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VARIATION OF FLUORIDE ION SOLVATION AND pF⁻ BUFFER PROPERTIES OF HF_2^-/HF AND HF/H^+ PAIRS IN ACETONITRILE-WATER MIXTURES

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SUMMARY

The F^- ion is weakly solvated in acetonitrile-water mixtures. In the mixture with 50% (mole) of water, the fluoride ion solvation transfer activity coefficient is $\log\gamma(F^-) = 5.1$; it increases up to 16.7 in anhydrous acetonitrile. In these two mixtures, the equimolar buffer HF/H^+ imposes pF^- values of 6.4 and 16.8 respectively and the HF_2^-/HF buffer system imposes pF^- values of 2.6 and 5.8. Variations of the solvation of HF_2^-, HF and H^+ species as a function of the water content of the mixtures are also determined.

INTRODUCTION

Reactions involving the exchange of the fluoride ion in aprotic media such as acetonitrile can be predicted from the pF^- scale and the E-pF^- diagrams [1,2]. The reactivity of many species can be modified by using pF^- buffers. Hydrofluoric acid (HF) which is both an acceptor (HF_2^-/HF) and a donor (HF/H^+) of the F^- ion is especially important since, contrary to many other systems as $CuF_{2(s)}/Cu^{2+}$, $FeF_{3(s)}/Fe^{3+}$..., these two pairs involve uniquely soluble species.

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Studies on equilibria involving halides give evidence of the increased reactivity of Cl^-, Br^- and I^- ions when transferred from water to aprotic solvents [3-8]. Since F^- ion is smaller, larger effects may be expected.
In this paper, we examine changes of the F^- reactivity and pF^- buffer properties of the two pairs HF_2^-/HF and HF/H^+ as a function of the water content of the CH_3CN-H_2O mixtures.

RESULTS AND DISCUSSION

Variation of solvation properties of the fluoride ion in the CH_3CN-H_2O mixtures.

Solvation transfer activity coefficients $\log\gamma^{w\to s}(A)$ characterizing the transfer of the species (A) from water (w) to the hydro-organic mixtures (s) are determined assuming the Strehlow hypothesis: $\gamma^{w\to s}(Fc^+) = \gamma^{w\to s}(Fc)$ [9].
$\log\gamma^{w\to s}(F^-)$ is calculated according to the relation :

$$\log\gamma^{w\to s}(F^-) = (E^w - E^s)/\ 59 \qquad (1)$$

where E^w is the potential (mV) of the fluoride specific electrode (FSE) in pure water and E^s (mV) its potential in the CH_3CN-H_2O mixture for an equal fluoride concentration.
This method has already been used by Vaillant [10] and Louis [11] to determine $\log\gamma(F^-)$ values in hydrofluoric acid-water mixtures and phosphoric acid-water mixtures respectively. It implies that the electrode has a linear response as a function of the fluoride concentration with a constant slope (59 mV per pF^- unit) in every mixture.
$\log\gamma^{w\to s}(F^-)$ is determined in each CH_3CN-H_2O mixture from the FSE potential relative to three concentrations: 10^{-4}, 10^{-3}, 10^{-2} M in fluoride. In pure water, the FSE response is given by the relation:

$$E(mV) = -237 + 59\ pF^- \qquad (2)$$

The results are given in the Table I along with log $\gamma^{w->s}(Cl^-)$ values determined by Cox [12] in the same mixtures.

TABLE I

Solvation transfer activity coefficients of F^- ions and Cl^- ions [12] in the CH_3CN-H_2O mixtures (comparison system: Fc^+/Fc).

