Thermochimica Acta, 122 (1987) 9-22
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMODYNAMIC PROPERTIES OF BINARY MIXTURES CONTAINING CYCLIC ETHERS.

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SUMMARY

Molar excess enthalpies H^E for binary mixtures (1,1,1-trichloroethane + oxolane, + oxane, + 1,3-dioxolane, + 1,3-dioxane and + 1,4-dioxane) were measured using a Picker flow microcalorimeter. For the 1,3-dioxolane mixture they were small and positive, $H^E(x_1 = 0.5) = 45$ J mol^{-1}, whereas for all the other systems they were negative, $H^E(x_1 = 0.5)$ from -100 J mol^{-1} to -650 J mol^{-1}. Their magnitude depended on the cycle size and the number of their oxygen atoms in the cycloether ring, as well as relative position.

The latter can also influence the symmetry of the curves. These results, together with those quoted in the literature on vapour-liquid equilibrium for cyclic ether + n-alkane and 1,1,1-trichloroethane + n-alkane, were interpreted in terms of molecular surface interactions using the Dispersive-Quasichemical model (DISQUAC), which is an extension of the quasichemical theory.

The interchange energy coefficients in the quasichemical approximation ($C^{quac}_{st,1}$ and $C^{quac}_{st,2}$) and in the zero approximation ($C^{disp}_{st,1}$ and $C^{disp}_{st,2}$) were calculated for each contact (s, t).

The DISQUAC model provided a fairly consistent description of molar excess enthalpies in function of concentration for all the binary mixtures investigated.

INTRODUCTION

In a previous paper [1] we reported molar excess heat capacities C_p^E and molar excess volumes V^E of the binary mixtures formed by oxolane (C_4H_8O), oxane

0040-6031/87/$03.50

($C_5H_{10}O$), 1,3-dioxolane (1,3-$C_3H_6O_2$), 1,3-dioxane (1,3-$C_4H_8O_2$) and 1,4-dioxane (1,4-$C_4H_8O_2$) each with trichloroethane.

We found that the symmetry and magnitude of C_p^E and V^E curves are influenced by structural factors and the number and relative positions of the oxygen atoms in the cycloether molecule. To obtain further information on the molecular interactions present in these mixtures, their molar excess excess enthalpies H^E have now been determined and analyzed in terms of group contribution theory in the surface interaction version proposed by Kehiaian et al.[2] .

Application of this model to binary mixtures requires the definition of a set of geometric parameters (total relative molecular volumes r_i and areas q_i , and the molecular surface fractions α_{si} of the type s surface on molecule i), a set of energetic parameters (interchange energy parameters for each pair of groups (s,t), $C_{st,1}$ and $C_{st,2}$) and the coordination number z, which depends on the degree of molecule orientation.

In a recent review, Kehiaian [3] showed that the group contribution method is very efficient in predicting and interpreting excess thermodynamic functions of liquid mixtures when an appropriate solution model is chosen. The simplest model for mixtures of non-polar liquids is the random mixing, rigid or pseudo-lattice model. However, it is inadequate for polar liquid mixtures interacting via permanent dipoles, because it assumes a random mixing breakdown (whence the importance of orientational effects). Encouraging results for this type of mixtures have been obtained with the quasi-chemical pseudo-lattice model [4-6], which uses a further parameter, i.e. the coordination number z to account for non-randomness.

With polar molecules of a certain complexity, the shape of the experimental curves cannot always be reproduced by adjusting z. The classic model does not consider the dispersive contribution (random) characterizing each contact. In addition, z is regarded as constant for all contacts. These drawbacks can be partly overcome by using the Dispersive Quasi-chemical model (DISQUAC).

In this extension of the quasi-chemical model, each polar or non-polar contact is characterized by a dispersive interchange parameter. The polar contacts are also assigned both z and a quasi-chemical interchange parameter.

