform(1) + 1,4-dioxane(2) system in terms of an "ideal associated solution" of chloroform(A), 1,4-dioxane(B), and two hydrogen-bonded complexes AB and A_2B. The solid—liquid phase diagram [4] for this system shows two eutectics, one at 196.9 K and $x_1 = 0.126$ and the other at 213.2 K and $x_1 = 0.375$. The maximum of the liquidus curve, between the two eutectics, at $x_1 = 0.333$ is characteristic of the formation of a compound A_2B at the solid state.

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Van Ness and Abbott [5,6] have determined the molar excess enthalpies of chloroform with oxolane, oxane, and 1,4-dioxane at 303.15 and 318.15 K. For these systems values of H^E are strongly exothermic and have a positive temperature coefficient.

In a recent series of publications [7—9] we have carried out a systematic study of molar excess enthalpies for mixtures of several cyclic mono- and diethers with n-alkanes of different chain length, with cycloalkanes, and with benzene and tetrachloromethane. For mixtures with n-alkanes and cycloalcanes the molar excess enthalpies are highly endothermic with a large increase when moving from cyclic monoethers to cyclic diethers. The exothermic character (with the exception of the CCl_4 + 1,3-dioxolane mixture which is slightly endothermic) of the CCl_4 + cyclic ethers mixtures has been attributed to the specific interaction of n—σ type between the oxygen atom (electron donor) and chlorine atom (electron acceptor).

In this paper we study the ability of cyclic ethers to act as a base in the formation of hydrogen bonding, measuring the molar excess heat capacities, C_p^E, and the 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), and 1,4-dioxane (1,4-$C_4H_8O_2$), each with chloroform.

EXPERIMENTAL

Heat capacity measurements

The molar heat capacities of pure liquids and their solutions have been determined by measuring the volumetric heat capacities in a Picker flow microcalorimeter. Details on the design of the instrument have been given in refs. 10 and 11. The microcalorimeter is essentially a thermal balance which directly measures the volumetric heat capacity of a liquid flowing through the working cell relative to that in the reference cell. The two cells (of identical construction) are each equipped with a Zener diode junction acting as heater and a thermal detector (thermistor).

Before entering the two cells, the liquids are thermostatted to ±0.5 mK and their temperature is controlled by a quartz thermometer (Hewlett-Packard, model 2801 A). While passing through the cells, at a flow rate of ca. 0.5 $cm^3\ min^{-1}$, both liquids are heated so as to have an equal increase in temperature of about 1 K. The power, W (ca. 20 mW), dissipated in the working cell is determined by measurement of the current through the Zener diode and the potential difference. Under these conditions the calorimeter is able to measure a variation of volumetric heat capacity C_p/V (V being the molar volume) between the liquids which flow in the two cells of $\pm 7 \times 10^{-5}$ $J\ K^{-1}\ cm^{-3}$. Initially, when the reference liquid of known volumetric heat capacity flows through both cells a steady state condition is reached. The liquid of unknown heat capacity is then put into the working cell while the other cell is still being crossed by the reference liquid.

The different volumetric heat capacities of the liquids alter the thermal balance and thus a thermal feedback circuit connected to the heaters and controlled by a bridge containing the detectors in adjacent arms changes the initial power supplied to the working cell, ΔW, to keep the temperature gradients equal in both cells. Under these conditions the volumetric heat capacity of the liquid under consideration is related to that of the reference liquid (subscript 0) by the equation

$$C_p/V = (C_p/V)_0 \times (1 + \Delta W/W) \tag{1}$$

The C_p/V value in eqn. (1) is an average value for the temperature increment (ca. 1 K) produced by the heating and coincides quite well with the volumetric heat capacity at the mean temperature. The initial temperature of the thermostat (297.65 K) is such as to lead to a mean temperature of 298.15 K.