% H_2O (mole)	H_2O (M)	log $\gamma^{w->s}(F^-)$	log $\gamma^{w->s}(Cl^-)$	Δ log $\gamma_{Cl,F}$ [a]
0	0	16.7	9.1	7.6
10	2.0	11.2	5.4	5.8
20	4.4	8.0	4.0	4.0
30	7.1	6.8	3.2	3.6
40	9.5	5.9	2.6	3.3
50	14.2	5.1	2.0	3.1
60	18.8	4.5	1.6	2.9
70	24.7	3.7	1.1	2.6
80	32.1	2.7	0.7	2.0
90	41.9	0.8	0.4	0.4
100	55.6	0	0	0

[a] $\Delta \log \gamma_{Cl,F} = \log \gamma^{w->s}(F^-) - \log \gamma^{w->s}(Cl^-)$

The desolvation of the fluoride ions increases rapidly with the acetonitrile content even when the water content is still high : log $\gamma^{w->s}(F^-)$ = 5.1 in the CH_3CN-50% H_2O mixture.

log $\gamma^{w->s}(F^-)$ values determined by Bhattacharya *et al.* [13] in acetonitrile-water mixtures with a low content of acetonitrile are higher than ours. The 4.0 value these authors give for the mixture CH_3CN-90% H_2O seems to us excessive considering the high water content.

The log $\gamma^{w->s}(F^-)$ value of 16.7 we determined in the anhydrous medium is slightly higher than that of 14.8 given by Coetzee *et al.* [14] who used $Et_4NF.2H_2O$ for their potentiometric determinations. The difference may be attributed to the degree of hydration of the fluoride ion.

It is shown in Table I that the desolvation of the fluoride ion is higher than that of the chloride ion. Such a property is common to all the aprotic solvent-water mixtures where the desolvation of the halides increases as their radius **decreases** [3,5,12,15].

The correlation which exists between $\log \gamma^{w\to s}(X^-)$ (X = F, Cl, Br, I) and the inverse of the crystallographic radius is illustrated in Fig.1. That confirms the first results given by Coetzee *et al.*[15] for the Cl^-, Br^- and I^- ions.

Variation of the HF_2^-/HF and HF/H^+ buffer properties in the CH_3CN-H_2O mixtures.

In order to characterize changes of the fluoride buffering ability of the HF_2^-/HF and HF/H^+ equimolar mixtures as a function of the water content, we determined the acidity constants (pK_1^s and pK_2^s) of the conjugate pairs HF_2^-/F^- and HF/HF_2^- corresponding to the equilibria:

$$2\,F^- + H^+ \Longleftrightarrow HF_2^- \qquad K_1^s = [H^+][F^-]^2/[HF_2^-] \qquad (3)$$

$$HF_2^- + H^+ \Longleftrightarrow 2\,HF \qquad K_2^s = [H^+][HF_2^-]/[HF]^2 \qquad (4)$$

The dissociation constants pK'^s_1 and pK'^s_2 relative to the equilibria:

$$HF_2^- \Longleftrightarrow F^- + HF \qquad (5)$$

$$HF \Longleftrightarrow F^- + H^+ \qquad (6)$$

are determined from pK_1^s and pK_2^s values according to the relations:

$$pK'^s_1 = (pK_1^s - pK_2^s)/2 \qquad (7)$$

$$pK'^s_2 = (pK_1^s + pK_2^s)/2 \qquad (8)$$

The potentiometric titration curves are measured at the hydrogen electrode. A 10^{-2} M fluoride solution ($Et_4NF.2H_2O$) is neutralized

