soap and V_0 is the molar volume of solvent. The results show that the solvation number increases with the increase of the concentration of soap. These results are in agreement with the results of other workers (*26–28*) reported for electrolytic solutions.

It is, therefore, concluded that the praseodymium valerate in a methanol–benzene mixture behaves as a weak electrolyte in dilute solutions below the cmc. The results show that there is a significant soap–solvent interaction in solution.

Registry No. Praseodymium valerate, 26176-68-1; benzene, 71-43-2; methanol, 67-56-1.

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Molar Excess Enthalpy for the Binary Systems 1,3-Dioxolane + 1,2-*trans*-Dichloroethylene, Tetrachloroethylene, or 1,1,2,2-Tetrachloroethane

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Molar excess enthalpy (liquid-phase enthalpy of mixing) for 1,3-dioxolane + 1,2-*trans*-dichloroethylene, + tetrachloroethylene, or + 1,1,2,2-tetrachloroethane binary systems is determined at atmospheric pressure and at 298.15 K. The experimental data were correlated by means of the Redlich–Kister expression, and the adjustable parameters were evaluated by the least-squares method. The cell model and the quasichemical approximation of the lattice theory of solutions were tested. Associations were inferred only for the 1,3-dioxolane + 1,2-*trans*-dichloroethylene system.

Introduction

The present work is a part of a long-term study of the molar excess enthalpy H^E of binary systems containing 1,3-dioxolane as common solvent (component 1). The main purpose of these investigations is to study the dependence of H^E on the substituted groups of the second component and to find a connection between the chemical structure of the compounds and their properties.

The cell model and the quasichemical approximation of the lattice theory of solutions have been tested to confirm the possible presence of associations for the systems in question.

Chemicals

1,3-Dioxolane (D; a Fluka product, purum, analytical grade 99%) was purified by refluxing for about 10 h on Na wires in N flow, excluding moisture, and then fractionated on a Vigreux column (*1*).

1,2-*trans*-Dichloroethylene (DCE; an Aldrich product, analytical grade 98%) was further separated from the residual cis isomer contained in the commerical mixture by fractional distillation (Widmar 30-plate column) over a 10% aqueous sodium hydroxide solution until the density was constant.

Tetrachloroethylene and 1,1,2,2-tetrachloroethane (TCE and TCA, respectively; C. Erba products, analytical grade 99.5% and 98.5%, respectively) were washed over an anhydrous solid, calcium sulfate, and distilled for 10 h.

All purified compounds were stored in dark bottles and preserved over molecular sieves type 3A (C. Erba).

Experimental Section

Density Measurements of Pure Components. Table I shows the experimental data of density ρ of pure liquids, which are necessary to evaluate fluxes and hence mole fractions in the calorimetric measurements. These values were determined with a two capillary glass pycnometer (volume, 31.41 mL at 298.15 K) calibrated with distilled mercury.

Table I. Densities ρ of Pure Chloro Compounds as a Function of Temperature T, Coefficients A and B, Equation 1, Correlation Coefficient R, and Root Mean Square Deviations $\sigma(\rho)$

	DCE		TCE		TCA	
	T/K	ρ/ (kg m^{-3})	T/K	ρ/ (kg m^{-3})	T/K	ρ/ (kg m^{-3})
	288.15	1267.5^a (1261.1)	297.15	1615.6	293.05	1595.4
	290.35	1263.7	298.15	1614.0^a (1614.3)	293.15	1595.4^a (1594.3)
	292.75	1259.6	300.45	1610.7	296.75	1589.8
	293.15	1258.9^a (1254.7)	301.15	1609.2	298.15	1587.7^a (1586.7)
	296.35	1253.6	303.15	1605.8^a (1606.3)	298.25	1587.5
	299.85	1247.5	304.25	1602.8	299.95	1585.0
	302.45	1242.3	306.95	1599.6	301.25	1583.1
	306.15	1236.5	310.05	1594.4	303.15	1579.9^a (1578.6)
			313.95	1588.1	306.25	1575.1
			315.35	1585.7	306.75	1574.3
A	1762.78		2104.76		2049.16	
B	1.71880		1.64622		1.54774	
R	0.99998		0.99890		0.99992	
$\sigma(\rho)$	0.08		0.59		0.10	

[a] Interpolated value eq 1; value in parentheses, ref 3.

