BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1807—1812 (1969)

Freezing of the Droplets of Aqueous Solution Aerosols

Yuhei Uzu and Isamu Sano

Department of Chemistry, Nagoya University, Nagoya

(Received October 4, 1968)

By atomizing aqueous solutions both of electrolytes and non-electrolytes, fog droplets of 8μ in diameter were prepared, and their freezing temperatures were measured in a thermostat-like cold chamber fitted with an electrically heated platinum wire. The results were compared with that obtained with fog droplets of pure water of the same size. It was found that non-electrolytes hardly influence the freezing, whereas electrolytes do a great deal. The freezing temperature rises in the presence of an electrolyte and varies with its concentration, the highest temperatures being observed at the concentrations around 1×10^{-4}M for 1-1 type electrolytes and at lower concentrations for 1-2 and 1-3 type electrolytes. K^+ is the most effective of the alkali metal cations having the same species of anion in common, and I^- of the halide anions having the same species of cation in common. Applying the theory of nucleation, the sizes of the hydrated K^+ and the critical nucleus developed from it for ice-nucleation were estimated to be about 6 and 21 Å in radius, respectively.

The formation of ice in supercooled water is a phenomenon of great interest from the physicochemical point of view. Although some sort of coherent picture about it is now beginning to emerge, the theory seems to be far from complete and, in addition, experimental evidence is confusing. Since an investigation of the phenomenon of ice-formation provides information on the nucleation mechanism in supercooled liquids and in supersaturated solutions, much work has been done concerning the roles of insoluble and soluble substances in promoting ice-nucleation in water. It has been found for the former[1] that they would act as a catalyst. Their surface concentrates water molecules to accelerate the phase transition, mainly because of the similarity of the crystallographic structure to that of ice, and partly through the electric force fields that are ionic or non-ionic according to the nature of the constituent of surface, imperfections such as growth steps, re-entrant corners or screw dislocations.

It is questionable, however, whether soluble substances promote ice-nucleation; few reliable data are available and many of the conclusions reached are contradictory to one another. This might be attributed to the difference in the purity of the water and aqueous solutions and the characteristics of the experimental procedures.

This report deals with the effects of soluble substances, electrolytes and non-electrolytes, upon the freezing temperature of a droplet of water, and shows, in the case of electrolytes, that the concentration and valence definitely affect the freezing temperature. Additional information is given about the functions of electrolyte ions in ice-nucleation in water.

Experimental Procedure and Results

The technique has been described in detail.[2,3] The fog droplets of water or aqueous solutions whose size is 8 μ in diameter were introduced into a thermostat-like cold chamber to be supercooled and the freezing temperature was determined by making use of a heated platinum wire as a detector

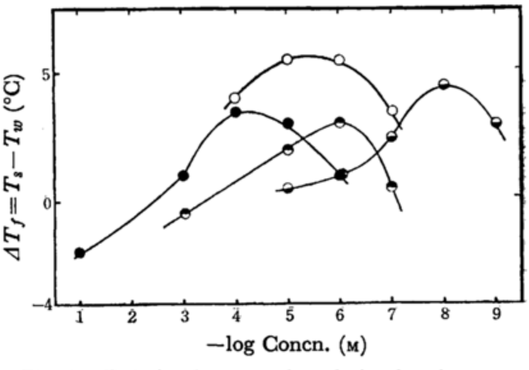

Fig. 1. Relation between the relative freezing temperature and the concentraion of electrolyte.
-●- KCl -○- K_2SO_4 -◓- Na_2SO_4
-◒- K_3PO_4

---

[1] N. H. Fletcher, *Austral. J. Phys.*, **13**, 408 (1960); *Discussions Faraday Soc.*, No. 30, 39 (1960).

[2] Y. Uzu, I. Sano and Y. Fujitani, *J. Colloid Sci.*, **18**, 697 (1963).

[3] Y. Fujitani, Y. Uzu and I. Sano, *J. Meteor. Soc. Japan*, **39**, 249 (1961); Y. Uzu and I. Sano, *ibid.*, **43**, 290 (1965).

of the droplets frozen.