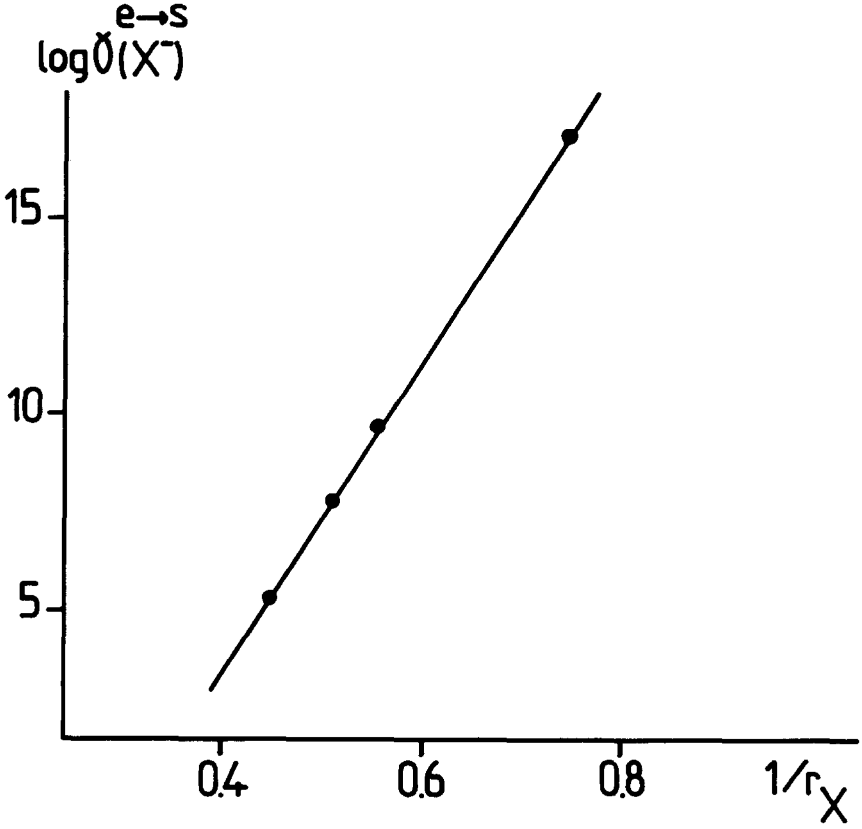

Fig. 1. Variation of the solvation transfer activity coefficient $\log\gamma^{w\to s}(X^-)$ ($X^- = F^-, Cl^-, Br^-$ or I^-) as a function of the inverse of the crystallographic radius.

by use of perchloric acid in the different CH_3CN-H_2O mixtures at constant **ionic strength** (Et_4NClO_4 10^{-1} M). The titration curves relative to the 10% and 20% water mixtures are presented in Fig.2.

In the anhydrous mixture, acid-base constants of the HF_2^-/F^- and HF/HF_2^- pairs are determined **by UV-Vis** spectrophotometry using p-nitrophenol (pKa = 20.7) and thymol blue (pKa = 13.4) as indicators [16].

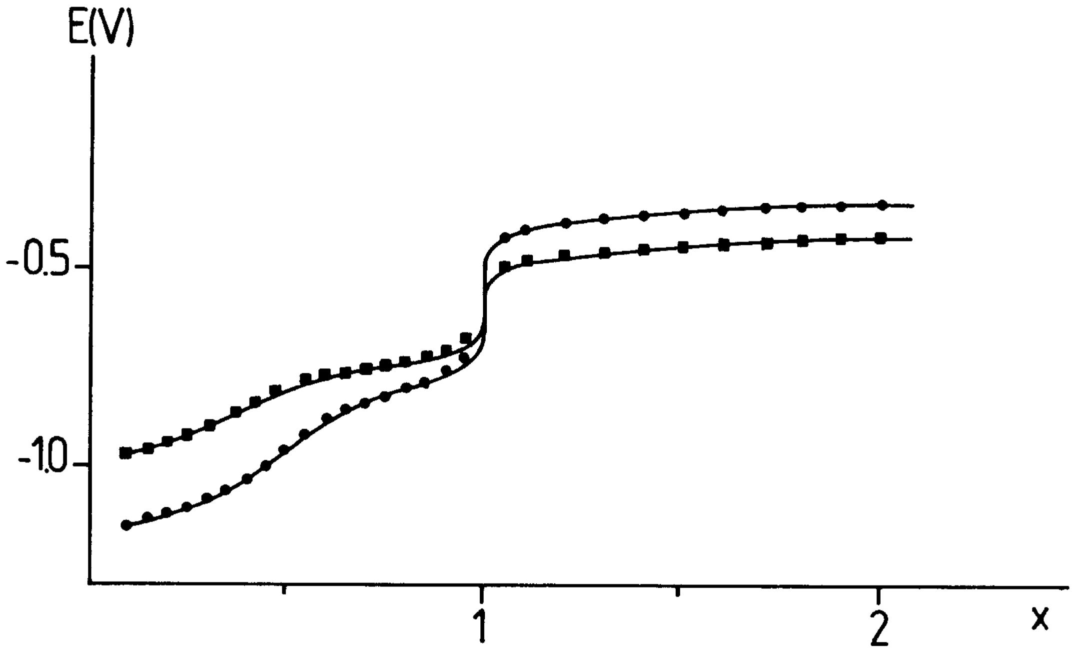

Fig. 2. Potentiometric titration curves of $Et_4NF.2\ H_2O$ (10^{-2} M) with $HClO_4$ in the CH_3CN-10% H_2O medium (•), in the CH_3CN-20% H_2O medium (■).
Et_4NClO_4 5.10^{-2} M. Hydrogen electrode.

