Table V. Molar Solubility Constants K_s for the Solubility of an Alkali-Metal Halide MCl in an Alkali-Metal Tetrachloroaluminate Melt $M'AlCl_4$ at 257 °C

MCl	$M'AlCl_4$	K_s = $[M^+][Cl^-]$, mol^2 L^{-2}	satn concn $[M^+]$, mol L^{-1}	$[Cl^-]$, mol L^{-1}
NaCl	$KAlCl_4$	6.78×10^{-3}	0.082	0.082
LiCl	$KAlCl_4$	6.4×10^{-5}	0.008	0.008
NaCl	$NaAlCl_4$	1.46[a]	8.653	0.169
KCl	$KAlCl_4$	3.22[b]	7.985	0.403

[a] An expression for pK_s vs. T in K was given[42] as a function $(A + \Delta C_p T)/(RT) - (B + \Delta C_p(\ln T))/R$, where $A = -11.850$ kJ mol^{-1}, $B = -352.81$ J mol^{-1} K^{-1}, and $\Delta C_p = 63.26$ J mol^{-1} K^{-1}. [b] An expression for K_s vs. T in K was given[10] as p$K_s = A/T - B$, with $A = 1030$ K and $B = 2.45$.

that is on the order of 100 for the case of sodium tetrachloroaluminate relative to potassium tetrachloroaluminate.

Consider the reaction

$$2AlCl_4^- \rightleftarrows Cl^- + Al_2Cl_7^- \qquad (7)$$

and the corresponding equilibrium constant, K_1

$$K_1 = \frac{[Cl^-][Al_2Cl_7^-]}{[AlCl_4^-]^2} \qquad (8)$$

which when expressed in concentrations depends on the temperature, the pressure, and the kind of alkali metal present.

The values of K_1 for $NaAlCl_4$ and $KAlCl_4$ have been determined as a function of temperature by means of the potentiometric method.[10,42] At 257 °C, approximate values of 7.8×10^{-7} and 5.0×10^{-9} can be estimated. We then obtain $K_1^{Na}/K_1^{K} = 156$, i.e. a ratio of the same order of magnitude as the one determined from the solubility experiments above.

The reason for the two ratios to be similar in magnitude is believed to be due to the occurrence of stronger $M^+\cdots Cl^-$ association in the Na^+ case than in the K^+ case. This association reduces the *effective* chloride concentration in the $NaAlCl_4$ melt relative to a $KAlCl_4$ melt with the same free chloride formality. In this way, the solubility product, K_s, for NaCl will be higher in $NaAlCl_4$ than in $KAlCl_4$ at saturation. The same argument applies for the case of the K_1's. The *effective* chloride concentration is lower in a melt containing a certain concentration of free chloride with Na^+ as the counterion than with K^+, and therefore a higher K_1 in the case of Na^+ than in the case of K^+ is necessary to obtain equilibrium.

For the case of LiCl saturation in $KAlCl_4$, we find that the solubility product ratio K_s(NaCl in $KAlCl_4$)/K_s(LiCl in $KAlCl_4$) is on the order of 100. Hence, the K_1 equilibrium constants corresponding to eq 7 should take approximately the ratio $K_1^{Li}/K_1^{Na} = 100$, if the above argument holds. With the above value of $K_1^{Na} = 7.8 \times 10^{-7}$, then K_1^{Li} should be approximately 7×10^{-5} or p$K_1^{Li} = 4.15$ at 257 °C. A pK_1^{Li} value of 4.0 has been determined by Torsi and Mamantov[24] at 250 °C. Data for other pairs of alkali metals are needed to see if this interesting agreement is a coincidence or a more general tendency.

The idea that the difference in solubility of NaCl in $NaAlCl_4$ and in $KAlCl_4$ is mainly due to the association between the cations and the *chloride* ions and to a much lesser extent due to association among the other ions can also be deduced by looking at the equilibrium (eq 9) found in acidic chloroaluminate melts. Øye

$$2Al_2Cl_7^- \rightleftarrows 2AlCl_4^- + Al_2Cl_6 \qquad (9)$$

et al.[43] devised a method to estimate the equilibrium constant for this reaction from Raman spectra. A value of 8×10^{-3} for the equilibrium constant corresponding to eq 9, K (expressed in Tempkin mole fractions), was found for the $KCl-AlCl_3$ system in the temperature range 170–240 °C. If the Raman spectra[44] obtained for $LiCl-AlCl_3$, $KCl-AlCl_3$, and $CsCl-AlCl_3$ in the same temperature range as above are compared, it is found that the equilibrium constant K does not vary more than by a factor of 2, depending on the cation. This estimate rests on the reasonable assumption that the scattering factors of the various aluminum chloride species are largely independent of the kind of cation. Our explanation for the relative constancy of K is that since K does not involve the chloride concentration, it can remain quite constant, independent of type of cation. Hence we consider the effect of the interaction between the cations and the chloroaluminate ions to be much smaller than that between the cations and the chloride ions.