The principal features of the results, also mentioned in our reports,[2,3] are as follows. It was found for electrolytes that a maximum appears in the change in relative freezing temperature with concentration. Some of the results are given in Fig. 1, where $\Delta T_f = T_s - T_w$ is the threshold freezing temperature of solution droplets relative to that of water droplets. The subscript symbols s and w refer to solution and water, respectively. Similar results have been obtained with other electrolytes such as $MgSO_4$, $CuSO_4$, $ZnSO_4$, $(NH_4)_2SO_4$. The results for non-electrolytes are illustrated in Fig. 2. ΔT_f takes a small negative value or zero in the concentration range studied, only becoming appreciable at higher concentrations.

Comparison of the results shown in Figs. 1 and 2 suggests that the change in relative freezing temperature found in electrolyte solution droplets might be due to the presence of ions. For a detailed study, we made measurements for 1×10^{-4} molar aqueous solutions of various electrolytes. The results are summarized in Fig. 3, in which almost all points represent the average of several measurements. It is clear that, for the 1-1 type electrolytes having the same type of cation, the relative freezing temperature rises with the size of the anion, the highest being observed for I^- and the lowest for Cl^-. For those having the same type of anion, the highest is found for K^+ among all the halides studied.

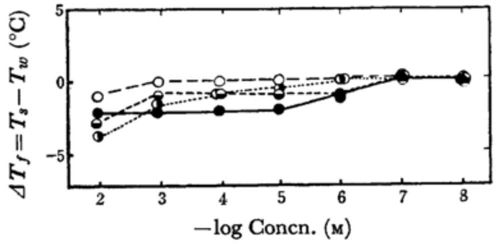

Fig. 2. Relation between the relative freezing temperature and the concentration of non-electrolyte.
-○- saccharose -◒- ethanol -◑- urea
-●- thiourea

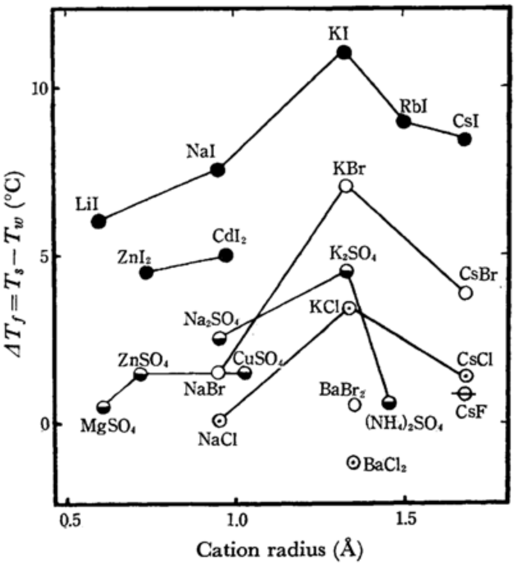

Fig. 3. Relation between the relative freezing temperature and the radius of cation.

Discussion

Two models as to the mechanism of freezing of the droplets of electrolyte solutions have been advanced lately.

1) Critical nuclei for ice-formation would be formed as the consequence of water molecules being attracted to electrolyte ions owing to their electric forces to be arranged around them in a fashion more or less similar to that in ice.

2) Critical nuclei would be insoluble particles which might have been either held tenaciously in water or introduced together with solute, and, in some cases those which might have been activated through reaction with solute.[4]

The results seem to be in line with model 1. Firstly, from the observation $\Delta T_f > 0$ for electrolytes, electrolyte ions could promote either the freezing of droplets by themselves or in cooperation with insoluble particles. Secondly, the finding that ΔT_f is nought in the case of non-electrolytes is evidence that ions alone can be active to effect ice-nucleation. This is supported by the fact that there is regularity, as shown in Fig. 3, in the relation between the relative freezing temperature and the cation radius. It should be added that insoluble particles, if present in water, might have little influence upon ice-nucleation. The reasons are: (1) ΔT_f might be positive in the case of non-electrolytes, if insoluble particles accelerated ice-nucleation. (2) Fogs were prepared with purified materials, such as water subjected to redistillation[2,3] and solutions filtered through 0.1 μ pore size millipore filter. (3) For the purpose of lessening the possibility of a droplet containing insoluble particles, droplets having the mean size as small as 8 μ in diameter were used. (4) To investigate the effect of insoluble particles, some measurements were conducted of the filtered water and 1×10^{-4} molar CdI_2 solutions, and also unfiltered ones. The freezing temperatures were found to be −29.0°C and −24.3°C for the former, and −28.5°C and −24.5°C for the latter.[*1]

From these considerations, we are led to the conclusion that the rise in relative freezing temperature is caused by electrolyte ions and not by insoluble

---

4) H. R. Pruppacher, *J. Chem. Phys.*, **39**, 1586 (1963).

