The effects of electrolytes on the depolarization of positive muons

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Measurements are reported of μ-e decay polarization in solutions of different strong electrolytes as a function of concentration. The data are interpreted within the framework of the muonium theory of depolarization of positive muons in a medium. The mechanisms of the various processes are discussed and the rate constants are determined for the interaction between muonium and a number of ions.

INTRODUCTION

Positive-muon depolarization in water and in water solutions of electrolytes is of considerable interest, above all because of the exceptional role of hydrogen in such systems. On the other hand, the behavior of the positive muon in polar liquids is somewhat unexpected if we confine our attention to conventional ideas. However, one would hope that a complete understanding of the depolarization mechanism will yield new and important information on the physical and chemical properties of water solutions of electrolytes. This refers chiefly to the interpretation of hydrogen reaction mechanisms.

The first measurements of the polarization of the positive muon in water and in water solutions (up to 0.1 mole/liter) were reported by Swanson,[1] who found that the polarization in water and in solutions was independent of the concentration of acids or bases (in the range pH = 1–12) and amounted to $P \approx 0.6$. We must note at once that both results give rise to certain questions. Firstly, since in pure water in weak magnetic fields the polarization is partly conserved, it might be thought that atomic muonium, formed during the slowing down of the positive muons, will rapidly enter into chemical reactions, forming a diamagnetic compound. It is not clear, however, which particular reaction is responsible for this process. Secondly, it is not at all clear why the addition of relatively high concentrations of hydrogen and hydroxyl ions does not affect the muonium depolarization processes.

Measurements of the polarization of positive muons in water were later performed by a number of workers.[2-6] The energy spectrum of positrons from muon decays and the initial polarization of the positive muon beam were measured in,[3,4] using very pure specimens, and the contribution due to mesons stopping in the target walls was reduced to a minimum. As a result, substantial statistical material was accumulated. There are, therefore, grounds for supposing that these data are the most accurate. There is good agreement with the measurements of positive muon polarization in water at room temperature, performed in the present work ($P = 0.623 \pm 0.004$).

The aim of the present research was to investigate positive muon depolarization in water solutions of electrolytes at high concentrations of the latter (right up to the saturation limit) since, in general, the introduction of a strongly dissociating electrolyte should undoubtedly affect the behavior of the positive muon (muonium) in the medium, and previous experiments[1] were performed with weak solutions.

EXPERIMENTAL DATA AND DISCUSSION

The experimental work was carried out on the synchrocyclotron at the Laboratory for Nuclear Problems, Joint Institute for Nuclear Research, using the positive-muon beam in the strongly focusing meson channel.[7] The experimental techniques and the processing of the data were described in detail in[8,9]. Figure 1 shows the experimental results on the positive-muon polarization in water solutions of acids and bases as a function of their concentration, and Figs. 2 and 3 show the analogous data for different salts which are strong electrolytes. We used magnetic fields of 50–100 Oe, perpendicular to the positive-muon spin. For the diamagnetic ions, the positive-muon polarization remained unaltered throughout the observation time (~6.5 μsec), i.e., we had a "residual" polarization in the sense defined in[10-12]. For paramagnetic ions, there is a slow (time scale of a few microseconds or more) depolarization,[13] and Fig. 3 shows the "residual" polarization at time t = 0. The rate of depolarization in solutions of paramagnetic ions is due to interactions between the magnetic moments of the positive muon and the ion, which is confirmed by the good agreement with NMR data (with suitable corrections).[13,14] Existing data thus indicate that, after 10^{-9}–10^{-8} sec, the positive muon is found either as part of a diamagnetic chemical compound or exists as a "free" or hydrated meson.

Let us summarize the main experimental results.

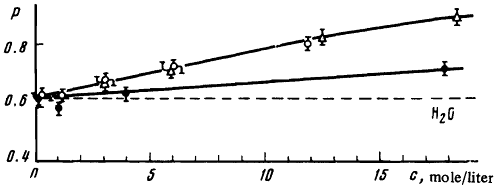

FIG. 1. Polarization of positive muons in water solutions of acids and bases as a function of their concentration: Δ–NaOH, ○–HClO₄, ●–H₂SO₄. Broken line–polarization for a pure solvent.

