On the Possibility of Concentrating Colloid by Means of Freezing at the Sedimentation Equilibrium State Attained in a Centrifugal Field

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In this note a suggestion has been made that the freezing of a colloid at the sedimentation equilibrium state attained in a centrifugal field could possibly be utilized as a means to concentrate the colloid. The argument is confined to the case in which the dispersion medium is water, and in which the concentration and molecular weight of the colloid, as well as the concentration of the electrolyte present in the colloid, are small.

The colloid is put into a cell and subjected to centrifuging (Fig. 1). After the sedimentation equilibrium has been reached, the temperature is lowered and the colloid in the cell is frozen. Centrifuging is then stopped and the frozen colloid is taken out of the cell and the part near the bottom is removed. This is put to stand at a temperature slightly above zero and the frozen colloid is brought back to a sol which has a concentration greater than the initial one. Starting from the ample quantity of the colloid and by repeating the procedure, it is possible to get a colloid of very high concentration, if the colloid does not change by being subjected to the freezing-thawing treatment.

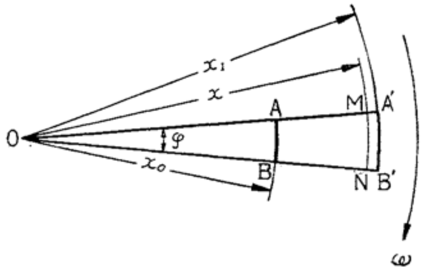

Fig. 1.

There are two factors which might influence the course of freezing of the colloid. They are hydrostatic pressure and concentration gradient. We know that the freezing point of water is lowered under pressure. The hydrostatic pressure of the colloid is the smallest at the top of cell AB and increases with x. Thus, when the temperature is lowered in equilibrium, ice formation will start at the top and then proceeds gradually along Ox. The fact that ice is lighter than water will also favor the tendency. In a dilute solution, the freezing point lowering is proportional to concentration. From this fact we understand that the freezing point of the colloid is the highest at the top AB and that it becomes lower with the increase of x. Thus, both the hydrostatic pressure and the concentration gradient favor the ice formation from the top AB toward the bottom A'B', acting in the tendency to enhance the concentration gradient.

How far the colloid is concentrated by this procedure can be estimated as follows: Let us consider the colloid in AA'B'B. The thickness of cell is taken as unity. The concentration gradient in the sedimentation equilibrium is given by

$$\frac{c}{c_0}=\frac{\alpha(x_1^2-x_0^2)}{e^{\alpha x_1^2}-e^{\alpha x_0^2}}\cdot e^{\alpha x^2}, \tag{1}$$

where c=concentration of colloid, c_0=initial concentration of colloid, x=distance from the axis of rotation, x_0=OA, x_1=OA', φ=sector angle, s=sedimentation constant of colloid, D=diffusion constant of colloid, ω=angular velocity, and $\alpha=\frac{s\omega^2}{2D}$.(1)

If we could take out the colloid contained in the part MA'B'N near the bottom of cell without disturbing the concentration gradient, then we have a colloid having a concentration greater than c_0. As a measure of the increase of the concentration, we make use of the *local average concentration*, a function of x, defined by

$$\bar{c}(x)=\frac{\text{total amount of colloid in MA'B'N}}{\text{volume of MA'B'N}},$$

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(1) S. Oka, *Proc. Phys.-Math. Soc. Japan*, **18**, 522 (1936). This formula was derived as the solution of a special case ($\partial c/\partial t=0$) of Lamm's differential equation of ultracentrifuging. A formula essentially the same, but without explicit use of sedimentation constant and diffusion constant, was given by Rinde before the publication of Lamm's equation. (Cf. H. Rinde, Dissertation, p. 176 (Upsala, 1928)). Oka's equation is used herewith for the sake of convenience.

or

$$\bar{c}=\frac{\int_0^{\varphi}\int_x^{x_1} cx\,dx\,d\varphi}{\frac{1}{2}\varphi(x_1^2-x^2)}. \tag{2}$$

This gives the average concentration of the colloid in MA′B′N at sedimentation equilibrium, and the ratio $\bar{c}/c_0$ gives the relative increase of the concentration. By means of (1), we obtain

$$\frac{\bar{c}}{c_0}=\frac{x_1^2-x_0^2}{e^{\alpha x_1^2}-e^{\alpha x_0^2}}\cdot\frac{e^{\alpha x_1^2}-e^{\alpha x^2}}{x_1^2-x^2}. \tag{3}$$

We see from this that

$$[\bar{c}]_{x=x_0}=c_0,\quad \lim_{x\to x_1}[\bar{c}]=[c]_{x=x_1}$$

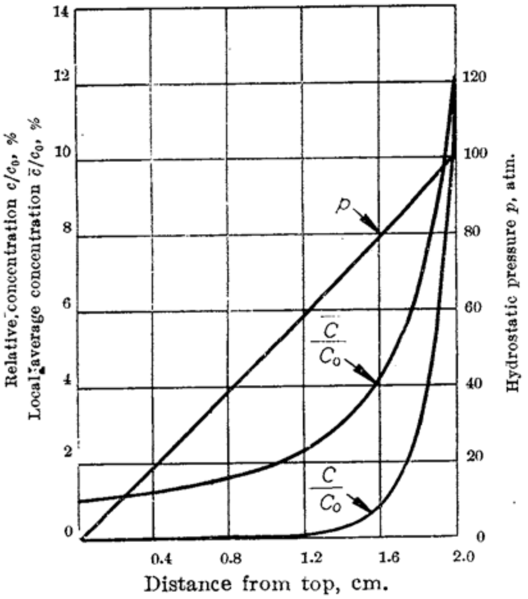

Fig. 2.

and $\bar{c}>c$ for $x_1>x>x_0$.

For the sake of illustration, an example is given. Put $M=10{,}000$, $V=0.75$, $\rho=1.00$, $x_0=5.0$ cm., $x_1=7.0$ cm., and r. p. m. $=30{,}000$ or $\omega=3{,}140$, where M = molecular weight, V = partial specific volume, and ρ = density. In order to use the formula (3), it is necessary to know the value of s/D. We find this by means of the sedimentation velocity formula

$$\frac{s}{D}=\frac{M(1-V\rho)}{RT},$$

where R and T have their usual meanings. Using the above data and assuming that $T=288$ we have $s/D=1.044\times10^{-7}$. The results obtained by using this value are given in Fig. 2.

The hydrostatic pressure p in the cell is given as a function of x by the following relation

$$p=\frac{\rho\omega^2}{3}\left(\frac{x^3-x_0^3}{x}\right). \tag{4}$$

The values of p calculated by this formula is also given in Fig. 2. From the Clausius-Clapeyron equation we understand that for the ice at 0°, the rate of freezing point lowering is −0.0076° per atmosphere. We see from Fig. 2 that the difference of freezing points at AB and A′B′ is about 0.8° corresponding to the hydrostatic pressure difference 101 Atm.

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