The great differences in the volumetric heat capacities $\{(C_p/V) - (C_p/V)_0\}$ of the pure liquids and their mixtures make disadvantageous the measuring system of a single reference over the whole mole fraction range since the calorimeter must be used at reduced sensitivity. For this reason, the calorimeter was used in the stepwise mode [12]. Each mixture, after measurement, was used as reference liquid for the following mixtures. The effects of small cumulative errors with this technique are largely compensated by the increased sensitivity of the measurements [13]. The molar heat capacities of all liquids were measured relative to cyclohexane (Fluka puriss. $\geqslant$99.5 mole %) using $C_p = 156.07$ J K^{-1} mole^{-1} as determined by Fortier et al. [11].

Density measurements

The densities of the pure liquids and the mixtures were determined with a vibrating tube densimeter [14] (from Sodev, Inc., Sherbrooke, Canada) operating under flow conditions. The liquid flows at constant rate in the vibrating tube during measurement. If there are no secondary effects resulting from the flow condition, the natural vibration period, τ, of the tube is related to the density, d, of the liquid by the equation [15]

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

where A and B are characteristic constants of the particular oscillator.

The density of one of the two pure liquids, for a given binary mixture, was measured relative to cyclohexane (Fluka puriss. $\geqslant$99.5 mole %) chosen as reference liquid; after which, densities of the mixtures and of the second liquid were measured relative to the first pure liquid. From eqn. (2) the density increment of solution against solvent is

$$d = (d - d_0) = B(\tau^2 - \tau_0^2) \tag{3}$$

were zero subscript refers to the solvent. Constant B of the densimeter was determined from eqn. (3) by measuring the vibration period of two fluids of perfectly known density. We generally used dry nitrogen at atmospheric pressure and degassed bidistilled water. The natural vibration period of the tube was measured with a high-resolution digital frequency meter (Schneider CF 700).

Substances

Oxane (Fluka, purum $\geqslant$98 mole %), 1,4-dioxane (C. Erba, puriss. $\geqslant$99.5 mole %), oxolane (Fluka puriss. $\geqslant$99.5 mole %), and 1,3-dioxolane (Fluka, purum $\geqslant$99 mole %) were further purified by fractional distillation over sodium wires. Chloroform (Fluka, puriss. $\geqslant$99.5 mole %) was 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. Possible error in the mole fraction is of the order of $\pm 1 \times 10^{-4}$.

RESULTS

Table 1 contains the molar excess volumes, V^E, of chloroform + oxolane, chloroform + oxane, chloroform + 1,3-dioxolane, and chloroform + 1,4-

TABLE 1

Volumes of mixing, V^E, at 298.15 K of binary chloroform + cyclic ether; x_1 is the mole fraction of chloroform

x_1	V^E (cm^3 mole^{-1})	x_1	V^E (cm^3 mole^{-1})
x_1 CHCl$_3$ + $(1-x_1)$ C_4H_8O			
0.0904	−0.093	0.6052	−0.337
0.1374	−0.136	0.6994	−0.294
0.2112	−0.200	0.7934	−0.229
0.3066	−0.269	0.8668	−0.155
0.4195	−0.324	0.9413	−0.073
0.5321	−0.343		
x_1 CHCl$_3$ + $(1-x_1)$ $C_5H_{10}O$			
0.1121	−0.089	0.6045	−0.237
0.1743	−0.132	0.7189	−0.185
0.3060	−0.205	0.7949	−0.145
0.3683	−0.229	0.8533	−0.099
0.4406	−0.249	0.9227	−0.058
x_1 CHCl$_3$ + $(1-x_1)$ 1,3-$C_3H_6O_2$			
0.1044	−0.080	0.6263	−0.282
0.1908	−0.144	0.7049	−0.255
0.2628	−0.200	0.7807	−0.211
0.3756	−0.259	0.8520	−0.144
0.4767	−0.296	0.9185	−0.086
0.5371	−0.304		
x_1 CHCl$_3$ + $(1-x_1)$ 1,4-$C_4H_8O_2$			
0.0390	0.007	0.3254	−0.078
0.0859	0.008	0.3734	−0.092
0.0868	0.006	0.4234	−0.123
0.1347	0.002	0.5295	−0.190
0.1518	−0.001	0.6148	−0.212
0.1808	−0.006	0.6969	−0.237
0.1916	−0.012	0.7896	−0.209
0.2362	−0.038	0.8577	−0.169
0.2718	−0.042	0.9201	−0.103