Dispersive and quasi-chemical terms are calculated independently and then summed. The DISQUAC model has been explained in detail in a recent paper [7] and need not be repeated here.

MATERIAL AND METHODS

The cyclic ethers: oxolane (puriss.>99.5 mole %), oxane (purum>99 mole %), 1,3-dioxolane (purum>99 mole %), 1,4-dioxane (puriss.>99.5 mole %) all Fluka, were further purified by fractional distillation on sodium wires, whereas trichloroethane (Fluka, purum>99 mole %) were used directly. All liquids were carefully dried over molecular sieves for at least two weeks before use. Gas chromatography analysis showed that purity of the distilled liquids was better than 99.5 % and that of trichloroethane and 1,3-dioxane was closely related to that indicate by Fluka.

H^E values were determined with a Picker flow calorimeter [8-10] equipped with separators in the liquid feed system [11] and use in a discontinuous manner[12] to obtain more precise enthalpies and molar fractions. For each selected position of the two pumps, the density of the solutions at the exit of the calorimeter was measured with a densimeter (mod. 03, Sodev, Canada) mounted in series. This type of assembly allows determination of molar fractions with greater precision than conventional methods.

Moreover, direct flow measurements gives more precise H^E values, expecially in dilute regions. All measurements were carried out at 298.15 K and atmospheric pressure with the calorimeter thermostated at± 0.005 K. In these conditions, the results obtained for the reference system benzene + cyclohexane are within 1% of the better results reported in the literature [13] .

The H^E values for each binary mixture are reported in Table I and fitted by the least squares method to the equation

$$H^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \qquad (1)$$

where x_1 is the molar fraction of trichloroethane.

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

$$(H^E) = \left\{ \sum [H^E_{exp} - H^E_{calc}]^2/(n-m) \right\}^{1/2} \qquad (2)$$

TABLE I

Experimental results of the molar excess enthalpies, H^E, in trichloroethane (1) + cyclic ether (2) mixtures at 298.15 K.

x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})	x_1	H^E (J mol^{-1})
		Trichloroethane (1) + Oxolane (2)			
0.0168	-35.5	0.2960	-551.2	0.7154	-514.0
0.0338	-68.3	0.3445	-594.8	0.7733	-444.8
0.0509	-98.2	0.3940	-626.9	0.8326	-354.1
0.0682	-135.4	0.4447	-647.3	0.8933	-244.1
0.1119	-224.3	0.4964	-652.2	0.9305	-166.8
0.1565	-314.7	0.5493	-636.8	0.9556	-119.2
0.2020	-408.0	0.6034	-661.5	0.9809	-49.7
0.2485	-490.1	0.6588	-571.8	0.9936	-17.6
		Trichloroethane (1) + Oxane (2)			
0.0203	-34.5	0.3364	-551.3	0.7511	-451.8
0.0405	-72.9	0.3878	-586.1	0.8034	-380.1
0.0608	109.9	0.4394	-605.3	0.8559	-297.3
0.0811	-148.8	0.4910	-612.0	0.9085	-201.2
0.1319	-245.2	0.5428	-606.7	0.9401	-141.0
0.1829	-342.1	0.5947	-588.4	0.9613	-98.3
0.2339	-425.2	0.6467	-553.9	0.9824	-44.0
0.2851	-502.8	0.6988	-506.2		
		Trichloroethane (1) + 1,3-Dioxolane (2)			
0.0267	6.2	0.2622	38.3	0.8029	26.8
0.0416	8.8	0.3077	41.3	0.8697	18.9
0.0566	12.2	0.4036	45.2	0.9112	13.5
0.0951	18.6	0.5068	45.4	0.9395	9.6
0.1348	24.4	0.6182	41.6	0.9682	5.4
0.1758	29.8	0.6773	38.0		
0.2183	34.2	0.7388	33.3		
		Trichloroethane (1) + 1,4-Dioxane (2)			
0.0375	-14.2	0.3510	-82.7	0.6693	-98.3
0.0564	-19.2	0.4024	-89.3	0.7248	-92.1
0.1039	-31.2	0.4544	-95.0	0.7811	-81.8

