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The Velocity Constants of Free Ions and Ion Pairs. II

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SUMMARY

The distribution of the intercharge distance of ion pairs was derived from a solvated ion pair model. The calculation was applied to a fluorenylsodium-tetrahydrofuran system, and the equilibrium constants for the equilibria, contact ion pairs ⇌ solvent separated ion pairs ⇌ free ions, were calculated. Furthermore, the enthalpy and entropy changes for the equilibria were derived. Agreement with experimental data was satisfactory.

INTRODUCTION

In a preceding paprer [1] the reactivities of ion pairs and free ions were theoretically studied, and the reactivity of ion pairs was shown to depend sensitively on the intercharge distance of ion pairs. The problem was recently discussed [2, 3] and the reactivities of two kinds of ion pairs, namely contact and solvent-separated ion pairs, were compared [4]. Distribution functions for the intercharge distance have previously been derived by Bjerrum [5] and Fuoss [6], but they could not give information on the two kinds of ion pairs because the problem of solvation around ion pairs was not considered. In the preceding paper [1], a "solvent atmosphere" model was presented, but it was much too simplified to account for the reactivities of the two kinds of ion pairs. A more exact distribution function will be presented in this paper, and the intercharge distance of ion pairs will be discussed in terms of solvation effect.

DERIVATION

Model of an Ion Pair

In the preceding paper [1], the distribution function for the intercharge distance R of an ion pair was given by

$$P(R)\,dR = e^{-\epsilon_R/kT}\,R^2 dR \Big/ \int_{r_I+r_{II}}^{R_c} e^{-\epsilon_R/kT}\,R^2\,dR \qquad (1)$$

where ϵ_R represents the potential energy of an ion pair with an intercharge distance R, k the Boltzmann constant, T the absolute temperature, $r_I + r_{II}$ the closest intercharge distance, and R_c the critical distance distinguishing free ions and ion pairs. According to our solvent atmosphere model [1], the potential energy of an ion pair is given by

$$\epsilon_R = \epsilon_i - (\epsilon_{BSR})_I - (\epsilon_{BSR})_{II} \qquad (2)$$

where ϵ_i represents the potential energy between an ion and its gegenion, ϵ_{BSR} the potential energy of a solvent atmosphere partially broken by an approach of an ion to its gegenion, and I and II are the ion and its gegenion, respectively.

For the calculation of ϵ_i and ϵ_{BSR}, we make the following assumptions:

1) The ion and its gegenion are rigid spheres with radii l_I and l_{II}, respectively.

2) The electric charge $z_I q$ is located at the center of a rigid sphere (radius r_I) as shown in Fig. 1.

3) The dielectric constant in the vicinity of ions is supposed to be much lower than the macroscopic one [7]. In the present model, the dielectric constant is unity within a radius a_I from the center of the electrically charged sphere as dotted in Fig. 1. Outside this area, the dielectric constant has the macroscopic value.

4) The Coulomb forces between an ion and its gegenion are

$$z_I z_{II} q^2 / DR^2 \tag{3}$$

the dielectric constant D being unity when the intercharge distance R is either a_I or a_{II}, whichever is smaller. Beyond this, the dielectric constant has the macroscopic value.

Potential Energy ϵ_i

From the definition, the potential energy between two ions constituting an ion pair ϵ_i is given by

$$\epsilon_i = \int_R^a \frac{z_I z_{II} q^2}{R^2} dR + \int_a^\infty \frac{z_I z_{II} q^2}{DR^2} dR$$

$$= z_I z_{II} q^2 \left\{ \frac{1}{R} - \left(1 - \frac{1}{D} \right) \frac{1}{a} \right\} , (r_I + r_{II} \leqq R \leqq a) \tag{4}$$

or

$$\epsilon_i = \int_R^\infty \frac{z_I z_{II} q^2}{DR^2} dR = \frac{z_I z_{II} q^2}{DR} , (a < R) \tag{5}$$

where a represents either a_I or a_{II}, whichever is smaller.

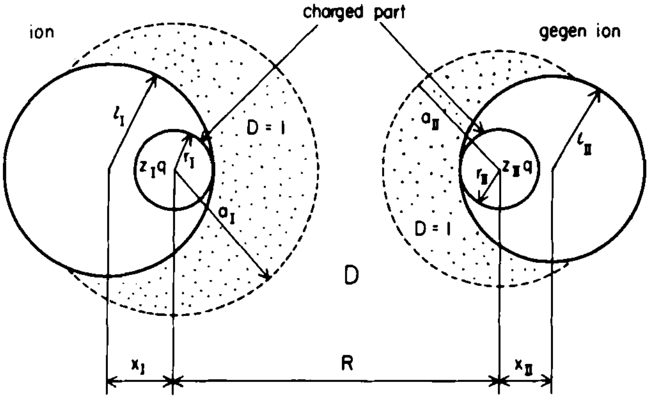

Fig. 1. Model of an ion pair.

