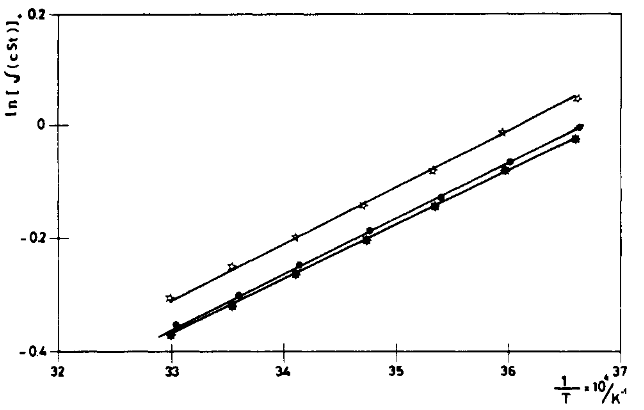

Figure 3. Kinematic viscosities of three ternary mixtures vs absolute reciprocal temperature. Experimental data: (●) (I); (☆) (II); (✱) (III). Calculated data: solid lines.

Table V. Andrade Constants for Kinematic Viscosity Correlation and Quality of Fit in the Temperature Range 273.15–303.15 K

system	A, cSt	B, K	$\delta(\nu)$, cSt	$(\Delta\nu\%)_{av}$
p-xylene, ν_1	0.028 21	962.83	0.0008	0.07
m-xylene, ν_2	0.028 37	948.50	0.0023	0.26
o-xylene, ν_3	0.019 54	1129.54	0.0031	0.25
p-xylene (1)/*m*-xylene (2)				
ν_{12}	0.025 65	987.21	0.0026	0.22
ν_{21}	0.028 78	948.62		
p-xylene (1)/*o*-xylene (3)				
ν_{13}	0.025 09	1013.77	0.0031	0.24
ν_{31}	0.023 75	1048.60		
m-xylene (2)/*o*-xylene (3)				
ν_{23}	0.029 16	962.67	0.0030	0.24
ν_{31}	0.029 17	986.10		
ternary mixtures				0.17 (I)
ν_{123}	0.031 23	941.67	0.0032	0.48 (II)
				0.45 (III)

Density predictions were carried out with the HBT method, the mean deviations between experimental and calculated values being always less than 0.3%. Figure 2 is a parity plot of measured and calculated binary and ternary densities for the xylene mixtures studied.

The correlation of the ternary kinematic viscosity data, over the temperature range 273.15–303.15 K, was performed with the Kalidas and Laddha expansion of the McAllister equation (*2*)

$$\ln \nu = x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + x_3^3 \ln \nu_3 + 3x_1^2x_2 \ln \nu_{12} + 3x_1^2x_3 \ln \nu_{13} + 3x_2^2x_1 \ln \nu_{21} + 3x_2^2x_3 \ln \nu_{23} + 3x_3^2x_1 \ln \nu_{31} + 3x_3^2x_2 \ln \nu_{32} + 6x_1x_2x_3 \ln \nu_{123} + R'^{\circ} \quad (3)$$

where once again R'° was set equal to zero for reasons identical with those given before for binary mixtures.

Equation 3 requires the knowledge of the binary interaction coefficient, ν_{123}, which must be assessed from experimental data. Therefore, assuming for this coefficient a temperature dependence as described by eq 2 and using pure-component and binary parameters, the two ternary Andrade constants, A_{123} and B_{123}, were calculated over the experimental data gathered for system I (Table IV). Mixtures II and III were used to evaluate the effectiveness of the McAllister method in the prediction of the viscosities of ternary systems. The average deviation found was about 0.37%. Figure 3 shows the experimental and calculated ternary viscosity data plotted as a function of the absolute temperature reciprocal.

The Andrade parameters required to estimate the kinematic viscosities of the ternary system, in the temperature range previously referred to, are shown in Table V along with the standard deviations, $s(\nu)$, and average percent deviations $(\Delta\nu\%)_{av}$. The accuracy with which the McAllister equation fits the viscosity data for binary mixtures of xylenes supports the use of this equation in the range of temperature studied. For liquid ternary mixtures, it also allows the estimation of viscosity data, over the whole concentration range, within acceptable margins of accuracy.

Registry No. *o*-Xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3.

