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Abstract

Full Text

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STUDY OF THE STATE OF RADIOACTIVE ISOTOPES IN EXTREMELY DILUTE SOLUTIONS BY THE DIFFUSION METHOD

At present the diffusion method is one of the principal methods for studying the state of chemical elements in solutions. However, if one does not count the early works ([1–3]), this method is used chiefly for studying the state of macroquantities of elements in solutions ([4–8]).

For a number of reasons–interionic interaction, the need to consider not only the motion of dissolved molecules and ions but also the motion of solvent molecules, dehydration phenomena, and others–the interpretation of experimental data in concentrated solutions is greatly complicated, and in some cases altogether impossible.

In the region of extreme dilution such difficulties do not arise, and the experimental diffusion coefficients may be regarded as quantities describing the independent motion of dissolved particles in an ideal solution.

Measurement of the diffusional ability of a series of radioactive isotopes in extremely dilute solutions* was used by us to study the polymerization of hydrolysis products and to determine the mean charge of the ions of these isotopes.

Experimental part

When measuring the diffusion coefficients of multicharged, hydrolyzing ions in extremely dilute solutions, it is necessary to find such experimental conditions as would make it possible to eliminate completely, or reduce to a minimum, the error caused by adsorption of these ions on the walls of the apparatus.

On the basis of the results of work by Starik and co-workers ([10]) on the study of the adsorption capacity of various ions as a function of solution acidity, and on a number of specially designed experiments, we found that when using the open-capillary method of Andersen and Saddington ([11]), in order to avoid the error caused by adsorption, the acidity of the solution must be: for Pu(IV) and Zr(IV), not less than 1 mole; for Th(IV), Ce(III), and Am(III), not lower than pH 2; and for Cs(I) and Sr(II), up to pH 11.5. For work in the region of

Fig. 1. Dependence of $D\eta/T$ on the acidity of the solution

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polymerization of hydrolysis products we used the method developed by Starik and Yurtov (24).

A comparison of the diffusion coefficients of Pu(IV) and Ce(III), measured by these two methods, showed that in three cases out of four the difference between the diffusion coefficients did not exceed 1%, and in only one case was it 4%. This enabled us once again to be convinced that neither adsorption nor the absence of stirring of the external solution in the open-capillary method introduces any noticeable error into the measurement results.

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* In studying diffusion, by extremely dilute solutions we mean solutions in which the concentration of the ions under investigation does not exceed 10^{-5} g-ion/l. Comparison of the diffusion coefficients of various ions calculated from the Nernst-Einstein equation and from the Gosting and Harned formula (9) showed that the difference between them does not exceed tenths of a percent.

As indicators for Cs, Sr, Ce, and Th, respectively, Cs^{137}, Sr^{90}, Ce^{144}, and Th^{234} were used. For preparing the solutions, twice-distilled water, distilled acids, and recrystallized salts were used. All working solutions were aged for 7 days. The viscosity of the solutions was determined with an Ostwald viscometer. All measurements were performed at $t = 25 \pm 0.05°C$. The concentration of the solutions did not exceed $1 \cdot 10^{-5}$ g-ion/l.

Fig. 1. Dependence of $D\eta/T$ on the acidity of the solution

In the theoretical works of Ottar (12) and Stokes (13), it is shown that the diffusion coefficient should be interpreted not as a function of mass, but as a function of the radius of the diffusing particle.

Then the change in the value of $D\eta/T$ in Fig. 1 represents, in essence, a change in the radius of the diffusing particles (or ions).

A sharp, discontinuous increase in the radius of the particles is observed for Zr(IV) near 0.3 mole HCl, for Pu(IV) at about pH 1.4, and for Th(IV) at about pH 3.7. It may be assumed that the inflection points on the curves $D\eta/T — \sqrt{C_{\mathrm{H}^+}}$ are due to polymerization of the hydrolysis products of the corresponding ions.

Let us assume that at these inflection points the solubility products (SP) of the corresponding hydroxides are reached. Then calculation by the formula $\mathrm{SP}_{\mathrm{Me(OH)4}} = [\mathrm{Me}^{4+}][\mathrm{OH}^-]^4$, substituting instead of $[\mathrm{Me}^{4+}]$ the total metal concentration C_M, gives: $\mathrm{SP}_{\mathrm{Th(OH)4}} 1 \cdot 10^{-46}$; $\mathrm{SP}_{\mathrm{Pu(OH)4}} = 1 \cdot 10^{-55}$; $\mathrm{SP}_{\mathrm{Zr(OH)4}} = 1 \cdot 10^{-59}$. The values of SP available in the literature are: Th $1 \cdot 10^{-50}$(16);

Fig. 2

Figure 2: Fig. 2

$1 \cdot 10^{-45}$(10); $1 \cdot 10^{-39}$(17). Pu $7 \cdot 10^{-56}$(15). Zr $6 \cdot 10^{-58}$(17), $8 \cdot 10^{-52}$(14). Comparison shows that the data calculated by us agree well with the SP values of Starik, Kasha, and Latimer.

