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Studies on Carbamoylation Reactions of Polyethylenimine and Its Low Molecular Weight Analogues with Cyanate Ions

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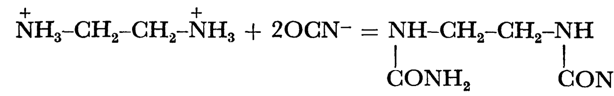
Carbamoylation reaction of ions of polyethylenimine and its low molecular weight analogues, *i.e.*, ethylenediamine, triethylenetetramine, and tetraethylenepentamine, with cyanate ions are investigated in the presence of simple-, micelle-, and poly-electrolytes and in their absence. The rate constants are practically independent of the valency of the cations and are much larger than that previously found for the ammonium cyanate reaction. Both of the activation enthalpy and entropy decrease with increasing valency of the cations. Added electrolytes are found to decelerate the reactions. The reactions of polycations are retarded more strongly by simple cations than by catalyst polycations, whereas those of simple cations are decelerated more effectively by polycations than by simple cations. The kinetic data are discussed thermodynamically in terms of the Brönsted theory and the activity coefficients of the reactant ions. The interaction parameters between reactant electrolyte and added electrolyte are also derived thermodynamically and discussed.

Interionic reactions in the presence of various electrolytes are interesting from the biological point of view and have been studied by many researchers (For a convenient review, see Ref. 1). In a previous paper,[2] we studied quantitatively the catalytic influence of polyelectrolytes for the ionic reaction between oppositely charged ionic species shown in Eq. 1, and also the electrostatic interactions between ions of polyelectrolytes and those of simple electrolytes.

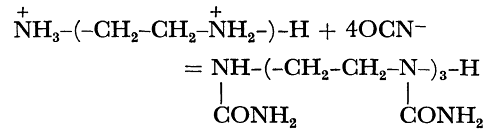
$$NH_4^+ + OCN^- = (NH_2)_2CO \qquad (1)$$

In this paper we obtain quantitative information on ionic reactions between ionic species of various charge types. For this purpose, the carbamoylation reactions of ethylenediamine, triethylenetetramine, tetraethylenepentamine and polyethylenimine with cyanate ions shown in Eqs. (2), (3), (4) and (5) are studied.



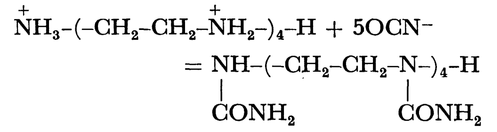
$$\overset{+}{N}H_3\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{N}H_3 + 2OCN^- = \underset{CONH_2}{NH}\text{-}CH_2\text{-}CH_2\text{-}\underset{CONH_2}{NH}$$

(2)



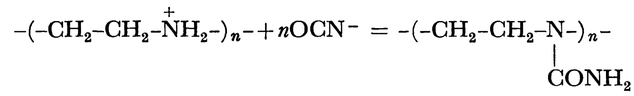
$$\overset{+}{N}H_3\text{-}(\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-})\text{-}H + 4OCN^- = \underset{CONH_2}{NH}\text{-}(\text{-}CH_2\text{-}CH_2\text{-}\underset{CONH_2}{N}\text{-})_3\text{-}H$$

(3)



$$\overset{+}{N}H_3\text{-}(\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-})_4\text{-}H + 5OCN^- = \underset{CONH_2}{NH}\text{-}(\text{-}CH_2\text{-}CH_2\text{-}\underset{CONH_2}{N}\text{-})_4\text{-}H$$

(4)



$$\text{-}(\text{-}CH_2\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-})_n\text{-} + nOCN^- = \text{-}(\text{-}CH_2\text{-}CH_2\text{-}\underset{CONH_2}{N}\text{-})_n\text{-}$$

(5)

The reactions (2) through (5) are simple reactions like reaction (1). After mixing silver cyanate with aqueous solutions of hydrochlorides of polyethylenimine and its low molecular weight analogues, the precipitate of silver chloride can be isolated from the reaction system. We obtain solutions containing reactant ions only, which is convenient for quantitative investigations. Since all the reactions (2) through (5) proceed between ionic species of unlike charges, the measurement of the electrical resistance of the reaction system offers a convenient and accurate technique for monitoring the reaction.