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Heat of Mixing of 1,3-Dioxolane + Trichloroethylene

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The excess molar enthalpy H^E of 1,3-dioxolane + trichloroethylene was measured in a flow microcalorimeter as a function of mole fraction x_1 of 1,3-dioxolane at 288.15, 298.15, and 313.15 K under atmospheric pressure. The H^E vs x_1 curves are S-shaped, with $H^E < 0$ over nearly the entire x_1 range, except at $x_1 \simeq 1$, and with positive molar excess heat capacity, $C_p^E = dH^E/dT$. This suggests complex formation in the liquid mixture.

Introduction

The present work is an extension of a series of previous investigations (*1*) on binary mixtures of a common solvent, 1,3-dioxolane. The main purpose of these studies is to obtain thermodynamic information as to the dependence of the molar excess enthalpy H^E on the nature of the groups of the second component. The group investigated in this paper is the chlorine of trichloroethylene.

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Table I. Densities ρ of Trichloroethylene as a Funciton of Temperature T, Standard Deviation $\sigma(\rho)$, and Correlation Coefficient R

T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
291.25	1467.59	301.35	1450.86
292.15	1466.03	303.35	1447.66[b]
293.55	1463.87[a]	304.95	1444.70
295.25	1461.21	307.15	1441.14
296.75	1458.52	310.35	1435.50
298.55	1455.57	312.65	1431.71
299.65	1453.72	315.45	1427.19

$\sigma(\rho) = 1.1 \times 10^{-4}$ kg m^{-3}; $|R| > 0.999$

[a] At T = 293.15, ρ = 1463.9 kg m^{-3} (*8*). [b] At T = 303.15, ρ = 1446.9 kg m^{-3} (*8*).

Chemicals

1,3-Dioxolane (Fluka product; purum, analytical grade 99%) was purified as described in ref 1. Trichloroethylene (C. Erba product; analytical grade 99.9%) was used without further purification. The pure liquids were stored over molecular sieves type 4A (C. Erba).

Experimental Section

The experimental H^E data reported in this paper were measured by means of an LKB Model 2107 flow microcalorimeter (LKB produkter AB, Bromma, Sweden) described elsewhere (*2*). Details on calibration, analytical measurements, and the accuracy of the results are given in refs 3 and 4. The calorimeter was tested with use of the standard cyclohexane + *n*-hexane mixture (*1*).

The densities ρ of the pure components, which are required to calculate the composition of the mixtures, were determined with a two-capillary glass pycnometer (*1*). The value obtained for trichloroethylene (Table I) can be represented by a straight line

$$\rho/(\text{kg m}^{-3}) = 1498.14 - 1.6777((T/K) - 273.15) \quad (1)$$

in the temperature range 291–315 K. The correlation coefficient R and the sample standard deviation $\sigma(\rho)$ are reported in Table I. The densities of 1,3-dioxolane have been determined in an earlier paper (*4*).

Results

The calorimetric data (Table II) were smoothed by using Redlich–Kister polynomials

$$H^E/(\text{J mol}^{-1}) = x_1x_2\sum_{k\geq 0} a_k(x_1 - x_2)^k \quad (2)$$

where the a_k's are the adjustable parameters obtained by least-squares analysis as described in ref 3.

Discussion

A literature survey shows no evidence of H^E for this system. As can be seen from Figure 1, the 1,3-dioxolane–trichloroethylene system shows negative values of H^E with a marked minimum at $x_1 \rightarrow 0.4$ for all temperatures, as well as a strong dependence on temperature.

Furthermore, the H^E vs x_1 curve shows an inversion of sign close to the 1,3-dioxolane-rich mixtures. This behavior is similar to that shown by 1,3-dioxolane–water (*5*) and 1,4-dioxane–water (*6*) and is due to the dilution effect on the hydrogen-bond complexes, as discussed in ref 5.

