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IONIC ASSOCIATION ON A POLYOXYETHYLENE CHAIN

Hiroshi AWANO,* Katsumichi ONO, and Kenkichi MURAKAMI
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira, Sendai 980

The equivalent conductivities, Λ, of potassium and sodium thiocyanate in ethanol and nitromethane solutions containing polyoxyethylene (POE) have been measured as a function of POE concentration, C_p, at 298.15 K. The Λ vs. C_p curves have peculiar features. These features have been explained in terms of the cooperative association of cation and anion on a POE chain.

The authors have investigated by conductometry the binding of alkali metal ions to polyoxyethylene (POE) in various solvents.$^{1)}$ It has been found that the equivalent conductivities of the alkali metal salts, Λ, monotonously decrease with increasing concentration of POE (monomer base mole), C_p. For methanol, acetonitrile, propylene carbonate, and sulfolane systems, the amount of the bound cation has been straightforwardly estimated from the decrease in Λ and analyzed on the basis of the one-dimensional lattice model. In these solvent systems, it is not necessary to take into account the contribution of anion to the decrease in Λ, since the specific interaction between cation and anion is virtually negligible. On the other hand, an additional complication arises in case that there exists ionic association on a POE chain. In this communication, the ion binding in such a complicated case is treated on the basis of the one-dimensional lattice model in the extended form.

The POE sample of the commercial grade (molecular weight 2×10^4) was used without further purification. Potassium and sodium thiocyanate were dried in vacuo before use. Ethanol was dried over molecular sieve 4A followed by distillation. Nitromethane was used without further purification. The conductance was measured at 3 kHz with a transformer bridge. All the measurements were performed at (298.15 ± 0.02) K.

Figure 1 shows the Λ vs. C_p curves for KSCN-ethanol system where the total salt concentration, C_s, is 10, 5, and 1 mmol dm^{-3}. Λ in the ordinate is divided by Λ_s, which is the value for C_p=0. Each curve has a minimum, particularly in large C_s. On the contrary, the Λ vs. C_p curve shows a monotonously decreasing feature for 5 mmol dm^{-3} NaSCN-ethanol system. Figure 2 shows the Λ vs. C_p curves for KSCN-nitromethane system where C_s=10, 5, and 1 mmol dm^{-3}. Each curve has a minimum in larger C_s, and the curve is shifted upward as C_s becomes larger. Figure 3 shows the Λ vs. C_p curves for NaSCN-nitromethane system where C_s=5 and 1 mmol dm^{-3}. After the curve experiences a minimum, Λ abruptly increases. Particularly, in the system of C_s=5 mmol dm^{-3}, Λ reaches the value 1.6 times as large as Λ_s.

The minimum observed in the Λ vs. C_p curve is inferred to be caused by the cooperative association of cation and anion on the POE chain. The minimum cannot be well reproduced through any procedures except the method based on the one-dimensional lattice medel. The authors present here an extended model by assuming the ionic association on the chain. Assume, first, that a site has energy 0 if nothing is bound (state $\underline{0}$), has energy E_c if a cation is bound (state $\underline{1}$), and has energy E_c+E_a if not only a cation but also an anion is bound (state $\underline{2}$). If μ_c and μ_a are the chemical potentials of the cation and the anion, then the normalized activity[1)] is defined, respectively, as

$$\xi = \exp[(\mu_c-E_c)/k_BT];$$
$$\eta = \exp[(\mu_a-E_a)/k_BT]. \qquad (1)$$

Assume, secondly, that interaction exists between the ith and the (i+m)th sites only when the both sites are in the state $\underline{1}$, and the interaction energy, J_m, is given by the Debye-Hückel potential:

$$J_m = e^2\exp(-\kappa r_m)/4\pi\varepsilon r_m, \qquad (2)$$

where r_m is the intersite distance[1)] and other symbols have usual meanings. If we truncate the range of the interaction to k sites, then the grand partition function, Ξ, is expressed in the following form:

