BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2797—2800 (1969)

The Adsorption of Cobaltous Ions on Glass Beads from Extremely Dilute Aqueous Solutions

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(Received April 4, 1969)

The adsorption of cobaltous ions on fine glass beads was measured for dilute aqueous $^{60}CoCl_2$ solutions with pH values from 2 to 10 and with concentrations from 10^{-6} to 10^{-10} mol/*l*. The amount of the adsorption of cobaltous ions on glass showed a maximum at pH near 9, and it was zero at both ends of the pH region for all the initial concentrations studied. This fact is considered to confirm the theory of radiocolloid formation by the so-called adsorption method. The mechanism of radiocolloid formation was further discussed in detail. The formation of radiocolloids was explained by the adsorption of cobaltous ions on foreign particles, while the formation of insoluble cobaltous hydroxide was ruled out. It was estimated from these measurements that a very minute amount of foreign particles is sufficient to adsorb cobaltous ions and to change a large franction of the solute to radiocolloid. It was emphasized that such an estimation can be made only by the measurement of the adsorption, expressed by the unit of mol/cm^2 as in the case of the present experiment, instead of the conventional unit of cpm/g or percent adsorption.

Several workers have reported that the radioisotope in a very dilute aqueous solution often behaves as a colloid or a coarser dispersion rather than as a true solution. Such a disperse system, called radiocolloid by Paneth,[1] forms far below the concentration usually believed to be the solubility of the substance in question. Two possibilities have been proposed for the formation: a true colloid formation from a supersaturated solution of the radioisotope,[1] and a colloid formation by the adsorption of dissolved radioisotopes on small colloid particles of a foreign substance which are accidentally introduced into the solution as fragments of the container wall[2,3] or as impurities present in the reagent or water used.

The formation of radiocolloids has been detected by means of filtration,[4] adsorption,[5] dialysis,[1,6] electrophoresis,[1,2] diffusion,[7] precipitation,[8] and by several other methods.[9] However, considerable ambiguities are inevitably introduced in the measurement of the concentration because of the extremely low concentration at which these experiments are carried out, and because of adsorption of the solute to the wall of the container or other surfaces that might come into contact with the solution. Thus, the published reports on radiocolloids are more or less qualitative in nature; quantitative studies concerning the behavior of the main constituent of radiocolloids are few. Recently, however, a radiotracer study of manganese adsorption on glass was reported, and radiocolloid formation was inferred.[10] Nevertheless, here, as in the other reports, the amount of adsorption and the concentration of solute are expressed in relative or conventional units which are unsatisfactory for the purposes of a more quantitative discussion. The present report will deal with a study of the radiocolloidal behavior of cobaltous ions paying attention to these facts. The cobaltous ion was chosen since the radiocolloid formation of cobalt has not yet been reported in spite of the wide use of 60-Co as a radiotracer. The explanation of the radiocolloid formation of 60-Co based upon the adsorption mechanism was attemtped. For this purpose, very many small glass spheres were added to an aqueous solution of $^{60}CoCl_2$ of a known concentration, and the amount of adsorption was exactly determined in the unit of mol/cm^2 at the

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[1] F. Paneth, *Kolloid Z.*, **13**, 297 (1913); *Z. Elektrochem.*, **31**, 5 (1925).

[2] T. Godlewski, *Le Radium*, **10**, 250 (1913); *Kolloid Z.*, **14**, 229 (1914).

[3] C. Rosenblum and E. W. Kaiser, *J. Phys. Chem.*, **39**, 797 (1935).

[4] G. K. Schweitzer and W. H. Jackson, *J. Chem. Educ.*, **29**, 513 (1952).

[5] I. E. Starik, *Z. physik. Chem.*, **157A**, 269 (1931).

[6] T. Sasaki and K. Osaka, This Bulletin, **32**, 490 (1959).

[7] J. S. Anderson and K. Sassington, *J. Chem. Soc.*, **1949**, 381.

[8] H. Lachs and M. Wertenstein, *Physik. Z.*, **23**, 318 (1922).

[9] C. Chamie, *Compt. rend.*, **184**, 1243 (1927); *ibid.*, **192**, 1277 (1931).

[10] P. Benes and A. Garba, *Radochim. Acta*, **5**, 99 (1966).

extremely dilute equilibrium concentration thus attained. These data enabled us to estimate the amount of foreign particles, which is extremely small but sufficient for adsorbing a large fraction of the cobaltous ions in a dilute solution and changing them into the radiocolloid.