TABLE I-continued

0.1521	-42.6	0.5604	-101.5	0.8381	-68.1
0.2503	-64.3	0.6145	-101.0	0.8959	-49.5
0.3004	-73.8				
		Trichloroethane (1) + 1,3-Dioxane (2)			
0.0182	-6.0	0.3061	-101.5	0.7947	-69.9
0.0643	-28.4	0.4608	-120.1	0.9140	-28.9
0.1112	-46.2	0.5684	-117.6	0.9747	-7.4
0.2071	-77.1	0.6796	-100.5		

where n is the number of experimental points and m the number of coefficients. The a_i and σ values obtained are given in Table II, while the equimolar values of G^E and H^E are reported in Table III.

TABLE II

Values of the least-squares coefficients a_i in equation (1) and standard deviation $\sigma(H^E)$ of the molar excess enthalpies, H^E, in trichloroethane (1) + cyclic ether (2) mixtures at 298.15 K.

cyclic ether	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)/J\ mol^{-1}$
Oxolane	-2595.0	280.0	-40.0	-871.0	621.0	3.6
Oxane	-2455.0	164.0	82.0	-688.0	419.0	2.9
1,3-Dioxolane	182.3	-257.0	5.5	-6.4	15.0	0.2
1,3-Dioxane	-482.1	10.4	79.9	81.8	44.1	1.0
1,4-Dioxane	-397.5	-128.2	3.1	7.0	-114.5	0.6

ESTIMATION OF INTERCHANGE ENERGY COEFFICIENTS AND DISCUSSION

In the DISQUAC approach, each non-polar contact (s,t) is characterized by its $C^{disp}_{st,1}$ (all $C^{quac}_{st,1} = 0$), while the polar contact (s,t) are characterized by a single z number and two sets of interchange energy coefficients $C^{quac}_{st,1}$ and $C^{disp}_{st,1}$ (1 = 1,2). The coefficients for the contacts (s,t) in our mixtures were determined by an iterative method from experimental values for the excess thermodynamic functions H^E and G^E. In this approach, it is primarily necessary to adjust z, since it affects the symmetry of the G^E and H^E vs x_1 curves.

The most serious shortcoming of the classic Guggenheim-Barker model was the observed dependence of z on the nature of the polar molecule. The model requires a single z value for all contacts. For its application to mixtures containing more than two groups, i.e. more than one type of contact (s,t) individually characterized by different values of z or by $z = \infty$, the same "average" z-value had to be taken [2] . With the DISQUAC model, we can avoid this inconsistency by givining the quasi-chemical terms the same z value and adjusting the appropriate amount of dispersive term for each contact (s,t).

For each selected value of z , the $C_{st,1}$ were calculated from the G^E experimental values for different quasichemical percentages of the contact (s,t). With $C_{st,1}$ constant, the $C_{st,2}$ were then adjusted, using the experimental H^E values at $x_1 = 0.5$ of the appropriate mixtures containing the pair of binary contacts (s,t) for the different quasichemical percentage of the contact (s,t). In this paper, z was taken as 4 for all contacts.

TABLE III

Molar excess Gibbs energies G^E and molar excess enthalpies H^E at 298.15 K and $x_1 = 0.5$ for trichloroethane + n-heptane,+ n-hexane and + five and six membered cyclic mono- and diethers mixtures. Comparison of calculated values using the coefficients $C^{disp}_{st,l}$ and $C^{quac}_{st,l}$ (l = 1,2) of Table IV with direct experimental values when available.