[*1] *Cf.* the Ph. D. thesis presented by Y. Uzu to the Nagoya University (1966).

particles which may be present in the droplets. Assuming that the nuclei are electrolyte ions more or less hydrated to build a layer of ice structure, we shall apply the theory of nucleation to our findings.

Macroscopic quantities such as interfacial energy have been used in the theory. Their use in assemblies containing molecules numbering from a few score to several hundreds is questionable. However, the theory is in good accord with experiment.

Application of the Nucleation Theory. According to the theory,[5] J, the rate of ice-nucleation or the rate at which the critical nuclei acquire an additional molecule to reach a size from which they grow directly toward ice particles, is given by

$$J = (\boldsymbol{k}T_s/\boldsymbol{h})n\cdot 4\pi r^{*2} \exp\{-(\Delta G^* + \Delta g)/\boldsymbol{k}T_s\}, \qquad (1)$$

where ΔG^* is the free energy of formation of the critical nuclei or the maximum free energy necessary for their creation, Δg the free energy of activation of water molecules for self-diffusion in water or across the water-ice boundary, n the number of water molecules in contact with unit area of the surface of critical nuclei whose radius is r^*, $\boldsymbol{k}$ Boltzmann's constant and $\boldsymbol{h}$ Planck's constant.

It is apparent in Eq. (1) that the rate J is much more sensitive to the magnitudes of ΔG^* and Δg in the exponential term as compared to the pre-exponential kinetic term, the magnitude of which is of the order of $10^{28}\ r^{*2}\ \mathrm{sec}^{-1}$ in the case of supercooled water as n is approximately equal to $3\times 10^{-8}\ n_0$, where n_0 represents the density of water expressed in number of molecules per cm^3.

ΔG^* may be expressed as

$$\Delta G^* = (4\pi/3)(r^{*3} - r_h^3)\Delta G_v + \Delta E_{st} + 4\pi(r^{*2} - r_h^2)\sigma + \Delta E_{el}, \qquad (2)$$

r_h being the radius of ions in hydrated state. ΔG_v means the change in free energy per unit volume of ice accompanying the phase transition from water to ice, ΔE_{st} the change in strain energy coming from water molecules fixed to form ice around the hydrated ions, σ the interfacial energy per unit area between the two phases, and ΔE_{el} the change in electrical energy of water molecules when they are subjected to phase transition.

Little is known about the strain energy ΔE_{st}. However, according to the structural models of liquid water, proposed theoretically by Bernal and Fowler,[6] Frenkel[7] and Frank and Wen-Yang Wen,[8] and confirmed experimentally by Dorsch and Boyd,[9] liquid water supercooled to temperatures below 4°C consists, with increasing degree of supercooling, of increasing number of molecules which constitute a structure closely resembling the structure of tridymite type ice, it follows that ΔE_{st} could be neglected.

Realizing that the hydration number of ion is 6 for K^+ and for I^-, it is difficult to imagine a surface for hydration layer. Thus the interfacial energy term, $4\pi r_h^2\sigma$ might be neglected.

For monovalent ion, the electrical energy change ΔE_{el} is calculated to be

$$\Delta E_{el} = (e^2/2D_s)(1/r_h - 1/r^*) + (e^2/2D_l) \times (1/r^* - 1/R) - (e^2/2D_l)(1/r_h - 1/R). \qquad (3)$$

It is assumed herewith that there are two successive layers of water molecules around a hydrated ion. Regarding the inner layer as ice and the outer as liquid, the electrical energy which would be held by a single layer of water molecules if it were wholly in liquid state, is subtracted from the electrical energy of two layers. In this equation, D_s is the dielectric constant of the inner layer having a thickness, r^*-r_h, D_l the dielectric constant of the outer layer extending to the surface of the droplet with radius R and the electronic charge e. Since $R \gg r^* > r_h$, ΔE_{el} can be written in a simplified form

$$\Delta E_{el} = (e^2/2)(1/D_s - 1/D_l)(1/r_h - 1/r^*). \qquad (4)$$

It is thus possible to transform Eq. (2), to a first approximation, into

$$\Delta G^* = (4\pi/3)(r^{*3} - r_h^3)\Delta G_v + 4\pi r^{*2}\sigma + (e^2/2)(1/D_s - 1/D_l)(1/r_h - 1/r^*). \qquad (5)$$

Δg was estimated by McDonald[10] to be nearly constant, the value being as small as about 4×10^{-13} erg/molecule in a limited range of temperature below 0°C.

