Elucidation of Concentrated Salt Effects on the Solvolysis Reactions of Typical S_N1 and S_N2 Substrates in Sulfolane–Water Mixed Solvent

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In a 50 vol % sulfolane–H_2O mixed solvent, extensive studies have been carried out of the concentrated salt effects on the solvolysis reaction rates of aliphatic halides and related compounds (RX). In the solvent system, the "pseudo" first-order rate constants (k/s^{-1}) of typical S_N1 substrates, 1-adamantyl chloride and bromide, or 2-adamantyl bromide, were increased exponentially by the addition of $MClO_4$ (M = Li and Na) and $M(ClO_4)_2$ (M = Mg and Ba); the extent of the cation effects increased as $Na^+ < Li^+ < Mg^{2+} \approx Ba^{2+}$, which was attributed to the "chemical" interaction between the metal ions and the leaving-group anions in the "aqueous" solution modified by the mixed-organic solvents and concentrated salts. Based on the Raman spectra, we discuss the distortion of the bulk water structure and the alteration of properties of water into those of a "non-aqueous" solvent with the addition of the organic solvents and concentrated salts ($LiClO_4$ and Et_4NBr) as well as with increasing temperature. However, the addition of non-metallic salts, i.e., Et_4NX ($X^- = ClO_4^-$, Cl^-, Br^-, and tosylate), caused decreases in the rates substantially, regardless of the leaving group (Cl or Br): the deceleration effects increasing as $ClO_4^- < Br^- < Cl^- < TsO^-$. The deceleration in the solvolysis rates with Et_4NX and R_4NBr (R = Pr and *n*-Bu) should be caused by mainly the further decrease in water activity of the solvents. In addition, we would like to report solvolyses accompanied by "ion exchange" reactions for the typical S_N2 substrates, hexyl chloride, bromide, and tosylate, in the sulfolane–H_2O solvent.

Electrolyte effects on reaction rates are believed to play an important role in the investigation of mechanisms. More than 40 years ago, however, Clarke and Taft[1] described that the validity of the theoretical treatment of salts had remained uncertain; a similar situation may have lasted until nowadays. In general, "indifferent" salts (or supporting electrolytes) are never involved directly in the equilibria or kinetics of reactions in solution. The effects by "indifferent" salts of lower concentrations ($<0.1\ \mathrm{mol\,dm^{-3}}$) in aqueous solution may be explained by the Debye–Hückel theory, which takes the electrostatic interaction into account. A corrected Debye–Hückel theory with size asymmetry and effective diameters has been discussed.[2]

Numerous studies have been performed to understand the salt effects on solvolysis reactions;[3] the Winstein's ion-pair scheme[4] has had strong impact in this field. A paper appeared[5] entitled "Correlation of Solvolysis Rates 50 Years Later" after the paper by Grunwald and Winstein of 1948.[6] However, the effects by concentrated salts ($>0.1\ \mathrm{mol\,dm^{-3}}$) have not been treated quantitatively and comprehensively. At higher ionic strength (μ), the reaction rate (k) can be expressed by

$$\log k = \log k_0 + b\mu, \tag{1}$$

where k_0 is the rate constant at infinite dilution (or $\mu = 0$); b is an empirical coefficient.[7] It is known that the rates of S_N1 solvolysis of alkyl halides and related compounds are subject to positive salt effects.[8] Bunton et al.[8] reported an exponential increase in the solvolysis rate of *t*-butyl bromide with increasing the concentration of $LiClO_4$. They concluded that anion effects are important but cation effects are small (for Li^+, Na^+, and Et_4N^+), and that the order of the effects of anions is $ClO_4^- > TsO^- \approx NO_3^- \approx Br^- \approx Cl^- \approx$ no salt $> F^- > OH^-$. However, Allen et al.[9] have reported a great difference in the salt effects of $LiClO_4$ and $n\text{-}Bu_4NClO_4$ on the solvolysis of 4-methoxybenzyl chloride in 85%(v/v) aqueous dioxane. The effects of $LiClO_4$ and LiCl in several organic solvents and water on the stereo-selectivity of products of the Diels–Alder reaction have been discussed:[10] the salt effects on Diels–Alder reaction kinetics have been reviewed.[11]