Solvation transfer activity coefficients $\log \gamma^{w\to s}(H^+)$ are determined from the measurement of the hydrogen electrode potential in the different mixtures. Those of the HF_2^- and HF species are calculated according to the relations (9) and (10) which result from the equilibria (3) and (4).

$$pK_1^s - pK_1^w = \log \gamma^{w\to s}(H^+) + 2 \log \gamma^{w\to s}(F^-) - \log \gamma^{w\to s}(HF_2^-) \quad (9)$$

$$pK_2^s - pK_2^w = \log \gamma^{w\to s}(H^+) + \log \gamma^{w\to s}(HF_2^-) - 2\log \gamma^{w\to s}(HF) \quad (10)$$

where pK^s and pK^w represent the constants in the CH_3CN-H_2O mixtures and in pure water respectively.
The results are given in Table II.

TABLE II

pK_1^s and pK_2^s acidity constants of the conjugate pairs HF_2^-/F^- and HF/HF_2^-, $pK'_1{}^s$ and $pK'_2{}^s$ dissociation constants of HF_2^- and HF and solvation transfer activity coefficients of the species F^-, H^+, HF_2^- and HF from water to CH_3CN-H_2O mixtures (21°C).

%H_2O (mole)	pK_1^s	pK_2^s	$pK'_1{}^s$	$pK'_2{}^s$	$\log \gamma(F^-)$	$\log \gamma(H^+)$	$\log \gamma(HF_2^-)$	$\log \gamma(HF)$
0	23.2	10.5	6.4	16.8	16.7	5.7 [a]	19.7	8.7
10	16.9	8.2	4.4	12.5	11.2	1.6	10.9	3.5
20	12.1	6.1	3.0	9.1	8.0	0.2	7.9	2.3
30	10.2	4.8	2.7	7.5	6.8	0.3	7.5	2.8
40	9.0	3.7	2.7	6.4	5.9	0.3	6.9	2.9
50	8.4	3.2	2.6	5.8	5.1	0.2	5.8	2.7
60					4.5			
70	7.5	2.5	2.5	5.0	3.7	0.0	3.7	1.9
80					2.7			
90					0.8			
100	3.8	2.6	0.6	3.2	0.0	0.0	0.0	0.0

[a] Reference 17

The strength of the bases F^- and HF_2^- increases markedly as the water content decreases. Such an effect can be accounted for the strong desolvation of these ions whose log $\gamma^{w->s}$ values are high and very close. On the contrary, the desolvation of the H^+ ion is only slightly affected by the water content in the still hydrated mixtures. The desolvation of the molecular species HF is much lower than that of the F^- and HF_2^- anions and does not vary much with the water content.

In the anhydrous medium, species in solution are generally much less solvated. In particular, the proton and HF are strongly desolvated when transferred from the 10% water mixture to the anhydrous solvent. Such a result seems logical since there are strong interactions between these species and the water molecules.

The $pK'_1{}^s$ and $pK'_2{}^s$ constants which represent the pF^- level of the equimolar buffers HF_2^-/HF and HF/H^+, give evidence that their pF^- values are very different in the weakly hydrated mixtures and in the anhydrous medium. In transferring from the 10% water mixture to the anhydrous medium, they increase from 3.0 to 6.4 for HF_2^-/HF buffer and from 9.1 to 16.8 for HF/H^+. In the case of mixtures with an higher water content, the pF^- value of the HF_2^-/HF buffer remains constant but that of the HF/H^+ buffer keeps on decreasing. Thus, the pairs HF_2^-/HF and HF/H^+ can be used as pF^- buffers both in anhydrous acetonitrile and in partially hydrated acetonitrile to maintain high pF^- values.

