Solvent Effects on the Thermodynamic Data for the Formation of the N,N-Dimethylacetamide–Iodine Adduct

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Abstract: Enthalpies and equilibrium constants for the reaction of N,N-dimethylacetamide, DMA, with iodine have been determined in the solvents benzene and methylene chloride. If the data in CH_2Cl_2 and C_6H_6 are evaluated ignoring solvent interactions, the DMA–I_2 enthalpy is calculated as -2.6 and -3.3 kcal mole^{-1}, respectively. These values are compared to -4.0 kcal mole^{-1}, the enthalpy of formation of the adduct in CCl_4. Calorimetric data are reported which enable determination of the solvation energies of the complexes in these solvents relative to those in CCl_4. A hydrogen bonding enthalpy of -2.2 ± 0.3 kcal mole^{-1} is measured for the DMA–CH_2Cl_2 adduct in CCl_4, and it is estimated that the DMA–I_2 complex is solvated to the extent of about -1 kcal mole^{-1} in methylene chloride.

The interaction of iodine with a variety of Lewis bases has been the subject of extensive review.[2] In general, investigations carried out on these systems have utilized an "inert" or nonpolar solvent such as carbon tetrachloride, cyclohexane, or *n*-heptane. Although some variation in the equilibrium constant for a specific iodine–donor system is observed in different inert solvents, the enthalpy of formation of the adduct is the same within experimental error. In addition, the enthalpy of formation of iodine adducts measured in the gas phase[3,4] has been found to be, within experimental error, identical with the enthalpy of formation of the corresponding adduct measured in an inert solvent. However, the gas phase equilibrium constants were quite different from those evaluated in CCl_4. These effects are also observed in other systems. For example, the formation constants for the 1:1 *s*-trinitrobenzene–naphthalene complexes have been measured in six inert solvents[5] and were found to be sensitive to the solvent employed while the enthalpy of formation of the adduct was not.

The effect of an interacting solvent on the formation constants for a series of complexes of tetracyanoethylene has been reported.[6] It was observed that the value of the equilibrium constant was markedly affected by the solvent in which the spectroscopic measurements were performed. After correcting the equilibrium constants relative to a "standard" solvent, $CHCl_3$, by treating the system as one involving competing equilibria between the acid and the solvent, much of the apparent deviation of *K* with solvent was removed. A similar approach was taken earlier by Foster for the determination of the association constants for two competing bases with an acid in nonpolar solvents[7,8] and has been recently treated rigorously by Tamres.[9] Although treatment of the data in terms of competing equilibria accounted for a large portion of the deviation of the equilibrium constants with a change in solvent for these systems, it is by no means the only effect to consider in order to describe the variation in *K* with solvent.

There are many instances in which the effect of solvation is ignored in the calculation of thermodynamic constants from data obtained in polar or donor solvents. This practice can lead to difficulty when enthalpies of adduct formation measured in polar solvents, such as methylene chloride, are compared directly with results from other systems in inert solvents.[10,11]

Consequently, it was of interest to select a model donor–acceptor system and evaluate the effects of different solvents on the thermodynamic data obtained. The N,N-dimethylacetamide–iodine system, which has been well characterized in carbon tetrachloride,[12] was selected for this study. Solvents of varying properties were utilized with carbon tetrachloride serving as the "standard" solvent. The solvents considered were methylene chloride, benzene, dioxane, and 3-methylsulfolane (3-methyltetrahydrothiophene 1,1-dioxide). Methylene chloride is a hydrogen bonding solvent with a dielectric constant of 9.08 at 20°, compared to a value of 2.24 at 20° for carbon tetrachloride.[13] Benzene, with a dielectric constant of 2.28 at 20°, is basic toward iodine, with a reported equilibrium constant for adduct formation of 0.15 l./mole at 25° in carbon tetrachloride.[14] The dielectric constant of 3-methylsulfolane has not been reported, but the value for sulfolane (tetrahydrothiophene 1,1-dioxide) has been determined as 44 at 30°.[15]

Experimental Section

Reagents. Fisher Spectranalyzed carbon tetrachloride was used without further purification.

Baker Analyzed Reagent methylene chloride was dried over anhydrous calcium sulfate for several days and then distilled at atmospheric pressure from a fresh quantity of the drying agent. The constant-boiling middle fraction was collected.

