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Quenching of the Scintillation from a γ-Irradiated Cyclohexane Solution Containing *p*-Terphenyl by Electron Scavengers, Positive Ion Interceptors and Some Hydrocarbons

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The luminescence from a cyclohexane solution containing *p*-terphenyl irradiated with ^{60}Co γ-rays has been quenched by various compounds. The quenching efficiencies were found to be in the following order; sulfur hexafluoride$\sim$carbon tetrachloride$>$nitrous oxide$>$ethanol$>$ammonia$>$carbon dioxide. These compounds are known in radiation chemistry as electron scavengers or as positive-ion interceptors. Cyclopropane and ethylene have also shown an appreciable quenching ability, but *n*-butane has shown scarecely any. These results have been explained by assuming that ionic reactions are responsible for the luminescence from a cyclohexane-*p*-terphenyl scintillator.

The mechanism of energy transfer occurring in a liquid organic scintillator has been a concern of many investigators.[1,2] The type of energy transfer seems to depend upon many factors, such as the kind of solvent molecule and the mode of excitation.

In an earlier short communication,[1] we have suggested the possibility that emission from a cyclohexane solution of *p*-terphenyl irradiated by γ-rays of ^{60}Co results from the ionic reactions occurring in the system. Such an ionic process had already been suggested by Kropp and Burton[3] as a possible mechanism, but the insight had not been pursued because the excitation-energy-transfer process was thought to be more plausible at that time.

In this paper, we intend to enlarge our remarks in the short communication[1] and to show more evidence for the participation of an ionic process in the formation of the scintillating state of *p*-terphenyl in cyclohexane.

Experimental

Research-grade cyclohexane purchased from the Wako Chemical Co. was passed through a 1 m column packed with silica gel and distilled twice at 80.8°C prior to use. Scintillation-grade *p*-terphenyl was purchased from the Nakarai Chemical Co. and used as supplied. The other compounds used as quenchers were all of a research grade and were used after usual purifications, such as bulb-to-bulb distillation.

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[1] T. Yoshida and S. Sato, This Bulletin, **40**, 2216 (1967).

[2] "Luminescence of Organic and Inorganic Materials," ed. by H. P. Kallmann and G. M. Spruch, John Wiley & Sons, New York (1962).

[3] J. L. Kropp and M. Burton, *J. Chem. Phys.*, **37**, 1742 (1962).

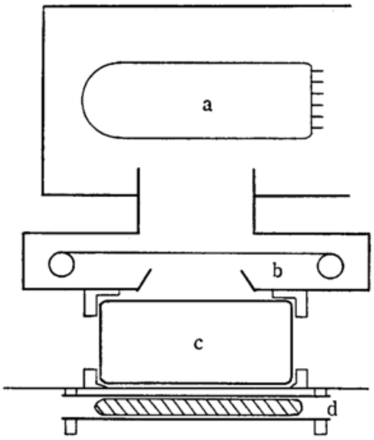

Fig. 1. Arrangement for measuring luminescence. a, Photomultiplier b, Photographic shutter c, Scintillator solution d, γ-Rays source (1 m Ci-^{60}Co).

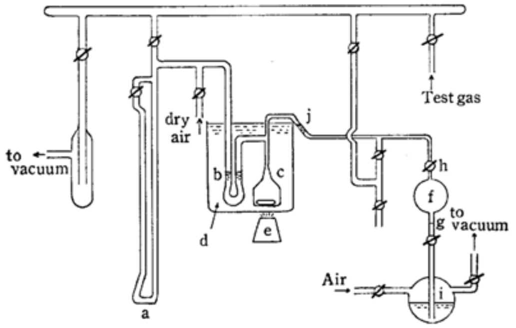

Fig. 2. Apparatus for measuring solubility. a, Mercury manometer. b, Mercury-filled U-tube, which balances the pressures of both sides. c, A flask of known volume (82 m*l*). d, Water bath. e, Magnetic stirrer. f, A glass flask (Volume is calibrated from the mark g to the stopcock h.). i, Mercury leveling bulb (Mercury goes up to the mark j when introducing a gas.).

A schematic diagram of the apparatus for the measurement of scintillation is shown in Fig. 1. Cyclohexane containing a constant amount of *p*-terphenyl was degassed by repeated freeze-pump-thaw cycles. At least five cycles were needed to obtain a constant emission intensity. Quencher gases were introduced with the aid of a liquid nitrogen trap after the pressure had been measured in a calibrated volume.

