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The Determination of the Critical Volume for the Free Motion of Solute Entities in an Aqueous Solution[1)]

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A certain volume of a solution, (20—30 Å)^3 per unit of solute entity, designated the "molecular space," is assigned as the necessary volume for the free motion of the solute. By the use of ESR, the actual size of the molecular space has been determined for the cupric ion and 2,2,5,5-tetramethyl-3-carbamoylpyrollidin-1-oxyl. It is pointed out that the concentrations of the important solutions in nature, such as sea water or human serum, may correspond to the moleuclar space of ions.

Solute entities in solution, such as ions or molecules, undergo diffusional and rotational motions in the solvent media. Those motions depend on the conditions of the solution, such as the concentration, the volume, the temperature, or the chemical propterties of the system, and the behavior of the solutes can be investigated by analogy with gaseous systems, where non-elastic and the elastic collisions characterize ideal and real gases. The free motion of the solute entity colud be defined as the motion in which the solute fulfils any one or a combination of the following conditions; 1) the motion is isotropic, 2) the solute does not exist as an ion-pair, 3) the solute is completely hydrated, or 4) the correlation time τ of the rotational motion obeys Debye's formula, $\tau_c = 4\pi\eta a^3/3kT$, where η is the viscosity of the solution; a, the ionic radius; k, the Boltzman constant, and T, the absolute temperature. Whether or not the solute entity is in the state of free motion can be seen by its NMR or ESR spectral features. This paper will report that a certain volume of a solution is required for the maintenance of the free motion of the solute entity. The minimum volume of a solution which allows the solute entity free motion is defined as V_c. The results of the investigation which has been carried out for the measurement of V_c will be presented.

In the investigation, the magnitude of V_c was evaluated first by the examination of the concentration dependence of the linewidths of the ESR spectra of aqueous cupric ions. In this experiment, the conditions of 1, 2, and 3 cited above were taken as measures of the free motion of ions. (Experiment 1).

We planned then to measure V_c more directly by the control of the space of the solution available to the solute entity. Two systems were adopted for this purpose, one silica gel (Experiment 2) and the other, cross-linked poly(vinylalcohol), PVA, gel (Experiment 3). One of the most notable findings of these experiments is that the magnitude of V_c is several times larger than the actual size of the solute entity. The relevance of this finding will be discussed with respect to the recent results of the measurement of the viscosity or the relaxation times of magnetic resonance. The significance of V_c in nature will also be discussed in the text.

Experimental

Experiment 1: Concentration dependence of the ESR linewidth of cupric ions in aqueous solutions. The ESR linewidth of cupric ions in aqueous solutions, ΔH, has been measured as the function of the concentration of ions. As the details of the experimental conditions have already been published elsewhere,[2)] they will not be repeated in this article for except Fig. 1. Figure 1 has been reproduced for convenience, and it has been augmented with some additional data and a recalibration of the scale of the linewidth.

It is evident in Fig. 1 that ΔH is not dependent on the concentration nor on the anion species in the range lower than about 0.1 M. This result has been interpreted in terms of the fact that the cupric ions are wholly hydrated in the concentration range lower than 0.1 M, whereas, in the higher concentration range, ion pairs are formed, resulting in the reduction and the anion dependence of ΔH. Hence, the conditions of the free motion, 1, 2, and 3, which have been raised in the introduction, are fulfilled, and 0.1 M can be taken as the limiting concentration which allows the free motion of ions.

This value of the critical concentration refers to a certain volume of solution (a cube of 20Å) per ion ($=1000$ ml$/2 \times 0.1 \times 6.02 \times 10^{23}$).

Experiment 2: ESR pattern of aqueous solutions of Cu^{2+} adsorbed in silica gel. In order to evaluate V_c more directly, another experiment was undertaken*** with the use of aqueous solutions of cupric sulfate spread over the surface of silica gel.