Fisher Spectranalyzed benzene was used without further purification.

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[1] Abstracted in part from the Ph.D. Thesis of R. J. Niedzielski, University of Illinois, 1963.

[2] See, for example, L. J. Andrews and R. M. Keefer, *Advan. Inorg. Chem. Radiochem.* 3, 91 (1961).

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[15] Phillips Petroleum Company, Product Bulletin.

Phillips Petroleum Co. 3-methylsulfolane was refluxed overnight over barium oxide under reduced pressure in a column packed with saddles. The constant-boiling middle fraction was retained. Vapor phase chromatography on an F and M Model 300 programmed temperature gas chromatograph with a silicone gum rubber static phase and helium carrier gas indicated only one component present.

1,4-Dioxane was dried over sodium metal for several days and then refluxed over a fresh quantity of sodium for several hours at atmospheric pressure in a column packed with glass helices. The constant-boiling middle fraction was saved.

Baker Analyzed Reagent iodine and Eastman White Label N,N-dimethylacetamide (DMA) were purified as previously reported.[12]

Calculations. The procedures for carrying out the spectrophotometric measurements and calculating the equilibrium constants and enthalpy values have been described.[16,17] The measurements were carried out on the low-energy side of the visible absorption band of free iodine. This position was chosen because it has been shown that the changes in the molar absorptivities of free iodine and complex with changing temperature are not significant in this region.[18] The calculation of the equilibrium constant for iodine–donor interaction was made using the equation[16]

$$K_{\text{obsd}}^{-1} = \frac{A - A_0}{\epsilon_c - \epsilon_I} - (C_I + C_D) + \frac{C_I C_D(\epsilon_c - \epsilon_I)}{A - A_0} \qquad (1)$$

where $(A - A_0)$ is the measured absorbance, C_I and C_D represent the initial concentrations of iodine and DMA, and ϵ_c and ϵ_I represent the extinction coefficients of complex and iodine. The quantity $(A - A_0)$ was measured directly by placing a solution of iodine and DMA in the sample cell and a solution of iodine of the same initial concentration in the reference cell.

The calorimetric procedure employed for the determination of ΔH and K for the DMA–CH_2Cl_2 system has been described.[19] For the consideration of competing equilibria, the following equations were utilized.

$$\text{A} + \text{B} \overset{K_2}{\rightleftarrows} \text{C} \qquad (2)$$

$$\text{A} + \text{S} \overset{K_3}{\rightleftarrows} \text{F} \qquad (3)$$

These simultaneous equilibria involve a species, A, which reacts with both B and the solvent, S, to form two products, C and F. In the case of the DMA–I_2 equilibrium in benzene, A represents I_2 and B represents DMA, since I_2 forms complexes with both B and S. In the case of the DMA–I_2 equilibrium in CH_2Cl_2, A represents DMA and B represents I_2.

The equilibrium constant which is calculated by ignoring eq 2 and 3 may be written

$$K_{\text{obsd}} = \frac{[\text{C}]}{[\text{A}^0 - \text{C}][\text{B}^0 - \text{C}]} \qquad (4)$$

in which symbols with superscripts represent initial concentrations and those without represent equilibrium concentrations of the various components. When the competing equilibria represented by (2) and (3) are considered, one obtains

$$K_2 = \frac{[C]}{[\text{A}^0 - \text{C} - \text{F}][\text{B}^0 - \text{C}]} \qquad (5)$$

$$K_3 = \frac{[\text{F}]}{[\text{A}^0 - \text{C} - \text{F}][\text{S}^0 - \text{F}]} \qquad (6)$$

If (a) $[\text{S}^0 - \text{F}] \cong [\text{S}^0]$ and (b) $[\text{A}^0 - \text{C}] \cong \text{A}^0$, eq 4 and 6 may be used to eliminate the unknowns [C] and [F] and eq 5 becomes