Mixture		G^E (J mol^{-1})		H^E (J mol^{-1})	
Trichloroethane (1) +		calc	exp	calc	exp
n-hexane (T = 333.15 K)	(2)	223	223[a]		
n-heptane	(2)	230		581	581[b]
Oxolane	(2)			-641	-649[c]
Oxane	(2)			-645	-614[c]
1,3-Dioxolane	(2)			70	46[c]
1,3-Dioxane	(2)			-123	-120[c]
1,4-Dioxane	(2)			-123	-99[c]

[a] From ref.[18]; [b] From ref. [17]; [c] This work.

For the chlorine-oxygen contact (d,e) in trichloroethene + cyclic ether, the best agreement between H^E_{exp} and H^E_{cal} was obtained for $z = \infty$(random mixing), probably because of mutual compensation between the polar groups: oxygen (-O-) and chlorine (-Cl). This means that (d,e) is characterized by its dispersive energy coefficients $C_{de,1}^{disp}$ only. This behaviour has already been observed in aliphatic aldehyde + chloroalkane mixtures [20].

Three types of surface are present in the mixtures formed by trichloroethane with fives and sixs membered cyclic mono- and diethers:

a, aliphatic ($-CH_2-$, $-CH_3$);

e, oxygen (-O-);

d, chlorine (-Cl).

Three sets of interchange energy parameters are thus necessary for the aliphatic-chlorine (a,d), aliphatic-oxygen (a,e) and oxygen-chlorine (e,d) contacts. These parameters can be calculated from the thermodynamic excess properties of appropriate mixtures. With regard to the aliphatic-oxygen contact, the G^E and H^E values of the n-alkane + oxolane and + 1,4-dioxane mixtures [14-16] were used, whereas for aliphatic-chlorine contact the H^E values for the trichloroethane + n-heptane mixture [18] , together with the liquid vapour equilibrium data at T = 333.15 K for trichloroethane + n-hexane mixture [18-19] , were employed.

For the oxygen-chlorine contact (e,d), our H^E values were used to calculating $C_{de,2}$ (see Table IV).

TABLE IV

Interchange energy coefficients $C_{st,l}^{disp}$ and $C_{st,l}^{quac}$ (l = 1,2) at 298.15 K for trichloroethane + cyclic ether mixtures.

Interchange Energy coefficient		Cyclic monoethers	Cyclic diethers
$C_{ae,1}$	(quac)	6.050	6.050
$C_{ae,2}$	(quac)	7.600	7.600
$C_{ae,1}$	(disp)	9.650	6.850
$C_{ae,2}$	(disp)	20.900	11.950
$C_{ad,1}$	(quac)	0.203	0.203
$C_{ad,2}$	(quac)	0.410	0.410
$C_{ad,1}$	(disp)	0.099[a]	0.099[a]
$C_{ad,2}$	(disp)	0.190[a]	0.190[a]
$C_{de,2}$	(disp)	13.050	9.450

[a] From ref. [2]

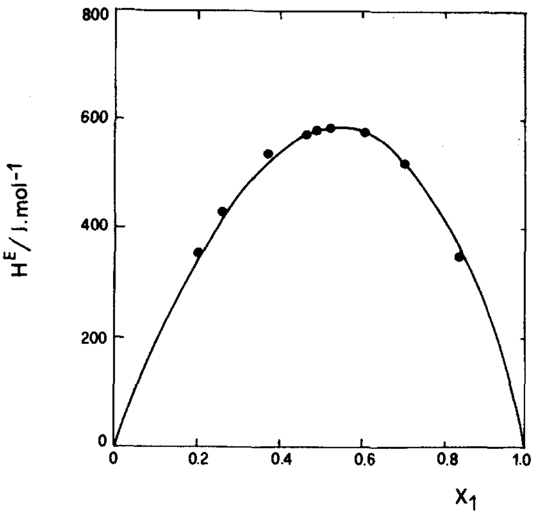

Fig.1. Comparison of the experimental and theoretical molar excess enthalpies, H^E, for the trichloroethane (1) + n-heptane (2) mixture at 298.15 K. Full line, predicted values; ●, experimental results.