Potential Energy $(\epsilon_{BSR})_I$

The potential energy $(\epsilon_{BSR})_I$ is the one of the solvent atmosphere partially broken by an approach of the gegenion to an intercharge distance R from its gegenion as shown in Fig. 1. The partial breaking of the solvent atmosphere implies a partial desolvation resulted by an approach of the gegenion.

According to the solvent atmosphere model [1], $(\epsilon_{BSR})_I$ is given by

$$(\epsilon_{BSR})_I = \int_V \sum_i^r \rho \, \Delta G_i^r \, dV$$

$$= 2\pi \int_{R+x_{II}-l_{II}}^{R+x_{II}+l_{II}} r^2 \left(1 - \frac{r^2 + (R + x_{II})^2 - l_{II}^2}{2r(R + x_{II})}\right) \sum_i \rho_i^r \, \Delta G_i^r \, dr \tag{6}$$

where V is the volume of the gegenion, ρ_i^r the density of the solvent molecule S_i at a distance r from the electric charge $z_I q$, ΔG_i^r the free energy of one S_i molecule at a distance r, and $x_{II} = l_{II} - r_{II}$. The density ρ_i^r and the free energy ΔG_i^r are formulated in our preceding paper [1] (by Eqs. 27 and 23, respectively). The free energy is given by

$$\Delta G_i^r = -\frac{D^r(D_{oi} + 2)}{2D^r + D_{oi}} \cdot |\mu_i| \cdot |E^r| \cdot L\left(\frac{D^r(D_{oi} + 2)}{2D^r + D_{oi}} \cdot |\mu_i| \cdot |E^r|/kT\right)$$

$$- \frac{3D^{r^2}(D_{oi} + 2)}{2(2D^r + D_{oi})(2D^r + 1)} \lambda_i E^{r^2} \tag{7}$$

where the suffixes i and r represent the solvent molecule S_i and the distance from the electric charge $z_I q$, respectively, D the dielectric constant of the solution, D_{oi} the internal dielectric constant of the solvent molecule S_i based on the electronic polarization, μ_i the dipole moment of S_i, E the electric field, L the Langevin function, and λ_i the isotropic electronic polarization of S_i. The second term of the right-hand side of Eq. (7) is assumed to be negligibly small,* and the angle between μ_i and E^r is furthermore assumed to be zero for simplicity. Hence, the free energy is given by

$$\Delta G_i^r = - \frac{D^r(D_{oi} + 2)}{2D^r + D_{oi}} \cdot |\mu_i| \cdot |E^r| \tag{8}$$

From the assumptions,

$$D^r = 1,\ |E^r| = \frac{|z_I|q}{r^2} \quad (r_I \leqq r \leqq a_I) \tag{9}$$

or

$$D^r = D,\ |E^r| = \frac{|z_I|q}{Dr^2} \quad (a_I < r) \tag{10}$$

Hence we have

$$\Delta G_i^r = - \frac{|\mu_I| \cdot |z_I|q}{r^2} \quad (r_I \leqq r \leqq a_I) \tag{11}$$

or

$$\Delta G_i^r = - \frac{D_{oi} + 2}{2D + D_{oi}} \cdot \frac{|\mu_i| \cdot |z_I|q}{r^2} \quad (a_I < r) \tag{12}$$

Equalizing the density ρ_i^r with $\rho_i^{R+x_{II}}$ for simplicity, and substituting Eqs. (11) and (12) into Eq. (6), we have

$$(\epsilon_{BSR})_I = -2\pi|z_I|q \left[1_{II} - \frac{(R + x_{II})^2 - 1_{II}{}^2}{2(R + x_{II})} 1\eta \frac{R + x_{II} + 1_{II}}{R + x_{II} - 1_{II}} \right] \cdot$$

$$\sum_i \rho_i^{R+x_{II}} \cdot \frac{D(D_{oi} + 2)}{2D + D_{oi}} \cdot |\mu_i| - 2\pi|x_I|q \left[\left\{ X - (R + x_{II} - 1_{II}) \right\} \left\{ 1 - \frac{X + (R + x_{II} - 1_{II})}{4(R + x_{II})} \right\} \right.$$

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*The assumption would be justified by the saturation phenomena of the electronic polarization under an extremely high intensity electric field in the vicinity of an ion. If the saturation occurs, the λ value should be drastically decreased. The error due to this assumption would be compensated for by assuming an area with D = 1.

$$-\frac{(R+x_{II})^2-l_{II}^2}{2(R+x_{II})}\ln\frac{X}{R+x_{II}-l_{II}}\Bigg]\sum_i\left\{(\rho_i^{R+x_{II}})_{D=1}-\rho_i^{R+x_{II}}\frac{D(D_{oi}+2)}{2D+D_{oi}}\right\}|\mu_i| \tag{13}$$

where

$$X=\begin{cases}R+x_{II}-l_{II}, & (a_I<R+x_{II}-l_{II})\\ a_I, & (R+x_{II}-l_{II}\leqq a_I=\leqq R+x_{II}+l_{II})\\ R+x_{II}+l_{II}, & (R+x_{II}+l_{II}<a_I)\end{cases}$$

The first term on the right-hand side in Eq. (13) is independent of the parameter a_I whereas the second term depends on a_I. The potential energy $(\epsilon_{BSR})_{II}$ is given by changing the suffix I into II in Eq. (13).