$$K_2 = K_{\text{obsd}}(1 + K_3\text{S}^0) \qquad (7)$$

Equations 5 and 7 express the "refined" equilibrium constant in the interacting solvent, *i.e.*, the constant corrected for the change in concentration of species A due to its reaction with the solvent. The enthalpy corresponding to eq 2, ΔH_2, was calculated for the system in the solvent benzene by the following procedure. The K and ΔH values obtained for the benzene–iodine complex in CCl_4 were employed for K_3 and ΔH_3. This is justified because the absorbance data in pure benzene pass through the common intersection in the K *vs.* ϵ plot for data obtained in CCl_4. This indicates a similar K in CCl_4 and C_6H_6. The value of K_{obsd} was calculated from absorbance data at a series of temperatures assuming the measured value at $\epsilon_c - \epsilon_I$ at room temperature is constant. Using K_3 calculated at each temperature from the benzene–iodine data in CCl_4, the value of K_2 at each temperature was obtained by substituting these quantities into eq 7. The enthalpy, ΔH_2, was evaluated from the temperature dependence of K_2 using the method of least squares. A similar procedure could not be employed for the DMA–I_2 system in CH_2Cl_2 because K_3 could not be obtained in CH_2Cl_2. In this system, the enthalpy calculated from the temperature dependence of K_{obsd} was corrected for the difference in heat of solution of DMA in CH_2Cl_2 and CCl_4. The resulting ΔH is the sum of the enthalpy of adduct formation in CCl_4 and the enthalpy of solvation of the complex by CH_2Cl_2 assuming, *vide infra*, that I_2 is solvated to the same extent in CCl_4 and CH_2Cl_2. For comparison, a similar quantity is reported for the system in benzene.

Error Analysis. Enthalpy values for the spectroscopic data were determined, and the error was calculated by the method of least squares. Errors are reported at the 95% confidence level. In an enthalpy experiment, in which a constant $\epsilon_c - \epsilon_I$ is assumed, the data fit the least-squares line extremely well. The principal source of error in this treatment is caused by the change in $\epsilon_c - \epsilon_I$ with temperature.

Results and Discussion

Equilibrium Constant Variations with Solvent. The data for the determination of the equilibrium constants for the DMA–I_2 system in different solvents are presented in Table I. The values reported as K_{obsd} were calculated using eq 1 and represent the equilibrium constants which would be reported if one chose to ignore the solvent interactions. In each case, K_{obsd} is much smaller than the equilibrium constant measured in CCl_4 ($K_{CCl_4} = 6.9$ l. mole^{-1}).[12]

In the benzene system, the refined equilibrium constant, K_2, is also reported in Table I. The reported[14] values of $K = 0.15$ l. mole^{-1} were used in the calculation of K_2. It is very interesting to point out that when the solvent equilibrium with iodine is taken into consideration, the refined equilibrium constant is approximately the same as that measured in CCl_4.

In order to calculate K_2 in methylene chloride, the equilibrium constant for the DMA–CH_2Cl_2 equilibrium in CH_2Cl_2 must be known. This equilibrium constant was measured in CCl_4 by using a calorimetric procedure for the simultaneous determination of K and ΔH. The data obtained are presented in Table II, and a value of $-\Delta H = 2.2$ kcal mole^{-1} for the heat of hydrogen bonding of methylene chloride with DMA in CCl_4 is obtained. If this equilibrium constant were to remain the same in the solvent CH_2Cl_2, a value of $K_2 = 23$ l. mole^{-1} would be calculated for the refined DMA–I_2 equilibrium constant. Actually, there is little reason to expect that the DMA–CH_2Cl_2 equilibrium constant will be the same in CH_2Cl_2 as it is in CCl_4. However, whatever the value of K_3 in CH_2Cl_2, K_2 must be greater than K_{obsd}, and K_2 most probably is larger than the DMA–I_2 equilibrium constant measured in CCl_4.

Effect of Solvent on Measured Enthalpies. The parameters affecting the measured enthalpies in a polar solvent relative to the values measured in CCl_4 can best be appreciated by consideration of the following enthalpy cycle

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Table I. Data[a] and Equilibrium Constants for DMA–I_2 at 25.0°

Solvent	λ, mμ	C_I, mole l.$^{-1}$	C_D, mole l.$^{-1}$	$-(A - A_0)$	$-(\epsilon_0 - \epsilon_1)$	K_{obsd}, l. mole^{-1}	[Solvent], mole l.$^{-1}$	K_2, l. mole^{-1}
Benzene	530	0.00920	0.0503	0.081				
		0.00920	0.1006	0.147	760 ± 30	2.6 ± 0.1	10.94	6.9 ± 0.4
		0.00920	0.2013	0.241				
	430	0.0912	0.0506	0.124				
		0.0912	0.1012	0.228	1162 ± 200	2.7 ± 0.4	10.94	6.9 ± 1.1
		0.0912	0.2024	0.370				
CH_2Cl_2	540	0.000941	0.0499	0.038				
		0.000941	0.0998	0.072	624 ± 40	1.4 ± 0.1	15.52	~23
		0.000941	0.1996	0.128				

[a] The values given for C_I, C_D, and $-(A - A_0)$ were averaged over several sets of data in order to minimize errors in the measurement of $-(A - A_0)$.

