Summary

pH titrations of the aquovanadyl ion, while inconclusive with respect to the exact stoichiometry of the basic solution species, place an upper limit of 3 mol of base/mol of vanadium(IV). An eight-line ESR spectrum shows the species to be monomeric, and ESR-inactive oligomers are ruled out by the linearity of an ESR Beer's law plot and the similarity of the slope of the plot to that for the aquovanadyl ion. Thus the basic solution species must be $VO(OH)_3^-$. Analysis of the Raman spectrum which shows the presence of the vanadyl group, V=O, and interpretation of the ESR and optical parameters show that $VO(OH)_3^-$ is structurally similar to the aquo ion $VO(H_2O)_5^{2+}$ with somewhat more covalent, and perhaps stiffer, equatorial V–O bonds. It thus appears that the two species are related by the ionization of three water protons, i.e.

$$VO(H_2O)_5^{2+} + 3OH^- \rightarrow VO(OH)_3(H_2O)_2^- + 3H_2O$$

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Registry No. $VO(OH)_3(H_2O)_2^-$, 56586-21-1; $VO(H_2O)_5^{2+}$, 15391-95-4.

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Kinetics and Mechanism of the Oxidation of Uranium(III) by Cobalt(III) in Perchlorate Media

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The kinetics of the oxidation of U(III) by Co(III) has been studied in perchlorate media. The rate law of the reaction was found to be given by the expression $-d[Co(III)]/dt = k_1[Co(III)][U(III)]$. The value of k_1 was determined as $(1.12 \pm 0.1) \times 10^6\ M^{-1}\ sec^{-1}$ at 20°C and ionic strength of 2.00 and was found to be independent of acid concentration at constant ionic strength. The temperature dependence of the reaction was studied in the range 11–31°C and the values of $\Delta H^‡$ and $\Delta S^‡$ were determined as 2.00 ± 0.25 kcal mol^{-1} and -25.6 ± 0.8 cal deg^{-1} mol^{-1}, respectively. In common with many other reactions of Co(III), the rate constant of this reaction is much lower than expected from the very high $\Delta G°$ value and plausible reasons for this observation are discussed.

Introduction

The chemical properties[1] and the kinetics and mechanisms of the oxidation–reduction reactions[2,3] of hexaaquocobalt(III) have been the subject of recent and comprehensive reviews. These have confirmed the earlier observation[4] that, although the experimental free energy change of activation ($\Delta G^‡$) for a series of Co(III) reactions at first decreases as predicted by the Marcus expression as the free energy change ($\Delta G°$) for the reaction becomes more negative, the values of $\Delta G^‡$ become essentially constant at 10 kcal mol^{-1} in reactions whose $\Delta G°$ value exceeds -40 kcal mol^{-1}. This behavior suggests some rate-limiting factor which is not normally included in the Marcus expression and which for reactions of Co(III) ions has often been identified as spin multiplicity restrictions involving the $Co^{III}(t_{2g}^6)$–$Co^{III}(t_{2g}^5e_g^1)$ equilibrium.[5]

As noted elsewhere,[5b] the determination of the activation parameters for other Co(III) reactions of high $\Delta G°$ values would be of interest and might provide further experimental verification of the above observation. Since preliminary experiments showed that the Co(III)–U(III) reaction with a $\Delta G°$ value of -55.7 kcal mol^{-1} [6] could be followed by stopped-flow techniques, this reaction was studied in perchloric acid solution.

Experimental Section

Reagents. Solutions of $UO_2(ClO_4)_2$, $NaClO_4$, and $HClO_4$ were prepared as reported elsewhere,[7] and the method of preparation and handling of the U(III) solutions was identical with that described previously.[8] A Co(II) stock solution was prepared from $Co(ClO_4)_2$

Table I. Effect of Initial Concentrations on the Second-Order Rate Constant k_1[a]

10^4[U(III)]$_0$, *M*	10^5[Co(III)]$_0$, *M*	No. of detns	$10^{-5}k_1$,[b] M^{-1} sec^{-1}
2.42	3.03	10	3.82 ± 0.11
2.42	5.82	10	4.02 ± 0.09
2.42	10.6	9	4.20 ± 0.10
1.21	6.41	9	3.61 ± 0.09
3.62	7.14	9	4.06 ± 0.12
7.25	6.64	10	4.56 ± 0.12
		Tot 57	Av 4.06 ± 0.31

[a] Conditions: 20°C, [H$^+$] = 0.20 *M*, ionic strength 0.20, reaction followed at 230 nm. [b] Average and standard deviation.