Since the solubilities of most gases in cyclohexane are not known, a separate apparatus was constructed for this measurement. A schematic diagram of it is shown in Fig. 2. The method is almost the same as that proposed by Loprest.[4] The apparatus for the preparation of scintillator solutions was constructed so as to be mercury free to avoid the possibility of the participation of dissolved mercury in the scintillation.

Results

Figure 3 shows the Ostwald absorption coefficients of five quencher gases (NH_3, N_2O, C_2H_4, CO_2, and SF_6) in cyclohexane as a function of the temperature. The other quenchers used (C_2H_5OH, CCl_4, cyclo-C_3H_6, and *n*-C_4H_{10}) were assumed to be completely soluble in cyclohexane. The values with nitrous oxide, carbon dioxide, sulfur hexafluoride, and ethylene were in good agreement with those previously measured.[5,6]

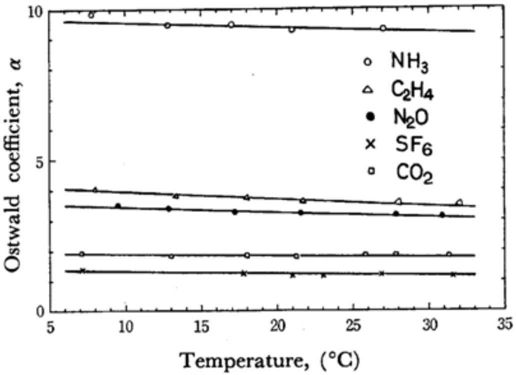

Fig. 3. Ostwald coefficients of quencher gases in cyclohexane as a function of temperature. (at 200 Torr)

In Fig. 4 the reciprocal of the emission intensity is plotted against the reciprocal of the concentration of *p*-terphenyl in cyclohexane. Such a linear relationship as has previously been reported by

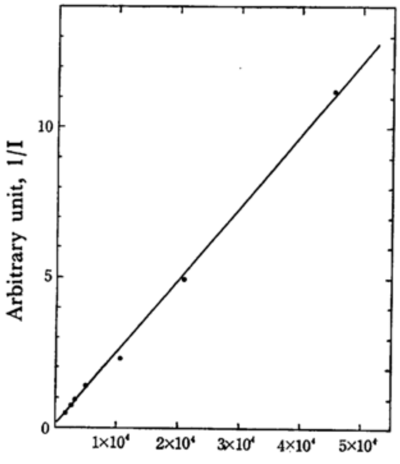

Fig. 4. Dependence of emission intensity on the concentration of *p*-terphenyl in cyclohexane.

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[4] F. J. Loprest, *J. Phys. Chem.*, **61**, 1128 (1957).

[5] S. Sato, T. Terao, M. Kono and S. Shida, This Bulletin, **40**, 1818 (1967).

[6] K. Kikuchi, S. Sato and S. Shida, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 561 (1963).

many investigators[7,8] is obtained. The slope/intercept ratio has been calculated to be 1.6×10^{-2} mol l^{-1}, a value which agrees reasonably well with the 1.3×10^{-2} mol l^{-1} reported by Burton *et al.*[7] Here, the emission from the quartz vessel and pure solvent has been substracted from the total emission. In the case of a 5.7×10^{-3} mol l^{-1} *p*-terphenyl solution, the emission from the vessel was 8.5%, and that from pure solvent was 6.9%, of the total emission.

In Figs. 5, 7, and 8, the relative emission intensities are plotted as a function of the mole fraction of the quenchers. The quencher gases in Fig. 5 are known in radiation chemistry as electron scavengers. An abnormal curve has been obtained with carbon tetrachloride; *i. e.*, the intensities of the emission from cyclohexane solutions containing high concentrations of carbon tetrachloride were lower than that from pure cyclohexane. The details are shown in Fig. 6, where the observed currents from the photomultiplier are plotted as a function of the concentration of carbon tetrachloride. Sulfur hexafluoride, which is as effective in quenching as carbon tetrachloride at low concentrations, did not have such an effect. In Fig. 7, the data with ammonia and ethanol are plotted. Their effects are obviously much weaker than strong electron scavengers, such as sulfur hexafluoride, carbon tetrachloride, and nitrous oxide. Figure 8 compares the quenching efficiencies of aliphatic hydrocarbons with those of electron scavengers. Since hydrocarbons were not effective in quenching, a low concentration of *p*-terphenyl was used. The quenching efficiencies of the hydrocarbons used are in the following order; cyclopropane, ethylene, and *n*-butane.