Table II. DMA–CH_2Cl_2 Equilibrium Constant and ΔH (26°)

DMA, mole l.$^{-1}$	CH_2Cl_2, mole l.$^{-1}$	Vol, ml	H^1, cal	ΔH, kcal mole^{-1}	K^{-1}, mole l^{-1}
0.05252	0.4116	100.0	−3.11		
0.05295	0.7877	100.0	−5.09	−2.2 ± 0.3	1.04 ± 0.2
0.05313	1.6020	100.0	−7.01		

Table III. Enthalpy Determination for DMA–I_2

C_I, mole l.$^{-1}$	C_B, mole l.$^{-1}$	[Solvent], mole l.$^{-1}$	$-(A - A_0)$	Temp, °C	K_{obsd}, l. mole^{-1}	K_2,[a] l. mole^{-1}	ΔH_{obsd}, kcal mole^{-1}	ΔH_2, kcal mole^{-1}
				In Benzene at 530 mμ				
0.000904	0.2034	10.94	0.237	25.2	2.57	6.81		
0.000901	0.2028	10.91	0.229	27.9	2.46	6.44		
0.000899	0.2024	10.89	0.220	30.9	2.32	6.02		
0.000894	0.2013	10.83	0.211	33.9	2.22	5.66		
0.000892	0.2007	10.80	0.203	36.2	2.12	5.33		
0.000890	0.2002	10.77	0.198	38.0	2.05	5.13	−3.30 ± 0.12	−4.14[a] ± 0.12
0.000888	0.1998	10.75	0.192	40.0	1.99	4.92		
0.000976	0.1782	10.98	0.235	25.4	2.59	6.85		
0.000974	0.1777	10.95	0.228	27.6	2.49	6.53		
0.000971	0.1772	10.92	0.221	29.8	2.40	6.23		
0.000969	0.1768	10.90	0.215	31.5	2.32	5.97		
0.000967	0.1764	10.87	0.209	33.4	2.24	5.72		
0.000964	0.1760	10.84	0.203	35.5	2.17	5.48		
0.000962	0.1755	10.81	0.197	37.6	2.09	5.24		
0.000960	0.1751	10.79	0.190	39.5	2.00	4.98		
				In Methylene Chloride at 540 mμ				
0.000946	0.2026		0.130	25.0	1.47			
0.000943	0.2021		0.126	27.0	1.42			
0.000941	0.2015		0.123	29.0	1.38			
0.000938	0.2009		0.120	31.0	1.35			
0.000936	0.2004		0.116	32.8	1.30			
0.000934	0.2000		0.114	34.6	1.28		−2.55 ± 0.10	
0.000986	0.1982		0.132	25.0	1.45			
0.000983	0.1976		0.129	27.1	1.42			
0.000981	0.1971		0.126	28.9	1.38			
0.000978	0.1965		0.122	31.2	1.34			
0.000911	0.1966		0.121	25.0	1.45			
0.000909	0.1962		0.118	26.7	1.41			
0.000906	0.1955		0.114	29.0	1.36		−2.67 ± 0.14	
0.000976	0.1961		0.118	32.7	1.29			
0.000973	0.1955		0.115	34.8	1.26			

[a] Calculated using $\Delta H_3 = -1.32$ kcal mole^{-1}: R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **77**, 2164 (1955).