Experimental

Solution. The radioisotope of cobalt was supplied by The Radiochemical Center, England, as a cobaltous chloride with a specific activity of 144 mCi/mg; it was isotopically diluted by an analytical-grade non-radioactive cobaltous chloride before use.

The water used was doubly distilled from a Hysil flask with nothing added after the reflux boiling and distillation with acid and alkaline permanganate respectively. Here, the adsorption of cobaltous ions by the wall of the container and the accidentally-introduced dust particles usually produce an error in the measurement at extremely low concentrations. To avoid this, a large quantity of carefully prepared fine glass beads was used as an adsorbent which had a far larger surface area than the surface area of the wall and of the dust particles introduced with the solvent water or reagents. The probable error due to the fine particles introduced together with the glass beads also turned out to be immaterial, as will be mentioned later. The present experiment enabled us to eliminate such an error and to attain an extremely dilute solution of a known concentration. The initial concentration was chosen in the range from 10^{-6} to 10^{-8} mol/l, and the equilibrium concentrations finally attained ranged from 10^{-8} to 10^{-10} mol/l. The concentration of cobaltous ions in the initial solution was determined by EDTA titration, using murexide as an indicator, while the amount of adsorption was determined from the change in the radioactivity of the supernatant solution due to the adsorption. Here, the loss of a solute by the adsorption on the wall of the pipet or of the container used for analysis was proved to be negligible, as will be discussed later.

Glass Beads. Beads of soda lime glass, ranging between 40 and 44 μ in diameter and with a specific surface area of about 593 cm^2/g, were used as an adsorbent. It is well known[11] that the glass surface has a considerable buffer action, and also that it often takes a fairly long time to attain the adsorption equilibrium. It was confirmed in the present study that, after the contact between the glass and the solution, a gradual change in the pH of the solution with the time was observed together with the change in the concentration of the cobaltous ions. Such a complication is not desirable for the present purpose of studying the adsorption behavior of cobaltous ions at various concentrations and pH values. For this reason, the glass beads were previously cleaned and equilibrated with the buffer solution according to the procedures shown in Fig. 1.

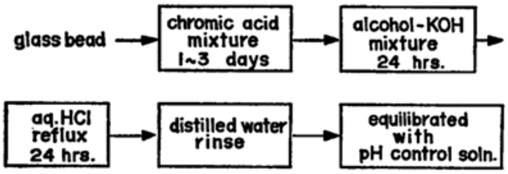

Fig. 1. Pretreatment of glass beads before adsorption.

The pH of the buffer solution in this figure was taken to be equal to that of the solution used for the adsorption measurement. The adsorption measurement was performed by immersing 2 g of the treated glass beads in 8 ml of 10^{-6} to 10^{-8} mol/l aqueous solution of cobaltous ions, and then by keeping it at 25±2°C with gentle stirring. At proper time intervals, the concentration of cobaltous ions of the supernatant solution was determined by radioactivity measurement using a Ten SA-100 Geiger Müller counter, the steady value of the counting rate was taken as the equilibrium. In this measurement, an aliquot of the solution was taken out by means of a constant-volume micropipet of 40 μl, placed on a circular Indian paper affixed to a glass plate, and dried completely under an infrared lamp before counting. The experiment previously performed by the present authors proved this counting technique to be satisfactory, especially for the measurement of 60-cobalt.[12] The errors due to the adsorption of cobalt on the glass surface of the pipet, errors which are unavoidable in this operation, turned out to be negligible when we compare the very slow rate of adsorption, which takes about 20 hr to attain equilibrium, with the short time of contact between pipet and solution.

Results and Discussion

The amount of the adsorption of cobaltous ions on a unit of the surface of glass, Γ, is expressed as the difference between the concentration of the solution before and after the adsorption multiplied by the volume of the solution:

$$S\Gamma = (C_i - C_e)V$$

or

$$\frac{S\Gamma}{C_i V} = 1 - \frac{C_e}{C_i} \tag{1}$$

where S expresses the total surface area of the glass beads; C_i and C_e, the initial and equilibrium concentrations respectively of the solution used for the adsorption experiment, and V, the volume of the solution. Equation (1) expresses the linear relation between C_e and $S\Gamma/C_iV$, the latter being the ratio of the total amount of adsorption to the total amount of the solute. This linearity is shown in Fig. 2 as a straight line for the three C_i's chosen in the present experiment. With the aid of this straight line we can obtain the $S\Gamma/C_iV$ values, and therefore Γ, from the observed C_e values. In the present experiment, starting from relatively high concentrations of 10^{-6} to 10^{-8} mol/l, low equilibrium concentrations of 10^{-8} to 10^{-10} mol/l were

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[11] G. G. Eichholz, Ann E. Nagel and R. B. Hughes, *Anal. Chem.*, **37**, 863 (1965).