Two types of experiment were performed: A) with the silica gel dipped in aqueous solutions of different concentra-

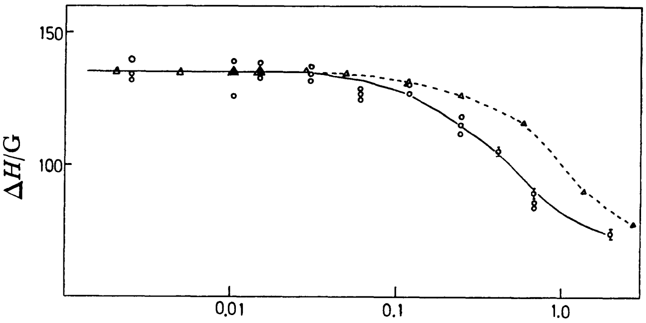

Fig. 1. Concentration dependence of the ESR line widths of aqueous Cu^{2+} ions.
—○— $CuSO_4$ aq. —△— $Cu(NO_3)_2$ aq.

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TABLE 1. CONTENTS OF WATER AND CUPRIC SULFATE ABSORBED IN SILICA GEL

Sample	Mother solution	H_2O g/g SiO_2	Cu^{2+} mM/g SiO_2
i	0.25 M	1.1	0.26
ii	0.5 M	1.1	0.56
iii	1.0 M	1.1	1.1

The values of water and cupric ions refer to those contained in the silica gel just after it is taken out of the mother solution and after it has been drained.

tions of cupric sulfates, and B) with thin-layered silica gel plates over which the cupric sulfate was developed. In both cases, the ESR of the cupric ions and the contents of ions and water in silica gel were measured.

Conditions of Experiment 2-A:

Silica gel: Wako Gel,

ESR: J 3BS Spectrometer, made by Japan Electron Optics Laboratory Co. X band, 100 kHz modulation.

Procedure. The silica gel was put in equilibrium with three aqueous solutions (i, ii, and iii) with concentrations of 0.25, 0.5, and 1.0 M respectively. No solution with a concentration lower than *ca.* 0.2 M was adopted in the present experiment because of the limitations of the ESR measurements. After filtration, the excess solution was gently removed as drainage. The contents of water and cupric ions in the samples as well as the ESR were measured at the same time at this stage. As a wet sample lowers the Q value of the ESR spectrometer, the sample size must be kept small. This condition brings another difficulty-that the number of cupric ions which are brought into the ESR cavity is reduced. Efforts were made to find out the optimal conditions. Another difficulty lay in the treatment of silica gel. The silica gel which had became wet with the solution showed a tendency to squeeze the solution out of the gel when it was treated for the transference into the capillary sample tube of ESR measurements. Efforts were made to transfer the wet silica gel into the capillary without any distortion. The results of the analysis are shown in Table 1.

Results of 2-A: In Table 1 it may be seen that the water content is the same for all three samples, 1 ml/gSiO_2. This value may be taken as the volume of solution which can "naturally" be held in silica gel. As the results of the analysis of the copper content also show that 1.1 ml of each mother solution is held in the silica gel, *ca.* a 1-ml solution over gSiO_2 would be a good value of water, with reference to the value of V_c. With the values of the surface of the silica gel from 4 to 6, m^2/gSiO_2†, a water layer 20±5 Å thick (=1 ml/4—6 m^2) is taken as the space which allows the solute ions "almost" free motion. The motion in the latter case is called "almost free" because the ions with the concentration of the experiment are assumed to be ion-paired to some extent. There was a slight worry that the samples might hold excess solution as a result of an incomplete removal of the drainage. Accordingly, Experiment 2-B was carried out, where the samples were assumed to be prepared in more homogeneous condition.

Experiment 2-B: Thin-layered silica gel plates were prepared on glass plates according to the usual technique of thin-layer chromatography. The thickness of the silica gel layers was assumed to be a few hundred microns. The silica gel used is the one same used in Experiment 2-A.

Two solutions of cupric sulfate with concentrations of 0.20 and 0.46 M were developed in the layers. After the development, each layer of silica gel was cut into 9 portions, equal in length, from the bottom to the top of the plate. The contents of water, cupric, and sulfate ions were measured as well as the ESR spectra for all samples. Table 2 presents the results of the measurement with respect to the bottom portion of the plates.

