The Self-diffusion Coefficient of Calcium Ion

in Aqueous Calcium Chloride Solution

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Abstract

The self-diffusion coefficient of calcium ion in calcium chloride aqueous so-lution was measured using ^{45}Ca as a radio-isotope of calcium by the cappillary method at 27.7°C.

Since the very large value of self-diffusion coefficient was found in 0.300M calcium chloride aqueous solution, notable concentration dependency is observed in spite of the previous similar studies for calcium ion.

1. Introduction

The self-diffusion is a phenomenon of diffusion of materials in the perfectry same media, such as transformation of water molecules in aqueous phase. In these cases we can obtain the rate of diffusion with some labelled materials.

Since the self-diffusion coefficients are intimately concerned with the movement of molecules in materials, measuring of the self-diffusion coefficients contributes much to ascertain a property and structure in solids, liquids and solutions.

As concentration gradient is not present in the self-diffusion, we need not take account of concentration change in the diffusion system, thereby the self-diff-usion coefficients can be treated to be constant in any concentration.

Though both diaphragm cell and capillary method are applied to measure self-diffusion coefficient in the liquids, a convenient capillary method for measur-ing in an unsteady state is chosen in this paper.

The capillary method was used by Anderson[1] at first and afterwards has been developed ,by Wang[2] for measuring the self-diffusion coefficients. By im-posing the integral boundary conditions of Fig. 1 on
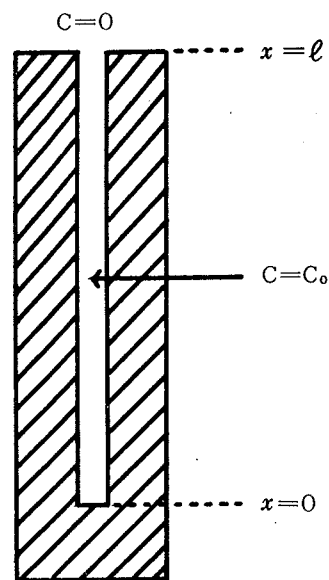

Fig. 1 Capillary method

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the Ficks equation and choosing an experimental condition to be $Dt/\ell^2 > 0.2$, epuation
(1) is obtained.[3]

$$2.303 \log \left(\frac{\pi^2}{8} \frac{C_{av}}{C_o} \right) = - \frac{\pi Dt}{4\ell^2} \tag{1}$$

where ℓ is the length of the capillary, Cav is the average concentration of the
tracer ion in the capillary at time t, Co is its initial concentration and D is the
self-diffusion coefficient.

The self-diffusion coefficient of calcium ion in aqueous solution has been measured
by Wang[4] and Matuura.[3] The former reported that the self-diffusion coefficients
slowely become lower with increasing calcium ion concentration, whereas the latter
found that the small maximum point exists at the concentration of 0.550M.

As the result of measuring in calcium chloride concentration between 0.258M
and 0.300M, the author found a large difference in their values of self-diffusion
coefficients and notable concentration dependency was recognized between two
concentration of calcium ion.

2. Experimental

2.1 Preparation of [45]Ca solution

[45]Ca solution* was placed in an evaporating dish and hydrochloric acid was ex-
pelled by exsiccation of the solution.

Five ml of natural calcium chloride solution prepared with distilled water was
poured in the dish. Exactry one ml of the sample solution was pipetted out, then it
was loaded to the column of finely meshed strongly acidic cation-exchange resin in
H type. After the column was treated with distilled water perfectly, the eluted
solution was titrated with a normal sodium hydroxide solution.

2.2 Measurement of self-diffusion coefficient

A natural calcium chloride aqueous solution in the same concentration with radio-
active one was prepared. The solution was poured in a four-necked flask shown
in Fig.2 and the flask was dipped in a thermostat. While allowing to stand in a
moment to attain the constant temperature with the solution in the flask, back-
ground was measured by means of G-M counter. For measurement of Co value, the
capillary was filled with [45]Ca solution with the aid of fine glass tube and [45]Ca
solution was instantly took out into a dish for radioactive measurement.