COMPARISON WITH EXPERIMENTS

Potential Energy Curves

To our knowledge, the most detailed investigation on ion pairs was presented for the system fluorenyl salts-tetrahydrofuran [4]. Our following discussion will be limited to this system, unless otherwise specified. It is known that the tetrahydrofuran molecule strongly solvates cations, but not anions; the sodium ion is considered to be strongly solvated by tetrahydrofuran. It may be assumed, therefore, that the fluorenyl anion has no solvent atmosphere in which dielectric constant is unity, and that the sodium cation is surrounded by a solvent atmosphere with D = 1, the thickness being the diameter of the spherical tetrahydrofuran molecule $2r_i$. The suffixes I and II represent the fluorenyl anion and the sodium cation, respectively. From these assumptions we have

$$a_I = r_I \quad \text{and} \quad a_{II} = r_{II} + 2r_i \tag{14}$$

as shown in Fig. 2.

From the definition, the potential energies are given by

$$\epsilon_i = \frac{z_I z_{II} q^2}{DR} \tag{15}$$

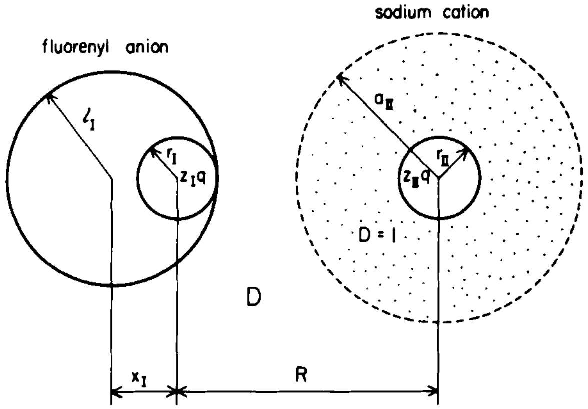

Fig. 2. Fluorenylsodium in tetrahydrofuran.

$$(\epsilon_{BSR})_I = -2\pi|z_I|q\left(r_{II} - \frac{R^2 - r_{II}^2}{2R}\ln\frac{R+r_{II}}{R-r_{II}}\right)\sum_i \rho_i^R \cdot |\mu_i| \cdot \frac{D(D_{oi}+2)}{2D+D_{oi}} \tag{16}$$

and

$$(\epsilon_{BSR})_{II} = -2\pi|z_{II}|q\left[l_I - \frac{(R+x_I)^2 - l_I^2}{2(R+x_r)}\ln\frac{R+x_I+l_I}{R+x_I-l_I}\right]\sum_i \rho_i^{R+x_I}\cdot\frac{D(D_{oi}+2)}{2D+D_{oi}}\cdot|\mu_i|$$

$$-2\pi|z_{II}|q\left[\left\{X-(R+x_I-l_I)\right\}\left\{1-\frac{X+(R+x_I-l_I)}{4(R+x_I)}\right\}-\frac{(R+x_I)^2-l_I^2}{2(R+x_I)}\ln\frac{X}{R+x_I-l_I}\right]$$

$$\sum_i\left\{(\rho_i^{R+x_I})_{D=1} - \rho_i^{R+x_I}\frac{D(D_{oi}+2)}{2D+D_{oi}}\right\}|\mu_i| \tag{17}$$

where

$$X = \begin{cases} R + x_I - l_I, & a_{II} < R + x_I - l_I) \\ a_{II}, & (R + x_I - l_I \leqq a_{II} < R + x_I + l_I) \\ R + x_I + l_I, & (R + x_I + l_I \leqq a_{II}) \end{cases}$$

and, from the definition of ρ_i^r given previously [1],

$$\rho_i^R = \rho_i^{R+x_I} = (\rho_i^{R+x_I})_{D=1} = \rho_i^\infty$$

The potential energy of an ion pair ϵ_R is given by substituting Eqs. (15), (16), and (17) into Eq. (2).

Based on the equations given above, the potential energy curves for fluorenylsodium in tetrahydrofuran are shown in Fig. 3. The curves are constructed with the parameters $r_I = 0.77$ Å (Pauling's radius of carbon atom), $r_{II} = 0.95$ Å (Pauling's ionic radius); $|\mu_i| = 1.68 \times 10^{-18}$ esu cm [8]; $\rho_i^\infty = 7.43 \times 10^{21}$ molecules/cm^3; $l_I = 5.14$ Å (the longest intramolecular distance × 1/2); $D_{0i} = 1.98$ (the square of the refractive index of tetrahydrofuran at 20°); $a_{II} = r_{II} + 2r_i = 7.31$ Å (r_i is calculated by the equation [1], $r_i^3 = 3.97 \times 10^{-25}$ M/d, where M represents the molecular weight, and d the density in g/cm^3); and D = 7.39 (25°), 7.88 (10°), 8.23 (0°), 8.60 (-10°), 9.00 (-20°), 9.43 (-30°), 9.91 (-40°), and 10.43 (-50°) [9]. As seen from Fig. 3, the potential energy curves have two minima at