This parameter can be modified by using acid-base pairs. For example, a 10^{-2} M hydrofluoric acid solution has a pF^- value of 9.4 in anhydrous acetonitrile; in the presence of the acid-base buffer $C_5H_5NH^+$ (10^{-2} M)/C_5H_5N (10^{-2} M) (pKa = 12.3 [18]), the pF^-

value decreases to 6.5. F^- ions are formed according to the reaction:

$$HF + C_5H_5N \Longleftrightarrow C_5H_5NH^+ + F^- \qquad (11)$$

which is characterized by the constant:

$$[C_5H_5NH^+][F^-]/[HF][C_5H_5N] = 10^{-4.5} \qquad (12)$$

In a similar way, the pF^- buffering ability of the HF_2^-/HF pair depends on the presence of a base (B). The equilibrium :

$$HF_2^- + B \Longleftrightarrow BH^+ + 2\ F^- \qquad (13)$$

shows that the addition of the base (B) in high concentration leads to decrease of the pF^- level.

The comparison of the pF^- scales in the acetonitrile-water mixtures allows characterization of the reactivity of HF_2^-/HF and HF/H^+ and of molar fluoride solutions (Fig.3). It increases in the case of HF_2^-/HF and fluoride solutions as the water content decreases since HF_2^- and F^- species are strongly desolvated. On the contrary, the reactivity of the HF/H^+ buffer varies little with the water content: the desolvation of the HF molecule remains close to that of the proton.

A comparison of the pH scales in the acetonitrile-water mixtures shows (Fig.4) that the variation of the basic strength of the HF_2^-/F^- pair as a function of the water content is larger than that of the HF/HF_2^- pair. For the first one, pH referred to water varies by 11.5 units on transferring from water to CH_3CN-10% H_2O mixture. For the second one, the variation is of 3.9 units. The