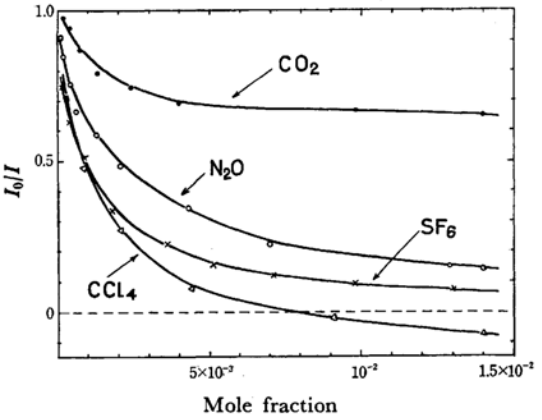

Fig. 5. Relative emission intensity from a 5.7×10^{-3} mol l^{-1} *p*-terphenyl solution as a function of the concentrations of electron scavengers.

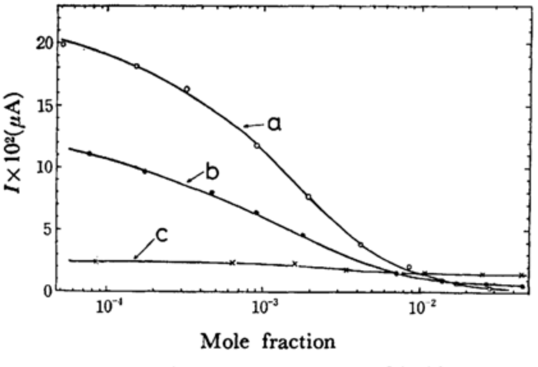

Fig. 6. Quenching by carbon tetrachloride. a, 5.7×10^{-3} mol l^{-1} *p*-terphenyl. b, 1.9×10^{-3} mol l^{-1} *p*-terphenyl. c, Pure cyclohexane.

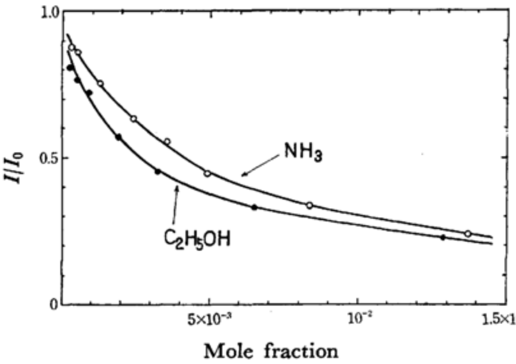

Fig. 7. Relative emission intensity from a 5.7×10^{-3} mol l^{-1} *p*-terphenyl solution as a function of the concentrations of positive ion interceptors.

By using the amplification factor of the photomultiplier and the geometry of the apparatus, the *G*-value of the luminescence has been estimated roughly. The values obtained range from 0.01 to 0.1 with a solution containing 5.7×10^{-3} mol·l^{-1} *p*-terphenyl.

Discussion

Dependence on the Concentration of *p*-Terphenyl. If the excitation-energy-transfer is operative as the mechanism of energy transfer occurring in the present system, a linear relationship between $1/I_0$ and $1/N_s$ can easily be obtained by the steady-state treatment, as Lipsky and Burton have already done.[9] Here, I_0 denotes the emission intensity, and N_s, the concentration of *p*-terphenyl. However, this linear relationship does not necessarily mean that the excitation-energy-transfer is the real mechanism. As has been stated in the earlier communication,[1] *p*-terphenyl molecules are known to capture electrons

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7) M. Burton, P. J. Berry and S. Lipsky, *J. chim. phys.*, **52**, 48 (1955).

8) M. Burton, M. A. Dillon, C. R. Mullin and R. Rein, *J. Chem. Phys.*, **41**, 2236 (1964).