(ROC-RIC) and analyzed for Co(II) and free acid concentrations by established procedures.[9,10] $Fe(ClO_4)_2$ solutions, used to analyze the Co(III) solutions as described below, were prepared by treating a solution of $FeSO_4$ (Merck) with a slight excess of the stoichiometric quantity of $Ba(ClO_4)_2$ (Merck), filtering the resulting precipitate, and determining the Fe(II) concentration by titration with standard Ce(IV) using ferroin indicator.

Co(III) solutions were prepared by electrochemical oxidation (platinum mesh anode) of suitably diluted samples of the Co(II) stock solutions.[11] The Co(III) concentration was determined before each run by treating a sample of the Co(III) solution with an excess of Fe(II) in the stopped-flow apparatus at 230 nm. At this wavelength and at the completion of the reaction Fe(III) is the only absorbing species. As the Fe(II)–Co(III) reaction displays a well-established 1:1 stoichiometry,[5b,12] the initial Co(III) concentration could be readily evaluated from the final absorbance and the measured extinction coefficient (3850 ± 50 M^{-1} cm^{-1}) of Fe(III) at this wavelength.

Measurement of Reaction Rates and Calculations. The reactions were followed at 230 nm using the stopped-flow apparatus and computerized data acquisition system described elsewhere.[8,13] The data were analyzed according to a second-order rate law, and plots of the integrated rate equation were excellent straight lines to 90% reaction. The combination of relatively low extinction coefficients and high rate constants made it necessary to operate the stopped-flow apparatus near its limit of sensitivity, so that the errors associated with the measured rate constant are somewhat higher than those obtained under more normal operating conditions.[7,8,13] All nonlinear least-squares analyses were carried out using the program of Lietzke,[14] the individual results being weighted according to the reciprocal of the square of the standard deviation.

Results

The reaction of Co(III) with U(III) (eq 1) can be followed

$$\mathrm{Co(III)} + \mathrm{U(III)} \xrightarrow{k_1} \mathrm{U(IV)} + \mathrm{Co(II)} \qquad (1)$$

by the oxidation of U(IV) to U(V) and ultimately to U(VI) (eq 2). To avoid this possibility, all rate measurements were

$$2\mathrm{Co(III)} + \mathrm{U(IV)} \rightarrow \mathrm{U(VI)} + 2\mathrm{Co(II)} \qquad (2)$$

carried out in the presence of a substantial excess of U(III). Under these conditions, a slight dependence of the experimental rate constant (k_1) on the initial U(III) concentration and on the product of the initial U(III) and Co(III) concentrations was observed. However, these dependencies are assumed to be artifacts and to be without mechanistic significance. For all determinations summarized in Table I, the average and standard deviation of k_1 was determined as (4.06 ± 0.31) × 10^5 M^{-1} sec^{-1} at 20°C for a solution of 0.20 *M* H$^+$ and of an ionic strength (*I*) of 0.20. The stoichiometry factor for these runs was determined as 1.1 ± 0.1 from the measured absorbance change in the course of these reactions and the independently determined extinction coefficients of the reagents and products.

Table II. Effect of Acid Concentration on the Value of the Second-Order Rate Constant k_1[a]

[H$^+$], *M*	Ionic strength	No. of detns	$10^{-5}k_1$,[b] M^{-1} sec^{-1}
0.10	0.50	9	5.80 ± 0.40
0.20		8	5.10 ± 0.33
0.30		8	5.41 ± 0.30
0.40		9	5.44 ± 0.18
0.50		7	5.41 ± 0.13
		Tot 41	Av 5.42 ± 0.35
0.20	1.00	9	7.80 ± 0.30
0.40		7	6.82 ± 0.16
0.60		9	6.37 ± 0.14
0.80		10	6.56 ± 0.15
1.00		11	7.84 ± 0.29
		Tot 46	Av 7.12 ± 0.60

[a] Conditions: [U(III)]$_0$ = 1.21 × 10^{-4} *M*, [(Co(III)]$_0$ = (4.50–6.00) × 10^{-5} *M*, 20°C, ionic strength maintained with $NaClO_4$. [b] Average and standard deviation.