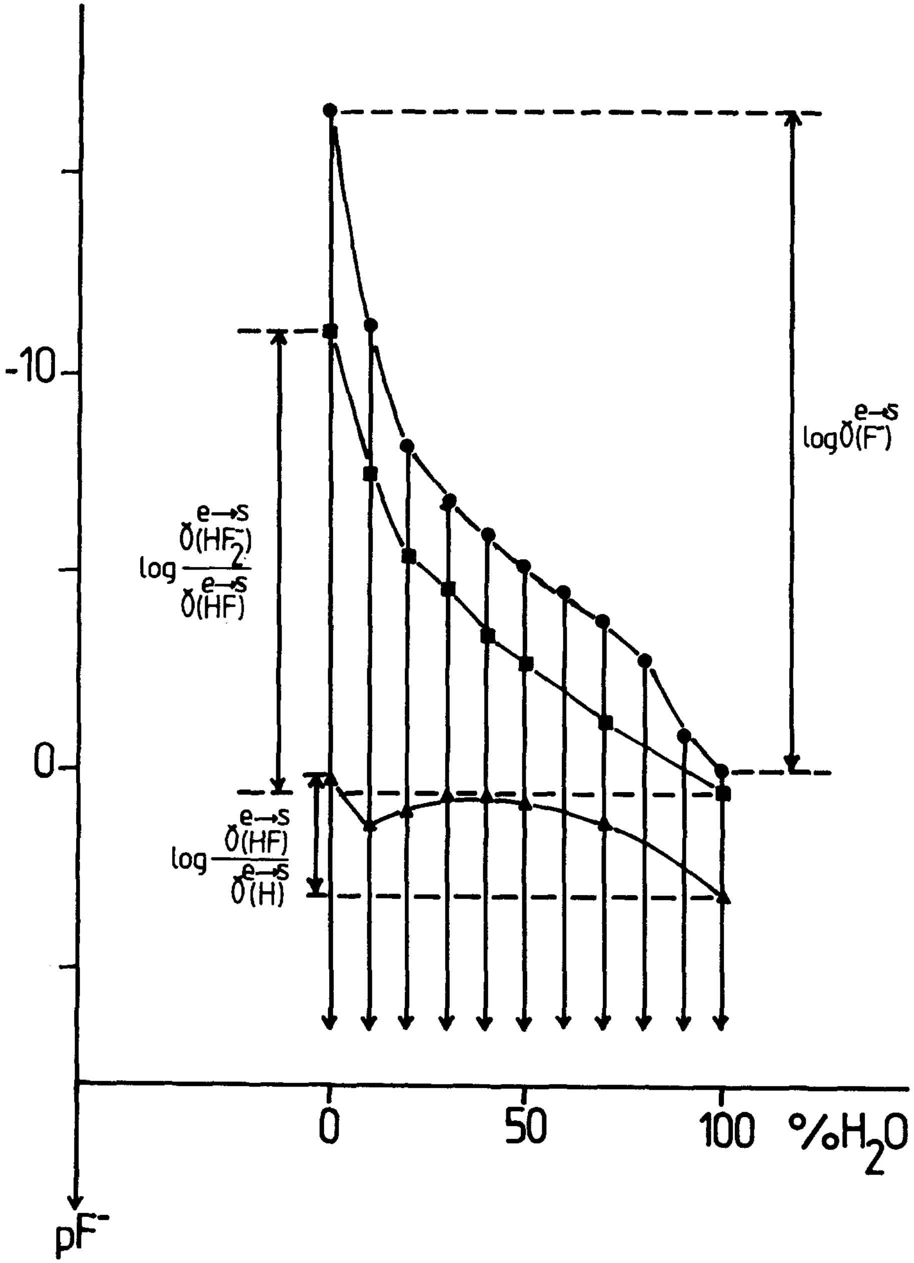

Fig. 3. pF^- level (referred to water) of the fluoride solution (1M) (Et_4NF or Bu_4NF) (●) and of the HF_2^-/HF (■) and HF/H^+ (▲) pairs in the CH_3CN-H_2O mixtures.