9) S. Lipsky and M. Burton, *J. Chem. Phys.* **31**, 1221 (1959).

in cyclohexane[10] and the negative ions formed may become precursors of excited *p*-terphenyl molecules. The reaction scheme is:

$$\mathrm{C} \rightsquigarrow \mathrm{C}^{+} + \mathrm{e} \qquad (1)$$

$$\mathrm{e} + \mathrm{T} \longrightarrow \mathrm{T}^{-} \qquad (2)$$

$$\mathrm{C}^{+} + \mathrm{T}^{-} \longrightarrow \mathrm{C} + {}^{1}\mathrm{T}^{*}\ (\text{or } {}^{3}\mathrm{T}^{*}) \qquad (3)$$

$${}^{1}\mathrm{T}^{*} \longrightarrow \mathrm{T} + h\nu \qquad (4)$$

Here, C and T denote cyclohexane and *p*-terphenyl molecules respectively. $^{1}\mathrm{T}^{*}$ and $^{3}\mathrm{T}^{*}$ denote excited singlet and triplet states of *p*-terphenyl. The former is responsible for the luminescence from the solution, while the latter may be deactivated without radiation to the ground state.[11]

For discussing the kinetics of the reactions occurring in a γ-irradiated solution, the steady-state treatment is not adequate, because the charged species produced are believed not to be distributed homogeneously in the solution.[12] A tentative treatment for such a system has recently been developed by Freeman[13] and this laboratory.[5,12] Using the formulation already described[12] with a little modification of the distribution function of the charged species, a linear relationship between $1/I_0$ and $1/N_s$ can be derived; the procedure is shown in the Appendix. In this treatment, the k ratio, which is the slope/intercept ratio of the linear relationship in Fig. 4, has the following relation:

$$k = \alpha/(zn^{0}_{-})$$

while

$$r_{av} = \alpha^{-1/3}\Gamma(4/3)$$

Here, n^{0}_{-} is the number of jumps which a "solvated" electron[5] makes when diffusing a unit distance. z is the coordination number, and r_{av} is the average initial distance between an electron and its parent ion. By substituting the observed value, 1.6×10^{-2} mol l^{-1} for k, we can obtain 70 Å for r_{av}. This value is in good agreement with the value, 50—60 Å, estimated previously from the data of an experiment using a different approach.[12]

The Effects of Electron Scavengers. In the previous communication[1] we have reported the effects of sulfur hexafluoride, nitrous oxide, and carbon dioxide. The reinvestigated data of these compounds agree well with the previous data. The quenching efficiencies are in the following order: sulfur hexafluoride, carbon tetrachloride, nitrous oxide, and carbon dioxide. This order seems to correspond to the order of the efficiency of electron scavenging in the gas phase.[14,15]

On the other hand, we have shown that the $G(\mathrm{H_2})$ from cyclohexane is suppressed by the addition of sulfur hexafluoride, nitrous oxide, or carbon dioxide, and that the concentration dependence of the effect is almost constant with any of the three electron scavengers.[5] This discrepancy may be explained as follows. In the scintillator system, we have *p*-terphenyl together with a quencher. Since the *p*-terphenyl molecule is known to capture an electron in cyclohexane,[10] a competition for electrons will occur between the two reactions, (2) and (5):

$$\mathrm{S} + \mathrm{e} \rightarrow \mathrm{S}^{-} \qquad (5)$$

Here, S denotes an electron scavenger. In such a system, electron-transfer reactions must occur when the electron affinities of T and S are different.

$$\mathrm{T}^{-} + \mathrm{S} \rightleftharpoons \mathrm{T} + \mathrm{S}^{-} \qquad (6)$$

If sulfur hexafluoride and carbon tetrachloride, which have high electron affinities, undergo a forward reaction, and carbon dioxide, which has a low electron affinity, does the reverse, the order of efficiencies shown in Fig. 5 can be explained.

If this reasoning is correct, the present experiment provides a method of determining the order of the electron affinities of some compounds. However, as will be seen below, complications airse.

At high concentrations of carbon tetrachloride, the luminescence from a cyclohexane solution of *p*-terphenyl was weaker than that from pure cyclohexane (Fig. 6). Since the origin of the luminescence from pure cyclohexane is difficult to explain,[*1] the mechanism of the quenching observed is far beyond our speculation. Obviously, further experiments using different approaches are needed on this problem.