[12] T. Seimiya and T. Sasaki, unpublished data.

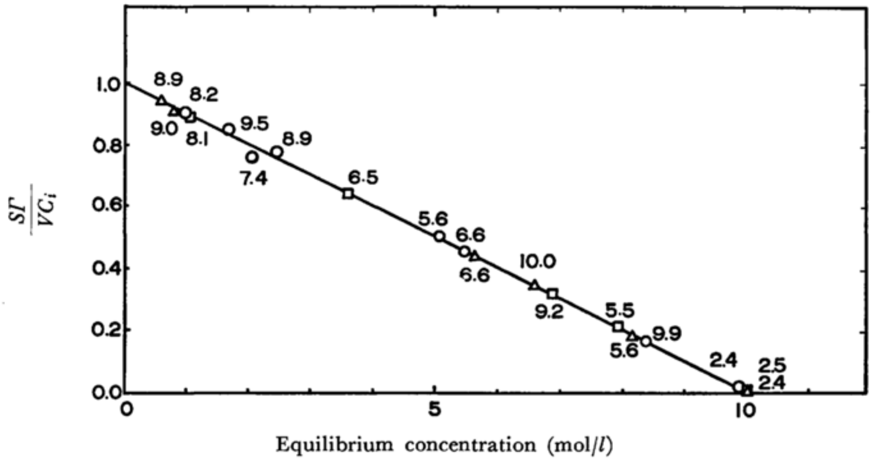

Fig. 2. Adsorption cobaltous ion on glass beads.

○ $\times 10^{-7}$ □ $\times 10^{-8}$ △ $\times 10^{-9}$

attained by adding a sufficient amount of an adsorbent. The points on the straight lines were located corresponding to the equilibrium concentrations thus obtained. The deviation of several plots from the straight line is due to the slightly different values of the corresponding C_i from those indicated in Fig. 2. The numbers indicated at the points in Fig. 2 show the pH values of the solutions at which the adsorption was equilibrated. The pH dependence of the adsorption of cobaltous ions on the glass surface is shown in Fig. 3. In this figure, the circles, squares, and triangles indicate the amounts of adsorption for the solutions of three different initial concentrations, 1×10^{-6}, 1×10^{-7}, and 1×10^{-8} mol/l respectively. The amounts of adsorption from these solutions are in the order of magnitude of 10^{-12}, 10^{-13} and 10^{-14} mol/cm^2 respectively, as is shown by the ordinate of this diagram. It may be noted that the use of glass beads as in the present experiment makes it possible to express the amount of adsorption in moles per area of glass surfaces instead of as cpm per weight of the powders or as mere percentages of the adsorption of the total solute present in the system, as has usually been done in similar studies.

As is shown in Fig. 3, all these plots can be brought near a common curve by a proper choice of the unit of the ordinate for each group of solutions with a different initial concentration. Thus, the adsorption behaviors of these solutions are quite similar towards the pH change in spite of the wide difference in initial concentrations and in the amount of adsorption. No indication of adsorption was observed at any pH lower than about 3. The adsorption increased with the pH and showed its maximum at a pH of about 9, regardless of the initial cobaltous-ion concentration. A further increase in pH sharply decreased the adsorption to zero at pH values of about 10. The amount of adsorption at its maximum is more than 90% of the total amount of solute——for instance, 95% of the cobaltous ions adsorbed from a 10^{-8} molar solution at pH values from 8 to 9, leaving a 10^{-10} molar solution in equilibrium with it. Here, we can confirm that a proportionality such as that expressed by;

$$\Gamma = kC_e \tag{2}$$

holds as a whole at any given pH and especially well at the pH of maximum adsorption. We can further confirm, at least from the 95% adsorption at pH values of about 9, that the fine dust particles which might be introduced together with the glass beads are negligible in amount, since the dust particles of such an origin, if they existed in a considerable amount, would adsorb as many cobaltous ions and keep them in a suspended state. Such a state should markedly increase the supernatant cobaltous-ion concentration and reduce the (apparent) fraction of the amount of adsorption far below 95%. As to the radiocolloid formation of cobalt, we can take the appearance of an adsorption maximum near pH 9 as a confirmation by the so-called adsorption method. The explanation based upon the mechanism of the formation of true insoluble colloidal particles of cobaltous hydroxide was first considered, but this is unacceptable since the equilibrium concentrations studied in the present experiment (at least 10^{-10} mol/l) are far below the solubilities of cobaltous hydroxide, $10^{-5.6}$—$10^{-7.4}$ mol/l, at pH values of about 9 as calculated from its solubility product.[13,14] The formation of cobaltic hydroxide, which is far more insoluble than cobaltous hydroxide, is also unlikely

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13) G. Charlot, "L'Analyse Qualitative et les Reactions en Solution," Masson et Cie., Paris (1957).