TABLE 2

Experimental results of the molar excess heat capacity, C_p^E, at 298.15 K for binary chloroform + cyclic ether; x_1 is the mole fraction of chloroform

x_1	C_p^E(JK^{-1} mole^{-1})	x_1	C_p^E(JK^{-1} mole^{-1})
x_1 CHCl$_3$ + $(1-x_1)$ C_4H_8O			
0.0904	1.231	0.6052	7.512
0.1374	1.814	0.6994	6.480
0.2112	3.000	0.7934	4.861
0.3066	4.722	0.8668	3.341
0.4195	6.687	0.9413	1.652
0.5321	7.655		
x_1 CHCl$_3$ + $(1-x_1)$ $C_5H_{10}O$			
0.1121	1.681	0.6045	7.578
0.1743	2.714	0.7189	6.072
0.3060	5.189	0.7949	4.753
0.3683	6.340	0.8533	3.466
0.4406	7.302	0.9227	2.041
x_1 CHCl$_3$ + $(1-x_1)$ 1,3-$C_3H_6O_2$			
0.1044	1.073	0.6263	6.027
0.1908	1.969	0.7049	5.821
0.2628	2.755	0.7807	5.092
0.3756	4.063	0.8520	3.942
0.4767	5.048	0.9185	2.444
0.5371	5.578		
x_1 CHCl$_3$ + $(1-x_1)$ 1,4-$C_4H_8O_2$			
0.0868	0.393	0.5295	5.105
0.1518	0.770	0.6148	5.855
0.1808	1.032	0.6969	5.952
0.2362	1.510	0.7896	5.147
0.3254	2.475	0.8577	3.853
0.4234	3.780	0.9201	2.483

TABLE 3

Values of the least-squares parameters, A_i, in eqn. (3) and standard deviation, σ, of the molar excess heat capacities and of the molar excess volumes in chloroform + cyclic ether mixtures at 298.15 K

System	Function	A_0	A_1	A_2	A_3	A_4	σ
Chloroform +	C_p^E	30.05	11.91	−25.93	−4.85	21.01	0.02
oxolane	V^E	−1.369	−0.204	0.217	0.119		0.002
Chloroform +	C_p^E	31.02	8.19	−25.86	−1.86	19.49	0.04
oxane	V^E	−1.001	0.047	0.276			0.003
Chloroform +	C_p^E	21.26	16.91	1.00	−6.44		0.04
1,3-dioxolane	V^E	−1.192	−0.204	0.319			0.004
Chloroform +	C_p^E	19.23	23.96	−0.112	−10.87		0.05
1,4-dioxane	V^E	−0.684	−1.054	−0.005	0.187		0.005

TABLE 4

Comparison of our results for $C_p^E(x = 0.5)$ of chloroform + cyclic ether mixtures with values of $\partial H^E/\partial T$ as estimated at approximately 298.15 K from the temperature variation of H^E for $x = 0.5$

System	C_p^E(J K^{-1} mole^{-1})	$\partial H^E/\partial T$(J K^{-1} mole^{-1})
Chloroform + oxolane	7.51	7.67 [5]
Chloroform + 1,4-dioxane	4.81	4.93 [6]