Since dried calcium chloride is hygroscopic in air, sodium fluoride solution was
added to the dish before evaporation and the whole matter was brought to dryness

*Chmical form, CaCl[2], supplied by Japanese Atomic Power Research.
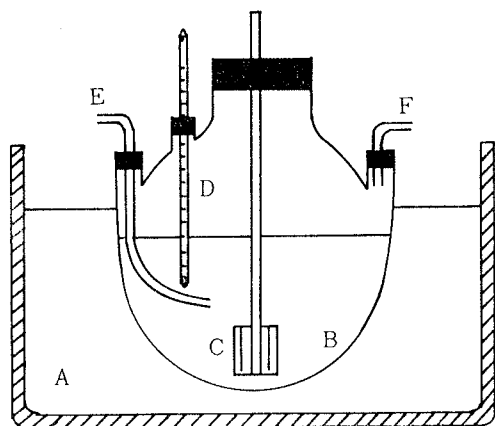[45]Ca; Half-life, 164days, β–emitter (0.256MeV)

Fig.2 Measuring apparatus of self-diffusion coefficient

A ; thermostat   B ; solution cell

C ; capillaries   D ; thermometer

E ; air inlet   F ; air outlet

under an infrared lamp. Radioactivity was measured by means of G-M counter too, and the value Co was estimated.

Then the capillary was filled with ^{45}Ca solution again, fitted to a glass rod and dipped in the flask slowly, thereby recording the time at which the diffusion was allowed to start.

Air was always being introduced in the flask to keep the system homogeneous during diffusion. After diffusion was completed, the Cav value was estimated by radioactive measurement of residual ^{45}Ca in the capillary.

3. Result

In the diffusion experiments previously carried out by other authors, mechanical stirring was applied in order to homonize the system, but in this case air was ventilated instead in order to avoid mechanical disturbance during diffusion.

The Co value before diffusion and Cav value after diffusion were put into equation (1) and the coefficient D was calculated as shown in the Table 1.

Table.1 The self-diffusion coefficient of calcium ion in aqueous calcium chloride solution

Capillary No.	ℓ [cm]	CaCl$_2$ Ccnoentration [M/L]	Co [CPM]	Cav [CPM]	D×10^{-5} [cm/sec]	The mean value of D×10^{-5} [cm/sec]
1	2.85	0.258	2439	1194	1.07	
2	1.80	0.258	1724	485	1.00	1.00
3	1.50	0.258	2684	517	0.92	
4	3.60	0.300	1522	1100	6.10	
5	3.35	0.300	2800	1840	7.00	6.30
6	2.00	0.300	2290	1120	6.00	

Diffuison temperature; 25.7°C

Diffusion time; 40.0 hrs

Back ground; 47 CPM.

Matuura et al[3] showed that the ratio of diffusion coefficients in 0.400M and 0.280M at 25°C was 1.309 ($D_{0.400}/D_{0.208}$), while Wang[4] obtained 0.844 ($D_{0.803}/D_{0.282}$) at the same temperature.

According to the author's experiment, the mean values of the self-diffusion coefficients in 0.258M and 0.300M of calcium chloride aqueous solution at 25.7°C were 1.00×10^{-5} and 6.30×10^{-5} respectively, and the ratio of their self-diffusion coefficients was calculated to be 6.30 ($D_{0.258}/D_{0.300}$). It is now clear that notable concentration dependency is observed between 0.258M and 0.300M in calcium chloride aqueous solution.

References

1) J. S. Anderson, K.Sadington ; J. Chem. Soc., **1949**, 381.
2) J. H. Wang ; J. Am. Chem. Soc., **73**, 510 (1951).
3) Ryohei Matuura, Ryosuke Shimozawa ; Memoirs of the Faculty of Science Kyushu University, **2**, 53 (1953).
4) J. H. Wang; J. Am. Chem. Soc., **75**, 1769 (1953).
5) T. A. Littlefield, N. Thorey; "Atomic and Nuclear Physics-An Introduction," P410, (1963).
   D. Van, Nostrand Company Ltd. London.