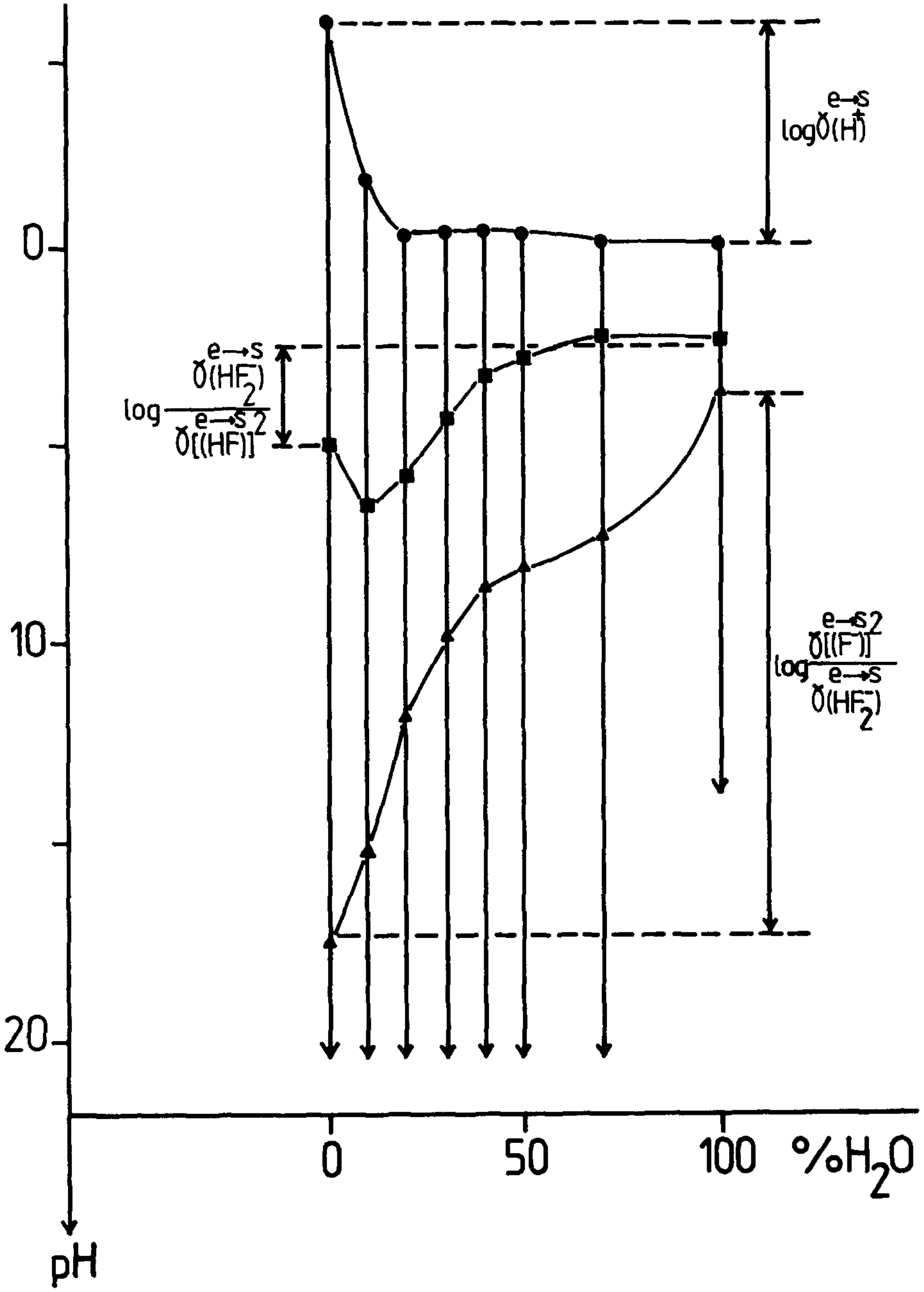

Fig. 4. pH level (referred to water) of 1M H^+ solution ($HClO_4$) (•) and of the HF/HF_2^- (■) and HF_2^-/F^- (▲) pairs in the CH_3CN-H_2O mixtures.

pH level of the HF/HF_2^- pair increases by 1.6 units when tranferring from the CH_3CN-10% H_2O mixture to the anhydrous medium due to the strong desolvation of the HF molecule between the two media.

It appears also from the Fig.4 that the reactivity of the free proton in solution remains the same in the presence of water, but increases notably in the anhydrous solvent.
In addition, F^- solvation transfer activity coefficients allow prediction of, for example, thermodynamical changes in the reducing power of metals whose fluorides are insoluble. For such redox systems as $MF_{2(s)}/M_{(s)}$ (M = Pb, Mg...) characterized by:

$$M_{(s)} - 2\ e^- + 2\ F^- \Longleftrightarrow MF_{2(s)} \qquad (14)$$

we have the relation:

$$E_o^s\ (mV) = E_o^w - 59 \log \gamma^{w->s}(F^-) \qquad (15)$$

Thus, in the presence of fluoride, the reducing power of lead and magnesium for example, is higher in the CH_3CN-20% H_2O mixture than in water since their normal potentials differ by 470 mV.
This result can also be used to calculate the solubility of fluorides whose solubility product in water and solvation transfer activity coefficients of the conjugate cations are known. For example, rubidium fluoride whose solvation transfer activity coefficient is assumed to be equal to 1 (Pleskov hypothesis) [19], is four times less soluble in the CH_3CN-20% H_2O mixture than in pure water.

CONCLUSION

The determination of the solvation transfer activity coefficient of fluoride: $\log \gamma^{w->s}(F^-)$ in the CH_3CN-H_2O mixtures gives evidence for the strong desolvation of the fluoride ion even in still hydrated mixtures. The log $\gamma^{w->s}(F^-)$ determined in anhydrous acetonitrile fits the relationship existing between log $\gamma^{w->s}$ of the halides and the inverse of the crystallographic radius. The pF^- buffering ability of the HF_2^-/HF and HF/H^+ pairs in these mixtures depends on the water content of the mixtures.

The pF^- level referred to water imposed by 1M fluoride solution and equimolar mixture HF_2^-/HF varies by 16.7 and 11.0 units respectively on transfer from water to anhydrous acetonitrile.

The pH scales established in these mixtures show the increase in basic strength of F^- and HF_2^- in the mixtures with a low water content.

