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Solubility of Alkyl Bromides in Aqueous Polymer Solutions

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The solubility of alkyl bromides (alkyl : ethyl, *n*-propyl, *n*-butyl and *n*-amyl) in aqueous solutions of neutral polymers and polyelectrolytes was measured and discussed. The polymers used were polyacrylamide (PAAm), polyvinylalcohol(PVA), polyethyleneglycol(PEG), polyvinylpyrrolidone(PVP), polyethylenimine(PEI) and polyacrylic acid(PAA) and its salts. The solubility of alkyl bromide increased linearly with concentration of neutral polymer in the order PAAm>PVP∼PEI>PEG>PVA∼PAA. Sodium salt of PAA decreased the solubility of alkyl bromide, but organic salts of PAA such as tetraalkylammonium salts increased it. Using the equation $\ln (S_0/S)=km_2$, the limiting Setchénow constant k was obtained for these systems. The results were accounted for in terms of the hydrophobic structural modifications of water and the direct dipole and/or hydrophobic interactions between solute and cosolute.

In a previous paper,[1] the solubility of non-polar solutes, *i.e.*, naphthalene and biphenyl, in aqueous polymer solutions was reported. It was revealed that solvent-solute interactions, *viz.*, the structural effects of polymers on water, were most influential in determining the solubility. The cosolute-cosolute interactions or the solute-cosolute interactions except for those mediated by solvent water molecules were found to be negligible. In this paper we report on attempts to estimate the comparative strength of the solute-cosolute or cosolute-cosolute interactions and that of the solvent-solute interactions in polymer solution when cosolute is polar by measurements of the solubility of alkyl bromides. Studies on the solubility of the polar cosolute in polymer solutions have been carried out,[2] but the cosolutes were complicated compared with the alkyl bromids we used.

Experimental

Materials. Neutral polymers used as solutes were polyacrylamide (PAAm, degree of polymerization ($\overline{DP}$)= 1800), polyvinylalcohol (PVA, $\overline{DP}$=1200, fractionated sample), polyethyleneglycol (PEG, $\overline{DP}$=140) and polyvinylpyrrolidone (PVP, $\overline{DP}$=220). Polyelectrolytes also used as solutes were sodium, tetramethylammonium (Me_4N–), tetraethylammonium (Et_4N–), tetra-*n*-propylammonium (Pr_4N–) and tetra-n-butylammonium (Bu_4N–) polyacrylates (PAA) obtained by neutralization of a polyacrylic acid(a product of Toa Gosei Chemicals Co., Nagoya, Japan, $\overline{DP}$= 640) with the corresponding hydroxide. Polyethylenimine (PEI, a product of Sumitomo Chemicals Co., Osaka, Japan, $\overline{DP}$=100) and unneutralized polyacrylic acid(PAA) were also used. Low molecular weight solutes were urea, tetramethylammonium bromide, tetraethylammonium bromide, tetra-*n*-propylammonium bromide and tetra-*n*-butylammonium bromide. Except for high molecular weight compounds, all the materials used were commercially available (Guaranteed reagent grade). Water was deionized by cation- and anion-exchange resins. Ethyl bromide (EtBr), *n*-propyl bromide (PrBr), *n*-butyl bromide (BuBr) and *n*-amyl bromide (AmBr) used as cosolute were further purified by distillation, and washed three times with water before use.

Solubility measurements. Excess cosolute was introduced into 20 ml test tubes containing 5 ml pure water or polymer solution with known concentration, wchich were sealed with stopper, shaken vigorously at first and placed for two to four days in a mechanical shaker in a thermostat at 25°C.

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[1] T. Okubo and N. Ise, *J. Phys. Chem.*, **73**, 1488 (1969).

[2] Cf. e. g., J. Eliassaf, F. Eriksson, and F. R. Eirich, *J. Polymer Sci.*, **47**, 192 (1960).