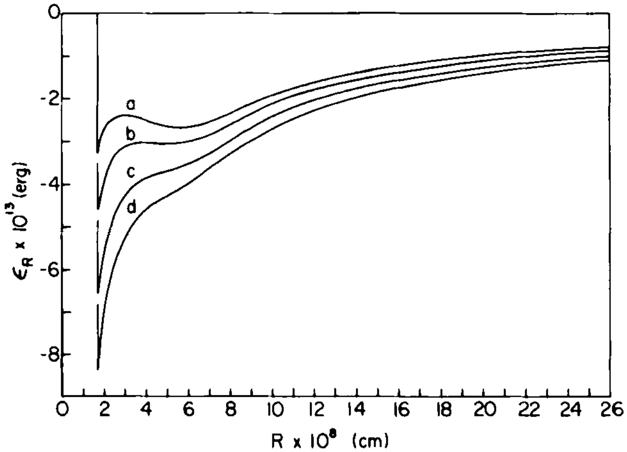

Fig. 3. Potential energy of an ion pair, fluorenylsodium in tetrahydrofuran, $a_{II} = 7.31$ Å. a, -50°; b, -30°; c, 0°; d, 25°.

low temperatures (and hence, at high dielectric constants). Even at -50°, however, the two minima do not appear to represent two thermodynamically distinct and chemically different entities, i.e., the contact or intimate ion pair and the solvent-separated ion pair, because the potential barrier for the mutual transfer from one minimum to another is too low; for the transfer from the higher minimum to the lower, the barrier is 0.26×10^{-13} erg/ion pair (= 0.4 kcal/mole). At 0 and 25°, the two kinds of ion pairs cannot be distinguished from the potential energy curves.

Grunwald [2] has presented a potential energy diagram with two minima corresponding to the two ion pairs, which is shown in Fig. 4 with changed units. On the other hand, the present paper shows that the two kinds of

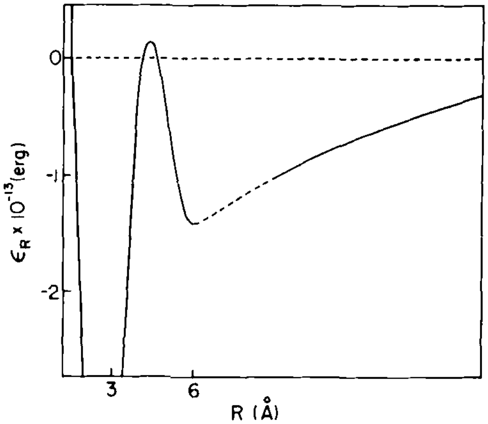

Fig. 4. Grunwald's diagram for the potential energy of an ion pair (D = 20).

ion pairs may not be generally distinguished from the potential energy curve in contrast with Grunwald's curve. Figure 5 shows the potential energy curves for various dielectric constants under the same conditions as fluorenylsodium in tetrahydrofuran. In the calculation, a constituent ion of an ion pair was assumed to be surrounded by a solvent atmosphere having a dielectric constant of unity; in other words, one ion (not both ions) constituting an ion pair is strongly solvated. From Fig. 5 it is seen that the two minima are not found at very high and low dielectric constants (curves a, b, e, and f), and that even the two minima of the curves for D = 10.43 and 13 (curves c and d) do not appear to represent the two thermodynamically distinct entitles because of very low potential barrier in between. The two kinds of ion pairs, it may be concluded, do not generally exist when only one ion pair is strongly solvated.

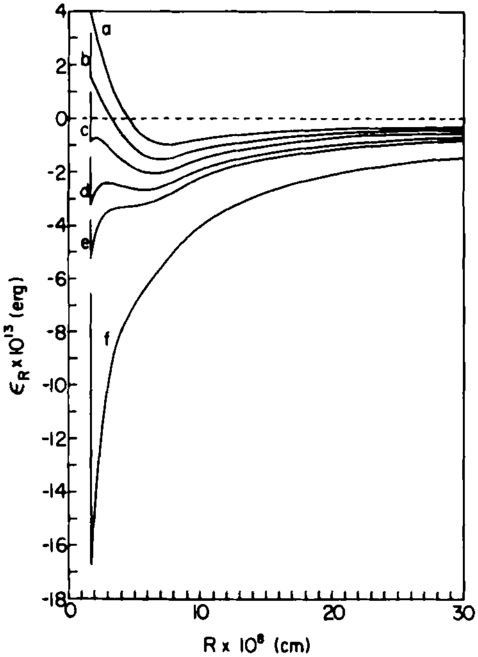

Fig. 5. Potential energy of an ion pair having strongly solvated constituent ion. a, D = 25; b, D = 17; c, D = 13; d, D = 10.43; e, D = 9; f, D = 5. For other conditions, see Fig. 3.