$$\begin{tikzcd}
\text{DMA (CCl}_4\text{)} & + \text{I}_2\text{ (CCl}_4\text{)} \arrow[r, shift left, "\Delta H_{\text{CCl}_4}"] & \text{DMA}\cdot\text{I}_2\text{ (CCl}_4\text{)} \arrow[l, shift left] \arrow[d, "\Delta H_\text{C}"] \\
\text{DMA (solv)} \arrow[u, "\Delta H_\text{B}"] & + \text{I}_2\text{ (solv)} \arrow[u, "\Delta H_\text{A}"] \arrow[r, shift left, "\Delta H_\text{obsd}"] & \text{DMA}\cdot\text{I}_2\text{ (solv)} \arrow[l, shift left]
\end{tikzcd}$$

in which ΔH_{obsd} is the measured enthalpy in the polar solvent and ΔH_B, ΔH_A, and ΔH_C represent the difference in enthalpy of solvation of the base, acid, and complex in the polar solvent and CCl_4. This cycle leads to the following equation

$$\Delta H_{obsd} = \Delta H_{CCl_4} + \Delta H_B + \Delta H_A + \Delta H_C \quad (8)$$

where ΔH_A and ΔH_B are usually endothermic and ΔH_C is exothermic.

First, the data in benzene will be considered. If the competing equilibrium with the solvent was considered negligible, ΔH_{obsd} would be taken as equivalent to the enthalpy of DMA–I_2 adduct formation in CCl_4. The data used in the calculation of ΔH_{obsd} are included in Table III. Since $\Delta H_{\mathrm{obsd}} = -3.3$ kcal mole^{-1} while $\Delta H_{\mathrm{CCl_4}} = -4.0$ kcal mole^{-1}, the competing equilibrium is important, *i.e.*, $\Delta H_{\mathrm{A}} + \Delta H_{\mathrm{B}} \neq -\Delta H_{\mathrm{C}}$. Correcting for the changes in the benzene–iodine equilibrium constant at each temperature produces the refined constant K_2. The value of ΔH_2 can be calculated from the temperature dependence of K_2. The value of ΔH_2 thus obtained is ΔH_{obsd} corrected for the temperature dependence of the change in the ratio of complexed to free iodine in benzene. In benzene as solvent, the benzene concentration is large and approximately constant leading to

$$K' = K_{\mathrm{obsd}}[\mathrm{C_6H_6}] = [\mathrm{complex}]/[\mathrm{I_2}]$$

Plotting the log K' *vs.* $1/T$ produces ΔH_{A}, the heat of desolvation of iodine by benzene. Consequently, $\Delta H_2 = \Delta H_{\mathrm{obsd}} - \Delta H_{\mathrm{A}}$, which gives

$$\Delta H_2 = \Delta H_{\mathrm{CCl_4}} + \Delta H_{\mathrm{B}} + \Delta H_{\mathrm{C}} \qquad (9)$$

The value of ΔH_2 is -4.1 kcal mole^{-1} and that of $\Delta H_{\mathrm{CCl_4}}$ is -4.0 kcal mole^{-1}, leading to the conclusion that the difference in the enthalpy of solvation of the base, ΔH_{B}, and the complex, ΔH_{C}, in benzene must be the same as in $\mathrm{CCl_4}$. Since the heat of solution of DMA in $\mathrm{CCl_4}$ and benzene is approximately the same (Table IV), there must be very little difference in the enthalpy of solvation of the complex, *i.e.*, the solvating properties of benzene and carbon tetrachloride are similar toward these materials. If this is true for most substances which are not Lewis acids, the range of systems which may be examined in poorly solvating solvents would be significantly increased for many compounds which are not soluble in $\mathrm{CCl_4}$ or hexane are soluble in benzene.

Table IV. ΔH_{soln} of DMA at 26°

DMA, moles added	C_{DMA}, mole l.$^{-1}$	C_{solvent}, mole l.$^{-1}$	Vol, ml	H^1, cal	ΔH_{soln}, kcal mole^{-1}
In $\mathrm{CH_2Cl_2}$					
	0.06073	15.64	100.4	−12.64	−2.08
	0.1024	15.57	100.8	−20.75	−2.03
$\Delta H_{\mathrm{soln}} = -2.0 \pm 0.2$ kcal/mole					
In $\mathrm{CCl_4}$					
0.000800	0.0080			0.39	0.49
0.00236	0.0316			1.19	0.50
0.00202	0.0518			1.08	0.53
$\Delta H_{\mathrm{soln}} = 0.5 \pm 0.1$ kcal/mole					
In Benzene					
0.000490	0.0490			0.58	0.14
0.00543	0.1033			0.52	0.10
0.00687	0.1720			0.59	0.10
$\Delta H_{\mathrm{soln}} = 0.1 \pm 0.05$ kcal/mole					