Experimental

Materials. The details of the preparation of silver cyanate were described earlier.[2] Polyethylenimine (PEI) was furnished by the Dow Chemicals Co., Michigan (Montrek 12). A molecular weight of 4500 was obtained from viscosity determination using an equation proposed by Jones, Langsjoen, Neumann and Zomlefer.[3] Dilute aqueous solutions of PEI were purified by passing them through columns of cation and anion exchange resins. The concentration of PEI was determined by a conductometric method. The fraction of tertiary amino groups was measured by acetylation to be 0.25.

The tertiary amino groups of PEI do not react with cyanate ions. The reaction velocity was determined from the conductance at very low conversions of the reaction in our experiments. The tertiary amines, which are partly responsible for the conductance, were therefore dealt with as reactant ions, in addition to the primary and secondary amino groups. The hydrochloride of PEI (PEI·HCl) was prepared by partial neutralization of PEI solution with HCl (degree of neutralization=0.92) to prevent the hydrolysis of the PEI salt. Ethylenediamine (ED), triethylenetetramine (TT), and tetraethylenepentamine (TP) were purified by distillation or recrystallization.[4] These bases were partially neutralized with HCl; the degrees of neutralization of ED, TT and TP were 0.77, 0.72, and 0.70, respectively. Sodium polyacrylate (NaPAA) was a product of the Toa Gosei Chemicals Co., Nagoya, Japan. The weight average degree of polymerization was 640. Dilute solutions of NaPAA were converted to the acid form by passing them through ion-exchange resin columns. Completeness of the conversion was assured by checking the atomic absorption spectrum of the solution for sodium ions. A copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS) was kindly

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[1] N. Ise, *Fortschr. Hochpolym. Forsh.*, **7**, 536 (1970).

[2] T. Okubo and N. Ise, *Proc. Roy. Soc.*, **A327**, 413 (1972).

[3] G. D. Jones, A. Langsjoen, M. M. C. Neumann, and J. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).

[4] N. Ise and T. Okubo, *J. Phys. Chem.*, **70**, 2400 (1966).

donated by the Nitto Spinning Co., Koriyama, Japan.[5] Sodium chloride, calcium chloride, and cetyltrimethylammonium bromide (CTABr) were guaranteed reagents.

Kinetic Measurements. A conductometric method was applied to the determination of the reaction rate.[6] The details of the experiments were described earlier.[2] The reactant solutions of ED·OCN, TT·OCN, TP·OCN and PEI·OCN were prepared by mixing hydrochloride solutions of the bases with silver cyanate. In all reaction mixtures, silver chloride, a by-product, was completely removed by filtration. Removal was checked by measuring the concentration of remaining silver chloride using an atomic absorption spectrophotometer. Thus, the filtrate is believed to contain reactant ions only. A cell of the Jones and Ballinger type (cell constant=7.64 cm^{-1}) was used together with a Wheatstone bridge.[8] The maximum experimental error of the resistance was ±0.1%. Kinetic measurements were carried out at 30, 40, and 50 °C and within 1% conversion. The error of our measurements was at the highest 3% of the reaction rate. The pH values of the reaction solution were between 5.5 and 7.5 during the reaction.

Results and Discussion

The second-order rate constants k_2 of the carbamoylation reactions are compiled in Table 1. The magnitude of k_2 was about the same for the four reactants studied, whereas it was 20 to 100 fold larger than that for the ammonium cyanate–urea conversion.[9] As is seen from the Table, the k_2 value decreases with increasing concentration and this tendency becomes more distinct with increasing valency of the reactant cations.

Table 1. The second-order rate constants for reactions of ED·OCN, TT·OCN, TP·OCN and PEI·OCN