Babko and Gridchina (23), using the dialysis method, studied the polymerization of Zr at a concentration of $1 \cdot 10^{-2}$ mol/l as a function of the concentration of $HClO_4$. If the value of the polymerization factor (or dialysis coefficient) in Fig. 2 is expressed as a function of the square root of the $HClO_4$ concentration, two intersecting straight lines are obtained. An analogous calculation of the SP from the point of intersection gives the value 10^{-59}.

Thus, the results obtained indicate that the quantities usually called PR, at least for concentrations of 10^{-5}-10^{-2} g-ion/l, may have the meaning of the onset of polymerization of hydrolysis products. For a more detailed consideration of the concept of PR, as well as of questions concerning the applicability of this concept to extremely dilute solutions, the data we have obtained do not provide sufficient grounds.

A sharp increase in the radii of the diffusing particles can now be explained as follows. When the PR of the corresponding hydroxide is reached, polymerization of the hydrolysis products begins. Polymeric products attain colloidal dimensions (1μ) not when the PR is reached, but at a somewhat lower concentration of H^+ ions; moreover, the interval between the pH at which the PR is reached and the pH at which particles of colloidal dimensions are formed increases in parallel with the decrease in the crystalline radius of the ion and reaches two pH units for Zr.

Fig. 2. Dependence of the relative change in D on the ion concentration at $[H^+] = 1M$

It does not appear possible to establish the nature of these colloidal particles solely on the basis of our measurements, although the formation of true, positively charged colloids may be assumed (21,22).

It is possible that the study of the diffusional capacity of elements near inflection points may serve as a method for determining the PR of hydroxides; moreover, the application of this method should be most useful for ions that are hydrolytically complex, such as the ions of polonium and protactinium.

From the data on measurements of the diffusion coefficients of Zr in the alkaline pH region, the formation of true, negatively charged colloids may be considered probable only after pH 7.5. Starik and Ampelogova (20) found that true colloids of Po predominate after pH 8. The works of Starik and Kositsyn (21,22) make it possible to suppose the existence of true colloids of Tl(III) and Ru(IV) also after pH 7.

The fact also attracts attention (Fig. 1) that, as the concentration of H^+ ions decreases, the curves $D\eta/T - \sqrt{C_{H^+}}$ seem to tend to merge at one point. This argues in favor of the idea that, as the polymerization process develops, the difference between the polymeric products is leveled out.

All this suggests that the region of existence of true colloids (at least for Th, Zr, Po, Tl, and Ru) is apparently determined only by the acidity of the solution.

When the acid concentration is increased from 0.3 to 3 mol/l, as is seen from Fig. 1, the diffusion rate of Zr, Th, and Pu does not change. In addition, the absolute value of this rate is practically the same for all three elements, although the crystalline radii of their ions and, consequently, their chemical character differ.

This once again confirms that the motion of ions in dilute solutions is determined chiefly by the structure of the solvent.

The increase in the value of $D\eta/T$ at high acid concentrations, observed in the case of Sr(II), Ce(III), and Pu(IV), is explained either by the nonideality of the solution and dehydration of the ions ([18,19]), or by a change in the composition of the complexes ([8]). Apparently, this question cannot be resolved on the basis of diffusion measurements alone, especially since in the case of Zr(IV) and Th(IV) no analogous increase is observed. Since in the case of self-diffu-

of adsorption or diffusion of labeled particles in an excess of foreign electrolyte, the composition of the solution along the diffusion path does not change; it may be expected that the decrease in the self-diffusion coefficients of charged ions with increasing concentration will be determined mainly by the magnitude of the mean charge of these ions.

Figure 2 gives the values of the relative decrease in the diffusion coefficients of a number of ions when their concentration is increased from 10^{-5} to 10^{-3} g-ion/l.

Extrapolation of the curves $D\eta/T - \sqrt{C_{H^+}}$ to zero concentration of H^+ ions in the case of Sr (II) and Ce (III) gives the values $D^{0*}_{Sr} = 0.784 \cdot 10^{-5}$ cm^2/sec and $D^{0*}_{Ce} = 0.616 \cdot 10^{-5}$ cm^2/sec. The corresponding values of D^0, calculated from the Nernst equation (1), are 0.789 and $0.619 \cdot 10^{-5}$ cm^2/sec, respectively. Therefore one may expect that the extrapolated values D^{0*} for other ions are also close to the values D^0 at infinite dilution.

Estimation of the charges of Sr (II), Ce (III), and Th (IV) from the Nernst equation

$$|z| = \frac{RT}{D^0 F^2}\lambda_0 \tag{1}$$

on the basis of the extrapolated values D^{0*} shows that the mean charge of Sr (II) $\simeq 2.0$, Ce (III) $\simeq 3.0$, and Th (IV) $\simeq 2.4$.

If the curves for Ce (III) and Sr (II) in Fig. 2 correspond respectively to charges 3 and 2, then the mean charge of Zr (IV) is close to zero, Pu (IV) $\simeq 2.2$, and Th (IV) $\simeq 2.4$.

Thus, measurement of the dependence of D on the concentration of the diffusing ion may make it possible to estimate the magnitude of its mean charge in a dilute solution.

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