In previous studies,[12–14] we have observed that for a typical S_N1 substrate, such as 1-adamantyl halides or *t*-butyl chloride, cation effects increase as $Et_4N^+ \ll Li^+, Na^+ < Mg^{2+}, Ba^{2+}$ for perchlorate salts in 80 vol % MeOH–H_2O ($\varepsilon_r = 49$),[12] 50 vol % acetone–H_2O ($\varepsilon_r = 55$),[13] and 50 vol % 1,4-dioxane–H_2O ($\varepsilon_r = 44$)[14] solvent systems. The cation effects were attributed to the interaction between the metal ions and the leaving-group anions of substrates. For the incredibly "strong" interaction between the metal ions and the simple anions in "aqueous" solutions, we have proposed a model[12] of water containing highly concentrated salts. This model can be outlined as follows: in a highly concentrated salt solution ($>5\ \mathrm{mol\,dm^{-3}}$), too many anions and cations exist to be fully solvated by H_2O molecules ($<55\ \mathrm{mol\,dm^{-3}}$); under such extreme conditions, the network of hydrogen bonding by the solvent water is almost distorted to give isolated H_2O molecules.

Isolated H_2O molecules are indeed very different from bulk water. The donicity, for instance, of isolated H_2O molecules is very small, DN = 18.0,[15] whereas the donor number of bulk water is reported to be $DN_{bulk} = 33$[16] or 42.3,[17] depending on the solution conditions. Erlich et al.[16] have noted that ^{23}Na NMR chemical shifts are concentration dependent for NaI and NaSCN. It is supposed that the DN_{bulk} value would

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approach DN = 18.0 with increasing concentration of a sodium salt if its solubility in water had no limit. We may stress that the donicity of ethers are very close (e.g., DN = 19.2 for diethyl ether)[15] to that of isolated H_2O molecules.

The main points proposed in our previous solvolytic studies[12–14] are as follows: (1) Highly concentrated salts would reduce the properties of bulk water (H–O–H) into those of a nonaqueous solvent, such as an ether (R–O–R). (2) In water-mixed solvents containing concentrated metal salts ($>1.0\,\mathrm{mol\,dm^{-3}}$), the exponential increase in solvolysis rates of S_N1 substrates are caused by the formation of carbocations through direct "chemical" interaction between metal ions and anions (X^-, from the substrate RX) in the modified solvent. (3) The solvolysis rates of S_N2 substrates are decelerated by concentrated salts because of the decrease in water activity. (4) Positive or negative salt effects can be correlated to the *m*-value (by Grunwald and Winstein)[18] of the substrates.

By means of voltammetry,[19] conductometry,[20,21] and UV–visible and NMR spectroscopies,[22–27] we have undeniably demonstrated that alkali metal and alkaline earth metal ions have "weak" but unexpectedly distinct chemical (i.e., covalent bonding or coordinating) as well as Coulombic interactions with many simple anions. This holds true not only in low permittivity media ($\mathcal{E}_r < 10$)[21] but also in higher permittivity media ($20 < \mathcal{E}_r < 65$) with poor solvating ability,[19,20] where the simple anions include halides, carboxylates, phosphates, sulfonates, etc. Coordination chemistry of the lithium ion with simple anions as well as cyclic ligands has been reviewed by Olsher et al.[28] Stable carbocations can be produced from trityl halides by the addition of the perchlorates salts of Li^+, Na^+, Mg^{2+}, (Ca^{2+}, Sr^{2+}), and Ba^{2+} in acetonitrile;[22–24] the carbocations have been detected by UV–visible,[22] ^1H and ^{13}C NMR spectroscopies.[23,24] For a fluoran-based black color former in acetonitrile, the color has been developed by the addition of the alkali metal or alkaline earth metal perchlorates[24] as well as phenol which is used as a normal color developer.

We have explained the large salt effects on the indicator acidity (or Hammett acidity function)[29] using *p*-(dimethylamino)azobenzene[25] and on the proton transfer from tropolone[26] or nitrophenols[27] to amine bases in acetonitrile solution in terms of the chemical interaction between the anions and M^+ or M^{2+}, not merely as ion-exchange reactions or the alternation between the contact ion pair (CIP) and the solvent-separated ion pair (SSIP).[27] Binder and Kreevoy[30] examined the interaction of Li^+ with a betaine dye, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate, and *p*-nitrophenolate in acetonitrile. Very recently, we obtained decisive ^1H NMR evidence of the formation of a "reversed-coordinated" species,[26] $(Li^+)_2L^-$, for the anions (L^-) from tropolone and hinokitiol (4-isopropyltropolone) in acetonitrile-d_3 but not in DMF-d_6.[31] The extraordinary chemical reactions with alkali metal and alkaline earth metal ions in higher permittivity media have been reviewed.[32] Fuoss and Kraus[33] have proposed the concept of "symmetrical" triple ion formation, which is based on electrostatic interaction between (spherical) ions in an electric field of low permittivity.