If the above given explanation, involving the cation–chloride ion association, is correct, it should apply also to other equilibria in chloroaluminate melts. Unfortunately, as far as we know, no other data is available for which one can compare equilibrium constants obtained in $NaAlCl_4$ and $KAlCl_4$ at the same temperature. For solutions of niobium(V) in tetrachloroaluminate melts in which the equilibrium (eq 10) applies, we were recently

$$NbCl_6^- \rightleftarrows NbCl_5 + Cl^- \qquad (10)$$

able to estimate[45] that the ratio between the equilibrium constants in $NaAlCl_4$ and $KAlCl_4$ is ~100 at 300 °C, in good agreement with the ideas given above. In order to evaluate the general character of such relations, more data are of course indispensable.

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Registry No. KCl, 7447-40-7; $AlCl_3$, 7446-70-0; $KAlCl_4$, 13821-13-1.

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Polarographic Studies on Iron(II) Complexes with Carbamide Derivatives Containing Alkyl Substituents

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Complexation reactions of Fe(II) with carbamide, H_2NCONH_2 (U), and its aliphatic derivatives such as $CH_3HNCONH_2$ (MeU), $C_2H_5HNCONH_2$ (EtU), $CH_3HNCONHCH_3$ (*sym*-Me$_2$U), and $C_2H_5HNCONHC_2H_5$ (*sym*-Et$_2$U) have been studied by the polarographic method. It has been found that, in these systems, there are formed complexes of the type $[Fe(H_2O)_{6-n}X_n]^{2+}$ (n = 1–6). With use of the method of De Ford and Hüme, stability constants β_j and K_j of these complexes were calculated.

Carbamide was well as most of its N-substituted derivatives do not show polarographic activity.[1-3] On the other hand, both carbamide and thiocarbamide reveal a catalytic effect on the behavior of other compounds; e.g. carbamide is used in polaro-

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graphic studies of protein neutralization[4] and Turian and co-workers[5] have shown that thiocarbamide is able to effect the process of electrode reduction of Fe(II). Carbamide complexes of various metals easily form polarographic waves. Using the polarographic method, Chatterjee and co-workers[6] have determined the composition of Cu(II) complexes with carbamide, and Singh and co-workers[7] have found the half-wave potentials for Ti(IV) ions combined in complexes with alkyl derivatives of carbamide with compositions 1:1 and 1:2.

It resulted from the studies on adsorption of carbamide and its derivatives[8-10] that, in the presence of iron ions, an increase in the adsorption of carbamide derivatives took place, which could evidence the adsorption of Fe(II) and Fe(III) complexes with these derivatives. Hence, it was necessary to carry out investigations aimed at finding compositions and stability constants of Fe(III) complexes[11] and, in the present work, of Fe(II) complexes with carbamide and its derivatives. The investigations were carried out with the systems $FeSO_4$–X–$NaClO_4$–H_2O, where X is carbamide, H_2NCONH_2 (U), or a carbamide derivative such as $CH_3HNCONH_2$ (MeU), $C_2H_5HNCONH_2$ (EtU), $CH_3HNCONHCH_3$ (*sym*-Me_2U), and $C_2H_5HNCONHC_2H_5$ (*sym*-Et_2U). The types of complexes and their stability constants may be determined by using the relationship[12-14]

$$\Delta E_{1/2} = E_{1/2}(\mathrm{c}) - E_{1/2}(1) = 2.3\,\frac{RT}{nF}(\log \gamma_{\mathrm{M}})\frac{I(\mathrm{c})}{I(1)}\sum_{j=0}^{N}\beta_j\frac{[\mathrm{X}]^j}{\gamma_{\mathrm{MX}_j}} \tag{1}$$

where $E_{1/2}(\mathrm{c})$ and $E_{1/2}(1)$ are the half-wave potentials of the complex ion and the free ion, respectively, $I(\mathrm{c})$ and $I(1)$ are the diffusion coefficients, β_j is an equilibrium constant of the $[\mathrm{MX}_j]/[\mathrm{M}][\mathrm{X}]^j$ type, and γ_{M} and γ_{MX_j} are the activity coefficients.