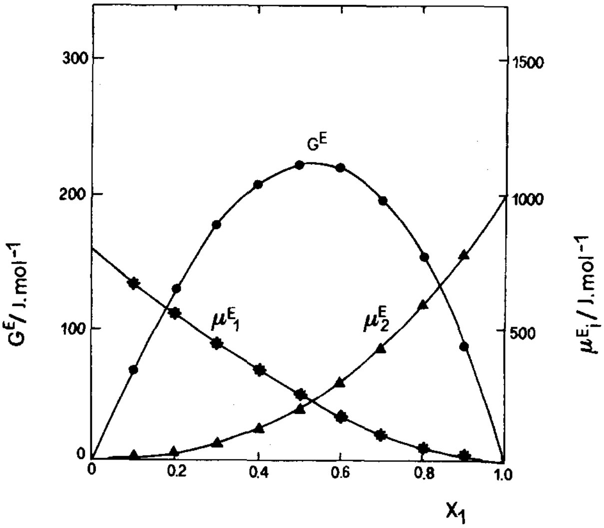

Fig.2. Comparison of the experimental and theoretical molar and partial excess Gibbs energies, G^E and μ_i^E, at 333.15 K for trichloroethane (1) + n-hexane (2) mixture. Full lines, predicted values; points, experimental results.

The most important points of this analysis are:

a) trichloroethane + n-alkane mixtures.

Comparison was limited to H^E at 298.15 K for the n-heptane mixture and to G^E at 333.15 K for the n-hexane mixture. If the contributions represented by dispersive parameters of the apolar CCl_4 + n-alkane mixtures [22] are regarded as dispersive and if the quasi-chemical contributions from the polarity of trichloroethane are added the curves calculated for H^E, G^E and μ_i^E are in good agreement with the experimental results (see figures 1 and 2). In other words, for the polychlorocompounds of general formulae R_x-C-Cl_y (x + y = 4), where x = 0 and y = 4 the aliphatic-chlorine interactions are assumed to be only of a dispersive type (% quac = 0), while if y diminuishes (e.g. y = 3, x = 1 as in trichloroethane) the quasi-chemical interactions increases (% quac > 0). Therefore, for the trichloroethane + n-alkane mixtures the dispersive interactions are evaluated with the $C_{ad,l}^{disp}$ (l = 1,2) parameters of the CCl_4 + n-alkane mixtures, whereas the quasichemical portion is obtained from the difference $X^E_{quac} = X^E_{exp} - X^E_{disp}$ (X = H, G).

b) Cyclic ether + n-alkane mixtures.

With 50 % dispersive and 50 % quasichemical for the aliphatic-oxygen (a,e) contact, satisfactory agreement is obtained between the calculated and experimental values of the excess thermodynamic functions, as can be seen in figure 3, in which G^E and H^E vs x_1 are reported for the 1,4-dioxane + n-heptane mixtures. The excess thermodynamic functions for this series of binary mixtures were calculated using two values of the $C_{ae,l}^{disp}$(l =1,2) parameters, since they are considerably affected by the number of oxygen atoms in the ring.

If there two oxygen atoms in the same molecule (1,3-dioxolane, 1,3-dioxane and 1,4-dioxane), in fact, the interchange energy coefficient decreases by approximately 40 % ("proximity effect"). As reported by Kehiaian et al. [22-23] this effect gives a negative contribution to H^E that decreases when the intramolecular distance between the two functional groups increases and tends to vanish when they are distant enough to be considered independently.

In this case the interchange energy parameters should be identical to those of the monofunctional compound. For the cyclic ethers this tendency is very weak.