$$\Xi = e\, U_k^N e', \qquad (3)$$

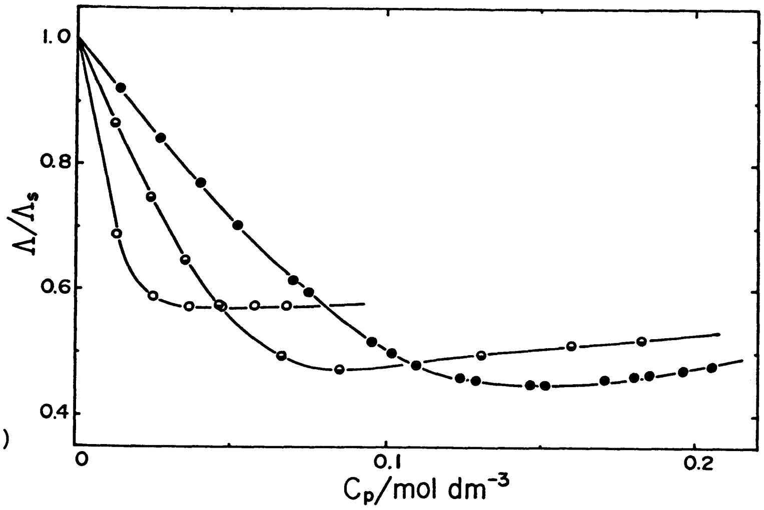

Fig. 1. Λ vs. C_p plots for KSCN-ethanol systems. ●, C_s=10 mmol dm^{-3}; ⊖, C_s= 5 mmol dm^{-3}; O, C_s=1 mmol dm^{-3}.

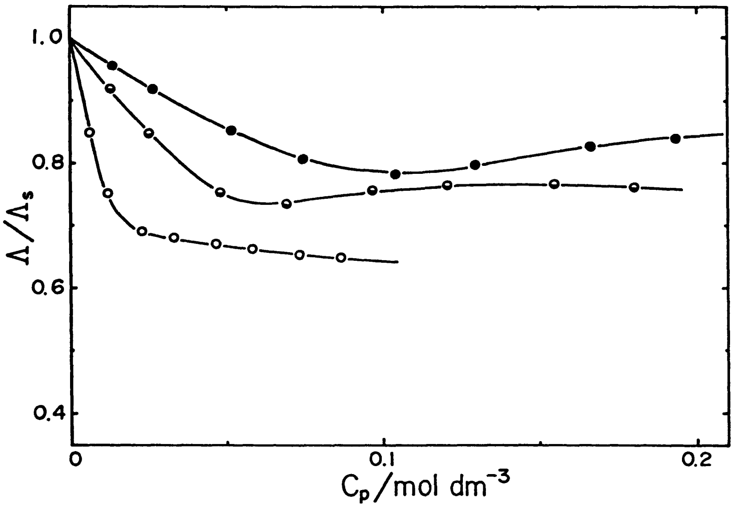

Fig. 2. Λ vs. C_p plots for KSCN-nitromethane system. ●, C_s=10 mmol dm^{-3}; ⊖, C_s=5 mmol dm^{-3}; O, C_s=1 mmol dm^{-3}.

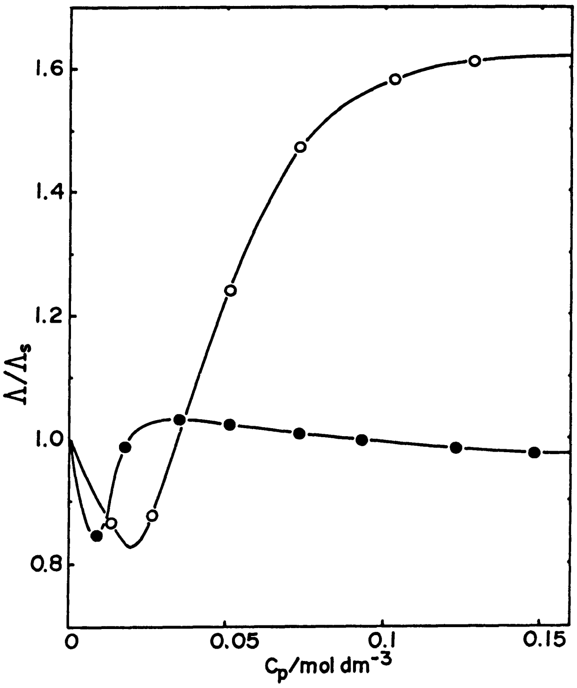

Fig. 3. Λ vs. C_p plots for NaSCN-nitromethane system. O, C_s=5 mmol dm^{-3}; ●, C_s=1 mmol dm^{-3}.