After equilibration, a small portion of the homogeneous layer was taken out with a syringe and analyzed by gas chromatography. The apparatus used was GCG-550T with a thermal conductivity detector of Yanagimoto Mfg. Co., Kyoto. The column used was 2.2 m × 3 mm ϕ. The stationary phase is Tide with carrier Neopak 1 A (mesh 60—80, products of Nishio Industry Co. Tokyo). The carrier gas was helium. The injection and detector temperatures were 125—135°C and 110°C, respectively. For ethyl bromide, *n*-pyropyl bromide, *n*-butyl bromide and *n*-amyl bromide, the column temperatures were 103, 100, 98 and 96°C, the helium flow rates 15, 20, 22.5 and 25 ml/min. and the bridge currents 100, 130, 150 and 200 mA, respectively. The solubilities of ethyl, n-propyl, n-butyl and n-amyl bromide are estimated to be 8.3×10^{-2}, 1.9×10^{-2}, 4.3×10^{-3} and 7.9×10^{-4} mol/l, respectively, at 25°C.

Rusults and Discussion

The solubilization[3] of *n*-butyl bromide in various neutral polymer solutions is shown in Fig. 1, in which

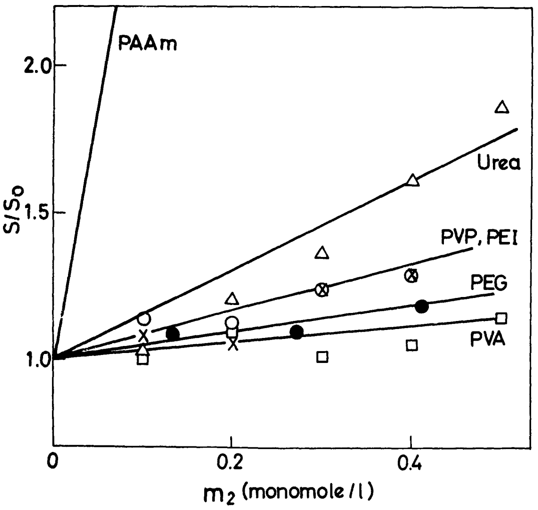

Fig. 1. Solubilization factor (S/S_0) of BuBr in various neutral polymer solutions at 25°C. ○: PVP, ×: PEI.

S_0 and S are the solubilities in pure water and in polymer solution, respectively, and m_2 is the polymer concentration. It is seen that S/S_0 becomes larger with increasing polymer concentration in the order:

$$\text{PVA} < \text{PEG} < \text{PVP} \sim \text{PEI} \ll \text{PAAm} \tag{1}$$

On the other hand, the order for the non-polar hydrocarbons such as naphthalene and biphenyl was[1]

$$\text{PAAm} < \text{PVA} < \text{PEG} < \text{PEI} < \text{PVP} \tag{2}$$

which was accounted for in terms of the iceberg enforcing effects. In other words, when an iceberg enhancing polymer is dissolved in water, a cage of water molecules is formed around the polymer solute, and the cosolute can then be incorporated within the same cage as the polymer. Thus, the solubility of the cosolute can be expected to be enhanced by the presence of iceberg enhancing polymers. The fact that the order (1) coincides with (2) except for PAAm indicates that the iceberg enforcing effect is still a main factor for the solubilization of polar cosolute as in the case of non-polar cosolute. Thus, the solute-solvent interactions are stronger than those between solute and cosolute or cosolute and cosolute. It should be recalled that PAAm solubilized most weakly non-polar cosolutes, whereas it solubilized most strongly polar cosolutes. This suggests that PAAm cannot greatly increase the solubility of polar cosolute by iceberg formation (carbamoyl groups of PAAm interfere with the formation) and some kind of complex formation of PAAm with alkyl bromide should exist. Solubilization of n-butyl bromide by urea is less strong than by PAAm, but fairly stronger than by other polymers. Thus, the carbamoyl groups contained both in PAAm and urea can be considered to interact strongly with butyl bromide by dipole-dipole interactions. The extent of the solubilization of butyl bromide by PVP, PEI, PEG and PVA is similar to that for naphthalene or biphenyl.

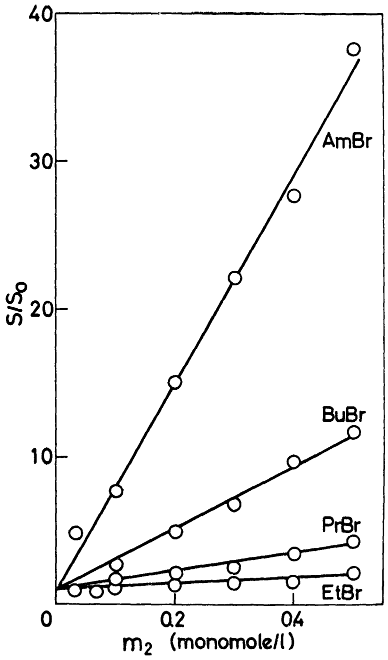

Fig. 2. Solubilization factor (S/S_0) of various alkyl bromides in polyacrylamide solution at 25°C.