Reactant	Concentration (mol·l^{-1})	k_2(l·mol^{-1}·min^{-1}) 30°C	40°C	50°C
ED·OCN	0.00766	0.816	—	—
	0.00957	0.830	1.78	3.27
	0.0139	0.709	1.63	—
	0.0184	0.638	1.43	—
	0.0232	0.632	1.43	—
	0.0312	0.592	1.27	—
	0.0411	0.588	1.19	—
	0.0822	0.514	—	—
TT·OCN	0.00425	1.270	—	—
	0.00890	0.955	2.08	3.76
	0.0142	0.706	1.71	—
	0.0171	0.712	1.47	—
	0.0213	0.592	1.38	—
	0.0282	0.526	1.14	—
	0.0366	0.489	0.96	—
	0.0784	0.261	—	—
TP·OCN	0.00417	1.341	2.63	—
	0.00872	0.964	1.60	2.85
	0.0140	0.721	1.23	—
	0.0167	0.701	1.12	—
	0.0209	0.559	1.03	—
	0.0277	0.465	0.836	—
	0.0360	0.390	0.706	—
	0.0780	0.208	—	—
PEI·OCN	0.00766	1.37	—	—
	0.00957	1.15	1.64	2.80
	0.0139	0.536	1.31	—
	0.0184	0.572	0.889	—
	0.0232	0.457	0.904	—
	0.0312	0.442	0.882	—
	0.0411	0.315	0.582	—
	0.0822	0.196	—	—

Table 2. Thermodynamic quantities for reactions of NH_4OCN, ED·OCN, TT·OCN, TP·OCN, and PEI·OCN at 40 °C

Reactant[a]	$\Delta G^{\neq}$ (kcal·mol^{-1})	$\Delta H^{\neq}$ (kcal·mol^{-1})	$\Delta S^{\neq}$ (cal·deg^{-1}·mol^{-1})
NH_4OCN[b]	23.6	22.9	−2
ED·OCN	20.6	12.9	−24.6
TT·OCN	20.5	12.8	−24.6
TP·OCN	20.6	10.1	−33.7
PEI·OCN	20.6	8.0	−40.2

a) Concentrations of the reactants are 0.00957, 0.00890, 0.00872 and 0.00957 mol·l^{-1} for ED·OCN, TT·OCN TP·OCN and PEI·OCN, respectively.

b) Okubo and Ise, Ref. 2.

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5) S. Harada and K. Arai, *Makromolek. Chem.*, **107**, 78 (1967).

6) It is clearly shown that the conductance method can give the "correct" rate constant of the carbamoylation reaction, even when the side reaction, especially carbonate formation (Eq. (A)) proposed by Wyatt and Kornberg exists.[7] If the carbonate really formed, the rate constant, k, from the conductance method is given by Eq. (B).

$$OCN^- + 2H_2O = HCO_3^- + NH_3 \tag{A}$$

$$\frac{-d\{[NH_4^+]+[OCN^-]+[HCO_3^-]\}}{2dt} = k\left\{\frac{[NH_4^+]+[OCN^-]+[HCO_3^-]}{2}\right\} \tag{B}$$

when the equivalent conductances of NH_4^+, OCN^- and HCO_3^- are approximately equal to each other and when the $[H^+]$ and $[OH^-]$ are negligible, *i.e.*, $[NH_4^+]=a-x$, $[OCN^-]=a-x-y$ and $[HCO_3^-]=[NH_3]=y$, where the notations a, x, and y are the same as those given in Ref. 7, Eq. (B) becomes

$$-\frac{d[NH_4^+]}{dt} = k[NH_4^+]^2 \tag{C}$$

Eq. (C) clearly shows that k obtained from the conductance is apparently "correct". Furthermore, it can be easily shown that the k from the conductance correlates with the rate constant of carbamoylation at infinite dilute, k_{u_0} by Eq. (D).

$$k = k_{u_0} f_1^2\left(\frac{a-x-y}{a-x}\right) \approx k_{u_0} f_1^2 \quad \text{at} \quad t \approx 0 \tag{D}$$

where f_1 is the activity coefficient of 1-valent ions. For the details of the derivation of Eqs. (C) and (D), the readers should consult the work of Wyatt and Kornberg. Thus, the conductance method is convenenient for the rate determination of the carbamoylation reaction.

7) P. A. H. Wyatt and H. L. Kornberg, *Trans. Faraday Soc.*, **48**, 454 (1952).

8) J. Jones and M. Ballinger, *J. Amer. Chem. Soc.*, **53**, 411 (1931).

9) J. C. Warner and E. L. Warrick, *ibid.*, **57**, 1491 (1935).

For example, the k_2 value of ED·OCN decreases by 40 percent with a ten-fold increase in the reactant concentration, whereas that of PEI decreases more than 80 percent. A quantitative explanation for the decreasing tendency will be described later.