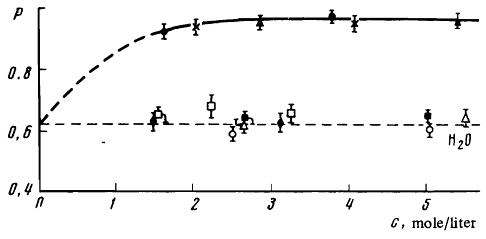

FIG. 2. Polarization of positive muons as a function of the concentration of diamagnetic compounds: ●–Mg(NO₃)₂, ○–MgCl₂, ▲–Ca(NO₃)₂, Δ–CaCl₂, X–Zn(NO₃)₂, □–ZnSO₄, ■–NaCl, ◆–glucose.

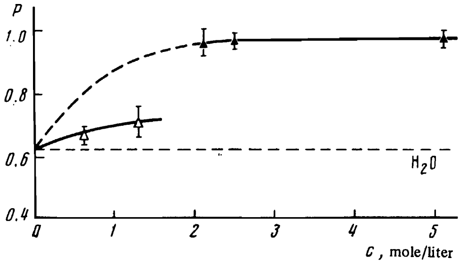

FIG. 3. Residual polarization of positive muons (at time t = 0) as a function of the concentration of salts with paramagnetic cations: ▲–$Cu(NO_3)_2$, ▲–$CuSO_4$.

1. The introduction into a solution of the anion NO_3^-, capable of oxidation-reduction reactions, sharply increases the residual polarization up to the limiting value, and the cation has a much smaller effect.

2. Saturation of the solution with the cations Ca^{++}, Zn^{++}, Mg^{++}, and Na^+ and the anions Cl^- and SO_4^{--} does not modify the polarization of the positive muons, as compared with the pure solvent.

3. The addition of the cations Fe^{+++},[3,15] Cu^{++}, and H^+ results in an increase in the polarization but to a different degree.

4. The positive-muon polarization increases with increasing concentration of the anions ClO_4^- and OH^-.

5. The introduction of nondissociating compounds (glucose) has no appreciable effect on the polarization.

As can be seen, the observed phenomena are quite varied. We shall, however, attempt to carry out an analysis based on the assumption that the thermalization of the positive muon in water or in water solution of an electrolyte is followed by the formation of muonium which then enters into different fast chemical reactions, the final byproduct of which is a diamagnetic compound incorporating muonium.

First, we note that the addition of the anion NO_3^- suppresses in an obvious fashion the other processes involving the participation of muonium. Consequently, the muonium very rapidly enters into a chemical reaction either with the ion NO_3^- or the HNO_3 molecules which may be present in dynamic equilibrium in solutions with a high concentration of NO_3^-. Although the last possibility is problematic, it is useful to include it as one of the possible hypotheses.

Thus, it is natural to assume that the fast reactions involving the reduction of the anion NO_3^- proceed as follows:

$$\mathrm{Mu}+\mathrm{NO_3^-}\to(\mathrm{OMu})^-+\mathrm{NO_2}. \tag{1}$$

The analogous reaction for hydrogen is well known in radiation chemistry.[16] The molecule HMuO is formed in the solution after muonium becomes part of the composition of the diamagnetic ion $(OMu)^-$. In this case, we have the possibility of slow depolarization of the positive muon in the solvate shell of the paramagnetic ion, for example, Cu^{++}. The isotope exchange process

$$\mathrm{Mu}+\mathrm{HNO_3}\to\mathrm{MuNO_3}+\mathrm{H}, \tag{2}$$

which competes with (1) is less probable, as already noted.

This example clearly illustrates the possibilities of the positive-muon method. Since the rate of the muonium reaction is directly proportional to the concentration of the NO_3^- ions, it is possible to measure the degree of dissociation of, say, the nitric acid and its salts. There is evidence in the literature for the incomplete dissociation of HNO_3 in water solutions with high concentrations.[17] According to our data, the degree of dissociation of the nitrates which we have investigated is roughly the same.