Table III. Ionic Strength Dependence of k_1[a]

Ionic strength	No. of detns	$10^{-5}k_1$, M^{-1} sec^{-1}	
		Obsd[b]	Calcd[c]
0.305	9	3.66 ± 0.09	3.81
0.405	9	5.08 ± 0.12	4.61
0.606	9	5.83 ± 0.18	5.94
0.806	10	6.57 ± 0.33	7.01
1.01	9	7.90 ± 0.27	7.93
1.31	10	8.35 ± 0.36	9.06

[a] Conditions: [U(III)]$_0$ = 1.81 × 10^{-4} *M*, [Co(III)]$_0$ = 4.50–7.50 × 10^{-5} *M*, [H$^+$] = 0.303 *M*, 20°C. [b] Average and standard deviation. [c] Calculated from eq 3 with log k_0 = 3.85 ± 0.11, *d* = 10.5 ± 0.9, *C* = 0.0, rms = 6.1%.

The acid dependence of the value of k_1 was studied in solutions of ionic strengths 0.50 and 1.00. The results obtained (Table II) suggest that within the experimental error the reaction rate constant at 20°C is independent of acid concentration, k_1 having a value of (5.42 ± 0.35) × 10^5 M^{-1} sec^{-1} (41 runs) in the acid concentration range 0.10–0.50 *M* at *I* = 0.50 and (7.12 ± 0.60) × 10^5 M^{-1} sec^{-1} (46 runs) in the acid concentration range 0.20–1.00 *M* at *I* = 1.00. The data are unfortunately insufficiently precise to exclude the possible presence of a minor acid-dependent reaction path, but the dominant, inverse acid dependence commonly encountered in reactions of Co(III) ions is clearly not observed in the present system.

The ionic strength dependence of k_1 (Table III) conformed well with the Debye–Huckel equation (eq 3) with $\Delta Z^2 = 18$,

$$\log k_1 = \log k_0 + [A\Delta Z^2 I^{1/2}/(1 + BdI^{1/2})] + CI \qquad (3)$$

$A = 0.5070$,[15] and $B = 0.3282$.[15] Because of the limited range of ionic strengths over which this reaction could be studied, the *C* term in the above expression was set equal to zero, and least-squares analysis of the data yielded values of 3.85 ± 0.11 for log k_0 and 10.5 ± 0.9 for *d* in the above expression, the root-mean-square deviation[16] (% rms) being 6.1%. These data may be used to obtain an extrapolated value of (1.12 ± 0.10) × 10^6 M^{-1} sec^{-1} for k_1 at 20°C and an ionic strength of 2.00.

The effect of temperature on the value of k_1 was studied over the range 11–31°C, at an acid concentration of 0.50 *M* and an ionic strength of 0.51 *M*. Analysis of the results (Table IV) in terms of the Eyring equation[17] (eq 4) gave values of

$$k_{\mathrm{obsd}} = \frac{kT}{h} \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \qquad (4)$$

2.00 ± 0.25 kcal mol^{-1} and −25.6 ± 0.8 cal deg^{-1} mol^{-1} for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ respectively, with a root-mean-square deviation of 2.0%.

Discussion

The absence of any measurable inverse acid dependence for the Co(III)–U(III) reaction is surprising in view of the marked preference for this path usually found in other reactions of the Co(III) ion.[4,5b,12,18] Only the oxidation of Np(V) by Co(III)

Table IV. Temperature Dependency of k_1[a]

Temp, °C	No. of detns	$10^{-5}k_1$, M^{-1} sec^{-1} Obsd[b]	$10^{-5}k_1$, M^{-1} sec^{-1} Calcd[c]
10.9	9	4.32 ± 0.06	4.33
15.5	10	4.59 ± 0.12	4.66
20.0	9	5.08 ± 0.09	4.99
25.2	9	5.24 ± 0.21	5.39
30.8	9	5.71 ± 0.26	5.84