Equation 1 may be written in the form

$$F_0(\mathrm{X}) = \mathrm{antilog}\left[\frac{0.4343nF}{RT}\Delta E_{1/2} + \log\frac{I(1)}{I(\mathrm{c})}\right] = \gamma_{\mathrm{M}}\sum_{j=0}^{N}\frac{\beta_j[\mathrm{X}]^j\gamma_{\mathrm{X}}^{\,j}}{\gamma_{\mathrm{MX}_j}} \tag{2}$$

and if the summation is developed

$$F_0(\mathrm{X}) = 1 + \beta_1[\mathrm{X}]\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{X}}}{\gamma_{\mathrm{MX}}} + \beta_2[\mathrm{X}]^2\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{X}}^2}{\gamma_{\mathrm{MX}_2}} + \ldots \tag{3}$$

The values of $F_0(\mathrm{X})$ are determined experimentally, and assuming the ratios between the activity coefficients to be unity, the values of the constants may be obtained by resolving the equation graphically according to the De Ford–Hüme method.[12]

Experimental Section

Reagents and Solutions. AnalaR grade reagents from PoCh-Gliwice were used, such as $NaClO_4$, $FeSO_4$, and H_2NCONH_2. The others were $CH_3HNCONH_2$ and $C_2H_5HNCONH_2$ from Loch-Light Laboratories Ltd., Colubrook, Bucks, England, $CH_3HNCONHCH_3$ from Loba Chemie Vien, and $C_2H_5HNCONHC_2H_5$ from Fluka AG, Buchs SG, Switzerland. The supporting electrolyte was a 0.2 mol/dm^3 solution of $NaClO_4$. The concentration of Fe(II) salts was constant, 3.597×10^{-3} mol/dm^3, in all the measurment series. The concentrations of carbamide derivatives were from 0.020 to 1.200 mol/dm^3. The ionic strength was constant ($\mu = 0.2$).

Table I. Half-Wave Potentials ($E_{1/2}$) for the Systems $FeSO_4$–X–$NaClO_4$–H_2O (X = H_2NCONH_2 (U), $CH_3HNCONH_2$ (MeU), $C_2H_5HNCONH_2$ (EtU), $CH_3HNCONHCH_3$ (*sym*-Me_2U), and $C_2H_5HNCONHC_2H_5$ (*sym*-Et_2U)

C_X, mol/dm^3	$-E_{1/2}$, V				
	U	MeU	EtU	*sym*-Me_2U	*sym*-Et_2U
0.02	1.3757	1.3755	1.3753	1.3752	1.3751
0.04	1.3765	1.3761	1.3757	1.3754	1.3753
0.06	1.3774	1.3766	1.3760	1.3757	1.3754
0.08	1.3782	1.3772	1.3764	1.3760	1.3756
0.10	1.3791	1.3778	1.3767	1.3764	1.3758
0.12	1.3800	1.3783	1.3771	1.3768	1.3760
0.14	1.3809	1.3790	1.3775	1.3773	1.3760
0.20	1.3838	1.3809	1.3788	1.3792	1.3769
0.30				1.3838	1.3794
0.40	1.3940	1.3892	1.3848	1.3897	1.3832
0.50				1.3958	1.3884
0.60	1.4044	1.3999	1.3956	1.4018	1.3940
0.80	1.4142	1.4121	1.4080		
1.00	1.4213	1.4240	1.4225		
1.20	1.4325	1.4347	1.4345		

Since the fact that carbamide and its aliphatic derivatives are weak bases was taken into account (p*K* constants change within the range from 0.88 for carbamide to 0.54 for *sym*-diethylcarbamide[15]), it was assumed that there would not be considerable changes in activity coefficients in the systems under investigation. It was also assumed that the high concentration of carbamide derivatives does not considerably change the concentration of free water in solution since, at their higher concentrations, a smaller number of water molecules takes part in the composition of the $[\mathrm{Fe(H_2O)}_{6-n}\mathrm{X}_n]^{2+}$ complexes being formed.

The use of Fe(II) salts in the form of sulfates could result in somewhat erroneous values of stability constants since Fe(II) also forms a complex with SO_4^{2-} with a composition 1:1 and stability constant of $\log \beta = 1.0$.[16] However, the error was rather low since the concentration of SO_4^{2-} ions was very low (0.0036 mol/dm^3), about 10 times lower than the lowest concentration of the carbamide derivative (0.02 mol/dm^3).

