that there is rapid exchange between any such hydrogen bonded acetone molecules and the bulk of the solvent whereas the water molecule is firmly held. Such an interaction can be reasonably described as solvation and cannot be regarded as being in principle any different from the weaker interaction that presumably exists between $BF_3.H_2O$ and $SbCl_5.H_2O$ and the solvent CH_2Cl_2. We were indeed fully aware of the possibility of ternary complexes and in fact we postulated the existence of the ternary complex $F_3B.OH_2.OH_2$ in order to explain the rapid proton exchange that occurs in the presence of water in excess of the 1:1 composition. Moreover, in a subsequent paper [3] we have discussed the $BF_3.MeOH$ and $BF_3.2MeOH$ complexes and have proposed a structure for the 1:2 adduct involving a weak hydrogen bond between the first directly bonded molecule and the second methanol molecule. Our work on this system has subsequently been repeated and confirmed.[4]

Bernander and Olofsson also claim that our statement that "acetone is much inferior to water as an electron pair donor to BF_3" is not corroborated by comparison of donor strengths towards $SbCl_5$. However, at low temperatures in excess acetone the NMR spectra of both the acetone.BF_3 and the $H_2O.BF_3$ complex can be observed directly in the same solution and it is quite clear that the equilibrium

$$H_2O + \text{acetone}.BF_3 \rightleftharpoons \text{acetone} + H_2O.BF_3$$

lies far to the right. Moreover, we observed proton-fluorine coupling in $BF_3.H_2O$ even in the presence of a large excess of acetone. Both of these observations clearly indicate that BF_3 is bonded to water much more strongly than to acetone and if a ternary complex does exist the primary bond must be between the BF_3 and a water molecule with the acetone molecule held weakly by hydrogen bonds to the water molecule. Bernander and Olofsson report thermochemical measurements demonstrating that $SbCl_5$.ester, $SbCl_5$.ketone, and $SbCl_5$.water complexes all have very similar stabilities and they make the assumption that this should also be true for the BF_3 adducts. Quite apart from the fact that this is inconsistent with our NMR results such an assumption is also not justified on the basis of previous work on the Lewis acidity of BF_3 with respect to different bases.[5] Indeed it is a well known problem in comparing the strengths of Lewis acids and bases that there is no absolute scale of relative basicities that is valid for all Lewis acids. Ethers, ketones, and water need not have the same relative donor strengths with respect to BF_3 as they do with respect to $SbCl_5$. There are examples of base strength reversal even between Lewis acids as similar as BF_3 and BCl_3,[6] and it has been found that even the replacement of a single fluorine in BF_3 by a chlorine can have striking effects on Lewis acid properties.[7]

If Bernander and Oloffson's conclusion that water and acetone have similar base strengths towards $SbCl_5$ is correct then their results taken in conjunction with ours, which show that acetone is a much weaker base towards BF_3 than is water, demonstrate once again that one cannot establish a single consistent set of base strengths towards different Lewis acids and in particular towards BF_3 and $SbCl_5$.

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A Simple Parameterfree Expression for the Activity Coefficient of Potassium Chloride in Water in the Range $0.1 \leq m \leq 4.8$

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The following expression [1] for the activity coefficient of a simple 1:1 electrolyte can be derived using in principle the same approach as that of Stokes and Robinson [2] but using the *molarity scale* instead of the molality scale used by them

$$\log y_A y_B = -\frac{2 \times 0.5115\sqrt{C}}{1+Ba\sqrt{C}} - 2\log\left[\frac{1}{d_0}\left\{d + 0.001C(2 \times 18.015 - M_{AB})\right\}\right] - \log S \quad (1)$$

where $S = \sum K_n a_w^n$ (2)

S "represents" the sum of all various hydrated species. a_w is the water activity, C is concentration in mol liter^{-1}, d_0 the density of pure water and d that of the solution. M_{AB} is the molecular weight of the solute. The first term in eqn. (1) represents the electrostatic part of the excess free energy, the second term is a scale factor connecting the mol fraction and molarity scales while the third term represents the excess free energy of hydration. S has the property

$$\frac{\mathrm{d}\log S}{\mathrm{d}\log a_w} = \bar{n} = \frac{\sum n K_n a_w^n}{\sum K_n a_w^n} \qquad (3)$$