TABLE 2. WATER CONTENT IN SILICA GEL JUST AFTER THE DEVELOPMENT OF THE SOLUTION OF CUPRIC SULFATE

Sample	Mother solution	H_2O Content just after development
iv	0.20 M	1.2 g/g SiO_2
v	0.46 M	1.0 g/g SiO_2

Results of 2-B. In Table 2 it may be seen that the two samples of thin-layered silica gel, iv and v, also hold about 1 ml (actually 1.2 and 1.0 ml) of the solution. Because the patterns of the ESR spectra are of a single line with a fairly good symmetry, it is certain that the cupric ions are in a state of almost "free' motion. Summarizing the results of A and B, the ions in the samples of both cases are in almost "free' motion in the water layer (20±5 Å thick) which is spread over the surface of the silica gel.

Experiment 3†† : *Use of the network of γ-irradiated PVA.* For the purpose of the measurement of V_c, the cross-linked network of polyvinyl alcohol, PVA, which was produced by the γ-ray irradiation was utilized. By the γ-ray irradiation of the aqueous solution of PVA, the latter molecules are cross-linked and form a three-dimensional network. The average distance between the end terminals of the PVA molecules, $\langle l \rangle$, can be controlled by the control of the concentration of PVA, C, and the total dose of the γ-rays, R. The value of $\langle l \rangle$ actually refers to the size of the hole in the network which can hold ions in the solution. Thus, the cross-linked PVA gel is used as a convenient medium for the control of the motion of the solutional ions. Some examples of the application have already been reported.[3]

The value of $\langle l \rangle$ may be calculated according to the following equation:[4]

$$\langle l \rangle = 2.5\times[(5.1\times10^8+1.37\times10^8\,C)/R]^{1/2}, \qquad (1)$$

where C refers to the value in g PVA per 100 ml of H_2O and R is in rads. In practice, the degree of the polymerization of PVA is about 2000, and C is 5 g PVA/100 g H_2O. The source of the γ rays is the University of Tokyo, the γ-ray source of Co-60 with 3000 Curies, and R is 2×10^6 rads. First in this experiment, a), the symmetry of the ESR spectra was examined by a comparison of the half-maximum linewidths of the two parts of the derivative curve. That is, after recording the derivative of the single line of the ESR absorption spectrum, the half-maximum linewidths, Δh_1 and Δh_2, were measured with respect to both the higher-field and lower-field parts (*cf.* Fig. 2), respectively. It was confirmed that the cupric ions in the gel of $\langle l \rangle$ almost equal to, or smaller than, 25 Å gave Δh_2 values for the lower field side derivative about 5% larger than the Δh_1 values for the higher-field side. However, the ions showed almost symmetric lines in the gel of $\langle l \rangle$ larger than 25 Å. That is, the V_c for Cu^{2+} ions was counted as about 25 Å.

In the b) experiment, the relative heights of the three hyperfine lines of the ESR signal of the radical were compared. The correlation time, τ_c, was then calculated by the use of the observed results and the following equation,[5] where the

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† Determined by the nitrogen gas adsorption.

†† This section forms a part of the B. Sc. thesis of Yasushi Kanaoka, University of Tokyo, 1975.

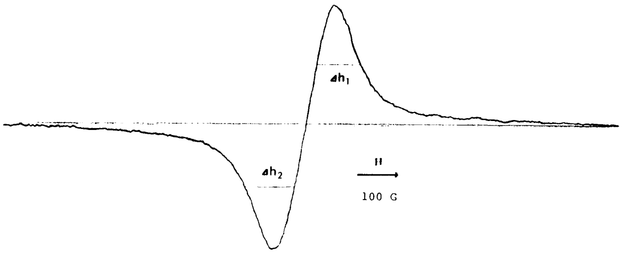


Fig. 2. Derivative of the ESR spectrum of Cu^{2+} 0.01 M solution in PVA gel of $\langle l \rangle = 20$ Å, where $\Delta h_1 > \Delta h_2$ by 5%. When $\langle l \rangle \geqq 25$Å, $\Delta h_1 = \Delta h_2$.