Apparatus and Measurement Methods. The measurments were performed by dc polarography, with a Square Wave Type OH-105 polarograph from Radelkis (Budapest, Hungary) in a three-electrode system with a dropping mercury electrode. The reference electrode was a saturated calomel electrode connected to the investigated solution through an electrolytic bridge filled with a 1 mol/dm^3 solution of $NaClO_4$. The third electrode was a platinum cylindrical net with a surface area of 1000 mm^2. The output of the capillary at a defined height level was 1.025 mg/s. The mercury drop time was adjusted with a Test Rapid Adapter from Radelkis to be 1 s. Experiments were carried out under an atmosphere of nitrogen that was previously purified from oxygen residues in a special deoxygenating system,[17] at a temperature of 298 ± 0.1 K. To the deoxygenated solution in a polarographic vessel containing the main electrolyte and the tested derivative was added a weighed portion of solid $FeSO_4$, followed by passing of nitrogen for 10 min, and then the polarogram was taken. The half-wave potentials were calculated by the least-squares method from the relationship $\log((i_d - i)/i) = f(E)$. The $E_{1/2}$ value scatter was within ±1 mV. The investigations were carried out in the presence of a small amount of gelatin, its concentration in the tested solution being 0.01%. Bulovova[18] has shown that gelatin present in a small amount damp maxima, providing reproducible polarographic waves that are easy to interpret.

Results and Discussion

The polarographic reduction of the ions $[\mathrm{Fe(H_2O)_6}]^{3+}$ proceeds in two stages: (I) the polarographic wave with a half-wave potential value of $E_{1/2} = +0.145 \pm 0.001$ V corresponding to reaction 4 of the electrode reduction of the aqua complex; (II) the po-

$$[\mathrm{Fe(H_2O)_6}]^{3+} + \mathrm{e}^- \rightleftharpoons [\mathrm{Fe(H_2O)_6}]^{2+} \tag{4}$$

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Table II. Numerical Stability Constants of the Fe^{2+}–X System (X = Carbamide or Carbamide Derivatives) Determined by the Polarographic Method[a]

stability constants	$[Fe(NH_2CONH_2)_n]^{2+}$	$[Fe(CH_3HNCONH_2)_n]^{2+}$	$[Fe(C_2H_5HNCONH_2)_n]^{2+}$	$[Fe(CH_3HNCONHCH_3)_n]^{2+}$	$[Fe(C_2H_5HNCONHC_2H_5)_n]^{2+}$
$\beta_1 = K_1$, L mol^{-1}	2.6 ± 0.5	1.8 ± 0.4	1.1 ± 0.2	0.7 ± 0.2	0.4 ± 0.2
β_2, L^2 mol^{-2}	8.0 ± 1.0	3.2 ± 0.8	1.8 ± 0.4	1.2 ± 0.5	0.8 ± 0.4
β_3, L^3 mol^{-3}	7.0 ± 1.0	5.0 ± 1.0	1.5 ± 1.0	19 ± 1.0	2.8 ± 1.0
β_4, L^4 mol^{-4}	15 ± 2	8 ± 2	2 ± 2	14 ± 2	12 ± 2
β_5, L^5 mol^{-5}	5 ± 2	11 ± 4	14 ± 4		8 ± 4
β_6, L^6 mol^{-6}	2 ± 2	13 ± 4	17 ± 4		
$K_2 = \beta_2/\beta_1$, L mol^{-1}	3.1 ± 1.0	1.8 ± 0.8	1.6 ± 0.4	1.7 ± 0.5	2.0 ± 0.4
$K_3 = \beta_3/\beta_2$, L mol^{-1}	0.9 ± 1.0	1.6 ± 1.0	0.8 ± 1.0	15.8 ± 1.0	3.5 ± 1.0
$K_4 = \beta_4/\beta_3$, L mol^{-1}	2.1 ± 2	3.6 ± 2	1.3 ± 2	0.7 ± 2	4.3 ± 2
$K_5 = \beta_5/\beta_4$, L mol^{-1}	0.3 ± 2	1.4 ± 4	7.0 ± 4		0.7 ± 4
$K_6 = \beta_6/\beta_5$, L mol^{-1}	0.4 ± 2	1.2 ± 4	1.2 ± 4		

[a] Conditions: $\mu = 0.2$; temperature 298 ± 0.1 K.

Table III. Stability Constants (L mol^{-1}) K_j of the Complexes of Fe(II) and Fe(III) with the Carbamide Derivatives Determined by the Polarographic Method[a]