Table II. Experimental Molar Excess Enthalpies H^E for 1,3-Dioxolane (1) + Trichloroethylene (2) at 288.15, 298.15, and 313.15 K as a Function of The Mole Fraction x_1 of 1,3-Dioxolane, Coefficients a_k, Equation 2, and Standard Deviations $\sigma(H^E)$

	T = 288.15 K		T = 298.15 K		T = 313.15 K	
	x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})	x_1	H^E/ (J mol^{-1})
	0.0387	−58.2	0.0386	−52.9	0.0387	−32.0
	0.0510	−74.0	0.0509	−67.9	0.0510	−46.6
	0.0970	−133.5	0.0968	−122.5	0.0970	−89.1
	0.1769	−213.3	0.1769	−190.7	0.1769	−138.1
	0.2438	−259.0	0.2438	−229.6	0.2438	−161.9
	0.3007	−285.0	0.3007	−248.4	0.3006	−179.4
	0.3921	−291.0	0.3921	−255.3	0.3920	−180.0
	0.4623	−278.7	0.4622	−244.9	0.4623	−169.8
	0.5633	−238.8	0.5633	−205.9	0.5632	−138.3
	0.6323	−199.9	0.6323	−170.8	0.6592	−95.8
	0.7207	−129.4	0.7207	−107.4	0.7296	−65.6
	0.7748	−96.1	0.7747	−79.8	0.7747	−42.8
	0.7947	−72.9	0.7946	−56.1	0.7946	−28.7
	0.8377	−40.6	0.8377	−30.2	0.8376	−8.0
	0.8856	−12.6	0.8856	−6.8	0.8856	7.6
	0.9117	−2.5	0.9117	1.1	0.9116	10.5
	0.9393	4.4	0.9393	5.5	0.9393	13.2
	0.9687	3.0	0.9687	3.1	0.9687	7.4
	0.9763	2.4	0.9763	2.4	0.9767	5.1
a_0	−1081.6		−907.9		−624.2	
a_1	830.9		676.1		544.9	
a_2	464.8		−240.2		−177.1	
a_3	−1339.4		353.3		399.5	
a_4	4210.1		1757.8		1410.4	
a_5	140.3		−1333.7		−356.1	
a_6	−3202.5		−234.8		−960.9	
$\sigma(H^E)$	3.8 J mol^{-1}		4.0 J mol^{-1}		3.7 J mol^{-1}	

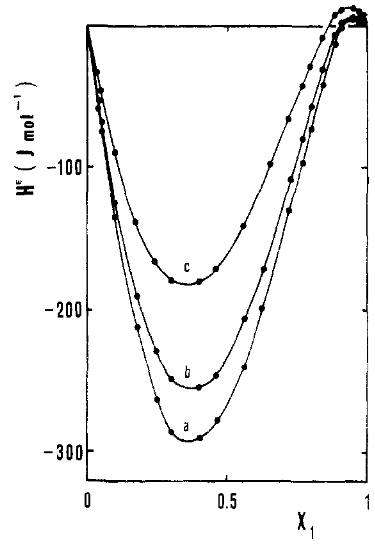

Figure 1. Molar excess enthalpy H^E of the 1,3-dioxolane–trichloroethylene system as a function of the mole fraction x_1 at 288.15 K (a), 298.15 K (b), and 313.15 K (c): (●) experimental values; (—) curves calculated by eq 2 with the parameters a_k of Table II.

A spectroscopic analysis (NMR) on the 1,3-dioxolane–trichloroethylene system and a theoretical study based on quantum mechanics have also been performed in order to obtain supplementary information on the association pattern. The results, which will be published in a separate paper, indicate the favorable formation of 1,3-dioxolane–trichloroethylene associations via a hydrogen bond between the negatively charged oxygens in 1,3-dioxolane and the positively charged hydrogen in trichloroethylene. The double bond and the presence of three electronegative Cl atoms in trichloroethylene are responsible for this last effect.

For a better understanding of the behavior of this mixture, we considered the 1,3-dioxolane + 1,1,1-trichloroethane system (*7*). In fact, the latter system shows a positive, nearly symmetric H^E vs x_1 curve with a maximum of 45 J mol^{-1}. This is consistent with weaker interactions between the O atom and the H atoms, where the latter are placed far from the three Cl atoms.

Glossary

a_k	coefficients in eq 2
H^E	molar excess enthalpy, J mol^{-1}
R	correlation coefficient
T	absolute temperature
x_i	mole fraction of component i (i = 1, 1,3-dioxolane; i = 2, trichloroethylene)

Greek Letters

ρ	density, kg m^{-3}
σ	standard deviation, ref 1

Registry No. 1,3-Dioxolane, 646-06-0; trichloroethylene, 79-01-6.