Figure 2 gives the solubilization of various alkyl bromides by PAAm. The solubility increases with the order:

$$\text{EtBr} < \text{PrBr} < \text{BuBr} < \text{AmBr} \tag{3}$$

In other words, the larger the molecular weight of the cosolute, the more remarkable the solubilization. We see that the solubility increases linearly with the concentration of PAAm in the concentration region 0—0.5 monomol/l.

The solubilization effect by various water-soluble polymers is demonstrated in the following. Figures 3, 4 and 5 show the solubility of EtBr, PrBr, BuBr and AmBr in the presence of PVP PEI and PEG, respectively. The solubility increases in the order shown by the relation (3) but not that of EtBr by addition of

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[3] In this paper the term "solubilization" refers to the solubility increase by addition of the third substances. The correct term is "hydrotropy".[4]

[4] F. A. Long and W. F. McDevit, *Chem. Revs.*, **51**, 119 (1952).

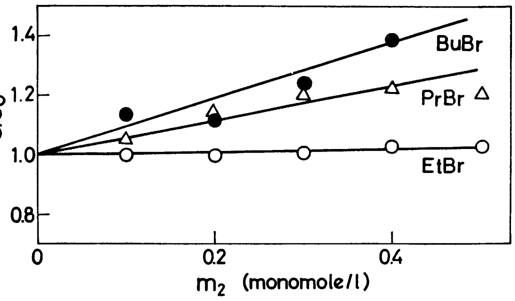

Fig. 3. Solubilization factor (S/S_0) of various alkyl bromides in polyvinylpyrrolidone solution at 25°C.

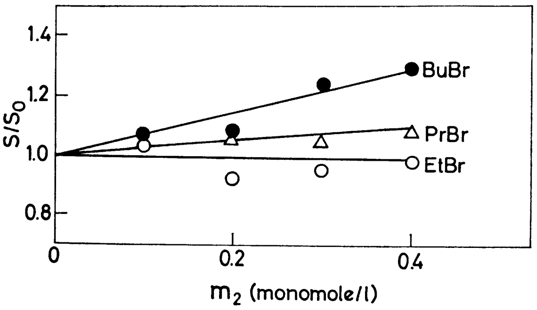

Fig. 4. Solubilization factor (S/S_0) of various alkyl bromides in polyethylenimine solution at 25°C,

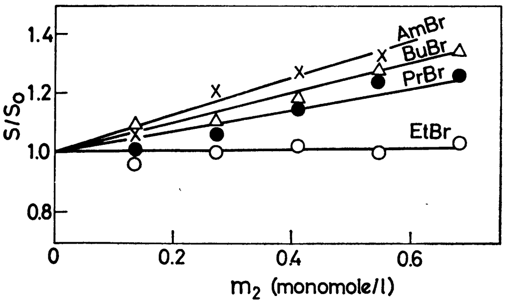

Fig. 5. Solubilization factor (S/S_0) of various alkyl bromides in polyethyleneglycol solution at 25°C.

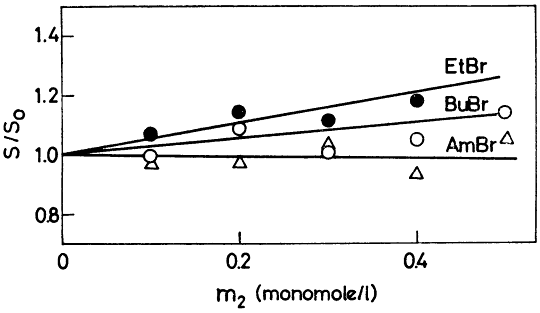

Fig. 6. Solubilization factor (S/S_0) of various alkyl bromides in polyvinylalcohol solution at 25°C.

these neutral polymers. Order (3) can be understood by the concept of the iceberg enforcing effect since it is known that the larger the volume of cosolute, the stronger the solubilizing effects.[1,4,5] Inequality (1) appears to hold also for PrBr. The specific interactions between polymer and cosolute such as dipole-dipole interactions do not seem to be significant in these polymers.