complexes	K_1	K_2	K_3	K_4	K_5	K_6
$[Fe(H_2O)_{6-n}(NH_2CONH_2)_n]^{2+}$	2.6	3.1	0.9	2.1	0.3	0.4
$[Fe(H_2O)_{6-n}(CH_3HNCONH_2)_n]^{2+}$	1.8	1.8	1.6	3.6	1.4	1.2
$[Fe(H_2O)_{6-n}(C_2H_5HNCONH_2)_n]^{2+}$	1.1	1.6	0.8	1.3	7.0	1.2
$[Fe(H_2O)_{6-n}(CH_3HNCONHCH_3)_n]^{2+}$	0.7	1.7	15.8	0.7		
$[Fe(H_2O)_{6-n}(C_2H_5HNCONHC_2H_5)_n]^{2+}$	0.4	2.0	3.5	4.3	0.7	
$[Fe(H_2O)_{6-n}(NH_2CONH_2)_n]^{3+}$	6.0	1.8	0.9	3.3	0.3	0.1
$[Fe(H_2O)_{6-n}(CH_3HNCONH_2)_n]^{3+}$	2.1	2.4	1.6	1.3	1.3	1.2
$[Fe(H_2O)_{6-n}(C_2H_5HNCONH_2)_n]^{3+}$	1.2	1.9	0.9	1.0	9.0	1.4
$[Fe(H_2O)_{6-n}(CH_3HNCONHCH_3)_n]^{3+}$	0.9	1.7	20.1	0.6		
$[Fe(H_2O)_{6-n}(C_2H_5HNCONHC_2H_5)_n]^{3+}$	0.6	2.0	2.9	4.6	0.8	

[a] Conditions: $\mu = 0.2$; temperature 298 ± 0.1 K.

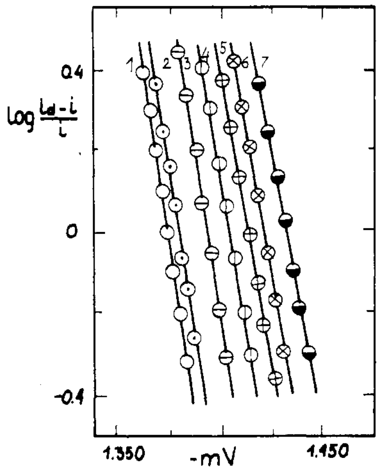

Figure 1. Plot of log $((i_d - i)/i) = f(E)$ for the system Fe(II)–H_2NCONH_2–$NaClO_4$–H_2O (Fe(II) concentration 3.597 × 10^{-3} mol/dm^3, $\mu \doteq 0.2$, $T = 298 \pm 0.1$ K). Concentrations of H_2NCONH_2 (mol/dm^3): (1) 0; (2) 0.1; (3) 0.4; (4) 0.6; (5) 0.8; (6) 1.0; (7) 1.2.

larographic wave with $E_{1/2} = -1.375 \pm 0.001$ V corresponds to reaction 5 of the electrode reduction of the aqua complex to free

$$[Fe(H_2O)_6]^{2+} + 2e^- \rightleftharpoons Fe + 6H_2O \qquad (5)$$

metal. This interpretation is in agreement with the results of polarographic investigation of waves for Fe(III) and Fe(II) complexes.[11,19] On the basis of the half-wave potential values $E_{1/2}$ calculated for the tested system (Figure 1, Table I), it was found that the values for reaction 6 depend on the concentration

$$[Fe(H_2O)_{6-n}X_n]^{2+} + 2e^- \rightleftharpoons Fe^0 + nX \qquad (6)$$

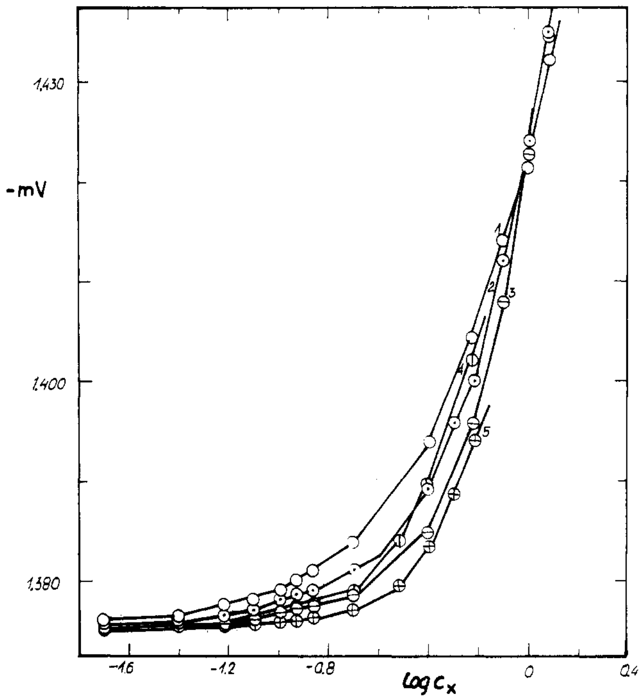

Figure 2. Plot of $E_{1/2} = f(\log C_X)$ for the system Fe(II)–X–$NaClO_4$–H_2O (Fe(II) concentration 3.597 × 10^{-3} mol/dm^3, $\mu = 0.2$, $T = 298 \pm 0.1$ K): (1) X = H_2NCONH_2; (2) X = $CH_3HNCONH_2$; (3) X = $C_2H_5HNCONH_2$; (4) X = $CH_3HNCONHCH_3$; (5) X = $C_2H_5HNCONHC_2H_5$.