The free energy ($\Delta G^{\ddagger}$), enthalpy ($\Delta H^{\ddagger}$), and entropy ($\Delta S^{\ddagger}$) of activation of the carbamoylation reactions are listed in Table 2. These parameters for the ammonium cyanate–urea conversion are also given in the Table from the previous publication.[2] The $\Delta G^{\ddagger}$ values of the carbamoylation reactions studied in the present work are constant within experimental error, being smaller than that for the NH_4OCN reaction. The $\Delta H^{\ddagger}$ values decrease sharply with increasing valency of the reactant cations. The electrostatic attractive forces between cations and anions become stronger with increasing valency and may decrease the activation energy. As is clearly shown in Table 2, $\Delta S^{\ddagger}$ decreases with increasing valency of the cations. The $\Delta S^{\ddagger}$ value is much smaller than that for the NH_4^+—OCN^- reaction. According to our previous study on the partial molal volume,[10,11] the PEI cation is hydrated electrostrictionally by two water molecules per repeating unit at the full degree of neutralization. On the other hand the ammonium ion is reported to be hydrated by three water molecules from compressibility measurement.[12] If these values are correct, the NH_4^+—OCN^- reaction should have larger $\Delta S^{\ddagger}$ than the polycation reaction. In addition to the dehydration factor, the local accumulation of OCN^- in the vicinity of the polycation by strong electrostatic attractive forces would result in small $\Delta S^{\ddagger}$ values for the PEI^+—OCN^- reaction.

The second-order rate constant for a reaction between ions can be represented as follows by Brönsted,[13,14]

$$k_2 = k_{2_0}\gamma_+\gamma_-/\gamma_X \tag{6}$$

where γ_+ denotes the single-ion activity coefficient of the amino groups of the macroion, and γ_- the single-ion activity coefficient of the cyanate anions. X indicates the activated complex. The reference value, k_{2_0}, is a limiting velocity constant at zero concentration of the reactant ions. For convenience, we discuss the rate constant by using a reference constant k_2^* which is the rate constant at 0.01 equiv. l^{-1} without foreign salt. The constant k_2^* is correlated with k_{2_0} by the equation

$$k_2^* = k_{2_0}\gamma_+^*\gamma_-^*/\gamma_X^* \tag{7}$$

where γ_+^*, γ_-^* and γ_X^* are the single-ion activity coefficients of the species indicated by the suffix at the reference concentration. From Eqs. (6) and (7) the following equation is derivable.

$$\log(k_2/k_2^*) = 2\log(\gamma_\pm/\gamma_\pm^*) - \log(\gamma_X/\gamma_X^*) \tag{8}$$

where $\gamma_\pm$ and $\gamma_\pm^*$ are the mean activity coefficients of the reactive groups which are related to the single-ion activity coefficients γ_+, γ_-, γ_+^* and γ_-^* by Eqs. (9) and (10) (see for example, Ref. 15)

$$\gamma_\pm^2 = \gamma_+\cdot\gamma_- \tag{9}$$

$$\gamma_\pm^{*2} = \gamma_+^*\cdot\gamma_-^* \tag{10}$$

The first and second terms of the right-hand side of Eq. (8) denote the changes of the activity coefficients of the reactant ion and activated complex, respectively, in going from the specified state to the reference state.

At this point we wish to try to estimate the activity coefficients of the reactant ions from the kinetic parameter, k_2, using Eq. (8). In the case of interionic reactions between ions of unlike signs and of the same valence (NH_4^+ and OCN^-, for example), the activated complex is considered to be neutral. The second term of the right-hand side of Eq. (8), therefore, can be safely neglected, compared to the first term, because the activity coefficients of neutral molecules are not so sensitive to changes in ionic concentration. In the present case, (Eqs. (2) to (5)), on the other hand, the complex is not neutral except in the final stage of the reaction. However, it is still expected that the second term of the right-hand side of Eq. (8) is much smaller than the first term. Thus we neglect the second term and obtain:

$$\log(k_2/k_2^*) = 2\log(\gamma_\pm/\gamma_\pm^*) \tag{11}$$

It should be noted here that γ is the single-ion activity coefficient of the amino groups of the macroion, and not that of the macroion (to be denoted as $\gamma_{\alpha+}$). The mean activity coefficient of polyelectrolyte ($\gamma_{\alpha\pm}$) is given by the following equation.