14) Landolt-Börnstein, "Physikalisch-chemische Tabellen," I. Erg., Verlag J. Springer, Berlin (1927).

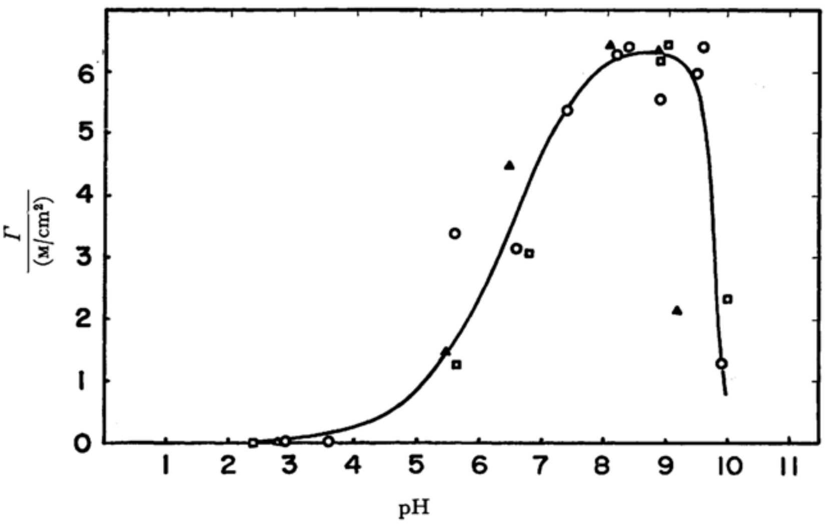

Fig. 3. Adsorption of cobaltous ion on glass beads.

	Γ	C_i
○	$\times 10^{-12}$	1.0×10^{-6}
□	$\times 10^{-13}$	1.0×10^{-7}
△	$\times 10^{-14}$	1.0×10^{-8}

considering the cobaltic-ion concentration in equilibrium with the cobaltous ion, which is calculated from the oxidation reduction potential measured for the solution used in the present experiment. Further, the electrodialysis data for the 10^{-4} molar cobaltous chloride solution which one of the present authors has formerly reported[6] showed that the colloid formation of cobaltous hydroxide is limited to the pH region slightly below the solubility of cobaltous ions calculated from the solubility product. From these facts, it can safely be concluded that true colloid of cobaltous hydroxide in any form cannot be considered to exist below the cobaltous-ion concentration of 10^{-9} mol/*l* at pH 9 and at 25°C.

On the contrary, though, we can numerically show the possibility of radiocolloid formation due to the adsorption of cobaltous ions on foreign particles. As has already been shown in the preceding section, about 95% of the solute is adsorbed by two grams of glass beads from 8 m*l* of a 10^{-8} molar aqueous solution at pH 9. Here the total area of the beads is 1186 cm². Now, simple calculation shows that as small an amount as about 6×10^{-6} g of glass particles of colloidal size (10^{-7} cm) in a 1 m*l* solution gives a 1186 cm² surface for an 8 m*l* sample solution, which just adsorbs 95% of the cobaltous ions in solution and keep them in a radiocolloidal state. It is quite conceivable that dust particles in such a small amount exist in ordinary water. Thus, the results of the above adsorption experiment with coarse glass beads indicate the possibility that the radiocolloid formation of cobalt in a dilute aqueous solution is due to the adsorption of the solute on a very small amount of foreign particles.

It should be emphasized in conclusion that the radiocolloid formation can be confirmed only by the exact measurement of the amount of adsorption expressed in the unit of moles per square centimeter and by using an adsorbent with a clearly defined total area and pH condition. Such a confirmation is impossible by the so-called adsorption method usually adopted; here the results are expressed merely by the percentage of adsorption or by the unit of moles per weight of the adsorbent, using irregular particles of an ill-defined surface area.