The quasichemical interchange energy parameters $C_{ae,l}^{quac}$ (l =1,2) for the cyclic mono- and diethers are slightly different. Only one value was therefore used

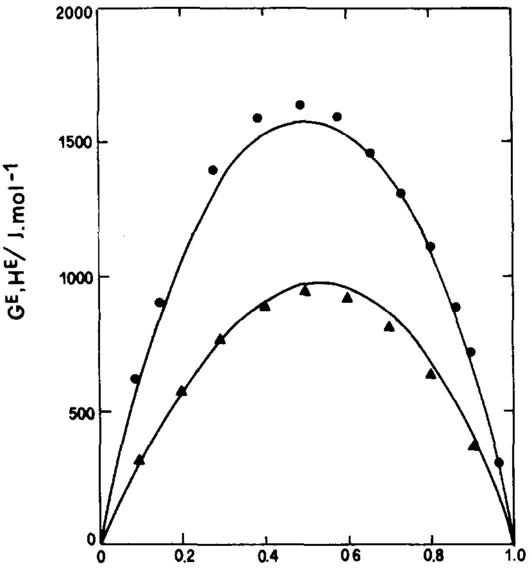

Fig.3. Comparison of the experimental molar excess enthalpies H^E(●) at 298.15 K and molar excess Gibbs energies G^E (▲) at 303.15 K, with the theoretical values for the 1,4-dioxane (1) + n-heptane (2) mixture. Full lines, predicted values; ●, ▲, experimental results.

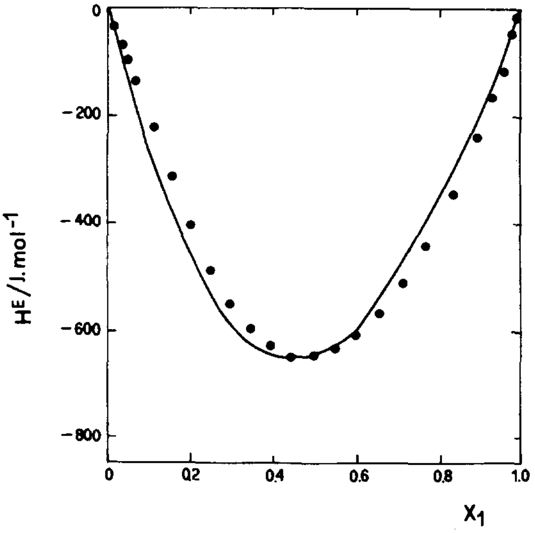

Fig.4. Comparison of the experimental and theoretical molar excess enthalpies H^E for trichloroethane (1) + oxolane (2) mixture at 298.15 K. Full line, predicted values; ● , experimental results.

for all the cyclic ethers.

c) trichloroethane + cyclic ether mixtures.

No G^E values have been reported for this series. It is thus impossible calculate the $C^{disp}_{ed,1}$ and $C^{quac}_{ed,1}$ accurately for the oxygen-chlorine contact.

An attempt get round this difficulty was made by using the G^E and H^E data available for the tetrachloromethane + cyclic ether mixtures. Several trials proved that it is pratically impossible to satisfactorily reproduce the H^E of our mixtures.

For our mixtures, we assumed that there is a compensation of polar effects and the oxygen-chlorine interactions were predominantly dispersive (100 %, with $z = \infty$). Since $C^{quac}_{ed,1} = C^{quac}_{ed,2} = 0$, H^E can be calculated independently of G^E .

The dispersive interchange energy coefficients calculated in this way are given in Table IV, while the calculated and experimental H^E are illustrated in figures 4, 5 and 6.

For all the mixtures considered in this paper, H^E values were calculated using one $C^{disp}_{ed,2}$ value for the two cyclic monoethers and another for the three cyclic diethers. The $C^{disp}_{ed,2}$ coefficient for the cyclic diethers decreased considerably (~ 30 %) compared with that for monoethers because of the so-called proximity effect. This effect could also be a function of the intramolecular distance between the functional groups, as shown by Kehiaian et al. [23] for the mixtures $Cl\text{-}(CH)_m\text{-}Cl + n\text{-}C_6H_{14}$,in which an increase of 90 % of the interchange energy parameters from m = 1 to m = 4 and ~ 60 % from m = 1 to m = 2 was observed.