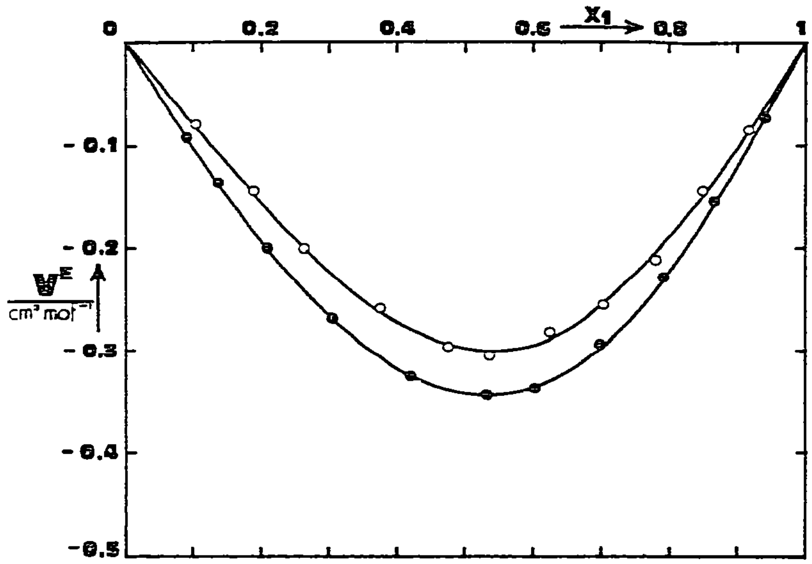

Fig. 1. Experimental molar excess volumes, V^E, of chloroform + cyclic ether mixtures plotted against mole fraction, x_1, of chloroform at 298.15 K. ○, Chloroform + oxolane; ●, chloroform + 1,3-dioxolane. The curves are calculated from eqn. (5) with coefficients from Table 3.

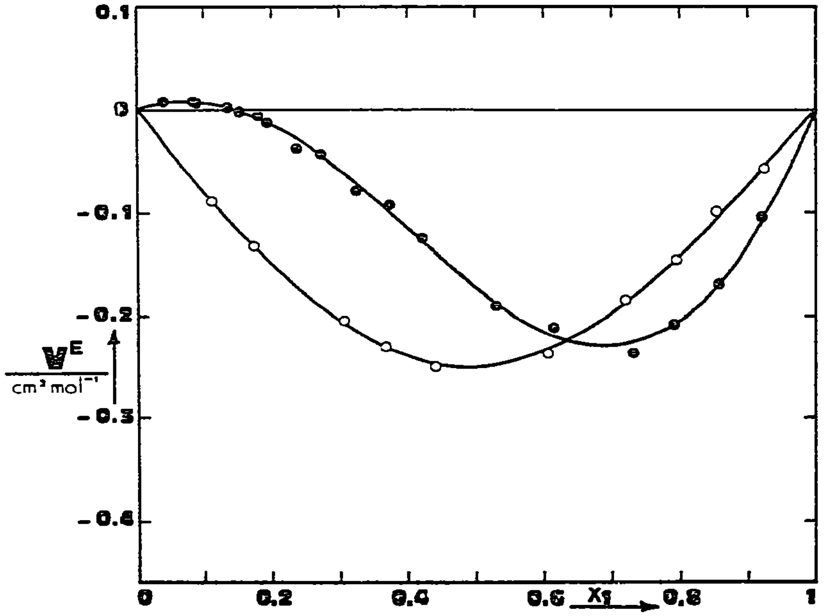

Fig. 2. Experimental molar excess volumes, V^E, of chloroform + cyclic ether mixtures plotted against mole fraction x_1 of chloroform at 298.15 K. ○, Chloroform + oxane; ●, chloroform + 1,4-dioxane. The curves are calculated from eqn. (5) with coefficients from Table 3.

dioxane obtained from the experimentally determined densities according to

$$V^E = x_1 M_1 \left(\frac{1}{d_m} - \frac{1}{d_1}\right) + x_2 M_2 \left(\frac{1}{d_m} - \frac{1}{d_2}\right) \qquad (4)$$

where x, M, and d are the mole fraction, the molar mass, and the density, respectively; the subscripts m, and 1 or 2, denote "mixtures" and pure component 1 or 2, respectively. Table 2 contains the experimental molar excess heat capacities, C_p^E, evaluated from the equation