$$\gamma_{\alpha\pm}^{\alpha+1} = \gamma_{\alpha+}\cdot\gamma_-^{\alpha} \tag{12}$$

where the effective valency of the macroions is α. Physicochemical measurements such as e.m.f. measurement give $\gamma_{\alpha\pm}$, not $\gamma_\pm$. Thus, the relation between $\gamma_{\alpha+}$ and γ_+ must be given to complete the discussion of the mean activity coefficients of the reaction systems. The chemical potential of the macrocations, $\mu_{\alpha+}$, is given by the sum of the chemical potentials of the reactive group i (the amino groups in the present case), μ_{+i},

$$\mu_{\alpha+} = \sum_{i=1}^{\alpha}\mu_{+i} \tag{13}$$

We assume here that the value of μ_{+i} is not dependent on the location of the group on the cation chain. Then we obtain,

$$\mu_{\alpha+} = \alpha\mu_+ \tag{14}$$

From Eq. (15) we have

$$\gamma_{\alpha+} = \gamma_+^{\alpha} \tag{15}$$

The relation between k_2 and $\gamma_{\alpha\pm}$, is therefore, given by

$$\log(\gamma_{\alpha\pm}/\gamma_{\alpha\pm}^*) = \frac{\alpha}{\alpha+1}\log(k_2/k_2^*) \tag{16}$$

By using Eq. (16), the mean activity coefficients of ED·OCN, TT·OCN, TP·OCN and PEI·OCN in aqueous media were calculated from the observed kinetic data (Fig. 1). The α value equals to Z[D.N.], where, Z and [D.N.] are the valency of reactive cation and the degree of neutralization, respectively. The α values of ED·OCN, TT·OCN, TP·OCN and PEI·OCN were 1.5, 2.9, 3.5 and 96.3, respectively. The

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[10] N. Ise and T. Okubo, *J. Amer. Chem. Soc.*, **90**, 4527 (1968).

[11] N. Ise and T. Okubo, *Kobunshi Kagaku* **27**, 193 (1970).

[12] J. F. Hinton and E. S. Amis, *Chem. Rev.*, **71**, 627 (1971).

[13] J. N. Brönsted, *Z. Phys. Chem.*, **102**, 169 (1922).

[14] J. N. Brönsted, *ibid.*, **115**, 337 (1925).

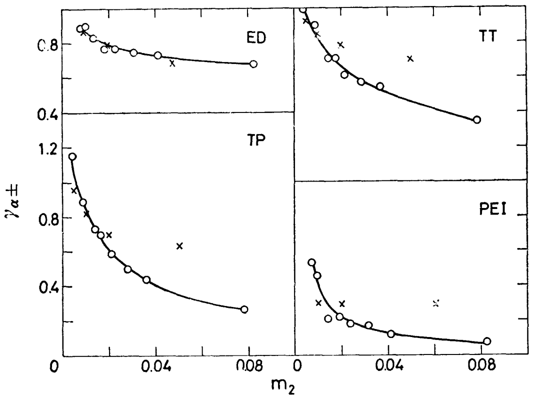

Fig. 1. $\gamma_{\alpha}\pm$ calculated from the kinetic data at 30 °C.
○: from the kinetic data
×: from e.m.f. measurements for hydrochlorides
(Ise and Okubo, Ref. 4)

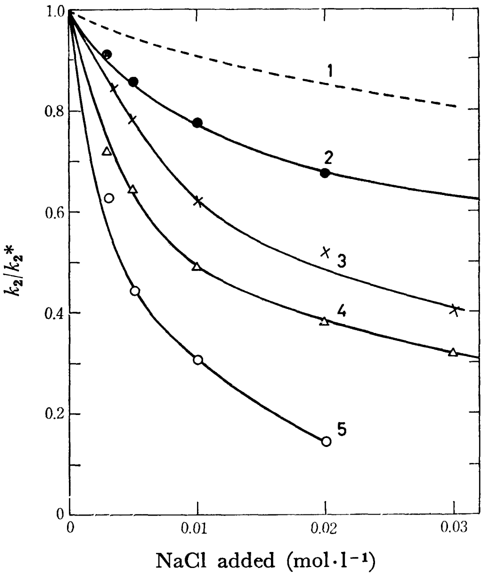

Fig. 2. Decelerating effect of NaCl at 30 °C.
[Reactant] = 0.01 mol·l^{-1}
Curve 1: NH_4OCN 2: ED·OCN 3: TT·OCN
4: TP·OCN 5: PEI·OCN