Recently, Holroyd has shown that nitrous oxide in a cyclohexane solution is decomposed by light irradiation at 1470 Å and has concluded that the excitation-energy transfer occurs from an excited cyclohexane molecule to nitrous oxide.[16] According to his estimation, the *G*-value of excited cyclohexane molecules in the γ-radiolysis of cyclohexane is 1.2, if the *G*-value of charge separation is assumed to be 3. In the present system, therefore, the process suggested by Holroyd may play a part in the reaction, especially at high concentrations of quenchers. However, since we are concerned with a qualitative correlation between the quenching of the scintillation and the electron or positive-ion scavenging of quenchers, we neglect the energy-transfer process for the sake of simplicity.

The Effects of Positive-ion Interceptors. Ammonia and ethanol are known to behave as

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[10] S. Arai and L. M. Dorfman, *ibid.*, **41**, 2190 (1964).

[11] F. B. Harrison and G. T. Reynolds, *Phys. Rev.*, **79**, 732 (1950).

[12] S. Sato, This Bulletin, **41**, 304 (1968).

[13] G. R. Freeman, *J. Chem. Phys.*, **46**, 2822 (1967).

[14] W. J. Holtslander and G. R. Freeman, *Can. J. Chem.*, **45**, 1649 (1967).

[15] J. M. Warman, *J. Phys. Chem.*, **71**, 4066 (1967).

[*1] The possibility that impurities in cyclohexane play a role in the scintillation of pure cyclohexane cannot be excluded.

[16] R. A. Holroyd, *ibid.*, **72**, 759 (1968).

proton scavengers in the radiation-induced reaction of hydrocarbons.[17,18] The reaction in cyclohexane may be described as follows:

$$RH + C_6H_{12}^+ \rightarrow RH_2^+ + C_6H_{11} \qquad (7)$$

Here, RH denotes ammonia or ethanol. In the present case, the reaction which interferes with the formation of excited *p*-terphenyl molecules may be as follows:

$$RH_2^+ + T^- \rightarrow RH + HT \qquad (8)$$

The radicals produced (HT) would not luminescence. The fact that ethanol is more effective than ammonia in quenching (Fig. 7) is consistent with the order of their efficiencies as proton scavengers.[18]

The Effects of Ethylene, Cyclopropane, and *n*-Butane. Recently, Stephenson *et al.* have shown that some diolefins can quench the fluorescence from excited aromatic compounds in *n*-hexane.[19] Therefore, ethylene could behave as a quencher as has been observed in the present experiment (Fig. 8). However, the concentration of dienes used in the above experiment is much higher than ours. Moreover, as is shown in Fig. 8, cyclohexane has been shown to quench the luminescence as much as ethylene. Cyclopropane is a paraffin and is not expected to quench an excited *p*-terphenyl molecule efficiently. On the other hand, *n*-butane is found to be much less effective even in quenching.

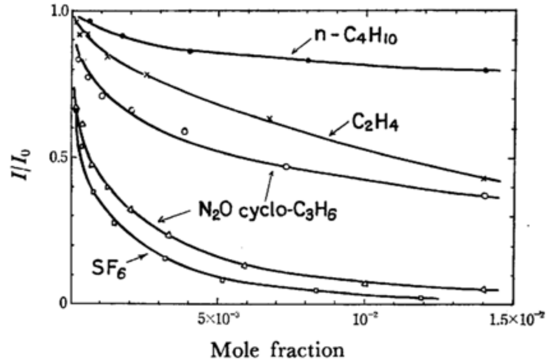

Fig. 8. Relative emission intensity from a 1.9× 10^{-3} mol l^{-1} *p*-terphenyl solution as a function of the concentrations of some hydrocarbons and electron scavengers.

Ausloos *et al.*[20] have recently uncovered a series of ion-molecule reactions occurring in the liquid phase:

$$C_6H_{12}^+ + RH \rightarrow C_6H_{11}^+ + RH_2 \qquad (9)$$

$$\searrow C_6H_{10}^+ + RH_3 \qquad (10)$$

Here, RH represents cyclopropane or ethylene. If these reactions occur in the present system, quenchings observed with cyclopropane and ethylene may be explained by a combination of the reactions (9) and (10) and the reaction (11):

$$C_6H_{11}^+ + T^- \rightarrow C_6H_{10} + HT \qquad (11)$$

Reaction (11) interferes with the formation of excited *p*-terphenyl. In the case of *n*-butane, reactions such as (9) and (10) have not been reported. Probably, they would not occur efficiently.