Figure 6 gives the experimental data for PVA. Solubilization is not so remarkable as in the case for naphthalene[1], and is in the order

$$\text{EtBr} > \text{BuBr} > \text{AmBr} \tag{4}$$

This indicates that the iceberg enforcing effect is unimportant on account of the interfering effect of OH groups with the iceberg formation,[1,6] and the interactions of the OH groups of PVA with polar cosolute (solute-cosolute interactions) certainly exist.

The Setchênow equation was reported to be valid for non-polar cosolute in various polymer solutions in dilute concentration regions, and the Setchênow constant, k, derived from the following equation was discussed in detail.[1]

$$\ln (S_0/S) = km_2 \tag{5}$$

For BuBr, $\ln(S_0/S)$ in various polymer solutions linearly decreased with increasing polymer concentration below 0.4 monomol/l except for PAAm solution. In the case of PAAm, deviation from linearity was found over 0.1 monomol/l, and the linearity between S/S_0 [not $\ln(S/S_0)$] and m_2 holds in the range 0—0.5 monomole/l (Fig. 2). The limiting Setchênow constants ($k/2.303$) derived for BrBu were −5.0, −0.31, −0.22, −0.21, −0.14 and −0.05 for PAAm, PVP, PEI, PEG, PAA and PVA, respectively.

Figure 7 shows the solubilization of BuBr in the presence of mixtures of PAAm and PVP. PAAm solubilized strongly BuBr whereas PVP did only weakly (Fig. 1). If no specific interaction exists between PAAm and PVP, the solubility should change as shown by the broken line. However, the solubility decreases at first with increasing PAAm and increases through a minimum. The decrease in solubilizing forces by mixing of PAAm and PVP may reflect that the polar carbamoyl groups of PAAm, which can solu-

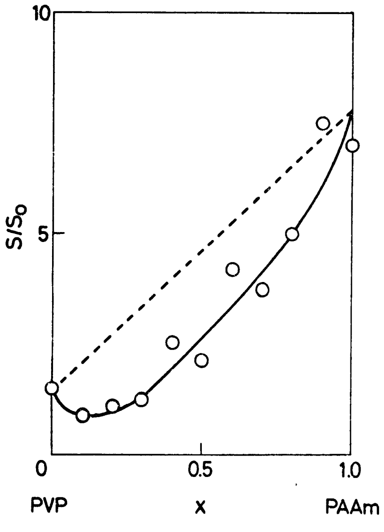

Fig. 7. Solubilization factor (S/S_0) of n-butyl bromide in mixture solution of polyvinylpyrrolidone and polyacrylamide at 25°C. $m_2=0.3$ monomol/l.

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[5] A. G. Leiga and J. N. Sarmousakis, *J. Phys. Chem.*, **70**, 3544 (1966).

[6] W. Y. Wen and J. H. Hung. *ibid.*, **74**, 170 (1970).

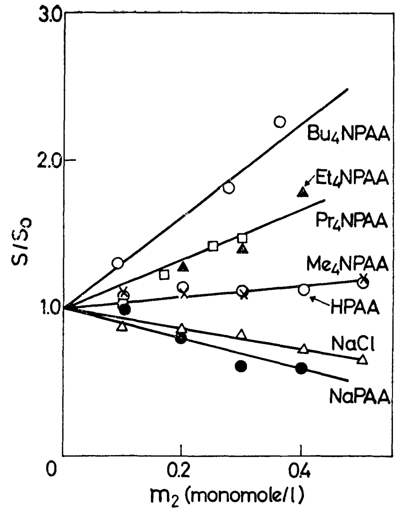

Fig. 8. Solubilization factor (S/S_0) of *n*-butyl bromide in various polyacrylate solutions at 25°C.