$\gamma_{\alpha}\pm^*$ values at 0.01 mol·l^{-1} were taken from the literature.[4] For comparison, the values of $\gamma_{\alpha}\pm$ from the e.m.f. measurements of the hydrochlorides, *i.e.*, ED·HCl, TT·HCl, TP·HCl and PEI·HCl are also given in the figure.[4] The $\gamma_{\alpha}\pm$ value of ED·OCN coincides with that of ED·HCl very well. The agreement between the $\gamma_{\alpha}\pm$ values of the cyanate and hydrochloride, however, becomes less satisfactory with increasing valency of the cations. This may be due to the fact that μ_{+i} depends for higher valence cations on the location of the reactive group i. Furthermore, the agreement is not good at higher concentrations, perhaps due to the specificity of the anions. Qualitatively, however, the concentration dependence of $\gamma_{\alpha}\pm$ derived from the kinetic data is satisfactory compared with that from the electrochemical measurements.

Now we turn to the catalytic action of added salts on the carbamoylation reactions. Figure 2 shows the decelerating effect of sodium chloride on the ED·OCN, TT·OCN, TP·OCN and PEI·OCN reactions. The data for NH_4·OCN by Warner and Warrick[9] are also given for comparison. The quantity k_2^* denotes the rate constant at $t=0$, at a reactant concentration of 0.01 mol·l^{-1} in the absence of the added salt. As is clearly seen from the Figure, the reactions of the higher valence cations with cyanate anions are retarded more effectively with sodium chloride than those of the lower valence cations.

Let us next discuss the interactions between reactant electrolyte and catalyst salt more quantitatively. For this purpose, it is convenient to use the interaction parameter, β_{23}, defined by Eq. (17).[16]

$$\beta_{23} = (1+\alpha)\partial \ln \gamma_{\alpha}\pm/\partial m_3 \tag{17}$$

were $\gamma_{\alpha}\pm$ and m_3 denote the mean activity coefficient of the reactant electrolyte and the concentration of sodium chloride, respectively. The β_{23} values obtained from the kinetic data by the use of Eq. (16) are compiled in Table 3. The negative value of β_{23} suggests that the interactions between the reactant electrolyte and the salt are electrostatic (see Refs. 17 and 18). The value of β_{23} increases with increasing concentration of sodium chloride, suggesting a weakening of the electrostatic forces with addition of sodium chloride. As is clearly seen, the magnitude of β_{23} increases strikingly with increasing valency of the reactant cations.

Table 3. Interaction parameter β_{23}
Component 2 : ED·OCN, TT·OCN, PEI·OCN
Component 3 : NaCl

m_3 (mol·l^{-1})	β_{23}			
	ED·OCN	TT·OCN	TP·OCN	PEI·OCN
0.003	−46.6	−151	−326	−11700
0.005	−38.5	−132	−192	−9100
0.01	−29.4	−84	−119	−8000
0.02	−14.7	−63	−93	−6000
0.03	—	−64	−89	—

The dependence of β_{23} on the valency of the reactant cations implies the following. The higher the valency of the reactant cations, the more strongly they attract chloride ions which in turn prevent the cyanate ions from approaching the reactant cations. This shielding effect of the chloride ions becomes greater as the reactant cations are more highly charged.

The catalytic action of a polyelectrolyte on the carbamoylation reactions of ED·OCN, TT·OCN, TP·OCN and PEI·OCN is portrayed in Fig. 3. The decelerating efficiency of DECS was about the same for all of the carbamoylation reactions studied, in contrast to the action of sodium chloride. This suggests that the interactions between the catalyst polyelectrolyte (*i.e.*, DECS) and reactant electrolyte (2–1, 4–1, 5–1,

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15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Butterworths, London (1959), Chapt. 2.

16) G. Scatchard, *J. Amer. Chem. Soc.*, **68**, 2315 (1946).

17) T. Okubo, N. Ise, and F. Matsui, *ibid.*, **89**, 3697 (1967).