Alternative Ionic Reactions to Form the Excited *p*-Terphenyl. So far, we have addopted *p*-terphenyl negative ions as the precursors of excited *p*-terphenyl molecules. However, since *p*-terphenyl has an ionization potential lower than cyclohexane, alternative ionic processes can be constructed for the formation of the excited *p*-terphenyl. One of these reaction schema is:

$$C \rightsquigarrow C^+ + e \qquad (1)$$

$$C^+ + T \rightarrow C + T^+ \qquad (12)$$

$$T^+ + e \rightarrow {}^1T^* \text{ (or } {}^3T^*) \qquad (13)$$

However, if this mechanism is the only process producing the excited *p*-terphenyl, the difference in quenching efficiency of the four electron scavengers cannot easily be explained. Therefore, reactions (12) and (13), should they occur, should be taken into account, along with the series of reactions from (1) to (4). In that case, the reaction (14) should probably be included also:

$$T^+ + T^- \rightarrow {}^1T^* \text{ (or } {}^3T^*) + T \qquad (14)$$

The data obtained in the present paper cannot make a possible decisive choice of a reaction scheme, but they do show that ionic processes seem to play an important role in the scintillation from a cyclohexane solution of *p*-terphenyl.

The authors are grateful to Professor S. Shida for his valuable suggestions.

Appendix

Electrons ejected into a cyclohexane solution by γ-ray irradiation drift toward the parent positive ions by means of the Coulombic interaction. On the way, a part of electrons will be scavenged by *p*-terphenyl. If the reaction is diffusion-controlled, the fraction (f_T) of electrons scavenged by *p*-terphenyl may be expressed as follows:[12]

$$f_T = 1 - \frac{1}{N}\int_0^\infty \phi(r)(1-N_s)^{zn}\text{-d}r$$
$$= 1 - \frac{1}{N}\int_0^\infty \phi(r)\exp(\beta r^3)\text{d}r$$

where N_s is the mole fraction of *p*-terphenyl, z is

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[17] F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

[18] J. W. Buchanan and F. Williams, *J. Chem. Phys.*, **44**, 4377 (1966).

[19] L. M. Stephenson, D. G. Whitten and G. S. Hammond, "The Chemistry of Ionization and Excitation," ed. by G. R. A. Johnson and G. Scholes, Taylor & Francis Ltd., London (1967), p. 35.

[20] P. Ausloos, A. A. Scala and S. G. Lias, *J. Am. Chem. Soc.*, **89**, 3677 (1967).

the coordination number, and n_- is the number of jumps which an electron makes in diffusion to the parent ion $(n_-=n_-^0 r^3)$.

$$\beta=\left(\frac{2z}{\sigma^2 r_c}\right)\left(\frac{D_-}{D_+ + D_-}\right)\log(1-N_s)$$
$$\simeq -\left(\frac{2z}{\sigma^2 r_c}\right)\left(\frac{D_-}{D_+ + D_-}\right)N_s$$

The symbols used here have been discussed in a previous paper;12) σ is the diameter of the cyclohexane molecule, r_c is defined by the $r_c=e^2/\varepsilon \boldsymbol{k}T$ relation, and D_- and D_+ are the diffusion coefficients of an electron and the parent positive ion in cyclohexane. $\phi(r)$ is the distribution function for ion pairs, for which we used the $r^2\exp(-\alpha r^2)$ function in the previous paper.12) With this function, the integration shown above cannot easily be carried out. Here, a modified function, $r^2\exp(-\alpha r^3)$,*2 is tentatively introduced for $\phi(r)$, so that the integration can easily be performed. The relation obtained is as follows:

$$f_{\mathrm{T}}=\beta/(\beta-\alpha)$$

According to the preceding discussion, I_o is proportional to f_{T}:

$$1/I_o \propto 1/f_{\mathrm{T}}=1-\alpha/\beta=1+k/N_s$$
$$k=\left(\frac{\sigma^2 r_c}{2z}\right)\left(\frac{D_+ + D_-}{D_-}\right)\alpha$$

Obviously, a linear relationship between $1/I_o$ and $1/N_s$ is obtained.

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*2 The distribution expressed by this function corresponds to that between $r^2\exp(-\alpha r^2)$ and the function calculated by Freeman.13)