We must now consider the third of the above five results. Here, the picture is quite clear. Oxidation-reduction reactions with ions of variable valency, or the charge transfer between muonium and the hydrated proton, may occur as follows:

$$\mathrm{Fe^{+++}}+\mathrm{Mu}\to\mathrm{Fe^{++}}+\mu^+, \tag{3}$$

$$\mathrm{Cu^{++}}+\mathrm{Mu}\to\mathrm{Cu^{+}}+\mu^+, \tag{4}$$

$$\mathrm{H^{+}}+\mathrm{Mu}\to\mathrm{H}+\mu^+. \tag{5}$$

In all cases, the positive muon (or hydrated meson) may form the HMuO molecule. Subsequently, the polarization may remain unaltered if paramagnetic centers are absent, but, when the latter are present (for example, Cu^{++}), slow depolarization processes will take place. Estimates of the influence of the isotope effect on the energy balance in the reactions are difficult because the heat of hydration of Mu^+ is unknown. At any rate, it is expected that this effect is relatively unimportant.

We now note an important fact which is due to the exclusive presence of the muonium atoms throughout the volume under investigation at a given time. If, for example, the elementary direct reaction (5) takes place, then the reverse reaction is simply excluded because of the absence of atomic hydrogen. This remark is, of course, valid for practically all the muonium reactions considered in this paper.

Comparison with experimental data on the dependence of the positive-muon polarization on the concentration of $HClO_4$ and H_2SO_4 (it is well known that $HClO_4$ completely dissociates even at high concentrations) shows that the reaction with H^+ occurs with a lower rate than with the ion Cu^{++}, while the reduction reaction with Fe^{+++} [3,15] has a maximum rate comparable with that for (1).

Several experiments performed on a solution of $NaClO_4$ show that, in this case, the polarization is slightly reduced as compared with $HClO_4$. Since the effect of the cation Na^+ is absent, it may be concluded that the probability of the reduction reaction for the ion ClO_4^- exceeds the probability of charge transfer between the positive muon and the proton. Experiments with H_2SO_4 (Fig. 1) confirm this qualitative conclusion. Finally, the effect of the hydroxyl ions OH^- in the alkali solution may be interpreted by assuming the formation of the ion $(OMu)^-$ through the intermediate stage of the molecular ion $(HMuO)^-$:

$$\mathrm{OH^-}+\mathrm{Mu}\to(\mathrm{HMuO})^-\to\mathrm{H}+(\mathrm{OMu})^- \tag{6}$$

A similar mechanism can be used to describe the behavior of muonium in pure water (in the absence of dissolved gases or other impurities). Here, the muonium atom becomes attached to the H_2O molecule (or the dimer H_4O_2) with the formation of the hydrated atom Mu. A similar conclusion on the hydration of the atom H in aqueous media was reported in connection with radiation chemistry in[18]. The next possible step is the formation of the diamagnetic molecule HMuO, as follows:

$$\mathrm{Mu}+(\mathrm{H_2O})_n\rightarrow\mathrm{Mu}(\mathrm{H_2O})_n\rightarrow\mathrm{HMuO}+\mathrm{H}+(\mathrm{H_2O})_{n-1}. \tag{7}$$

There is a further hypothetical possibility,[4] namely, the presence of dimeric associations in the liquid phase allows the migration of the unpaired electron over the hydrogen bond. In this case, once the muonium stage is completed, there is a substantial reduction in the critical magnetic field in the hydrated radical, which is essential for breaking the coupling between the magnetic moments of the electron and the positive muon, and the result of this is that the latter will precess with the "free" meson frequency.

It is clear that all the experimental results can be adequately explained by the hypothesis that short-lived muonium is formed in the water, but further accumulation of experimental data is very desirable so that a more complete verification of the hypothesis may be carried out. We note that for diamagnetic ions and for pure water there is apparently no reason to suppose that the relaxation frequency of the electron spin in muonium (characterized by the parameter ν in[10-12]) is different from zero. However, the presence of paramagnetic ions (for example, $\mathrm{Cu^{++}}$) may lead to a change in the electron-spin relaxation frequency, and this must be taken into account in calculations.