EXPERIMENTAL

Acetonitrile (S.D.S. Puran A.R.) was dehydrated on molecular sieves (3 Å) for 48 hours. Its water content, determined by the Karl-Fisher coulometric method, did not exceed $5\ 10^{-4}$ M.
All the solutions of anhydrous compounds were prepared and kept in a glove box under a dry argon atmosphere.
The electrolyte Et_4ClO_4 (Fluka, A.R.) was recrystallized twice in ethanol and dried under vacuum at 60°C for 16 hours.
$Et_4NF.2H_2O$ (Fluka, A.R.) used as an electrolyte in hydrated mixtures was recrystallized twice in acetonitrile and benzene. In the anhydrous medium, Bu_4NF fluoride solutions were prepared from Bu_4NI and AgF.
The 1M perchloric acid solution was prepared from the 70-72% $HClO_4$ commercial solution (Merck, A.R.). A 0.1 M perchloric acid solution in acetic acid was used in the case of anhydrous acetonitrile.
p-Nitrophenol and thymol blue were Aldrich (A.C.S.) reagents.

The potentiometric measurements were realized with a Tacussel Aries 10000 millivoltmeter. The indicating electrode was either the fluoride specific electrode Orion 94.09.00 or the hydrogen electrode prepared as recommanded by Charlot *et al.* [20]. The reference electrode was the half cell $Ag_{(s)}/AgClO_4$ 10^{-2} M, Et_4ClO_4 10^{-1} M, CH_3CN.

For the spectrophotometric measurements, we used a UV-Vis DU7 Beckman spectrophotometer.

REFERENCES

1 F. Bazine and J. Bessiere, submitted to Electrochimica Acta.
2 *idem*, in preparation.
3 M. L'Her, D. Morin-Bozec and J. Courtot-Coupez, J. Electroanal. Chem. Interf. Electrochem., 61 (1975) 99.
4 M.H. Abraham , Monatsch. Chem., 110 (1979) 517.
5 B.G. Cox, G.R. Hedwig, A.J. Parker and D.W. Watts, Austr. J. Chem., 27 (1974) 477.
6 A.J. Parker, U. Mayer, R. Schmid and V. Gutmann, J. Org. Chem., 43 (1978) 1843.
7 S. Ahrhland, K. Nilsson and B. Tagesson, Acta Chem. Scand. A, 37 (1983) 193.
8 J.Y. Cabon, M. L'Her and J. Courtot-Coupez, J. Chem. Res.(S) (1981) 196; (M)(1981) 2433.
9 **H. Strehlow, in J.J. Lagowski (ed.), Electrode potentials in non-aqueous solvents, The chemistry of non-aqueous solvents, Vol. 1, Academic Press, New York, 1966.**
10 A. Vaillant, J.D. Devynck and B. Tremillon, J. Electroanal. Chem. Interf. Electrochem., 57 (1974) 219.
11 C. Louis, Thèse de Doctorat d'Etat ès-Sciences Physiques, Nancy, France, 1983.
12 B.G. Cox, A.J. Parker and W.E. Waghorne, J. Phys. Chem.,78 (1974) 1731.
13 A. Bhattacharya, K. Das and K.K. Kundu, Bull. Chem. Soc. Japan., 54 (1981) 2194.
14 J.F. Coetzee and M.M. Martin, Anal. Chem., 52 (1980) 2412.
15 J.F. Coetzee and J.J. Campion, J. Am. Chem. Soc., 89 (1967) 2517.
16 I.M. Kolthoff, M.K. Chantooni Jr.and M. Bhowmik, Anal. Chem., 39 (1967) 315.
17 Y. Marcus, 'Ion solvation' Wiley Interscience, New York, 1985, p.166.
18 O. Popovych and R.P.T. Tomkins, Wiley Interscience, New York, 1981, p.63.
19 V.A. Pleskov, Upsekhi. Khim., 16 (1947) 254.
20 G. Charlot, J. Badoz-Lambling and B. Tremillon, Les Réactions électrochimiques. Méthodes électrochimiques d'analyse, Masson et Cie, Paris, 1959, p.47.