Temperature stabilization is within 0.05 K, and the estimated uncertainty of ρ is 0.1 kg m^{-3} for DCE and TCA and about twice this value for TCE.

The density of D has already been reported in an earlier paper (*2*) while those of DCE, TCE, and TCA, determined at atmospheric pressure, are assessed by means of the following formula

$$\rho/(\mathrm{kg\ m^{-3}}) = A - B(T/\mathrm{K}) \qquad (1)$$

The coefficients of eq 1 were obtained by a best fit of our experimental density data with a straight line and are reported in Table I with their correlation coefficients R and root mean square deviations $\sigma(\rho)$.

Agreement with the literature data is given in Table I.

Calorimetric Measurements. The molar excess enthalpies for the three systems D + DCE, D + TCE, D + TCA were measured at 298.15 K by a flow microcalorimeter Model 2107, LKB Produkter AB, described in ref 3. Full automatic burets ABU (Radiometer, Copenhagen, Denmark) were used to pump the pure liquids into the flow-mixing cell. Details of calibration and analytical measurements are given in ref 2.

The microcalorimeter was electrically calibrated before use and calibration subsequently checked by using the standard cyclohexane + *n*-hexane mixture (*4*): the discrepancy between measured and published data was less than 0.5% over the central range of composition.

The estimated accuracy is about 1% for H^E data and 0.0005 for the mole fractions.

The experimental data for the three binary mixtures are reported in Table II and Figure 1.

Correlation of the Calorimetric Data. For all three binary systems, the correlation expression for H^E is provided by the Redlich-Kister equation (*5*)

$$[H^E/(\mathrm{J\ mol^{-1}})]/X_1X_2 = \sum_{k=0}^{n-1} a_k(X_1 - X_2)^k \qquad (2)$$

with n the number of the adjustable parameters a_k.

The a_k values were evaluated by means of a least-squares method, the objective function being

$$\phi = \sum_{i=1}^{N} W_i\eta_i^2 \qquad (3)$$

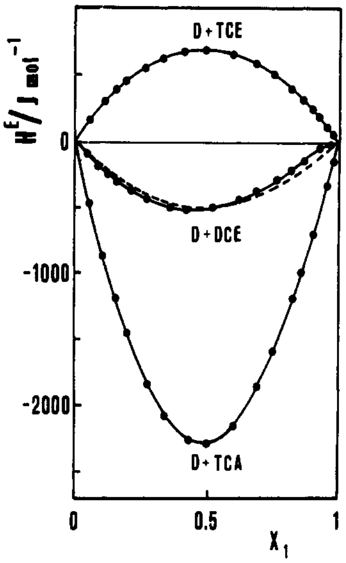

Figure 1. Molar excess enthalpy, H^E, of 1,3-dioxolane (1) + chloro compound (2) as a function of the mole fraction of 1,3-dioxolane at 298.15 K. Points, experimental data; curves, results calculated with the parameters of Table II (dashed curve, cell model calculation (*10*)).

Table II. Experimental Molar Excess Enthalpy H^E of 1,3-Dioxolane (1) + Chloro Compound (2) Systems as a Function of the Mole Fraction X_1 of 1,3-Dioxolane at 298.15 K, Coefficients a_k in Equation 2, and Standard Deviations σ (J mol^{-1}), Equation 4

	D + DCE		D + TCE		D + TCA	
	X_1	H^E/ (J mol^{-1})	X_1	H^E/ (J mol^{-1})	X_1	H^E/ (J mol^{-1})
	0.0441	-96	0.0577	169	0.0592	-471
	0.0845	-179	0.1091	300	0.1119	-878
	0.1217	-253	0.1551	391	0.1589	-1194
	0.1559	-308	0.1967	455	0.2012	-1450
	0.2170	-387	0.2686	564	0.2742	-1841
	0.2698	-442	0.3287	623	0.3350	-2096
	0.3566	-502	0.4234	682	0.4304	-2266
	0.4249	-513	0.4947	691	0.5019	-2295
	0.5257	-507	0.5949	662	0.6018	-2159
	0.6244	-444	0.6878	585	0.6939	-1848
	0.6891	-381	0.7460	510	0.7514	-1591
	0.7688	-283	0.8150	403	0.8193	-1186
	0.8160	-226	0.8546	326	0.8581	-984
	0.8693	-140	0.8981	240	0.9007	-707
	0.9301	-30	0.9216	186	0.9478	-328
	0.9638	-10	0.9463	125	0.9732	-139
			0.9742	79		
a_0	-2037.7		2759.3		-9117.3	
a_1	541.4		-164.2		762.2	
a_2	1022.2		125.7		2647.7	
a_3	806.6		-129.5			
σ	6.36		5.05		23.4	