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Conductivity and Viscosity of Molten Mixtures of Ferric Nitrate Nonahydrate with Hydrates of Calcium, Cadmium, Magnesium, and Zinc Nitrates

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The conductivity and viscosity of molten mixtures of ferric nitrate nonahydrate with hydrates of calcium, cadmium, magnesium, and zinc nitrates have been measured as a function of temperature and composition. Both conductivity and fluidity exhibit a non-Arrhenius temperature dependence for all the compositions and have been described in terms of three-parameter equations $\Lambda = A_{\Lambda} \exp[-B_{\Lambda}/(T - T_{0,\Lambda})]$ and $\phi = A_{\phi} \times \exp[-B_{\phi}/(T - T_{0,\phi})]$. A_{Λ}, B_{Λ}, $T_{0,\Lambda}$, A_{ϕ}, B_{ϕ}, and $T_{0,\phi}$ are empirical parameters characteristic of the medium. The deviations from ideal behavior in transport properties have been interpreted considering ion–ion, ion–water, and water–water interactions. The results suggest the existence of a hydration–dehydration phenomenon in these mixed hydrated melts.

Introduction

The behavior of molten hydrated salts has been discussed considering the existence of large weak field cations of the type $M(H_2O)_n^{z+}$ and anions; this has been evidenced by spectral (*1*, *2*) volumetric and transport studies (*3*–*8*). In binary molten mixtures of hydrated salts, as divalent metal nitrates are added to trivalent metal nitrates, the differences in charge, radius, and polarizability of the cations result in a competition for preferential orientation of water dipoles and anions toward the cation having high cationic potential (z/r), leading to ion association and a hydration–dehydration phenomenon (*9*, *10*). In order to investigate these interactions in hydrated salt mixtures, the conductivity and viscosity of molten mixtures of divalent and trivalent nitrates have been studied. This communication reports the observations made on molten mixtures of ferric nitrate nonahydrate with hydrates of calcium, cadmium, magnesium, and zinc nitrates.

Experimental Section

AnalaR (BDH) grade chemicals were used. The water of hydration was determined by volumetric titration by using EDTA with an accuracy of ±0.02 mol/mol of cation. The average number of moles of water of hydration per mole of the salt (R) was 9.08 for ferric nitrate, 4.12 for calcium nitrate, 4.15 for cadmium nitrate, 6.02 for magnesium nitrate, and 6.22 for zinc nitrate. Mixtures were prepared by adding calculated amounts of the salts, melted and matured for 3 h.

A Beckman conductivity bridge (Model RC 18A, precision 0.03%) based on Wien's bridge principle, provided with a CRT null detector and Wagner ground, operating at an ac frequency of 1 kHz, was employed to measure the solution resistance. A single capillary dip-type conductivity cell with plantinized platinum electrodes was employed. The cell constant was determined with 0.1 and 1.0 mol dm^{-3} KCl solutions at 25 °C from the data of Jones and Prendergest (*11*). Redetermination of the cell constant after five to six runs showed no appreciable change. The expected accuracy of the conductivity data is ±0.3%.

A three-limb UCF-viscometer was employed for viscosity measurements. It essentially consists of receiving, measuring, and auxiliary tubes arranged parallel to one another to form the suspended level arrangement in a triangular fashion, which reduced the effect of back-pressure. The measuring arm had two small bulbs with fiducial marks between them. The size of the bulb and the length and diameter of the capillary were such that the efflux time for the flow of ca. 2 mL of solution ranges between 120 and 300 s. Viscometers were calibrated in the temperature range 278–363 K with use of triple-distilled water, 20% and 40% sucrose solutions, and 98% glycerol solution. Typical values of viscometer constants ranged between 0.003 and 0.0075 cP. Accuracy of the viscosity data is estimated to be better than ±0.5%.

A liquid paraffin thermostat of 20-L capacity was used. Temperature was controlled and known with a precision of ±0.05 °C. Data were recorded both in heating and cooling cycles at ca. 5–10-deg intervals.

Results and Discussion

Conductivity (κ) and viscosity (η) of molten mixtures of $Fe(NO_3)_3 \cdot 9H_2O$ with $M(NO_3)_2 \cdot RH_2O$ (M = Ca, Cd, Mg, Zn) have been measured over available composition and temperature

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