Fig. 6 shows the potential energy of an ion pair at various dielectric constants calculated on the assumption that two constituent ions of an ion pair are strongly solvated. The curves at high dielectric constants, for example curve a, are similar to Grunwald's diagram shown in Fig. 4, and the two kinds of ion pairs appear to be thermodynamically distinguishable; the two minima of the curves at equilbrium distances of about 3 and 7 Å represent a contact ion pair and a solvent separated ion pair, respectively. Apparently, the curves at lower dielectric constants, however, do not have the two minima.

When either ion of an ion pair is not strongly solvated, the potential energy is shown in Fig. 7. Apparently, the curves at various dielectric constants do not have two minima.

Considerations given here indicate that the two kinds of ion pairs, contact or intimate ion pairs and solvent separated ion pairs, can hardly be distinguished from the potential energy curve; it seems possible that they

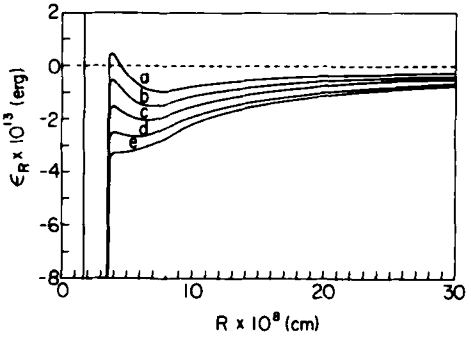

Fig. 6. Potential energy of an ion pair composed of two strongly solvated ions. a, D = 25; b, D = 17; c, D = 13; d, D = 10.43; e, D = 9; a_I = 4 Å. For other conditions, see Fig. 3.

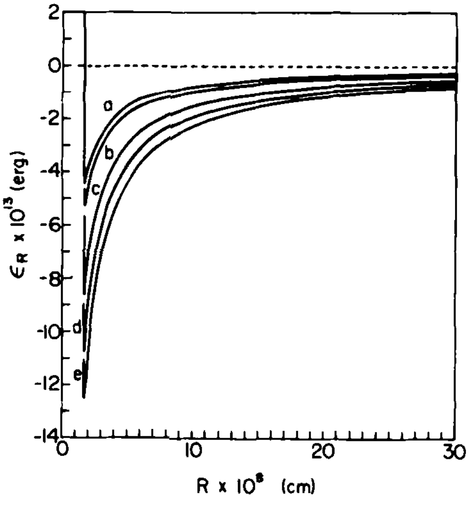

Fig. 7. Potential energy of an ion pair in the case that either ion of an ion pair is not strongly solvated. a, D = 25; b, D = 17; c, D = 13; d, D = 10.43; e, D = 9; $a_I = r_I$; $a_{II} = r_{II}$. For other conditions, see Fig. 3.

are distinguishable only when both ions of an ion pair are strongly solvated in solvents of high dielectric constant. Thus, the exact distinction between the two kinds of ion pairs is generally implausible, although the concept is convenient to describe the distribution of the intercharge distance of ion pairs. Szwarc et al. [10] were led to the similar conclusion on experimental basis.

Distribution of the Intercharge Distance

According to Bjerrum's theory [5], the probability of finding a gegenion in a shell with radius R and thickness dR around the central ion is given by

$$Q(R)\,dR = \frac{4\pi N[C]_a}{1000}\, e^{-\epsilon_R/kT} R^2\, dR \tag{18}$$

where N represents the Avogadro number and $[C]_a$ the electrolyte concentration. Using Eqs. (2), (16), (17), and (18), the $R^2 e^{-\epsilon_R/kT}$ term is plotted in Fig. 8 against R for the fluorenylsodiumtetrahydrofuran system (at -30°). The curve has two minima at distances of about 3 (R_B) and 32 Å (R_C). Here, R_C is the critical distance distinguishing between free ions and ion pairs. Similarly, it is possible to distinguish the two kinds of ion pairs by using R_B. In this paper, in order to compare the present theory with the experimental results by Hogen-Esch and Smid,[4] the two kinds of ion pairs will be defined as follows:

$r_I + r_{II} < R < R_B$	contact ion pair
$R_B < R < R_C$	solvent separated ion pair
$R_C < R$	free ion

Figure 9 shows the distributions for the fluorenylsodiumtetrahydrofuran system at different temperatures. It is apparent that the curves at lower temperatures (-50 ~ -10°) have a minimum in a distance range $r_I + r_{II} < R < R_C$. The minimum disappears at higher temperatures (0 ~ 25°). The two kinds of ion pairs are seen not to be distinguishable from each other at higher temperatures.

It is interesting that the logarithm of R_B can be represented by a linear relation with temperature, as seen from Fig. 10. The R_B values at higher temperatures cannot be determined from Fig. 9, but can be estimated by an extrapolation of the log R_B - T plot (see the broken line in Fig. 10). The results are shown in Table 1.