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

Where C_p, C_{p_1}, and C_{p_2} are the molar heat capacities of the mixture and of components 1 and 2, respectively. In Tables 1 and 2 x_1 denotes the mole fraction of chloroform. The experimental results for each of excess functions, X^E,

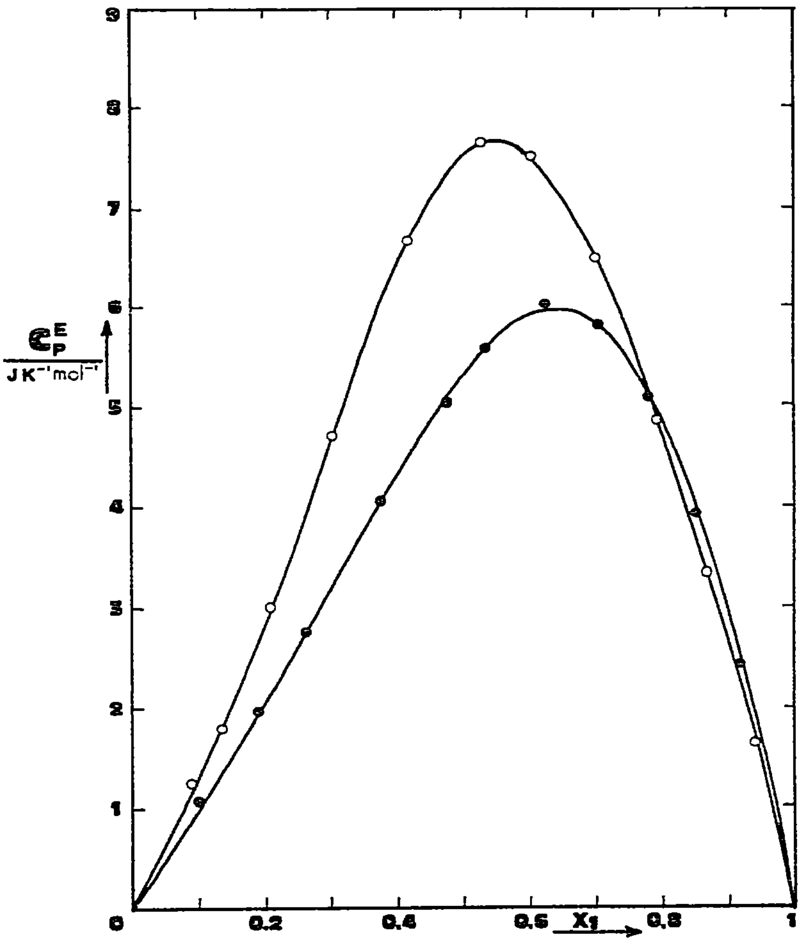

Fig. 3. Experimental molar excess heat capacities, C_p^E, of chloroform(1) + cyclic ether(2) mixtures at 298.15 K. ○, Chloroform + oxolane; ●, chloroform + 1,3-dioxolane. The curves are calculated from eqn. (5) with coefficients from Table 3.

were fitted to the equation

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

The parameters A_i and the standard deviation, defined by

$$\sigma = \left\{ \sum \delta_i^2/(n-m) \right\}^{1/2}$$

where $\delta_i = \{X^E\,(\text{expt.}) - X^E\,(\text{calc.})\}$ is the deviation of the ith experimental point from the smooth curve, n is the number of points, and m is the number of parameters, are given in Table 3.