where N is the number of experimental points in the calorimetric measurements, the residual η_i is the difference between the two sides of eq 2, with H^E taken from Table II, and W_i is the weight of the residual (*2*). Table II includes the values of these parameters with their sample standard deviations σ, defined as

$$\sigma = (\phi_{\min}/(N - n))^{0.5} \qquad (4)$$

where $\phi_{\min}$ is the minimum value of ϕ and n is the number of parameters. References 2 reports the calculation procedure and details on evaluation of the weights W_i.

Discussion of the Results and Conclusions

Figure 1 shows the experimental calorimetric data for the binary systems of D with DCE, TCE, and TCA. Systems D + DCE and D + TCA show negative values of H^E, with minima of −500 and −2100 J mol^{-1}; instead D + TCE shows positive values of H^E with a maximum of about 700 J mol^{-1}.

The H^E vs X_1 curves are almost symmetric for the D + TCE and D + TCA systems, whereas the curve referring to D + DCE is quite different for $X_1 \rightarrow 0$ and $X_1 \rightarrow 1$, showing, in the D-rich range, a trend to inversion of sign.

It is noteworthy to stress that sign inversion is evident in the D + trichloroethylene system previously studied (*6*), that is, when the second component has three Cl atoms substituting the H atoms in ethylene (one more than DCE), whereas complete Cl of substitution (D + TCE) does not lead to sign inversion and H^E is kept positive.

Though the trend of sign inversion seems connected to strong interactions between dissimilar molecules, but not necessarily of hydrogen bond type (*7*), we suggest that sign inversion in the H^E curve for the system D + trichloroethylene is due to the hydrogen bonding resulting from the interaction between the O atoms of D and the H atom of trichloroethylene, considering that a large positive charge is induced on this H atom by the double bond and the three electronegative Cl atoms. This situation is much more evident in the D-water system where H bonding is the accepted cause of the sign inversion in the H^E vs X_1 curve (*8*).

However, when all the H atoms of ethylene are substituted with Cl (as in the case of TCE), no hydrogen bonding being possible, the H^E curve is positive and symmetrical.

The D + TCA system (negative H^E with a minimum of −2100 J mol^{-1}) may be compared with the D + 1,1,1-trichloroethane mixture, showing positive H^E with a maximum of about 46 J mol^{-1} (*9*). This considerable difference in behavior is due to the much poorer induction effect of Cl vs H atoms in 1,1,1-trichloroethane, as compared to that of to TCA.

An attempt to describe the three systems of this paper by means of the cell model (*10*) and the quasichemical approximation of the lattice theory (*11*) was carried out, using model parameters fitted to the maximum of the H^E versus X_1 curves.

The calculated curves are almost the same for both theoretical models and very close to the experimental data for the systems D-TCA and D-TCE (maximum percentage difference about 5%) and are not shown in Figure 1.

Instead, the D + DCE system shows larger deviations between calculated and experimental curves, especially for $X_1 > 0.5$, though limitation of the theories may lead to such an extent of discrepancy.

This result confirms the previous conclusions on the D + DCE system, whose peculiar characteristic is similar to that of the D + trichloroethylene mixture where intra- and intermolecular associations have been assumed (*14*) to account for the calorimetric behavior.

Glossary

a_k	parameters in eq 2
D	1,3-dioxolane, component 1
DCE	1,2-*trans*-dichloroethylene, component 2
H^E	molar excess enthalpy (molar liquid-phase enthalpy of mixing), J mol^{-1}
N	number of experimental points, eq 3
T	absolute temperature, K
TCA	1,1,2,2-tetrachloroethane, component 2
TCE	tetrachloroethylene, component 2
W_i	weight of residual η_i, eq 3
X_i	mole fraction of component i (i = 1, 1,3-dioxolane; i = 2, chloro compound)

Greek Symbols

ρ	density, eq 1, kg m^{-3}
σ	sample standard deviation, eq 4
ϕ	objective function in the least-squares analysis, eq 3

Registry No. D, 646-06-0; DCE, 156-60-5; TCE, 127-18-4; TCA, 79-34-5.

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