We have found that potassium iodide is most active. Thus for K^+, both r^* the size as critical nucleus and r_h the size in hydrated state were estimated by virtue of Eqs. (1) and (5).

Calculation of r^* and r_h of K^+. For this purpose, we require the relations

---

5) R. Becker and W. Döring, *Ann. Phys.*, **24**, 719 (1935); **32**, 128 (1938); J. Frenkel, "Kinetic Theory of Liquids," Oxford Univ. Press, Oxford (1946), p. 366; D. Turnbull and J. C. Fischer, *J. Chem. Phys.*, **17**, 71 (1949); B. J. Mason, "The Physics of Cloud," Oxford Univ. Press, Oxford (1957), p. 129; N. H. Fletcher, "The Physics of Rainclouds," Cambridge Univ. Press, Cambridge (1962), p. 214.

6) J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

7) J. Frenkel, "Kinetic Theory of Liquids," Oxford Univ. Press, Oxford (1946), p. 366.

8) H. S. Frank and Wen-Yang Wen, *Discussions Faraday Soc.*, No. 24, 133 (1957).

9) R. G. Dorsch and B. Boyd, *U. S. Nat. Adv. Comm. Aero. Washington, Tech. Note*, No. 2532 (1951).

10) J. E. McDonald, *J. Meteor.*, **10**, 416 (1953).

$$\partial \ln J/\partial r^* = 0, \qquad \partial \ln J/\partial r_h = 0. \tag{6}$$

Denoting by ΔS_v the entropy of fusion per unit volume of ice at 273°K and by $\Delta T_s (=273-T_s)$ the degree of supercooling, it follows through thermodynamical arguments that $\Delta G_v = -\Delta S_v \cdot \Delta T_s$. ΔS_v is evaluated to be approximately 1.22×10^7 erg/°K·cm³. Denoting by ΔH_∞ the heat of fusion per unit mass of bulk ice and by ΔH_r that corresponding to the nucleus ice of radius r^*, we have thermodynamically[10] $\Delta H_r = \Delta H_\infty - (2\sigma/\rho r^*)$, where ρ is the density of ice that could be regarded to be practically independent of temperature and size. It follows that

$$\Delta G_v = -\rho/273(\Delta H_\infty - 2\sigma/\rho r^*)\Delta T_s. \tag{7}$$

By substituting Eq. (7) into Eq. (5) and carrying out differentiation, regarding T_s and Δ_g as constant, we obtain

$$\begin{aligned}&2kT_s/r^* + (4\pi/3)(\rho/273)\Delta T_s\{3r^{*2}(\Delta H_\infty - 2\sigma/\rho r^*)\\ &\quad + (r^{*3}-r_h{}^3)(2\sigma/\rho r^{*2})\} - 8\pi r^*\sigma\\ &\quad - (e^2/2)\,(1/D_s - 1/D_l)1/r^{*2} = 0,\end{aligned} \tag{8}$$

$$\begin{aligned}&(4\pi/3)(\rho/273)\Delta T_s(\Delta H_\infty - 2\sigma/\rho r^*)3r_h{}^2\\ &\quad - (e^2/2)\,(1/D_s - 1/D_l)1/r_h{}^2 = 0\end{aligned} \tag{9}$$

In order to calculate r^* and r_h of K⁺ from Eqs. (8) and (9), we use the following data

$T_s = 253$°K,[*2] $\Delta T_s = 20$°K, $\rho = 0.92$ g/cm³,
$\Delta H_\infty = 79.7$ cal/g, $\sigma = 22$ erg/cm²,[11]
$D_s = 3$, $D_l = 96$.