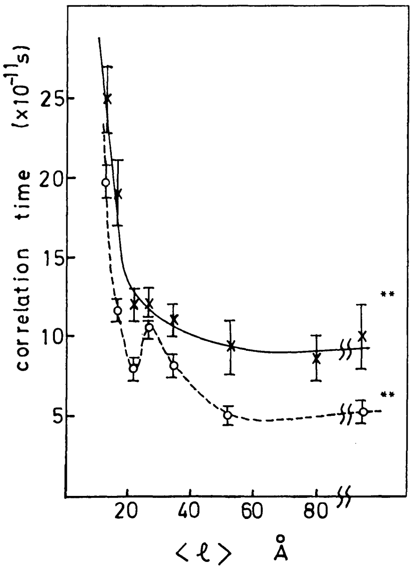
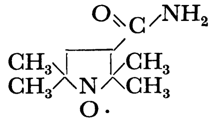


Fig. 3. Correlation time, τ_c, for the motion of 2,2,5,5-tetramethyl-3-carbamoylpyrrolidin-1-oxyl, TMCA, as the function of the molecular space in PVA gel.



—×—: 0.01 M in PVA gel, —○—: 0.001 M in PVA gel, **: τ_c in bulk solution.

values of the hyperfine constants of A_{xx}, and A_{zz} were obtained from the literature:[6]

$$\tau = \left[\left(\frac{h(0)}{h(1)}\right)^{1/2} + \left(\frac{h(0)}{h(-1)}\right)^{1/2} - 2\right] \times \frac{3\pi\Delta\nu(0)}{2C_2}, \qquad (2)$$

where $C_2 = 2\pi/9[A_{zz} - A_{xx}]^2$ and where h refers to the derivative height of each hyperfine line. The results of the measurement are shown in Fig. 3, where a marked increase of τ_c is seen in the gels of $\langle l \rangle$ lower than about 20 Å.

Discussion

According to the results of all the experiments shown above, it is evident that a certain volume of a solution, $(20 \pm 5)^3$ Å per unit solute entity, is required for the free motion of the solute entity of a simple structure, like Cu^{2+} or a low-molecular-weight compound. A problem of current interest is the fact that V_c is several times larger than the real size of the solute entity. This fact may have some connection with the discussion related with the microviscosity, which assumes the presence of a structural sphere surrounding the solute entity.[7] It may also be related to the discussion which has recently been made in the field of magnetic relaxation.[8] It should be stressed that V_c has been measured directly in the present investigation, unlike as in former investigations of microviscosity or magnetic relaxation. Further investigation will be necessary for a real understanding of the structure of V_c. Another point to be noted in this article is the possible significance of V_c in nature. As one considers the situation of the solute entity, where it is held in the concentration range of V_c, the whole system of the solution is assumed to be stabilized by the buffer action of the solute entity. That is, in the solution where the solute entity just holds the space of V_c, each individual solute entity behaves as free from the others and also as free from the external system. Nevertheless, it should easily respond to the action of the external system, for the concentration is not far from the condition which produces the mutual interaction of the solutes or the reaction with the external system. In connection with this statement, reference may be made to the fact that the concentrations of the salt in the important solutions in nature fall in the range of the concentration of V_c. For example, the concentration of the human serum is about 0.1 M, that of the silk worm egg is 0.1 M,[9] and that of the sea water is about 0.5 M. In addition to this, we may refer to the work of Ehrenberg.[10] He assumed the case of an adult human with a body of weight of 70 kg, 50 kg of water and 20 kg other materials, mainly organic. He evaluated the total interface of the macromolecules (and membranes) to be of the order of 10—100 km² (10^7—10^8 m²). If one spreads, according to this formula, the 50 kg of water in an uniform layer over this area, the thickness of the layer becomes 5—50 Å. He assumes that there would be, on the average, less than 20 water molecules between the most distant point in the water and the surface.

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