where N is the number of site per chain, e and e' are the row and the column vectors:

$$e = (1,1,\ldots,1); \quad {}^{t}e' = (1,0,\ldots,0),$$

and U_k is the statistical weight matrix whose order is 3^k. The degree of binding of cation and anion, that is, the probability that the ion is bound to a site, is formally given, respectively, by

$$\theta_c = (\partial \ln \Xi / \partial \ln \xi)_{\eta}/N; \quad \theta_a = (\partial \ln \Xi / \partial \ln \eta)_{\xi}/N. \tag{4}$$

The binding constant for cation and anion is defined, respectively, as

$$K_0^c = [(\mu_c^{\ominus} - E_c)/k_B T]; \quad K_0^a = [(\mu_a^{\ominus} - E_a)/k_B T], \tag{5}$$

where $\mu_c^{\ominus}$ and $\mu_a^{\ominus}$ are the standard chemical potentials of cation and anion. Combining Eqs. 1 and 5, the concentration of the free cation and anion is expressed as follows:

$$C_c = \xi / K_0^c y_{\pm}; \quad C_a = \eta / K_0^a y_{\pm}, \tag{6}$$

where $y_{\pm}$ is the mean ionic activity coefficient. Introducing the ionic association constant, K_A, we have from Eq. 6 the following equation:

$$C_p = \frac{C_s - (1 + K_A y_{\pm} \xi / K_0^c)\, \xi / K_0^c y_{\pm}}{(1 + K_A y_{\pm} \xi / K_0^c)(\theta_c - \theta_a)/4 + \theta_a/4}, \tag{7}$$

$$\eta = K_0^a y_{\pm} \frac{C_s - \theta_a C_p/4}{1 + K_A y_{\pm} \xi / K_0^c}. \tag{8}$$

The factor 4 appearing in Eqs. 7 and 8 means the number of monomer units composing a site.[2] Equations 4, 7, and 8 are simultaneous equations with respect to η, θ_c, θ_a, and C_p if ξ is fixed. Although these equations cannot be analytically solved, the self-consistent solution can be obtained by an iterative method. Thus, the equivalent conductivity to be observed is calculated by the use of Eq. 6 as follows:

$$\Lambda = (C_c \lambda_c + C_a \lambda_a)/C_s, \tag{9}$$

where λ_c and λ_a are the ionic equivalent conductivities, which

Table. Ionic association constants

Solvent	KSCN	NaSCN
Ethanol[a)]	47.53	32.32
Nitromethane[b)]	109.3	1591

a) Ref. 3. b) Ref. 4.

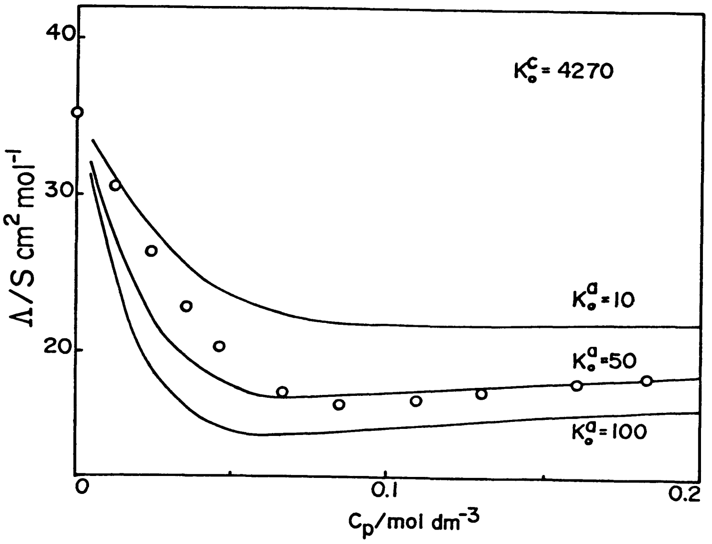

Fig. 4. Calculated Λ vs. C_p curves for 5 mmol dm^{-3} KSCN-ethanol system, together with the observed plots.