As has been stated, the concentration of the solution is of the order as low as 10^{-4} mol/*l*, so all the above values except those for ΔT_s and consequently T_s could be approximated by the characteristics of water. It should be mentioned that the value of D_l, 96, is obtained by extrapolation of the values at room temperature down to −20°C. The result is

$$r^* = 20.6\ \text{Å}, \qquad r_h = 6.1\ \text{Å}.$$

It is of interest examine how r^* and r_h vary with σ and D_l. Using the following approximate equations instead of Eqs. (8) and (9),

$$\begin{aligned}&\partial \ln J/\partial r^* \simeq \partial \ln \Delta G^*/\partial r^* \simeq (4\pi/3)(\rho/273)\Delta T_s\\ &\quad \times \{3r^{*2}\Delta H_\infty - (2\sigma/\rho)2r^*\} - 8r^*\pi\sigma\\ &\quad - (e^2/2)\,(1/D_s - 1/D_l)1/r^{*2} = 0,\end{aligned} \tag{10}$$

$$\begin{aligned}&\partial \ln J/\partial r_h \simeq \partial \ln \Delta G^*/\partial r_h \simeq (4\pi/3)(\rho/273)\Delta T_s\\ &\quad \times \Delta H_\infty 3r_h{}^2 - (e^2/2)(1/D_s - 1/D_l)1/r_h{}^2 = 0,\end{aligned} \tag{11}$$

TABLE 1. VARIATION OF r^* AND r_h AS FUNCTIONS OF D_l AND σ

D_l	D_s	σ (dyne/cm)	r^* (Å)	r_h (Å)
96	3	24	22.6	6.0
4			22.5	4.3
96	3	22	20.7	6.0
4			20.6	4.3
96	3	20	18.9	6.0
4			18.7	4.3
96	3	18	17.1	6.0
4			16.9	4.3
96	3	22	20.6	6.1

we find the results as shown in Table 1. The values given in the lowest line are obtained by Eqs. (8) and (9). They are recorded in order to confirm the accuracy of Eqs. (10) and (11).

It is seen from the table that, while the value of r^* hardly changes with D_l, it is largely dependent upon σ, being in the range of 17 to 23 Å for all the probable magnitudes of σ and in close agreement with that for supercooled water at −20°C which is shown in Table 2[12] together with those at other temperatures. As regards r_h, it remains effectively constant irrespective of the variation in σ, changing with D_l within the range of 6 Å which is usually admitted as plausible.

TABLE 2. RADIUS OF THE CRITICAL NUCLEUS FOR ICE FORMATION IN A DROP OF PURE WATER

Temperature (°C)	Radius of water drop (cm)	σ (dyne/cm)	Radius of critical nucleus (cm)
0	∞	23.8	∞
−10	∞	22.8	4.20×10^7
	10^{-6}	22.8	4.88
−20	∞	21.8	2.08
	10^{-6}	21.8	2.26
−30	∞	20.7_5	1.38
	10^{-6}	20.7_5	1.46
−40	∞	19.7	1.03
	10^{-6}	19.7	1.08

The calculated values of r^* and r_h are found to be of the right order of magnitude. Further, it is known that the thickness of the ionic atmosphere around K⁺ in a solution of the concentration 1×10^{-4} mol/*l* is approximately 300 Å. This is much larger than the radius of the critical nucleus, 21 Å. Hence we might regard K⁺ alone as the center of the ice nucleus. Thus, we have ignored the presence of I⁻ in the solution.

---

[11] L. Dufour and R. Defay, "Thermodynamics of Clouds," Academic Press, New York (1963), p. 226.

[*2] The freezing temperatures actually observed for the potassium iodide solution droplets were around −20°C.

[12] L. Dufour and R. Defay, "Thermodynamics of Clouds," Academic Press, New York (1963), p. 150, 176.

The Influence of K^+ on the Structure of Water. There are some factors of interest. One is that a potassium iodide containing water droplet freezes, as shown in Fig. 3, at a temperature about 10°C higher than that at which a potassium iodide not containing droplet of the same size freezes. This means that the critical nucleus in water which is supposed to be only of 14 Å in radius (Table 2) might make rapid development to 21 Å if potassium iodide is present at a concentration of the order of 10^{-4} mol/l. It has been observed that all the cations other than K^+ freeze at temperatures lower than that for K^+ (Fig. 3). This suggests their higher ΔG^* values.

In spite of many publications on the structure of liquid water as well as electrolyte solutions, no definite conclusion has been reached. However, utilizing the information obtained herewith, we are able to give additional interpretation.