Further, we may postulate that a very small but direct "chemical" interaction between M^+ or M^{2+} and simple anions, such as halide, occurs even in aqueous or organic-aqueous solutions if they are in the "dihydrogen ether" ([R](H)–O–(H)[R])[14] conditions. In order to support our proposal of previous solvolytic studies,[12–14] we examined the effects of various types of salts, $MClO_4$, $M(ClO_4)_2$, and R_4NX, on the solvolysis reactions of typical S_N1 and S_N2 substrates in a 50 vol % sulfolane–H_2O solvent. Coincidentally, it must be very important to distinguish the tetraalkylammonium ion (R_4N^+) possessing no coordination ability from metal ions (M^+ or M^{2+}) and to distinguish the perchlorate ion (three-dimensionally symmetrical anions, including PF_6^- and BF_4^-) from other anions (X^-), such as halides or tosylate. During the conductometric studies in aprotic solvents,[20] we noticed that the cation of Et_4N^+, and not a metal ion, can form a strong electrolyte, regardless of the kind of anions; similarly, the anion of ClO_4^- forms a strong electrolyte even though the counter cation is a metal ion. This principle in aprotic solvents stands even for concentrated salts in aqueous–organic solvent systems, at least for exploring kinetic phenomena.

The substitution (or "ion exchange") of leaving groups with added salt anions for the typical S_N2 substrates, hexyl chloride, bromide, and tosylate, were examined thoroughly in the 50 vol % sulfolane–H_2O solvent system.

Results and Discussion

Effects of Metallic and Non-Metallic Salts on the Solvolysis Rate of 1-Adamantyl Chloride. Figure 1 shows the change in the solvolysis rate of 1-adamantyl chloride with the addition of alkali metal or alkaline earth metal perchlorates in a 50 vol % sulfolane–water mixed solvent at 55 °C. The "pseudo" first-order reaction rate constant ($k/\mathrm{s^{-1}}$) increased exponentially with increasing concentration of $LiClO_4$ or $NaClO_4$, i.e., linearity between $\log(k/\mathrm{s^{-1}})$ and the concentration of $MClO_4$ was observed. With $Mg(ClO_4)_2$ or $Ba(ClO_4)_2$, although linearity was observed at lower salt concentrations, the slope appeared to become lower somewhat at higher salt concentrations. The effects of cations increased as $Na^+ <$

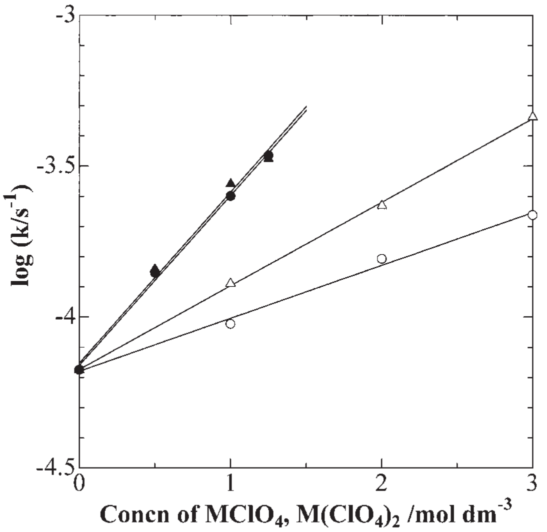


Fig. 1. Changes in the solvolysis rate constants of 1-adamantyl chloride with the addition of various salts in 50 vol % sulfolane–H_2O at 55 °C: (○) $NaClO_4$; (△) $LiClO_4$; (●) $Mg(ClO_4)_2$; (▲) $Ba(ClO_4)_2$.