[a] Conditions: $[U(III)]_0 = 1.81 \times 10^{-4}$ M, $[Co(III)]_0 = (3.50\text{–}6.10) \times 10^{-5}$ M, $[H^+] = 0.50$ M, ionic strength 0.50. [b] Average and standard deviation. [c] Calculated using the Eyring equation with $\Delta H^{\ddagger} = 2.00 \pm 0.25$ kcal mol^{-1} and $\Delta S^{\ddagger} = -25.6 \pm 0.8$ cal deg^{-1} mol^{-1}, rms = 2.0%.

has been reported[19] to be independent of acid concentration, even though the rate of this reaction was relatively slow ($k = 300 \pm 3$ M^{-1} sec^{-1}, at $[H^+] = 2.0$ M and 25°C).

A comparison of the rate constants and rate parameters of the reactions of U(III) with uncomplexed aquo ions studied to date shows (Table V) that, despite its more negative $\Delta G°$ value, the appropriate values obtained for the Co(III) reactions are surprisingly similar to those measured for the Fe(III) reaction. This observation would suggest that the mechanisms of the two reactions are the same, and, by analogy,[8] an outer-sphere electron transfer may be tentatively suggested for the Co(III)–U(III) reaction.

Examination of the rate constants summarized in Table V also suggests that the value found for the Co(III) reaction is much lower than might be expected from its $\Delta G°$ value of −55.7 kcal mol^{-1}. This is a commonly made observation for reactions of Co(III), which has been more formally expressed[2,4] by noting that a plot of $\Delta G^{\ddagger}$ against $\Delta G°$ for the *acid-independent reaction paths* of a series of reactions of Co(III) tends to approach a limiting value of approximately −10 kcal mol^{-1} for $\Delta G^{\ddagger}$ as $\Delta G°$ becomes very negative. As shown in Figure 1, the results obtained for the U(III)–Co(III) reaction (point 12) fit the trend shown by the other reactions of Co(III) (points 1–11 and 13, open circles) very well. For comparison, the theoretical relationship, calculated[4] from the Marcus expression for the Co(III) reactions is shown by the broken line.

Inclusion in Figure 1 of the appropriate values for a series of reactions not involving Co(III) ions (points 14–31, solid circles) suggests that the above observation is not confined to the reactions of Co(III) ions. Although there is some obvious scatter in the data[33] and further results in the high $-\Delta G°$ range are clearly required, it is surprising that for reactions involving a very wide variety of metal ions the values of $\Delta G^{\ddagger}$ follow a trend similar to that found for reactions of Co(III). There is also an indication of a limiting value of 9–10 kcal mol^{-1} for $\Delta G^{\ddagger}$ as $\Delta G°$ becomes highly negative. It may be noted, however, that the recently reported[34] rate constants for the reaction of Tl^{2+} ions with Co^{2+}, Fe^{3+}, Mn^{2+}, Fe^{2+}, and Co^{3+} and particularly the Tl^{2+} disproportionation reaction with a bimolecular rate constant of 5.5×10^8 M^{-1} sec^{-1} at 25°C fit the above plot only approximately. The significance of these results is difficult to evaluate with certainty at this time since some of the reported reaction rates may include contributions from a reaction path having an inverse acid concentration dependence. This effect could be quite significant at the relatively low acid concentrations (0.25–0.50 M) at which these measurements were made.