of ligand in solution and are displaced with an increase in concentration in the tested system. The diagram $E_{1/2}$–log C_X where C_X is the carbamide derivative concentration, becomes a curve (Figure 2); it is evident, therefore, that Fe^{2+} and carbamide form

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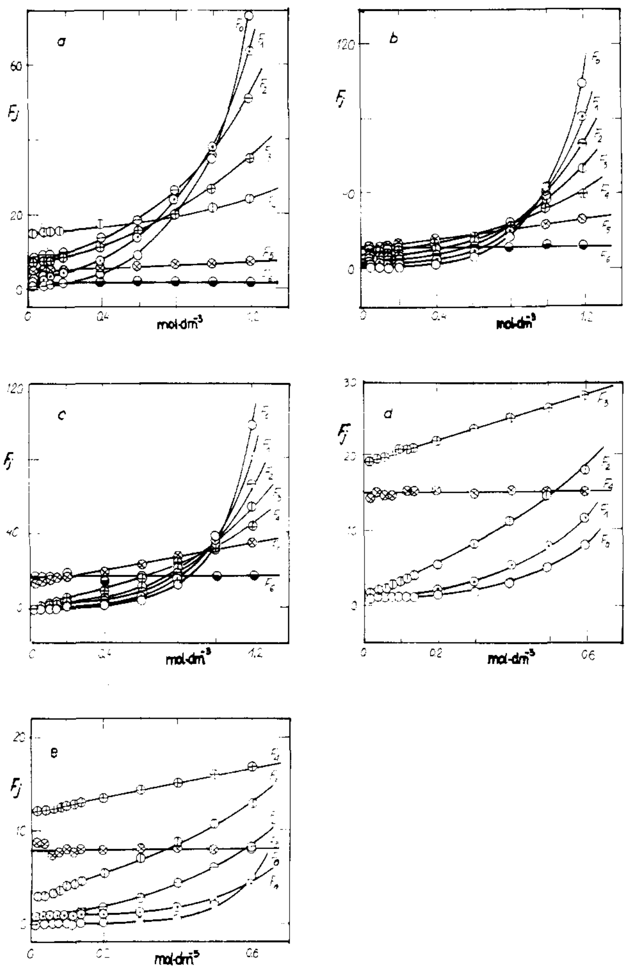

Figure 3. Plot of $F_j = f(C_X)$ for the complexes $[Fe(H_2O)_{6-n}X_n]^{2+}$ (Fe(II) concentration 3.597×10^{-3} mol/dm³, $\mu = 0.2$): (a) X = H_2NCONH_2; (b) X = $CH_3HNCONH_2$; (c) X = $C_2H_5HNCONH_2$; (d) X = $CH_3HNCONHCH_3$; (e) X = $C_2H_5HNCONHC_2H_5$.

various complexes, the stability constants of which are very close to each other. The results (Figures 2 and 3) show[20] that six complexes of the type $[Fe(H_2O)_5X]^{2+}$, $[Fe(H_2O)_4X_2]^{2+}$, $[Fe(H_2O)_3X_3]^{2+}$, $[Fe(H_2O)_2X_4]^{2+}$, $[Fe(H_2O)X_5]^{2+}$, and $[Fe(X)_6]^{2+}$ may be formed. The values of their constants β_j and the stability constants $K_j = [MX_j]/[MX_{j-1}][X]$ of the reaction $MX_{j-1} + X \rightleftharpoons MX_j$ are given in Tables II and III.

The data given in Tables II and III point out that the stability of Fe(II) coplexes with carbamide derivatives containing alkyl substituents is rather low, considerably lower than that of analogous Fe(III) complexes, which is probably associated with the lower charge of the central ion in the complex. The stability constants K_1 of the Fe(II) and Fe(III) complexes with carbamide derivatives decreases in the series

U > MeU > EtU > *sym*-Me$_2$U > *sym*-Et$_2$U

The values of K_2 for the Fe(II) complexes decrease in the order U, MeU, and EtU, and then they show a slight tendency to increase for the disubstituted derivatives. A similar direction of changes in shown by the K_2 values of Fe(III). A clear increasing tendency of complex stability is observed also at K_3 and K_4 for both iron ions and disubstituted derivatives.

Maximum stability of complexes for both iron ions takes place at K_3 for *sym*-Me$_2$U, at K_5 for the monoethyl derivative, and at K_4 for diethylcarbamide. But for urea maximum stability occurs at K_2 for Fe(II) and at K_1 for Fe(III) ions and for the monomethyl derivative at K_4 for Fe(II) and at K_2 for Fe(III).