In Table 4 our values of C_p^E $(x = 0.5)$ calculated from eqn. (6) for the chloroform + oxolane and chloroform + 1,4-dioxane systems are compared with the values derived from published results for H^E at different tempera-

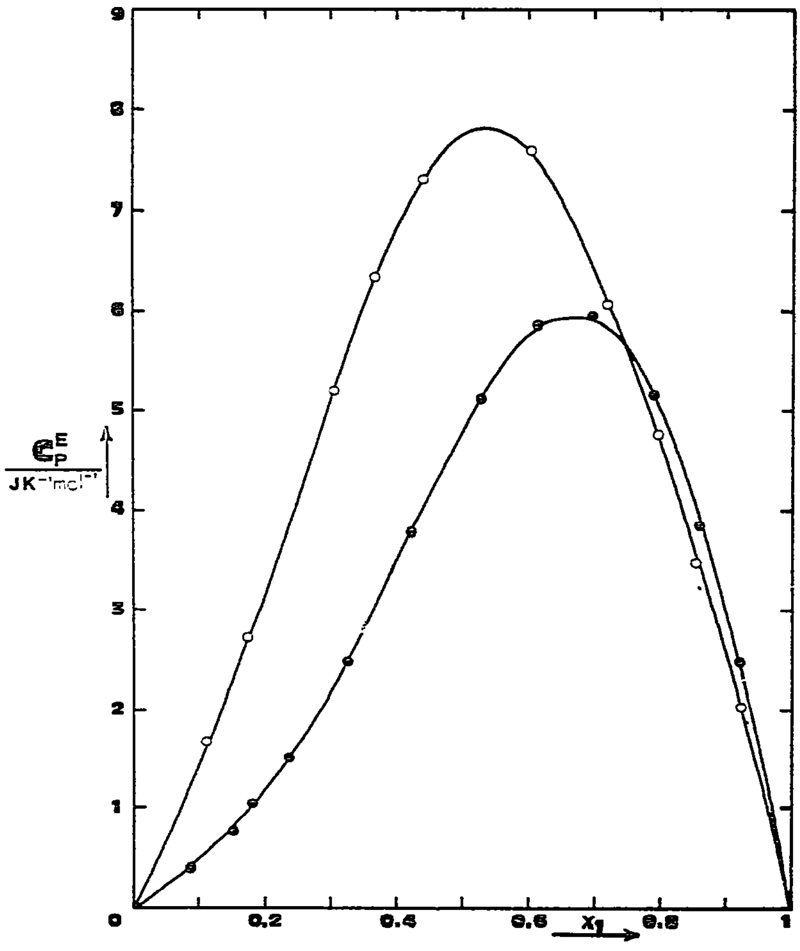

Fig. 4. Experimental molar excess heat capacities, C_p^E, of chloroform(1) + cyclic ether(2) mixtures at 298.15 K. ○, Chloroform + oxane; ●, chloroform + 1,4-dioxane. The curves are calculated from eqn. (5) with coefficients from Table 3.

tures, since $C_p^E = \partial H^E/\partial T$. For these two systems $\partial H^E/\partial T$ at $x = 0.5$ has been derived from highly accurate data of H^E reported by Van Ness and Abbott [5,6]. The values of H^E given by Becker and Kiefer [16] for the chloroform + oxolane and chloroform + oxane systems and those by McGlashan and Rastogi [3] for the chloroform + 1,4-dioxane system show considerable scatter from the Van Ness data, and have not been considered. The present results for C_p^E are in good agreement with the values of $\partial H^E/\partial T$ derived from the H^E values reported by Van Ness and Abbott. The experimental results for V^E and C_p^E are plotted against the mole fraction of $CHCl_3$ in Figs. 1—4.