With knowledge of a, the distance of closest approach, S can be computed from (1). It is found that $\bar{n}$ computed for the system NaCl – H_2O approaches 5 independent of the ion-size parameter. This indicates that what may be regarded as primary hydration numbers can be obtained for many salts independent of any knowledge of the ion-size parameter a. Following a suggestion by Pitzer [3] it was decided to use the Bjerrum q-value for the ion-size parameter *i.e.* the term Ba in eqn. (7) becomes 1.176 for all 1:1 electrolytes.

With this choice it is found that for KCl – H_2O at 25 °C

$$\bar{n} \approx n \approx 4 \qquad (4)$$

and eqn. (1) reduces to

$$\log y_{K^+}y_{Cl^-} = \frac{2 \times 0.5115\sqrt{C}}{1+1.176\sqrt{C}} - 2\log\left[\frac{1}{0.99707} \times (d - 0.038525C)\right] - 4\log a_w \qquad (5)$$

At 25 °C $d_0 = 0.99707$ g ml^{-1}.

This is in principle a parameter-free expression because the term 1.176 is constant and the equilibrium constant for the formation of the tetrahydrate is equal to unity by definition, otherwise the activity coefficient will not approach unity at infinite dilution. The number 4 is deduced from the application of eqn. (3) to the experimental data and has a simple physical meaning unlike the fractional hydration numbers arrived at by Stokes and Robinson.[2] The activity coefficient product $y_{K^+}y_{Cl^-}$ can be transformed into $\gamma_\pm$ from

$$\gamma_\pm = (y_{K^+}y_{Cl^-})^{\frac{1}{2}}C/0.99707m \qquad (6)$$

where m is the stoichiometric molality of the solution. In Table 1 experimental values for $\gamma_\pm$ are compared with those computed from eqns. (5) and (6). The activity and osmotic coefficient data used have been taken from the compilation of Robinson and Stokes [4] and the density data from International Critical Tables.[5] As seen in Table 1 experimental and calculated values agree to within ±0.75 % at most. Most of the data agree to better than ±0.5 %. Similarly it is found for RbCl that eqn. (1) fits to within ±2 % up to 4.5 m finding $\bar{n} = n = 3$ from eqn. (3). If a small extent of ion-pairing is assumed to occur the data can be fitted to within ±0.5 % up to 3.5 m beyond that the values deviate about 1 – 3.5 %. Ion-pair formation will add a term $+2\log\alpha$ to eqn. (1) where α is the degree of dissociation of the ion-pair. For CsCl the data definitely indicate ion-pair formation. For CsCl the hydration number is around three as for RbCl. For NH_4Cl the primary hydration number are two and seven plus some secondary hydration describable by an infinite series of complexes from $n = 8$ and two parameters, the equilibrium constant for the formation of the octahydrate and the constant ratio between consecutive equilibrium constants. A similar approach also fits salts like $LiNO_3$ (to within ±5 % up to 13 m) NaBr, NaI, KBr and KI studied so far. NaCl seems to need two primary hydrates 5 and 7 together with a slight secondary hydration.

While the present approach rather satisfactorily deals with the hydration part of the

Table 1. Comparison of experimental activity coefficients for KCl – H_2O with those calculated from eqns. (4) and (5).