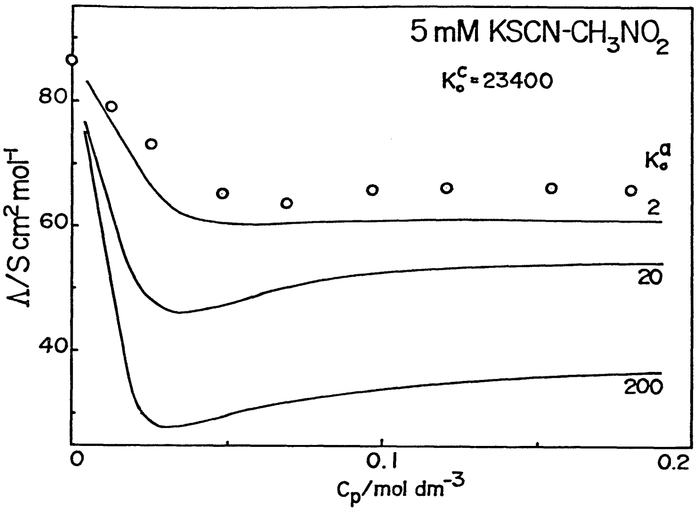

Fig. 5. Calculated Λ vs. C_p curves for 5 mmol dm^{-3} KSCN-nitromethane system, together with the observed plots.

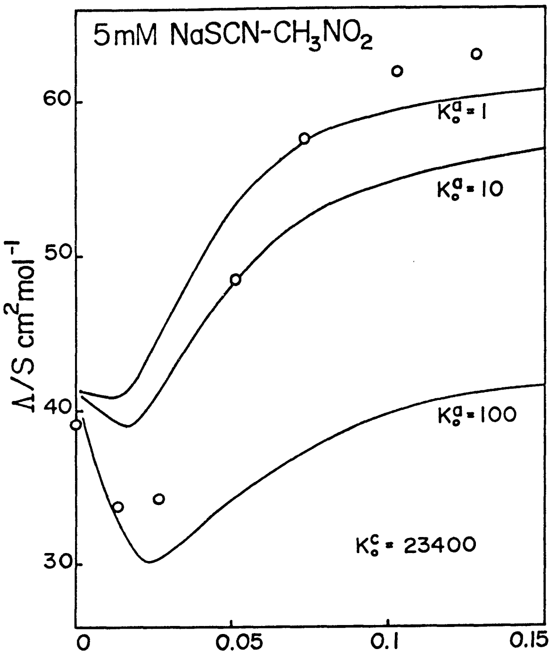

Fig. 6. Calculated Λ vs. C_p curves for 5 mmol dm^{-3} NaSCN-nitromethane.

are imaginary ones assuming that ionic association would not occur, and are obtained by applying the Onsager limiting law to the limiting ionic equivalent conductivities cited in the literature.[3,4]

K_A is obtained from the equivalent conductivity data cited in the literature[3,4] by the use of the Fuoss-Kraus method. The results are shown in Table. K_0^c is obtained for KSCN systems by extrapolating the relationship between log K_0^c and $\mu_c^{\ominus}$ established for other solvent systems.[1] The unpredictable constants are substituted by proper values on trial. The calculated curves are shown in Figs. 4-6. Given $K_0^a \sim 50$ for KSCN-ethanol and $K_0^a \sim 20$ for KSCN-nitromethane systems, and $K_0^c \sim 10^4$ and $K_0^a \sim 10$ for NaSCN-nitromethane system, the feature of the curve can be roughly reproduced. It is concluded that the cooperative association of cation and anion occurs on the POE chain.

Whereas K_A is much smaller in ethanol than in nitromethane, K_0^a is found to be larger in ethanol than in nitromethane. Kay et al.[5] pointed out that the association constant is larger for a larger cation in basic and hydrogen bonding solvent, such as ethanol, and it is smaller for a larger cation in neutral and acidic solvent, such as nitromethane. The fact previously mentioned is consistent with this tendency, if a bound cation, surrounded by a POE skeleton, is regarded as a large ion.

References

1) H. Awano, K. Ono, and K. Murakami, Bull. Chem. Soc. Jpn., to be submitted for publication.
2) K. Ono, H. Konami, and K. Murakami, J. Phys. Chem., 83, 2665 (1979).
3) M. Barak and H. Hartley, Z. Phys. Chem., A165, 272 (1933).
4) C. P. Wright, D. M. Murray-Rust, and H. Hartley, J. Chem. Soc., 1931, 199.
5) R. M. Kay, D. F. Evans, and M. A. Matesich, "Solute-Solvent Interactions," J. F. Coetzee and C. D. Richie ed, Marcel Dekker, New York (1976), Vol. 2, Chap. 10.

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