Table 1. "Pseudo" First-Order Reaction Rate Constants of the Solvolyses for Typical S_N1 Substrates in the Presence of Various Salts in the 50 vol % Sulfolane–H_2O Solvent

Substrate	Temp/°C	Salt[a]	k/s^{-1}	log(k/s^{-1})	Δ log(k/s^{-1})[b]
1-Adamantyl chloride	55	No salt	6.69×10^{-5}	−4.17	—
	55	$LiClO_4$	1.14×10^{-4}	−3.94	+0.23
	55	$NaClO_4$	9.49×10^{-5}	−4.02	+0.15
	55	$Mg(ClO_4)_2$	2.52×10^{-4}	−3.60	+0.57
	55	$Ba(ClO_4)_2$	2.76×10^{-4}	−3.56	+0.61
	55	$Ni(ClO_4)_2$	1.08×10^{-4}	−3.97	+0.20
	55	$Co(ClO_4)_2$	8.24×10^{-5}	−4.08	+0.09
	60	No salt	1.08×10^{-4}	−3.97	—
	60	Et_4NClO_4	6.49×10^{-5}	−4.19	−0.22
	60	Et_4NCl	4.26×10^{-5}	−4.37	−0.40
	60	Et_4NBr	5.92×10^{-5}	−4.23	−0.26
	60	Et_4NOTs[c]	2.14×10^{-5}	−4.67	−0.70
	60	Pr_4NBr	2.71×10^{-5}	−4.57	−0.60
	60	n-Bu_4NCl	7.55×10^{-6}	−5.12	−1.15
	60	n-Bu_4NBr	1.29×10^{-5}	−4.89	−0.92
2-Adamantyl bromide	80	No salt	8.10×10^{-6}	−5.09	—
	80	$LiClO_4$	1.22×10^{-5}	−4.91	+0.18
	80	$NaClO_4$	1.20×10^{-5}	−4.92	+0.17
	80	$Mg(ClO_4)_2$	2.24×10^{-5}	−4.65	+0.44
	80	$Ba(ClO_4)_2$	2.03×10^{-5}	−4.69	+0.40
	80	Et_4NClO_4	6.53×10^{-6}	−5.19	−0.10
	80	Et_4NCl	4.00×10^{-6}	−5.40	−0.31
	80	Et_4NBr	5.45×10^{-6}	−5.26	−0.17
	80	Et_4NOTs[c]	3.29×10^{-6}	−5.48	−0.39

a) The salt concentration of 1.0 mol dm^{-3}, except for transition-metal salts of 2.0×10^{-3} mol dm^{-3}. b) $\Delta \log(k/\mathrm{s}^{-1}) = \log(k_1/\mathrm{s}^{-1})$[with salt] $-$ $\log(k_0/\mathrm{s}^{-1})$[no salt] for each substrate. c) p-Toluenesulfonate (tosylate) salt.

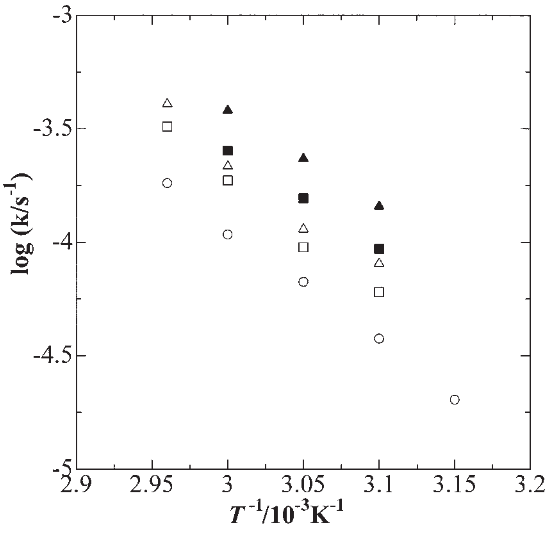
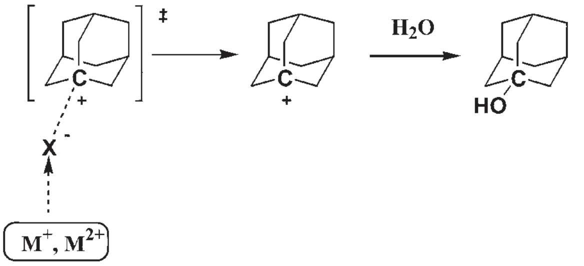


Fig. 2. Arrhenius plots of the solvolysis reaction of 1-adamantyl chloride in 50 vol % sulfolane–H_2O: (○) no salt; (△) 1.0 mol dm^{-3} $LiClO_4$; (▲) 2.0 mol dm^{-3} $LiClO_4$; (□) 1.0 mol dm^{-3} $NaClO_4$; (■) 2.0 mol dm^{-3} $NaClO_4$.



Scheme 1. The solvolysis of 1-adamantyl halide in the presence of alkali metal and alkaline earth metal ions in the modified "aqueous" solution.

$Li^+ < Mg^{2+}$, Ba^{2+} (cf. Table 1).