m	γ_{exp}	γ_{calc}
0.1	0.7698	0.7651
0.2	0.7181	0.7130
0.3	0.6875	0.6824
0.4	0.6657	0.6611
0.5	0.6492	0.6453
0.6	0.6365	0.6329
0.7	0.6262	0.6228
0.8	0.6176	0.6145
0.9	0.6101	0.6075
1.0	0.6038	0.6016
1.2	0.5933	0.5921
1.4	0.5856	0.5852
1.6	0.5800	0.5800
1.8	0.5758	0.5761
2.0	0.5728	0.5732
2.2	0.5707	0.5713
2.4	0.5694	0.5702
2.6	0.5687	0.5696
2.8	0.5686	0.5696
3.0	0.5689	0.5702
3.2	0.5698	0.5711
3.4	0.5711	0.5725
3.6	0.5725	0.5743
3.8	0.5745	0.5764
4.0	0.5768	0.5789
4.2	0.5793	0.5817
4.4	0.5820	0.5848
4.6	0.5848	0.5881
4.8	0.5879	0.5918

excess free energy the electrostatic term is rather uncertain. It should be emphasized that the choice of the Bjerrum q-value is rather arbitrary although it seems to be a useful compromise giving a self-consistent description of the systems studied so far. It is quite possible that some other choice (choices) for the distance of closest approach may emerge in the future.

A detailed account of this work will be published elsewhere.

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Dinuclear Hydrolysis Complexes of Uranium(IV)

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X-Ray scattering measurements on acid and hydrolyzed uranium(IV) perchlorate solutions [1] have shown that polynuclear complexes are formed in the hydrolyzed solutions. The U–U distance within the complexes was found to be 4.00 Å. This distance is similar to the Th–Th distance found in hydrolyzed thorium(IV) nitrate solutions [2] and in the dinuclear complex $Th_2(OH)_2(NO_3)_6(H_2O)_6$ in which the Th atoms are joined by double hydroxo bridges.[3] It seems likely, therefore, that in the hydrolysis complexes in the uranium(IV) perchlorate solutions the uranium atoms are bound together by the sharing of two hydroxo groups.

Table 1. Results of the chemical analysis.

	Observed value	Calculated value for $U_2(OH)_2(ClO_4)_6(H_2O)_{13}$
% UO_2	41.4	40.27
% Cl_2O_7	38.3	40.92
% H_2O	20.0	18.81
Density	3.1$_3$	3.091 ($z=4$)

In an attempt to obtain more information on the structures of the uranium(IV) hydrolysis complexes, two different basic perchlorates, obtained from the solutions used for the X-ray scattering measurements, have been investigated. For one of these a preliminary crystal structure determination has shown that it contains discrete dinuclear hydrolysis complexes.

The crystals, which can be obtained from solutions with a OH^-/U^{4+} ratio between about 0.2 and 0.5, are very soluble in water and are unstable outside the mother liquor, which makes their separation from the mother liquor difficult. The analysis, which is given in Table 1 leads to the formula $(UO_2)_2(Cl_2O_7)_3(H_2O)_x$ ($x \sim 13$).

From Weissenberg and precession photographs the unit cell was found to be monoclinic. The derived values for the unit cell dimensions were refined by a least squares procedure with the use of a Guinier powder photograph, taken with Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å) with Si as internal standard ($a = 5.4301$ Å). The values found were $a = 26.084(4)$ Å, $b = 9.493(1)$ Å, $c = 16.945(3)$ Å, and $\beta = 136.63(1)$ Å. Systematically absent reflections were hkl for $h+k = 2n+1$ and $h0l$ for $l = 2n+1$. This is characteristic for the space groups No. 15, $C2/c$ and No. 9; Cc.

Difficulties were encountered in getting good intensity data since the crystals seemed to be unstable under X-ray exposure and, therefore, absorption corrections could not be done. From intensities estimated visually by comparison with an intensity scale and corrected for Lorentz and polarization factors the Patterson projections along the three axes of the unit cell were calculated. An apparently unique interpretation of all the possible U–U peaks could be obtained by assuming the eight uranium atoms in the unit cell to occupy the position 8(f) in the centrosymmetric space group $C2/c$. Electron density projections along the three axes of the unit cell confirmed the correctness of the derived positions. A least squares refinement of the uranium positions with the use of the 180 observed $h0l$ and $hk0$ reflextions lead to an R value of 0.24 and the final parameter values were $x = 0.095$; $y = 0.075$; $z = -0.079$.

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