In the methylene chloride system, the data used for the calculation of ΔH_{obsd} are also included in Table III. In this case, $\Delta H_{\mathrm{obsd}} = -2.6$ kcal/mole, which is again much smaller than $\Delta H_{\mathrm{CCl_4}}$. This indicates that the data must be corrected for the competing equilibrium with the solvent. The procedure used to calculate ΔH_2 in the benzene system could not be used for the methylene chloride system since the DMA–$\mathrm{CH_2Cl_2}$ equilibrium constant in the solvent $\mathrm{CH_2Cl_2}$ is not known. However, it is possible to measure ΔH_{B}, the difference in the heat of solution of liquid DMA in $\mathrm{CH_2Cl_2}$ and $\mathrm{CCl_4}$, directly. The analog to eq 9 in the methylene chloride system is

$$\Delta H_2 = \Delta H_{\mathrm{CCl_4}} + \Delta H_{\mathrm{A}} + \Delta H_{\mathrm{C}} \qquad (10)$$

in which ΔH_2 includes the correction for the interaction of DMA with methylene chloride, *i.e.*

$$\Delta H_2 = \Delta H_{\mathrm{obsd}} - \Delta H_{\mathrm{B}} \qquad (11)$$

The data for the measurement of $-\Delta H_{\mathrm{B}}$ are given in Table IV and lead to a value of $\Delta H_2 = -5.1$ kcal/mole^{-1}. This calculation of ΔH_2 compares favorably with that value estimated by use of the relationship

$$\Delta H_{\mathrm{obsd}} = \Delta H_2 - \Delta H_3 \qquad (12)$$

which applies if all of the DMA is complexed by methylene chloride. The data for the calculation of ΔH_3 are included in Table II and lead to a value of $\Delta H_2 = -4.8$ kcal mole^{-1}. The observation that ΔH_2 is not equal to $\Delta H_{\mathrm{CCl_4}}$ suggests that solvation effects other than hydrogen bond formation with the donor are important in methylene chloride.

Since the electronic spectra of iodine in $\mathrm{CH_2Cl_2}$ and $\mathrm{CCl_4}$ are similar, we shall assume that there is no significant contribution to the enthalpy difference in these two solvents from iodine complexation. Since methylene chloride most likely does not form a single defined adduct with the DMA–$\mathrm{I_2}$ complex, we shall attribute this -1.1 kcal mole^{-1} as due to nonspecific solvation of this complex. This enthalpy value is appreciable when compared to the enthalpy differences of many adducts measured in the solvent $\mathrm{CCl_4}$, demonstrating that neglect of nonspecific solvation can lead to erroneous conclusions.

The equilibrium between DMA and iodine was also investigated in the solvents 3-methylsulfolane and dioxane. These results indicate that the reaction of iodine with various donors to produce $\mathrm{I_3^-}$ can be incorporated into the coordination model for nonaqueous solvent behavior.[20] This model focuses attention on the donor and solvating properties of the solvent in accounting for the extent of anion dissociation from a solute. In the donor–iodine system, it is found that strong donors, *e.g.*, $\mathrm{(C_2H_5)_3N}$, displace iodide from iodine resulting in the formation of $\mathrm{I^+}$ (solvated) and $\mathrm{I_3^-}$. In dilute solutions of the strong donor $\mathrm{(C_2H_5)_3N}$, iodide is displaced even in the poor solvating solvent hexane. At equivalent concentrations, DMA is not a strong enough donor to displace iodide. Toward iodine, 3-methylsulfolane is a weak donor with a measured[21] enthalpy of adduct formation in $\mathrm{CCl_4}$ of -2.3 kcal mole^{-1}. However, 3-methylsulfolane has a high dielectric constant and is expected to be a good solvating solvent, *i.e.*, one that will undergo nonspecific interactions with solutes and will facilitate charge separation. When iodine is added to 3-methylsulfolane (or when mixtures of DMA and $\mathrm{I_2}$ are investigated in this solvent), extensive formation of $\mathrm{I_3^-}$ results. In contrast to this behavior, $\mathrm{I_3^-}$ is not detected when $\mathrm{I_2}$ (or mixtures of DMA and $\mathrm{I_2}$) is dissolved in pure 1,4-dioxane as solvent. The enthalpy of formation of the dioxane–iodine adduct in $\mathrm{CCl_4}$ is[22] -3.1 kcal mole^{-1}, so it is a better donor than 3-methylsulfolane. However, the dielectric constant of 1,4-dioxane is 2.2 (25°),

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(21) R. Niedzielski, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1963.