DISCUSSION

As shown in Figs. 1 and 2, molar excess volumes, V^E, for the mixtures of chloroform + oxolane, + oxane, and + 1,3-dioxolane are all negative with a minimum at $x \sim 0.5$. For the chloroform + 1,4-dioxane system V^E is still negative but the curve is skewed toward high chloroform mole fractions ($x_{CHCl_3} \simeq 0.66$). The relative order of the molar excess volumes for the mixtures of chloroform with five- and six-membered cyclic mono- and diethers is 1,4-dioxane > oxane > 1,3-dioxolane > oxolane. The cyclic diethers, at $x = 0.5$, have molar excess volumes less negative (~10% for five-membered and ~30% for six-membered) than those of the corresponding cyclic monoethers. For five-membered cyclic mono- and diethers we have V^E values which are more negative (~30% for monoethers and ~42% for diethers at $x = 0.5$) compared to six-membered mono- and diethers. The molar excess heat capacities for the same systems (Figs. 3 and 4) are strongly positive with a maximum at $x_{CHCl_3} \simeq 0.55$ for the chloroform + cyclic monoethers and at $x_{CHCl_3} \simeq 0.66$ for the chloroform + cyclic diethers mixtures. The relative order of excess heat capacities is oxane ~ oxolane > 1,4-dioxane ~ 1,3-dioxolane. For the chloroform + cyclic monoethers mixtures there is a notable increase (~30%) in the C_p^E maximum compared to the corresponding cyclic diethers.

The curves of the excess heat capacities of the mixtures of chloroform with five- and six-membered cyclic monoethers (like those for mixtures with five- and six-membered cyclic diethers) are very similar, with the maximum of C_p^E at the same mole fraction. The volumetric data and molar excess heat capacities show that in all the systems we have studied there is strong interaction between unlike chemical species with the formation of hydrogen bonding.

A comparative study of the extent of the hydrogen bonding in chloroform + oxolane and chloroform + oxane mixtures from the analysis of the excess thermodynamic functions (H^E, G^E, S^E, C_p^E, V^E) must take into account the contribution to excess thermodynamic properties of molecular interactions which take place in pure liquids. In fact, the thermodynamic excess functions of the mixtures are the result of a series of structural and energetic factors characteristic of the solution and of pure liquids.

Molar excess enthalpies, H^E, at 298.15 K for the oxolane and oxane mixtures with an inert solvent like *n*-heptane are endothermic [7] (790 J mole^{-1} for oxolane and 598 J mole^{-1} for oxane) and indicate that molecular interactions between oxolane molecules are stronger. Excess enthalpy, at equimolecular concentration, for the chloroform + oxolane system is more exothermic (~5%) than the chloroform + oxane system. If one also considers the greater endothermic contribution to excess enthalpy of the mixtures which comes from the stronger interactions in pure oxolane, it can be deduced that the exothermic contribution of the hydrogen bonding formation is more consistent in the chloroform + oxolane mixture.

The molar excess volumes for these two systems are negative, in agreement with the formation of the AB complex. The greater volume contraction for the chloroform + oxolane mixture cannot, however, be attributed exclusively to stronger molecular interactions since differences in shape and size of the two cyclic monoethers have contributions which overlap the previous ones. For the chloroform + cyclic diether systems our C_p^E and V^E values show that there are strong specific interactions between unlike molecules.

For the chloroform + 1,4-dioxane system the heats of mixing and excess Gibbs free energies [3] at 323.15 K are negative. The excess entropies obtained from the relation $S^E = (H^E - G^E)/T$ are also negative and suggest strong solute—solvent interactions. The curves of the molar excess heat capacity and molar excess volume for this system show a maximum and a minimum, respectively, at a mole fraction corresponding to the stochiometric composition of the $1,4\text{-}C_4H_8O_2 \cdot 2\ CHCl_3$ complex. H^E, G^E, and TS^E also have curves which are skewed towards high mole fraction of $CHCl_3$.

For the chloroform + 1,3-dioxolane system, the V^E curve is less asymmetric than that of 1,4-dioxane, while the molar excess heat capacities show a very similar trend. Unfortunately H^E, G^E, and the solid—liquid phase diagram are not available for this system. Our results could suggest that the complex $1,3\text{-}C_3H_6O_2 \cdot 2\ CHCl_3$ is also formed in this case.

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