Figure 11 shows the temperature dependence of the proportion of the contact ion pairs and of the solvent separated ion pairs. Here, the ordinate represents the distribution function relative to that at 3 Å. From Fig. 11

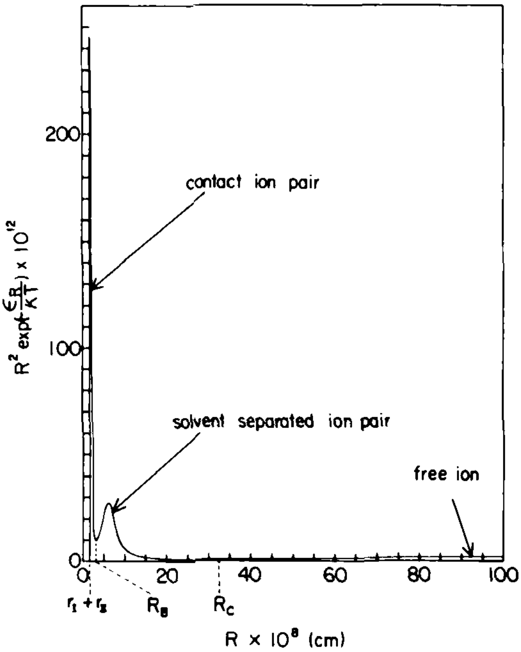

Fig. 8. Distribution of the intercharge distance, fluorenylsodium in tetrahydrofuran, at -30°. $r_I + r_{II}$ closest distance; R_B, critical distance distinguishing between contact ion pairs and solvent separated ion pairs; R_C, critical distance distinguishing between ion pairs and free ions.

it is apparent that the proportion of the solvent separated ion pair to the contact ion pair increases with decreasing temperature. The dielectric constant generally increases with decreasing temperature whereas the thermal energy decreases. Thus the temperature dependence of the distribution shown above indicates a predominant role of the dielectric constant over the thermal energy.

In this respect, we can show how the distribution is not sensitively influenced by changing temperature at a given dielectric constant. The values of the distribution function calculated at 30 and -30° for D = 9.43 are shown in Fig. 12. The 60° temperature difference does not give appreciable change for the distribution.

Dissociation Constants

Let us assume equilbria between contact ion pairs and solvent separated

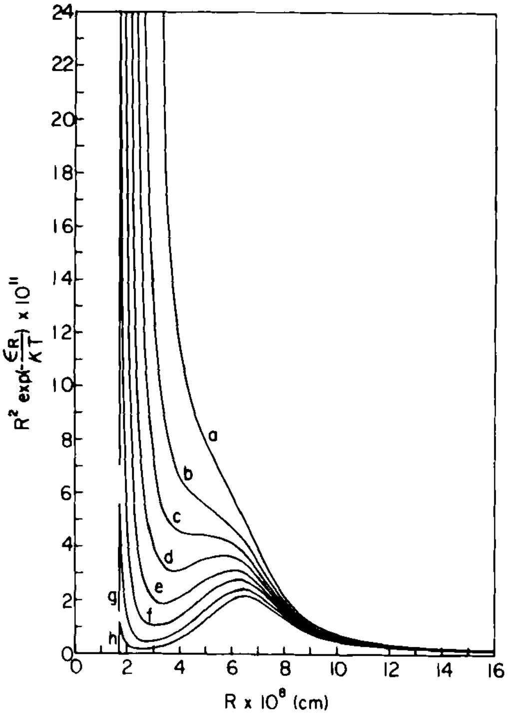

Fig. 9. Temperature dependence of the distribution. Fluorenylsodium in tetrahydrofuran. a, 25°; b, 10°; c, 0°; d, -10°; e, -20°; f, -30°; g, -40°; h, -50°.

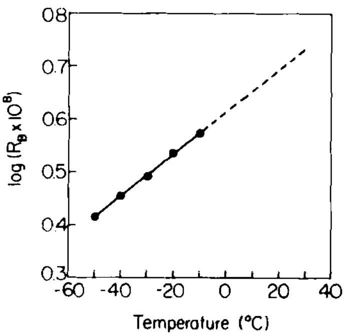

Fig. 10. Critical distance R_B and temperature. R_B is the critical distance distinguishing contact ion pairs from solvent separated ion pairs.

Table 1. Critical Distance R_B, Fluorenylsodium in Tetrahydrofuran

Temperature (°C)	$R_B \times 10^8$ cm
-50	2.60
-40	2.85
-30	3.10
-20	3.40
-10	3.75
0	4.10
10	4.49
25	5.15

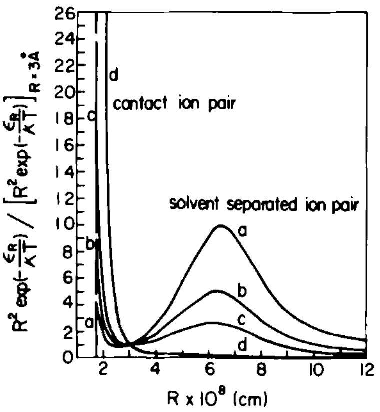

Fig. 11. Distributions at various temperatures, fluorenylsodium in tetrahydrofuran. a, -50°; b, -40°; c, -30°; d, +25°.

