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Report:

*Background***:** The investigations on the properties of nonaqueous and aqueous-organic electrolytes carried out by our research group in the last years have been so far prompted by specific demand of thermodynamic and transport quantities for the important intercorrelated fields of electrochemistry, corrosion and electroanalysis. Now, however, the data set so achieved is so wide and consistent to prompt us to plan their experimental and theoretical systematization for an interpretative study of the effect of solvent nature and properties on the structure of the solvation sphere and therefore on the thermodynamic and transport properties of the electrolyte solutions considered. In this context, extremely appealing was the possibility of combining the clues on solvation sphere obtained by electrochemical methodologies with a direct spectroscopic investigation of the solvation sphere structure. To this aim EXAFS is a most appropriate technique.

Experimental: In order to study the competition between water and acetonitrile in the solvation cage of alkali and alkali-earth cations we have studied the following solutions:

RbTF 0.1 m in (water + acetonitrile) with 0, 25, 50, 75, 100% in acetonitrile (target ion: Rb)
CsTF 0.1 m in (water + acetonitrile) with 0, 25, 50, 75, 100% in acetonitrile (target ion: Cs)
$Sr(TF)_2$ 0.06 m in (water + acetonitrile) with 0, 25, 50, 75, 100% in acetonitrile (target ion: Sr)
$Ba(TF)_2$ 0.1 m in (water + acetonitrile) with 0, 25, 50, 75 % in acetonitrile (target ion: Ba)

where TF = triflate ($CF_3SO_3^-$). We have chosen this counter-anion to increase the solubility of the salts in the above solvent mixtures, as suggested by D'Angelo and coworkers[1]. The triflate salts have been synthesized in our laboratories, before the experiment, using triflic acid and the appropriate alkali compounds.

Moreover, in order to investigate the role of the anion in the solvation cage we have studied the following solutions:

$BaCl_2$ 0.1 m in water (target ion: Ba^{2+}); CsCl 0.1 m in (water + acetonitrile) with 0, 75 % in acetonitrile (target ion: Cs^+); CsBr 0.1 m in (water + acetonitrile) with 0, 75 % in acetonitrile (target ion: Cs^+); CsF 0.1 m in (water + acetonitrile) with 0, 75 % in acetonitrile (target ion: Cs^+); RbI 0.1 m in (water + acetonitrile) with 0, 50, 75 % in acetonitrile (target ion: I^-)
(The last spectrum plus the Xe one also afforded a comparison in the regular atomic number sequence: I, Xe, Cs, Ba). Some of the solutions have been prepared in our laboratories before the experiment and some have been prepared in the Gilda Chemical Laboratory using commercial high purity grade chemicals. The solutions were kept in an appropriate Teflon cell (1 or 2.5 cm length) with Kapton windows, specifically made by the Gilda Group in Grenoble. We have recorded one spectrum for each solution (except in the case of 100%-pure solvent, water or acetonitrile, where we have recorded 2 or 3 spectra showing very good reproducibility) using the Gilda Beamline (BM8) at the K-edge energies of the target cations: Rb^+, Cs^+, Sr^{2+} and Ba^{2+} (plus I^- and Xe). The high quality of the recorded spectra is adequate to the multiple scattering contribution analysis which is essential in our case because of the linear structure of the acetonitrile molecule (CH_3–C≡N) and which we are now performing using the program GnXAS by Di Cicco and Filipponi. From a first qualitative survey, the spectra recorded confirm our expectations upon the solvation cage of the above cations. In particular we observe only a small EXAFS signal in the case of Cs^+ with respect to the Xenon one, which indicates poor or no solvation at all, consistently with our electrochemical investigations. Comparing EXAFS spectra for the four cations, we observe an increasing modulation (i.e. solvation) with increasing charge and decreasing radius, as expected by both theory and indirect experimental evidencies. The spectra of the same cations in different mixed solutions look quite similar at first approach, although some differences can be observed, expecially after background subtraction. Only an exhaustive data processing will likely allow us to precisely assess these differences. So far we started the analysis of the aqueous Rb^+ solution. In this case we observe two spectral edges due to multiple electron excitation, which are eliminated in the background subtraction. The preliminary result of this analysis is a distorted octahedral structure around the cation with the two longitudinal water molecules at 2.56 Å and the four planar ones at 2.86 Å. This confirms what other authors[2,3] have already found by other methods, although with small differences. In fact, they found six water molecules around the Rb^+ ion at approximately the same distance, but they were not able to resolve two different distances, probably due to the lower concentration of their samples and to the mediocre acquisition of the raw spectra. In the case of pure acetonitrile the fitting procedure leads to an octahedral structure with six molecules at 2.90 Å. The contribution of the multiple scattering here is high. This is not surprising and is due to the "focusing effect" which enhances the three body paths in quasi-linear three body configurations. But, if we suppose a perfect linear structure, we have a too high contribution. Therefore we have to consider an angle N-C-C of approximately 134°. This is probably due to a possible contribution of the triple bond in the charge compensation of the Rb^+ ion. This is in accordance with previous works[1].
The above first results are the object of the following meeting presentations:

1. L. Falciola, M. Liotto, P.R. Mussini, T. Mussini, P. Pelle, F. D'Acapito and S. Colonna: "Solvation sheaths of large alkali and alkali earth cations in (water+acetonitrile) solvents: a combined electrochemical and EXAFS investigation"; oral presentation at the Joint Meeting of the Physical Chemistry and Electrochemistry Divisions of the Italian Chemical Society. (Ferrara, (I), 23-28 giugno 2002)
2. L. Falciola, P.R. Mussini, T. Mussini, F. D'Acapito and S. Colonna: "EXAFS investigation of solvation sheaths of large alkali and alkali earth cations"; oral presentation at the 17th IUPAC Conference on Chemical Thermodynamics. ICCT '02 (Rostock (D), July 28 - August 02, 2002).

References:

1) P.D'Angelo, N.V. Pavel; *J. Chem. Phys.*, 111 (11), **1999**, 5107-5115.
2) J.L.Fulton, D.M. Pfund, S.L. Wallen, M. Newville, E.A. Stern, Yanjun Ma; *J. Chem. Phys.*, 105 (6), **1996**, 2161-2166.
3) Y. Kubozono, A. Hirano, H. Maeda, S. Kashino, S. Emura, H. Ishida; *Z. Naturforsch.*, 49a, **1994**, 727-729.