(22) J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952).

and one would expect dioxane to be a poor solvating solvent. These observations indicate the importance of both solvent donor strength and solvating ability in accounting for anion displacement.

In conclusion, it must be emphasized that solvent interactions make significant contributions to the measured enthalpy values of adduct formation. Specific interactions between the solvent and a reacting species significantly change the observed equilibrium constant and enthalpy; even contributions from nonspecific solvation have pronounced effects. Therefore, great care must be taken before comparing enthalpies measured in different solvents. The interpretation of changes in the equilibrium constant with changes in solvent appears formidable at present. Although the equilibrium constant appears to increase, as expected in a more polar solvent, little else can be said about the changes in the equilibrium constant in different solvents. Until a better understanding of all the factors affecting the equilibrium constant is reached, it is hazardous to interpret small differences between equilibrium constants measured in various solvents.

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The Hydrolytic Polymerization of Iron(III)

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Abstract: Hydrolysis of ferric nitrate with bicarbonate leads to solutions which contain a discrete high polymeric component. This component has been isolated by gel filtration and characterized. The weight-average molecular weight of the polymer, as determined with the analytical ultracentrifuge, is 1.4×10^5. Its empirical composition corresponds to $Fe(OH)_x(NO_3)_{3-x}$, where x lies between 2.3 and 2.5. Polymer size and composition are nearly independent of the degree of hydrolysis of the ferric nitrate solutions between 1.0 and 2.0 base equiv/mole of Fe. Formation of the polymer is rapid, while dissociation is very slow. Although ferric hydroxide precipitates from partially hydrolyzed ferric nitrate solutions within a few days, solutions of the isolated polymer remain clear indefinitely. Electron microscopy reveals that the polymer particles are isolated spheres, most of which are close to 70 A in diameter.

The hydrolysis of ferric ion, a problem of very long standing in solution chemistry, has been considerably clarified in recent years. On the basis of a careful potentiometric study, Hedström[2a] proposed that the initial product of hydrolysis in perchlorate solution is primarily a dimer, $Fe_2(OH)_2^{4+}$. This result was corroborated by Mulay and Selwood[2b] who established that the dimer is essentially diamagnetic, indicating strong electronic interaction between the ferric ions. Although considerable quantities of base (bicarbonate) can be added to ferric perchlorate before a lasting precipitate is produced, Hedström found that solutions containing more than about 0.5 equiv of base per mole of iron gave drifting potentials, and he attributed the drift to incipient precipitation of ferric hydroxide. Feitknecht and Michaelis[3] observed in fact that all iron(III) solutions to which base has been added, even those studied by Hedström, are unstable with respect to eventual precipitation of various forms of ferric hydroxides. This two-phase system reaches an apparent equilibrium after 200 hr as indicated by Biedermann and Schindler,[4] who obtained a reproducible solubility product constant for ferric hydroxide from hydrolyzed ferric perchlorate solutions.

It is evident, therefore, that the hydrolytic polymerization of ferric ion, which begins with the formation of $Fe_2(OH)_2^{4+}$, continues, with time, to the precipitation of ferric hydroxide. There remain the questions of mechanism of polymerization and chemical composition of the intermediates.

Diffusion measurements with partially hydrolyzed solutions of iron salts led Jander and Winkel[5] to suggest that polynuclear iron–hydroxy complexes were present. These complexes were thought to contain from 1 to 50 metal atoms. More generally, however, it is felt that these intensely colored solutions contain colloidal ferric hydroxide of indeterminant composition.

We wish to present evidence that the hydrolysis of ferric nitrate can lead to formation of a high molecular weight polymer of composition $[Fe(OH)_x(NO_3)_{3-x}]_n$ where x lies between 2.3 and 2.5 and n is of the order of 900. This polymer has been isolated and characterized.

Experiments and Results

The Preparation of Hydrolyzed Iron Solutions. Most solutions were prepared by dissolving a weighed amount of reagent ferric nitrate (Mallinckrodt) in a small volume of distilled water and adding the requisite

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