ion pairs, between contact ion pairs and free ions, and solvent separated ion pairs and free ions as follows:

$$\begin{tikzcd}
\text{contact ion pairs} \arrow[rr, leftrightarrow, "K_C"] \arrow[dr, leftrightarrow, "K_i"] & & \text{free ions} \\
& \text{solvent separated ion pairs} \arrow[ur, leftrightarrow, "K_S"'] &
\end{tikzcd} \tag{19}$$

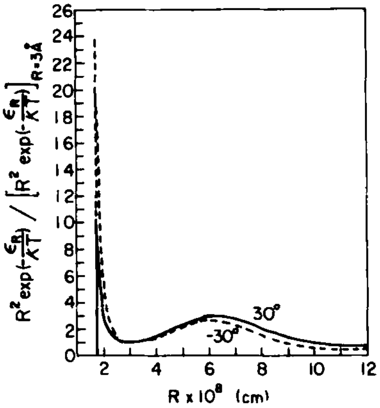

Fig. 12. Temperature dependence of the distribution. (—), 30°; (– –), -30°; D = 9.43. See Fig. 3 for other conditions.

K_i, K_C, and K_S represent the respective dissociation constants. According to Bjerrum's theory, the constants are given by

$$K_i = \int_{R_B}^{R_C} e^{-\epsilon_R/kT} R^2 \, dR \Big/ \int_{r_I+r_{II}}^{R_B} e^{-\epsilon_R/kT} R^2 \, dR \qquad (20)$$

$$K_C = \frac{1000}{4\pi N} \Big/ \int_{r_I+r_{II}}^{R_B} e^{-\epsilon_R/kT} R^2 \, dR \qquad (21)$$

and

$$K_S = \frac{1000}{4\pi N} \Big/ \int_{R_B}^{R_C} e^{-\epsilon_R/kT} R^2 \, dR \qquad (22)$$

where $r_I + r_{II}$, R_B, and R_C were defined in Fig. 8.

Since it is assumed that ion pairs consist of the contact ion pairs and the solvent separated ion pairs, the equilibrium

$$\text{ion pairs} \underset{}{\overset{K_d}{\rightleftarrows}} \text{free ions} \qquad (23)$$

can be characterized by the dissociation constant K_d as follows,

$$K_d = \frac{1000}{4\pi N} \Big/ \int_{r_I + r_{II}}^{R_c} e^{-\epsilon_R/kT} R^2 \, dR \tag{24}$$

according to the Bjerrum theory. From Eqs. (20), (21), (22), and (24), these dissociation constants are related to one another

$$K_i = K_C/K_S \tag{25}$$

and

$$\frac{1}{K_d} = \frac{1}{K_C} + \frac{1}{K_S} \tag{26}$$

The integrations in Eqs. (21) and (22) can be carried out with Simpson's equation.* The results obtained are given in Table 2. The K_i and K_d were calculated with Eqs. (25) and (26), respectively. The experimental data reported by Hogen-Esch and Smid [4]are also given in Table 2. Our theoretical value of K_d at 25° is in a good agreement with experimental result, but the agreement becomes less satisfactory with decreasing temperature. This tendency is most noticeable for K_C. In other words, our distribution function for contact ion pairs is an underestimation at lower temperatures. The dielectric constant to be used for the calculation of the intercharge energy term ϵ_i at lower temperatures may be smaller than the macroscopic dielectric constant. The dielectric constant in the vicinity of an electric charge would decrease with decreasing temperature because the solvation of an ion becomes more stable; on the other hand, the macroscopic dielectric constant increases generally with decreasing temperature. Furthermore,

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*Simpson's equation is given by

$$\int_a^b y \, dx \approx \frac{h}{3} (y_0 + 4y_1 + 2y_2 + 4y_3 + \ldots + 2y_{n-2} + 4y_{n-1} + y_n)$$

For the integrations in Eqs. (21) and (22), h was taken as 10^{-10} and 10^{-8} cm for distances ranging between 1.72 and 4.00 Å and between 4.00 Å and R_C, respectively. An h value of 10^{-10} cm was taken for the range between 4.00 Å and R.

Table 2. Dissociation Constants of Fluorenylsodium in Tetrahydrofuran

Temp. (°C)	$K_c \times 10^7$ (mole/l)		$K_s \times 10^4$ (mole/l)		$K_i \times 10^3$		$K_d \times 10^7$ (mole/l)	
	Theor.	Obs.[a]	Theor.	Obs.[a]	Theor.	Obs.[a]	Theor.	Obs.[a]
25	6.174	6.31[b]	0.6889	0.124[b]	8.961	50[c]	6.119	6.17
10	29.84	14.0	0.6519	0.145	45.77	112	28.53	12.6
0	86.29	24.4	0.6711	0.156	128.6	156	76.46	21.1
-10	246.3	46.2	0.6978	0.186	352.9	250	182.0	37.0
-20	784.7	95.2	0.7776	0.220	1,009	436	390.6	66.6
-30	2,586	212	0.8718	0.264	2,966	795	651.9	118
-40	9,735	518	1.003	0.343	9,710	1,510	909.0	206
-50	41,250	1190	1.152	0.393	35,808	3,020	1,121	298

[a] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 318 (1966).