For K_1 the trend in the stability of the Fe^{2+} and Fe^{3+} complexes is clear. The change in stability constants might be associated with the decrease in the electron density (δ^-) on the oxygen atom in the carbonyl group >C=O due to polar and stearic effects ($\sum\sigma^*$) of alkyl substituents, where the value ($\sum\sigma^*$) is a sum of inductive and resonance effects.[21] The relationship $K_j = f(\sum\sigma^*)$ illustrated in Figure 4 shows that the stability of the investigated complexes decreases with the drop in $\sum\sigma^*$ values. The highest changes in the stability constants K_1 are observed in the complexes with monosubstituted derivatives. The two-stage course of the relationship $K_j = f(\sum\sigma^*)$ (Figure 4) proves that the highest changes in the electron density on the oxygen atom in the carbonyl group are brought about by the introduction of the first alkyl substituent, i.e. $-CH_3$. The introduction of a larger substituent or another one causes also a decrease in the electron density in the donor group but to a much smaller extent (Figure 4). It follows from the comparison of the inductive and resonance efects of alkyl substituents that the observed changes in the electron density can be mainly accounted for by the resonance effects of those substituents, diminishing the electron donor character of groups in the series of substituents[21]

$NH_2 > NHCH_3 > NHC_2H_5 > N(CH_3)_2 > N(C_2H_5)_2$

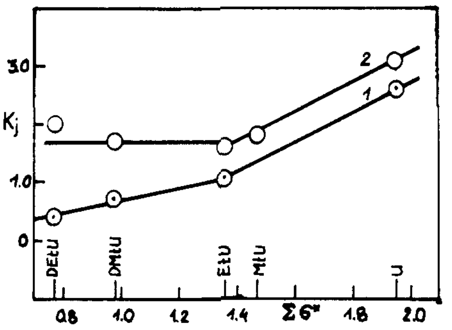

Figure 4. Plot of $K_j = f(\sum\sigma^*)$ for (1) $[Fe(H_2O)_5X]^{2+}$ and (2) $[Fe(H_2O)_4X_2]^{2+}$.

The observed changes in the stability constants of complexes, and particularly the changes in the maximum stability, being very interesting, are probably associated with the structures of these complexes. Further studies on this point will be continued in our next works. The direction of changes in the stability constants of Fe^{2+} and Fe^{3+} complexes for K_2, K_3, K_4, etc. is closely associated with the observed changes in the adsorption of carbamide derivative in the order[8]

U > MeU > EtU > *sym*-Me$_2$U > *sym*-Et$_2$U

The addition of Fe(II) or Fe(III) ions to the derivatives brings about considerable increase in the adsorption in comparison with the adsorption of pure carbamide derivatives.[8-10] The greatest changes in adsorption are observed in the disubstituted derivatives and the lowest in urea. These changes evidence the formation of complexes whose adsorption takes place with the participation of observed ligand $(X)_{ads}$: $[Fe(H_2O)_{5-n}X_n(X)_{ads}]^{2+}$ and $[Fe(H_2O)_{5-n}X_n(X)_{ads}]^{3+}$. The formation of such a complex can bring about an increase in its stability.

On the basis of the studies of the adsorption of carbamide and its derivatives as well as on the results obtained, one can conclude that the adsorption of both ligands and complexes can affect the equilibrium reactions taking place in solution. A strong adsorption of the given carbamide derivative on the electrode and the formation of complex with the participation of adsorbed derivative can influence the stability of complexes being formed. Our interpretation remains in good agreement with the results of other authors[5,22] who studied the effect of ion adsorption on the stability of complexes. They have also assumed the existence of complexes with the participation of adsorbed ligand.

To sum up, we can state that the changes in the stability of Fe(II) complexes with carbamide derivatives $[Fe(H_2O)_{6-n}X_n]^{2+}$

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for $n > 1$ do not conform with expectations and the direction of changes observed in the case of complex **1**: $[Fe(H_2O)_5X]^{2+}$ (X = carbamide derivative). However, they are closely associated with the changes in adsorption of carbamide derivatives, and their analysis allows us to conclude that the strong adsorption of carbamide derivatives brings about the increase in the stability of complexes due to the formation of complexes with the participation of adsorbed ligand: $[Fe(H_2O)_{5-n}X_n(X)_{ads}]^{2+}$.