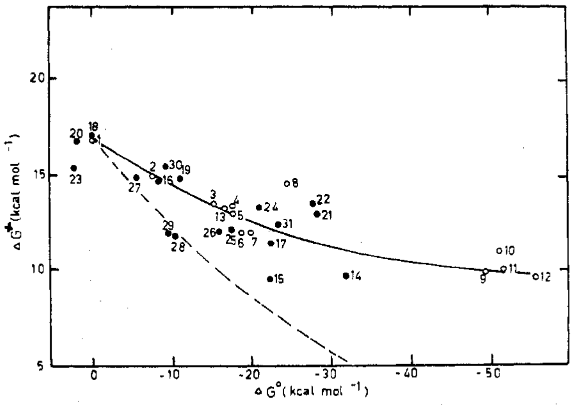

Figure 1. Plot of the free energy of activation ($\Delta G^{\ddagger}$) vs. the free energy of reaction ($\Delta G°$) for a series of acid-independent reaction paths: open circles, reactions involving Co(III) ions; filled circles, reactions of metal ions other than Co(III); solid line, curve of best fit for the Co(III) reactions; broken line, theoretical relationship calculated from the Marcus expression for the Co(III) reactions. Points 1–11 are from ref 2 and 4. The remaining points are as follows: 12, U(III)–Co(III) (this work); 13, Co(III)–Np(V);[19] 14, U(III)–Fe(III);[8] 15, U(III)–V(IV);[8] 16, U(III)–V(III);[8] 17, Np(III)–Np(VI);[20] 18, Fe(III)–Fe(II);[21] 19, V(IV)–Mn(III);[22] 20, Pu(III)–Pu(VI);[23] 21, Eu(II)–Fe(III);[24] 22, Cr(II)–Fe(III);[25] 23, Np(III)–U(VI);[26] 24, Np(VII)–V(IV);[27] 25, Mn(III)–Fe(II);[28] 26, U(III)–U(VI);[20] 27, V(II)–U(VI);[29] 28, U(VI)–Eu(II);[30] 29, U(VI)–Cr(II);[7] 30, V(II)–Cu(II);[31] 31, V(V)–Ti(III).[32]

The data summarized in Figure 1 would suggest that the factors limiting the maximum rate of the reactions of the Co(III) ion to a value of approximately 2×10^6 M^{-1} sec^{-1} may also be found in other reactions having a highly negative $\Delta G°$ value. If this observation can be further confirmed, it would seemingly eliminate the Co(III) low-spin–high-spin preequilibrium as responsible for the limiting value of $\Delta G^{\ddagger}$ for the reactions of Co(III) ions.

The origin of this limiting value in the context of the Co(III) reactions has been discussed[4] in terms of Rosseinsky's[35] modification of the Marcus equation. Although this essentially empirical interpretation could be plausibly extended to include the reactions of ions other than Co(III), the limitations inherent in the applicability of the Marcus equation to reactions of highly negative $\Delta G°$ values[36] with the possibility of "inverted" chemical behavior have been stressed on several occasions.[36,37]

Other factors which may contribute to the limiting value

Table V. Rate Constants and Rate Parameters of Some Reactions of U(III)

Activation process	$\Delta G°$, kcal mol^{-1}	k, M^{-1} sec^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	$S^{\ddagger}$,[c] cal deg^{-1} mol^{-1}	$S^{\ddagger}/Z$, cal deg^{-1} mol^{-1}
$V^{3+} + U^{3+} \rightarrow [\ ^{6+}]^{\ddagger}$ [a,f]	−8.6	54.2 ± 3.7	14.8	9.77 ± 0.62	−17.1 ± 2.1	−118.3	−19.7
$V^{3+} + U^{3+} + H_2O \rightarrow [\ ^{5+}]^{\ddagger} + H^+$ [a,f]	+11.0	278 ± 2	13.9	9.48 ± 0.29	−15.0 ± 1.0	−97.3	−19.5
$UO_2^{2+} + U^{3+} \rightarrow [\ ^{5+}]^{\ddagger}$ [b]	−15.8	$(1.20 \pm 0.04) \times 10^4$	11.9	4.15 ± 0.07	−26.1 ± 0.3	−85.1	−17.0
$VO^{2+} + U^{3+} \rightarrow [\ ^{5+}]^{\ddagger}$ [a,f]	−22.3	$(3.66 \pm 0.20) \times 10^5$	9.6	6.04 ± 0.43	−12.3 ± 1.5	−80.1	−16.0
$Fe^{3+} + U^{3+} \rightarrow [\ ^{6+}]^{\ddagger}$ [a,f]	−31.8	$(3.92 \pm 0.20) \times 10^5$	9.7	1.53 ± 0.89	−27.7 ± 3.0	−139.9	−23.3
$Co^{3+} + U^{3+} \rightarrow [\ ^{6+}]^{\ddagger}$ [d]	−55.7	$(1.12 \pm 0.10) \times 10^6$ [e]	9.5	2.00 ± 0.25	−25.6 ± 0.8	−140.0	−23.5