18) F. Matsui, N. Ise, and T. Okubo, *Polym. J.*, **1**, 64 (1970).

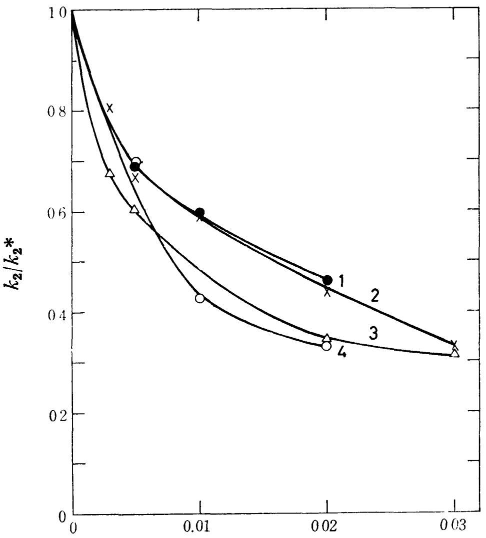

Fig. 3. Decelerating effect of DECS at 30 °C.
[Reactant] = 0.01 mol·l⁻¹
Curve 1: ED·OCN 2: TT·OCN
3: TP·OCN 4: PEI·OCN

100–1 valence types) are relatively similar in spite of the large range in the cation valency. The valency of the DECS cations (degree of polymerization about 2000) is much higher than the valencies of the reactant cations (2∼100). The attractive forces between the DECS cations and the cyanate anions, therefore, are much stronger than those between the reactant cations of various valencies and Cl^-. Thus, the difference in the strength of the interactions between the reactant cations and Cl^- may not strongly affect the retarding effects by the DECS cations.

The retarding influences of simple-, micelle-, and polyelectrolytes on the carbamoylation reactions of ED·OCN and PEI·OCN are compared in Table 4. For ED·OCN, the catalytic effect was the weakest for calcium chloride and increased in the order:

$$CaCl_2 < NaCl < CTABr < DECS < NaPAA \qquad (19)$$

On the other hand, the retarding effect on the PEI·OCN reaction was in the order:

$$DECS < CTABr < NaCl < CaCl_2 \qquad (20)$$

Table 4. Decelerating effect of various salts on the ED·OCN and PEI·OCN reactions at 30 °C
[Reactant] = [Added salt] = 0.01 mol·l⁻¹

Added salt	k_2/k_2^*	
	ED·OCN	PEI·OCN
NaCl	0.77	0.31
$CaCl_2$	0.93	0.25
CTABr	0.58	0.36
DECS	0.60	0.43
NaPAA	0.12	—

Generally speaking, the retarding action of the added salt is strong when the valencies of reactant cations and salt cations differ greatly from each other. These results are accounted for as follows. The fact that CTABr and DECS are more effective retarders than sodium chloride and calcium chloride in the ED·OCN reaction can be understood if we consider that these macrocations attract cyanate ions more strongly than Na^+ and Ca^{2+}. Sodium chloride is more effective than calcium chloride since the concentration of the chloride ions, which we recall do not favor the approach of cyanate ions to ED cations, is lower in the presence of Ca^{2+} than in the case of Na^+. The ED cations are less effectively shielded by calcium chloride than by sodium chloride, so that the ED·OCN reaction is decelerated less strongly by the former than by the latter.

For the PEI·OCN reaction, the situation is also interpretable by similar considerations. The chloride ion concentration around the PEI cations should be lower in the presence of DECS and CTABr cations than in the case of Na^+ and Ca^{2+} as a result of the attractive interaction between the macrocations and chloride ions, and of the very strong repulsive interaction between the macrocations and PEI cations. Thus, DECS and CTABr are not strong retarders in the PEI·OCN reaction. This situation is consistent with the activity data for the ternary systems, water–polyelectrolyte(2)–salt(3),[1,18] indicating that addition of low molecular weight salts as the third component 3 produces more efficient shielding effect on the polyelectrolyte (component 2) than that of another polyelectroylte (component 3). We have no reasonable explanation for the higher efficiency of calcium chloride as compared to sodium chloride. In summary, we state that the reactions of polycations are more effectively decelerated by coexisting simple cations than by catalyst polycations, whereas reactions of simple cations are retarded more strongly by polycations than by simple cations.

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