[b] Obtained by extrapolation of the plot of log K against 1/T.

[c] Calculated from Eq. (25).

it should be noted that the definition of the two kinds of ion pairs in the present theory is different from that adopted by Hogen-Esch and Smid [4]. Our definition is based on the distribution of the intercharge distance as mentioned above, whereas the entities corresponding to the wavelength of 356 and 373 mμ were defined by the Syracuse group as contact ion pairs and solvent separated ion pairs, respectively. It would be interesting to estimate the R_B value which can furnish good agreements between the observed and theoretical values of K_i. Since an excellent agreement was obtained at 25° between the observed and theoretical values of K_d, which is not dependent on R_B, we calculate the R_B value from the observed K_i value at this temperature by using Eq. (20). The result is R_B = 2.34 Å. The R_B value calculated in the previous section was 5.15 Å at 25°. Although the reason for the disagreement between these two R_B values is not clear at present, it is noteworthy that R_B = 2.34 Å gives $K_C = 6.46 \times 10^{-7}$ and $K_S = 0.125 \times 10^{-4}$ at 25°, which are in excellent agreement with the observed values.

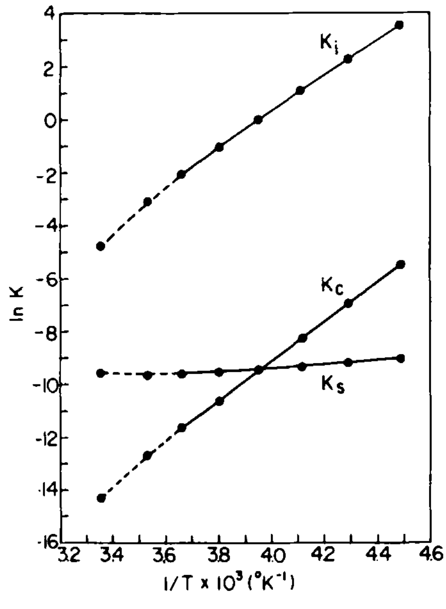

Fig. 13. Temperature dependence of the dissociation constants, fluorenylsodium in tetrahydrofuran. K_i, contact ion pair ⇌ solvent separated ion pair. K_C, contact ion pair ⇌ free ion. K_S, solvent separated ion pair ⇌ free ion.

Figure 13 shows the calculated temperature dependence of the dissociation constant K, which was given in Table 2 as the theoretical value. The enthalpy change, determined from the slope of the curve, is nearly constant over the temperature range between 0 and -50°. From Fig. 13, we obtain $-\Delta H_C = 10.34 \times 10^{-13}$ erg/ion pair (= 14.86 kcal/mole), $-\Delta H_S = 1.049 \times 10^{-13}$ erg/ion pair (= 1.507 kcal/mole), and $-\Delta H_i = 9.291 \times 10^{-13}$ erg/ion pair (= 13.35 kcal/mole). The experimental results [4] obtained from the absorption spectra were $-\Delta H_C = 9.5$ kcal/mole, $-\Delta H_S = 1.9$ kcal/mole, and $-\Delta H_i = 7.6$ kcal/mole. The agreement is satisfactory.

The entropy changes are estimated from the equaiton

$$\Delta S = (\Delta H + RT \ln K)/T \tag{28}$$

where R represents the gas constant. The entropy changes are given in Table 3. Apparently the entropy change from contact ion pairs into free ions ΔS_C and that from contact ion pairs into solvent separated ion pairs ΔS_i are negative over all the temperature range studied. The entropy change from solvent separated ion pairs into free ions ΔS_S is positive on the contrary. This indicates that the entropy increases in the order: solvent

Table 3. Entropy Change,
Fluorenylsodium in Tetrahydrofuran

Temp. (°C)	ΔS_C (e.u.)	ΔS_S (e.u.)	ΔS_i[a] (e.u.)
25	-21.51	11.19	-32.70
10	-27.27	11.04	-38.31
0	-31.30	10.78	-42.08
-10	-35.45	10.50	-45.95
-20	-39.98	10.06	-50.04
-30	-44.65	9.59	-54.24
-40	-50.02	9.04	-59.06
-50	-55.74	8.48	-64.22

[a] $\Delta S_i = \Delta S_C - \Delta S_S$.

separated ion pairs < free ions < contact ion pairs. The entropy change ΔS_i in Table 3 decreases with decreasing temperature. This indicates that the number of the additional solvent molecules immobilized by formation of the solvent separated ion pair increases with decreasing temperature.

The experimental value [4] of ΔS_i at 25° is about -33 e.u. which is in close agreement with our result, -32.70 e.u.

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