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Electrochemical and Spectroelectrochemical Studies of Monomeric Rhodium(III) Porphyrins in Nonaqueous Media

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The electrochemistry and spectroelectrochemistry of $(TPP)Rh(NH(CH_3)_2)Cl$ and $(TPP)Rh(NH(CH_3)_2)_2{}^+Cl^-$ were investigated in benzonitrile, THF, and pyridine. In benzonitrile, both of these six-coordinated Rh(III) complexes undergo two reductions and two oxidations at room temperature. No oxidations are observed in THF or pyridine (due to the limited solvent window), but two reductions are observed for the two complexes in each of these solvents. The first reduction is followed by a rapid chemical reaction, which generates a diamagnetic species that appears to be a rhodium(II) dimer. The second reduction is a two-electron reaction that produces another diamagnetic species. Electronic absorption spectra indicate the second reduction is at the porphyrin π system. The two oxidations generate the cation radical and dication of the Rh(III) compounds and give electronic absorption and ESR spectra similar to those of other metalloporphyrin π radical cations and dications. On the basis of the electrochemical and spectroscopic results, an overall oxidation–reduction scheme was formulated.

Introduction

Numerous communications have appeared in the literature that report the synthesis of rhodium(III) and rhodium(II) porphyrins,[1-14] but very little is known about the electrochemistry of these complexes. No electrochemical data has ever been reported for the reduction of rhodium(III) or rhodium(II) porphyrins, and only a single paper has been published that reports electrooxidation of rhodium(III) porphyrins.[15] One of the few examples of a monomeric rhodium(II) porphyrin species, identified by ESR and elelctronic absorption spectra, was reported in a recent paper.[16] The four-coordinate $(TPP)Rh^{II}$ was generated by flash photolysis in 2-methyltetrahydrofuran and is stable only at 77 K. Five-coordinate rhodium(II) porphyrins with bound NO and O_2 ligands have been reported in the literature, but these species are often described as containing a rhodium(III) ion.[15]

In this paper, we report the electrochemical properties and spectral characterization of bis(dimethylamine)(tetraphenylporphinato)rhodium(III) chloride, $(TPP)Rh(NH(CH_3)_2)_2{}^+Cl^-$, and (dimethylamine)(chlorotetraphenylporphinato)rhodium(III), $(TPP)Rh(NH(CH_3)_2)Cl$. These complexes will be abbreviated as $(TPP)Rh(L)_2{}^+Cl^-$, and $(TPP)Rh(L)Cl$ where L = dimethylamine.

Experimental Section

Instrumentation and Methods. IR spectra were measured on a Perkin-Elmer 1330 infrared spectrophotometer. UV-visible spectra were recorded on a Hitachi 110 spectrophotometer or a Tracor Northern 1710 holographic optical spectrometer/multichannel analyzer. NMR spectra were taken on a Varian FT-80 spectrometer. ESR spectra were recorded on an IBM Model ED-100 electron spin resonance system. A YSI Model 31 conductivity bridge was used to perform conductivity measurements. Cyclic voltammetric and polarographic measurements were obtained by using an EG&G Princeton Applied Research Model 174A/175 polarographic analyzer/potentiostat coupled with an EG&G Model 9002A X-Y recorder for potential scan rates less than 500 mV/s or a Tektronix 5111 storage oscilloscope for scan rates equal to or larger than 500 mV/s. The working and counter electrodes used were platinum, except in the case of the thin-layer spectroelectrochemical cell, where a gold-minigrid electrode was used. Potentials were all measured vs. a saturated calomel electrode (SCE), which was separated from the bulk of the solution by means of a fritted-glass-disk junction. Potential measurements were also made vs. the ferrocene/ferrocenium (Fc/Fc^+) couple for the purpose of evaluating liquid-junction-potential differences between different solvents. Low-temperature experiments were performed by cooling the cell with a dry ice/acetone bath to a constant temperature, monitored by a thermocouple. Bulk controlled-potential coulometry was carried out on an EG&G Princeton Applied Research Model 174 potentiostat/Model 179 coulometer system, coupled with a Shimadgu R-12 laboratory recorder. Thin-layer spectroelectrochemical measurements were made wth an IBM 225/2A voltammetric analyzer coupled with a Tracor Northern 1710 spectrometer/multichannel analyzer.

Materials. $RhCl_3{\cdot}3H_2O$ was purchased from Matthey Bishop, Inc., Malvern, PA. All solvents used in the synthesis of the rhodium porphyrins were either reagent or chemical grade. For the electrochemical and spectroscopic measurements, spectroscopic grade pyridine (py) was distilled over KOH. Reagent grade benzonitrile (PhCN) was vacuum-distilled over P_2O_5 before use. Spectroscopic grade THF was used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Eastman Kodak Co., twice recrystallized from ethyl alcohol, and stored in a vacuum oven at 40 °C. Unless otherwise noted, 0.1 M TBAP was used as a supporting electrolyte for the cyclic voltammetric measurements while 0.5 M TBAP was used for bulk solution electrolysis and 0.2 M TBAP was used for the spectroelectrochemical measurements.

Syntheses of the rhodium complexes were performed by literature

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