It is certain that an electrolyte ion could, owing to its ability of fixing water molecules oriented around itself through its electric forces, exhibit a function to break the structure of water. The structure breaking function should depend, firstly, on the size of ion, and secondly, on the extent of misfit. Here we have introduced the misfit as a measure of the disparity between the water structure contiguous to an ion and the ice structure to be formed from it. This might help interpret the finding that T_s for cations smaller than K^+ falls down in the same way as for those larger than K^+ (Fig. 3), the misfit being taken to be greater for an ion differing more largely in size from a water molecule. Addtional reference must be made to the finding,[13] provided by the studies of electrolyte solutions using X-ray diffraction technique, that ions such as K^+, NH_4^+ and OH^- which are close in size to water molecules have virtually no influence upon the structure of water, whereas those such as Li^+, Na^+ and Cl^- the sizes of which are decisively different from water molecules exert a more or less positive disturbance to the water structure owing to their structure breaking function. Moreover, according to the studies[14] of the self-diffusion of water in electrolyte solutions, both Cs^+ and Li^+ are the structure breakers, and this is particularly the case with Cs^+. Water molecules in the vicinity of Cs^+ display a mobility higher than that characteristic of those in pure water, indicating that the water structure has been made unstable by the presence of an ion. In the case of Li^+, water molecules are bound to the ion, yielding hydration members which are in strained state and hardly display mobility.

We conclude that an ion, which could be included in the water structure with least influence upon it and which could attract water molecules by electric forces to arrange them at least in an ice-like structure, can establish a certain extent of order in supercooled water so that it serves as a critical nucleus in ice formation. As a matter of fact, we observed that the most effective ion is K^+.

The Role of I^- in Ice-nucleation. Hitherto, we have discussed the rise in freezing temperature of water droplets in the presence of electrolytes, taking the behavior of cations alone into consideration. It might now be asked what about anions. It has been shown in Fig. 3 that, for anions having a common cation, their ice nucleability increases with the size of anion in such a way as $I^- > Br^- > Cl^-$. These anions should possess weaker electric fields around them because of their larger size as compared to cations. This might imply that it is next to impossible for anions to fix water molecules so as to form a critical nucleus. The water molecules around anions are supposed to be in situations similar to those of the water molecules around Cs^+, the size of which is large enough to impart them large mobilities. It is therefore possible for an anion to make contribution to the function of a cation in that the former allows water molecules to be taken away by the latter.

Concerning the roles of anions, there are views[15,16] worthy of mention. Anions are mostly of considerable polarizability on account of their large size, so that they might affect the structure of the surface of a water droplet as well as the structure of the interface between solid ice and liquid water. Once favored with these positions, they would act to reduce the strain there, thus facilitating ice formation. The polarizability was taken to be in the order $I^- > Br^- > Cl^-$, which is in line with that for the nucleability.

Concluding Remarks

We have examined the influence of the electrolyte concentration upon the freezing temperature of water droplets, and have indicated some of the results in Fig. 1. On the basis of these results, we conclude that there exists an optimum in electrolyte concentration, at which the droplets freeze most readily to give the highest freezing temperature. The optimums have been determined to be 1×10^{-4} mol/l or thereabout for 1-1 type electrolytes and to be at lower concentrations for 1-2 and 1-3 type electrolytes, though it would be necessary to make more exact determinations by future measurements for the latter two. Similar reports have been presented by some investigators[15] with a number of electrolytes, in which little account has been taken of the function of ions, and the greater part of

---

[13] G. W. Brady, *J. Chem. Phys.*, **33**, 1079 (1960).

[14] J. H. Wang, *J. Phys. Chem.*, **58**, 686 (1954).

[15] C. L. Hosler and C. R. Hosler, *Trans. Am. Geophys. Union*, **36**, 126 (1955); R. G. Pena, J. V. Iribarne and E. M. Achaval, *J. Atmos. Sci.*, **19**, 302 (1962).

[16] W. A. Weyl, *J. Colloid Sci.*, **6**, 389 (1951).

discussion has been given assuming the presence of insoluble particles in water.

It would be significant to search for reasons for the occurrence of the optimum in freezing temperature. It seems to us that the decrease in freezing temperature on the higher concentration side arises from the structure of water being broken down by a large number of cations so that the nuclei could grow with considerable difficulty. The finding that the optimums for 1-2 and 1-3 type electrolytes appear at lower concentrations might be attributed to the presence of more cations in water as compared with the case of 1-1 type electrolytes having the same concentration.