The Arrhenius plots, as shown in Fig. 2, of the solvolysis reaction (45–65 °C) of 1-adamantyl chloride in the 50 vol % sulfolane–H_2O solvent gave 100.1, 99.8, and 103.8 kJ mol^{-1} activation energies (E_a) for no salt, 1.0 mol dm^{-3} $LiClO_4$, and $NaClO_4$, respectively. The Arrhenius plots for 2.0 mol dm^{-3} of the salts gave similar values, suggesting that the S_N1 mechanism without salt remains even in the presence of concentrated salts. The $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ values at 55 °C were evaluated to be 97.4, −29.5, and 107.0 (R = 0.998) for no salt, 97.0, −24.4, and 105.0 (R = 0.990) for 1.0 mol dm^{-3} $LiClO_4$, and 101.0 kJ mol^{-1}, −14.2 eu, 105.7 kJ mol^{-1} (R = 0.997) for 1.0 mol dm^{-3} $NaClO_4$, respectively.

As shown above, the solvolysis rate of 1-adamantyl chloride increased remarkably in the presence of concentrated salts in spite of the (expected) decrease in the activity of solvent water. The observed results can be accounted for by the reaction mechanism in Scheme 1: First of all, the properties of the sulfolane–water or bulk water should be altered to be those of a "non-aqueous" solvent by the concentrated salts; the "chemi-

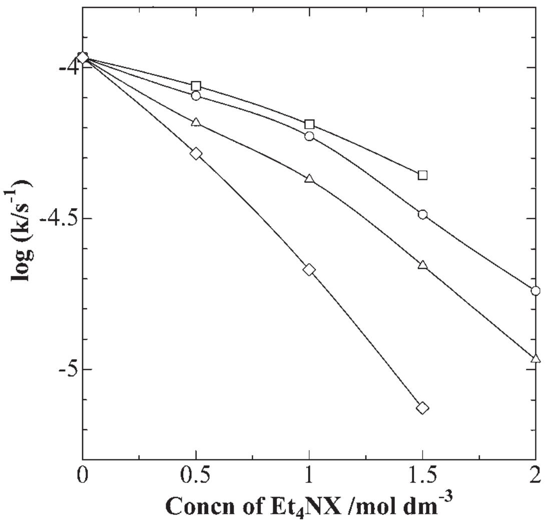


Fig. 3. Changes in the solvolysis rate constants of 1-adamantyl chloride with the addition of various salts in 50 vol % sulfolane–H_2O at 60 °C: (○) Et_4NBr; (△) Et_4NCl; (□) Et_4NClO_4; (◇) Et_4NOTs.

cal" interaction may operate between M^+ or M^{2+} and the chloride of (or from) the substrate to produce the 1-adamantyl cation in the deformed solvent; the 1-adamantyl cation can react with H_2O promptly, even if the activity of water is weakened.

The effects of non-metallic salts on the S_N1 solvolysis rate were examined in the same solvent. Figure 3 shows the change in the solvolysis rate of 1-adamantyl chloride with increasing the concentration of $Et_4N^+X^-$ ($X^- = ClO_4^-$, Cl^-, Br^-, and TsO^-) at 60 °C. All the tetraethylammonium salts caused deceleration in the solvolysis rate; the tosylate with the most bulky among the four anions caused the most remarkable decrease in the $\log(k/s^{-1})$ value of -0.70, i.e., the solvolysis rate decreased to be one-fifth at 1.0 mol dm^{-3} of the salt, compared with that in the absence of the salt [$\log(k/s^{-1}) = -3.97$] at 60 °C. The tetraethylammonium salts caused the deceleration effect in the order of $ClO_4^- < Br^- < Cl^- < TsO^-$ for the anions. The effects must be brought by the decrease in the activity of solvent water; that is, the solvolysis reaction in the present system should be initiated by the attack of water molecules towards the substrate in order to produce the carbocation. The solvation abilities of the anions may result in the difference of "effective" water activities.

Similar but more remarkable deceleration in the solvolysis rate was observed with other tetraalkylammonium bromides (R_4NBr: R = Pr and *n*-Bu). The longer the chain in tetraalkylammonium bromide, the more remarkable the deceleration of the solvolysis rate as $Et_4N^+ < Pr_4N^+ < n\text{-}Bu_4N^+$: $\log(k/s^{-1})$ values with 1.0 mol dm^{-3} bromide salts were -4.23, -4.57, and -4.89, respectively, at 60 °C. The chloride salt of *n*-Bu_4N^+ caused slightly larger deceleration ($\log(k/s^{-1}) = -5.12$) than the bromide salt (cf. Table 1).