We shall now carry out some quantitative estimates, using the theoretical formalism developed in[11,12]. Since the magnetic fields used in the experiments are low, the absolute polarization may be used in the simpler formula for the polarization in longitudinal fields:[12]

$$\frac{P}{2(1-P)}=\frac{1+2\nu\tau}{(\omega_0\tau)^2}+\frac{{}^1\!/_2+x^2}{1+2\nu\tau}. \tag{8}$$

In this expression τ is the mean lifetime of muonium as a polarized system, $^1\!/_2\nu$ is the mean reciprocal of the relaxation time for the electron spin in the muonium atom in the medium, ω_0 is the hyperfine splitting frequency for muonium in the medium, $x = (\omega'/\omega_0)(1+\xi)$, $\omega' = eH/mc$ is the Larmor frequency of the electron spin in the external magnetic field, and $\xi = m_{\mu^+}/m_e \approx 1/207$ is the ratio of the magnetic moments of the positive muon and electron.

We emphasize that τ, ν, ω_0 are determined by the properties of the medium and are phenomenological parameters which must be established experimentally. It is well known that, in vacuum, $\omega_0 = 2.8\times 10\ \mathrm{sec}^{-1}$ and the corresponding critical magnetic field produced by the positive muon at the point at which the electron is located is $H_0 = 1585$ Oe.

Neglecting x^2 in (8) in comparison with unity, we obtain the following final expression:

$$\frac{P}{2(1-P)}=\frac{1+2\nu\tau}{(\omega_0\tau)^2}+\frac{1}{2(1+2\nu\tau)} \tag{9}$$

The same formula can, of course, be obtained from the formulas given in[12] for the polarization in perpendicular magnetic fields under the condition $x \ll (2/\omega_0\tau) + (4\nu/\omega_0)$.

Assuming that for pure water $\nu\tau \ll 1$, we obtain $\omega_0\tau(\mathrm{H_2O}) = 1.75 \pm 0.04$ ($P = 0.623 \pm 0.004$). The value of the hyperfine splitting frequency can be determined, for example, from the dependence of the polarization on the longitudinal magnetic field. However, for water, as for other covalent diamagnetic compounds,[19,20] there is no reason to expect any difference between the values of ω_0 in the muonium atom and in vacuum. In this case, the characteristic time for the interaction between muonium and water molecules is $\tau = (6.25 \pm 0.13)\times 10^{-11}$ sec. The experimental results can be used to estimate the characteristic interaction times (rates of the corresponding reactions) between muonium and different ions.

Rate constants for reactions between muonium and ions in water solutions

Cation	$k\cdot 10^{-8}$, Liters/mole·sec	Anion	$k\cdot 10^{-8}$, Liters/mole·sec	Cation	$k\cdot 10^{-8}$, Liters/mole·sec	Anion	$k\cdot 10^{-8}$, Liters/mole·sec
$\mathrm{Cu^{++}}$	56	$\mathrm{NO_3^-}$	170	$\mathrm{Zn^{++}}$	$\leqslant 2$	$\mathrm{Cl^-}$	<1
$\mathrm{H^+}$	6	$\mathrm{OH^-}$	18	$\mathrm{Mg^{++}}$	<1	$\mathrm{SO_4^{--}}$	<1
$\mathrm{Ca^{++}}$	<1	$\mathrm{ClO_4^-}$	12	$\mathrm{Na^+}$	<1		

The results of the calculations are listed in the table (the absolute rate constant for the reaction between muonium and an ion is $k = 1/\tau c$ where c is the concentration of the ion in mole/liter). We note that the quantity ν for the paramagnetic ion $\mathrm{Cu^{++}}$ is small in comparison with corresponding rate of the chemical reaction stabilizing muonium. It is estimated that $\nu(\mathrm{Cu^{++}}) < 10^8\ \mathrm{sec}^{-1}$ (for the paramagnetic ion concentration of one mole/liter) which is not inconsistent with the data on the rate of spin-exchange interactions with the $\mathrm{Cu^{++}}$ ion.[13]

CONCLUSIONS

The substantial change in the residual polarization of positive muons when strong electrolytes are introduced into solution appears to us to reveal a broad and promising field for research. The study of positive-muon depolarization in a medium may turn out to be a very convenient and powerful method of investigating physical and chemical processes in highly concentrated solutions, in the elucidation of the kinetics of chemical reactions in solution, and in the determination of the dissociation constants for strong electrolytes and the rates of reactions between muonium and ions. The hypothesis proposed in this paper, namely, the existence of short-lived muonium in water, and the above method of determining the phenomenologic parameters of the theory of depolarization of positive muons in a medium, extend the possibilities of the muonium method.

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