[a] Conditions: $[H^+] = 1.00$ M, $I = 2.00$, 20°C. [b] Data taken from ref 20. Conditions: $[H^+] = 0.10$ M, 25.1°C. [c] The formal ionic entropy of the activated complex as defined in ref 25. $S°$ values obtained from ref 12, except $S°_{U(III)}$ which has been calculated as −42.1 cal deg^{-1} mol^{-1} by R. J. Hinchey and J. W. Cobble, *Inorg. Chem.*, 9, 922 (1970). [d] Conditions: $[H^+] = 0.50$ M, $I = 0.50$. [e] Extrapolated value. [f] Taken from ref 8; the process refers to the formation of the activated complex $[VOHU]^{5+}$, i.e., involves the reaction of a hydrolyzed species.

of $\Delta G^{\ddagger}$ include the possibility of a tunneling mechanism,[37] the involvement of a precursor complex of the type discussed in detail elsewhere,[2] or work terms which may include coulombic repulsion and solvent effects.[2,4] Although the reorganization of the inner coordination sphere prior to the electron transfer is not considered[38] to be as necessary for reactions of strongly negative ΔG° values as it is for reactions in which ΔG° is near zero, the observation that the limiting value of $\Delta G^{\ddagger}$ is found for reactions involving ions of a variety of properties suggests that solvent effects, possibly involving the secondary as well as the primary coordination sphere, may be involved.

The value of k_1 extrapolated to an ionic strength of zero is 7.08×10^3 M^{-1} sec^{-1}, which is slightly less than half the value of 1.7×10^4 M^{-1} sec^{-1} calculated from the Debye equation[39] for the diffusion-controlled limit for a reaction between two 3+ ions with an average radius of 4 Å. Although the derivation of the Debye equation assumes a structureless dielectric medium and will be only approximate, the above agreement may suggest that a diffusion-controlled limit is reached in the case of the U(III)–Co(III) reaction. An approach to a diffusion-controlled limit in a Co(III) reaction would be further evidence against the participation of a high-spin–low-spin preequilibrium.[40] However, the Debye equation involves the product (Z_1Z_2) of the charge carried by the reacting ions, and our observation that the limiting rates for the reactions of Co(III) with V(II), Eu(II), and Cr(II) as well as U(III) are all similar suggests that the value of the product Z_1Z_2 does not strongly influence the observed rate constant.

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Study of the Fused-Salt System Ammonium Chloride–Sodium Tetrachloroaluminate

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Experiments in which total vapor pressures generated by mixtures of ammonium chloride and sodium tetrachloroaluminate have been measured as a function of temperature have been used to derive information about the thermodynamic characteristics of this fused-salt system. At low mole fractions of NH_4Cl the principal component of the equilibrium vapor above the liquid at temperatures below 650 K is hydrogen chloride, with only small partial pressures of the ammine, NH_3AlCl_3, and ammonia present. Data correlate well when melts are treated as an ideal mixture of the ionic species with ammine molecules interspersed on adjacent cation–anion sites. Results are compared with an earlier study of the NH_4AlCl_4–NH_3AlCl_3 system. The reaction of ammonia with $NaAlCl_4$ has also been studied.

Introduction

In a recent study of the complex formed between ammonium chloride and aluminum chloride vaporization of NH_4AlCl_4 was found to occur by formation of the ammine, NH_3AlCl_3, and hydrogen chloride.[1,2] The ammine and the complex are miscible in the liquid phase over a significant concentration range at temperatures near the melting point of NH_4AlCl_4 (305°). Total pressures generated by the vaporization reaction

$$NH_4^+(l) + AlCl_4^-(l) = NH_3AlCl_3(g) + HCl(g) \qquad (1)$$

were found to correlate well by treating the liquid phase as an ideal mixture of the ammine, with each molecule presumed to occupy a combined cation and anion site, and the ionic complex. A preliminary study of such mixtures when an excess of NH_4Cl was also present suggested that the ionic solution model was still applicable although the "Henry's law" properties of liquid NH_4Cl at low concentrations in the complex liquid phase appeared somewhat different from those expected for pure liquid NH_4Cl.

The study of these interesting mixtures has now been ex-