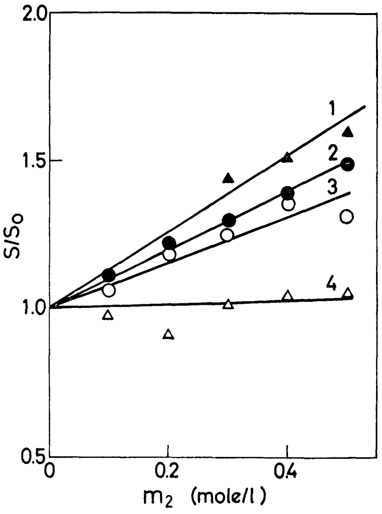

Fig. 9. Solubilization factor (S/S_0) of *n*-butyl bromide in various tetraalkylammonium bromide solutions at 25°C. 1 : Bu_4NBr, 2 : Pr_4NBr, 3 : Et_4NBr, 4 : Me_4NBr.

bilize alkyl bromide, combine with the polar side chain groups of PVP and the effective carbamoyl groups decrease. It is probable that complex formation takes place between PAAm and PVP. The behaviour of the desolubilization of the mixture of PVP and PAAm seems to be specific since the cosolute is more strongly solubilized by mixing of solutes than by individual solute.[7,8,9]

Figure 8 gives the solubility of BuBr in the presence of polyacrylic acid or its salts. The sodium polyacrylate and sodium chloride salt-out, whereas tetraalkylammonium salts show salting-in effects. It is seen that the solubility increases with increasing number of carbon atoms in organic gegenions, or with increasing hydrophobicity. The tendency has been observed for naphthalene and biphenyl.[1] The results indicate that the salting-in effect on the polar cosolute is also mainly determined by the hydrophobic interactions of solute with water molecules. The Setchénow constants ($k/2.303$) of BuBr were 0.54, -0.14, -0.49, -0.49, -0.88 for NaPPA, Me_4NPAA, Et_4NPAA, Pr_4NPAA and Bu_4NPAA, respectively.

Extensive study has been carried out on low molecular weight tetraalkylammonium salts.[6,10-14] We studied the solubilization effect for alkyl bromides by tetraalkylammonium bromide. Figure 9 shows the influence of the bromide on BuBr. The solubilization becomes stronger in the order

$$Me_4NBr < Et_4NBr < Pr_4NBr < Bu_4NBr \quad (6)$$

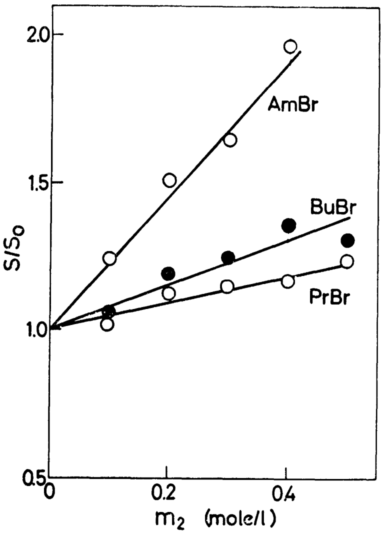

Fig. 10. Solubilization factor (S/S_0) of various alkyl bromides in tetraethylammonium bromide solution at 25°C.

This order was also found for tetraalkylammonium polyacrylates, but the strength of the solubilization is weaker by the bromide than by polyacrylate. Order (6) is the same as that found by Wen an Hung[6] for butane. This also indicates that hydrophobic interactions between the salts and water are the main factor determining the solubility of polar cosolutes (alkylbromide) as was the case for non-polar cosolute.

Figure 10 gives the solubilization data of n-propyl, n-butyl, and n-amyl bromides by tetraethylammonium bromide. The S/S_0 value is larger for larger alkyl groups. This is easily understood by the McDevit and Long equation,[15] which shows that the Setchénow coefficient is a linear function of the volume of the cosolute.

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7) J. W. McBain and K. E. Johnson, *J. Amer. Chem. Soc.*, **66**, 9 (1944).

8) R. S. Stearns, H. Oppenheimer, E. Simon, and W. D. Harkins, *J. Chem. Phys.*, **15**, 496 (1947).

9) N. Ise and T. Okubo, unpublished results.

10) J. O'M Bockris, J. Bowler-Reed, and J. A. Kitchner, *Trans. Faraday Soc.*, **47**, 184 (1951).

11) R. L. Berger, Jr. and F. A. Long, *J. Phys. Chem.*, **60**, 1131 (1956).

12) N. C. Deno and C. H. Spink, *ibid.*, **67**, 1347 (1963).

13) A. Ben-Naim, *ibid.*, **71**, 1137 (1967).

14) H. E. Wirth and A. LoSurdo, *ibid.*, **72**, 751 (1968).

15) W. F. McDevit and F. A. Long, *J. Amer. Chem. Soc.*, **74**, 1773 (1952).