In our case, the $C^{disp}_{ed,2}$ coefficient was scarcely affected by the relative position of the two oxygen atoms in the molecule of the cyclic diethers, we therefore used only one $C^{disp}_{ed,2}$ value for both 1,3-dioxane and 1,4-dioxane.

Introduction of a $-CH_2-$ group between the two functional groups did not produce the same effect as that observed for the linear chain compound, probably because of the particular structure of the cyclic compound.

Figure 6 shows that the experimental and calculated results were in good agreement for the trichloroethane + 1,3-dioxane mixture, whereas with 1,4-dioxane some deviations, probably due to the proximity effect, were observed.

For the other mixtures (figures 4,5 and 6) the agreement between H^E and H^E may be considered satisfactory, especially if one takes into account the

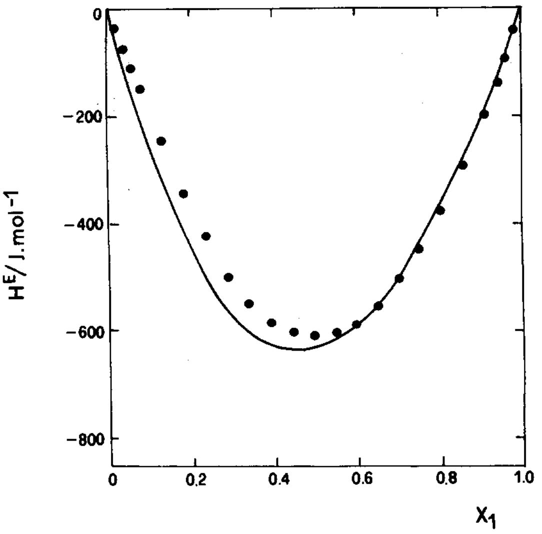

Fig.5. Comparison of the experimental and theoretical molar excess enthalpies H^E for trichloroethane (1) + oxane (2) mixture at 298.15 K. Full line, predicted values; ● , experimental results.

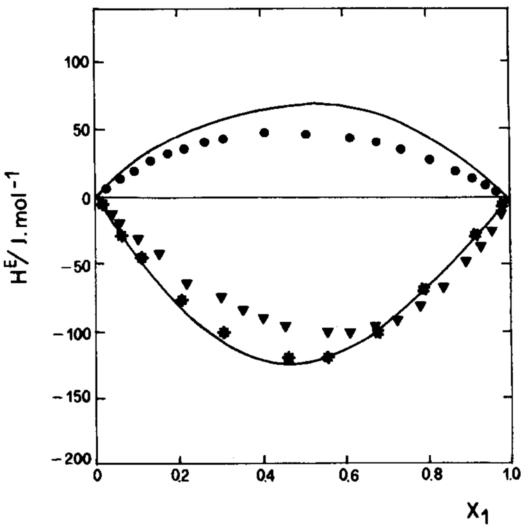

Fig.6. Comparison of the experimental and theoretical molar excess enthalpies H^E for trichloroethane (1) + cyclic diether (2) mixtures at 298.15 K. Full lines, predicted values; ● ,1,3-dioxolane; ▲ , 1,4-dioxane; *, 1,3-dioxane.

considerable complexity of these mixtures with their three types of contact surface, the structural differences between fives and sixs membered cyclic ethers, for which the same interchange energy coefficient was used, and the lack of experimental data for G^E for the trichloroethane + cyclic ether mixtures, for which the oxygen-chlorine contact was assumed to be completely dispersive. These two approximations could be responsable for the symmetry differences between the calculated and experimental curves observed for some systems.

Acknowledgement. We gratefully acknowledge the support of the Italian National Research Council. We also wish to thank Prof. J.P.E. Grolier (University of Clermont-Ferrand) for allowing the author to join his research for two months, and for the encouragement he gave to this project.

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