Chemical Interaction between Anions and Metal Ions. No interaction, except for the Coulombic force, should operate between the halide ions (X^-) and alkali metal (M^+) or alkaline earth metal ions (M^{2+}) of lower concentrations in aqueous solution at room temperature. Therefore, it must be quite natural that someone is suspicious that the interaction between X^- and M^+ or M^{2+} in the 50% aqueous solution causes cleavage of the $C^{\delta+}$–$X^{\delta-}$ covalent bond. Rudakov and Kozhevnikov[34] have reported exponential increases in the solvolysis rates of *t*-butyl halides in EtOH–H_2O mixed solvents with the complex formation constants (e.g., $K = [MX]/[M^+][X^-]$) of transition-metal halides, such as of Ag^+, Bi^{3+}, Cd^{2+}, Pb^{2+}, Tl^+, Co^{2+}, Mn^{2+}, Cu^{2+}, Ga^{3+}, or Zn^{2+}. On the other hand, Cox and Maskill[35] have discovered the solvolyses of *t*-butyl iodide catalyzed by I_2 in aqueous ethanol; the same effect, but to a smaller extent, is also found for *t*-butyl bromide in the solvent. We would like to note that polyhalogen ion formation, such as I_3^- and I_2Br^- (e.g., $I_2 + Br^- \rightleftharpoons I_2Br^-$), in the solution can account for the catalytic effects by I_2. The stability of the polyhalogen ions has been reported to decrease as $I_3^- > I_2Br^- > Br_3^-$.[36]

As a reference study, the effects of transition-metal salts were examined; with the assistance of the complex formation between a transition-metal ion and halide ions (X^-), the $C^{\delta+}$–$X^{\delta-}$ bond may be cleaved to produce the reaction intermediate species (the carbocation). Upon the addition of a small amount of $AgClO_4$ to 1-adamantyl chloride in 50 vol % sulfolane–H_2O at 55 °C, precipitation of AgCl occurred to disturb further titration with NaOH.

The addition of Ni^{2+} at very low concentrations [$(2.0–4.0) \times 10^{-3}$ mol dm^{-3}], however, caused an increase in the solvolysis rate of the substrate. The slope, $\log(k/s^{-1})$ vs concn of the metal ion, was extremely larger than that for $LiClO_4$ or $Mg(ClO_4)_2$: the slope of 96.5 for Ni^{2+}, cf., 0.28 and 0.56 for Li^+ and Mg^{2+}, respectively. Cobalt(II) perchlorate also caused a linear increase in the $\log(k/s^{-1})$ of 1-adamantyl chloride in the same solvent system; however, the slope for Co^{2+} ($\Delta \log k/\Delta c$ = ca. 40) was smaller than that of Ni^{2+}. The difference in the acceleration effects between Ni^{2+} and Co^{2+} can be explained by the complex formation (chemical interaction) abilities of Ni^{2+} and Co^{2+} with Cl^- in aqueous solution: $\log \beta_2 = 0.34$ and -0.2 for $NiCl_2$ and $CoCl_2$, respectively, at room temperature, where β_2 is the overall formation constant of $M^{2+}(Cl^-)_2$.[37] Halide salts (Cl^- and Br^-) of Ni^{2+} and Co^{2+} caused no obvious differences in the solvolysis rate constants, compared with the perchlorate salts. Strong acids, such as $HClO_4$ and HCl, of $(2.0–4.0) \times 10^{-3}$ mol dm^{-3} also caused exponential increases in the rate constants with $\Delta \log k/\Delta c$ = ca. 25.

The above results indicate that complex formation with transition-metal ions can extract the Cl^- ion from 1-adamantyl chloride, which may induce the exponential increase in the solvolysis rate constant with the metal ion concentration. We imagine that the "special salt effect" proposed by Winstein et al.[4] might be brought by the "direct" chemical interaction between $Li^+(ClO_4^-)$ and benzenesulfonate anions from substrates in lower permittivity media, such as acetic acid. Raman spectral evidences will be given in the final section to show the distortion of hydrogen-bonding structure of aqueous solution with the addition of organic solvents and concentrated salts or with increasing temperature.

On the Solvolysis Rate of 2-Adamantyl Bromide. Another typical S_N1 substrate, 2-adamantyl bromide, in the same solvent system was subject to similar acceleration effects by the metal perchlorates as shown in Fig. 4. The solvolysis rate con-

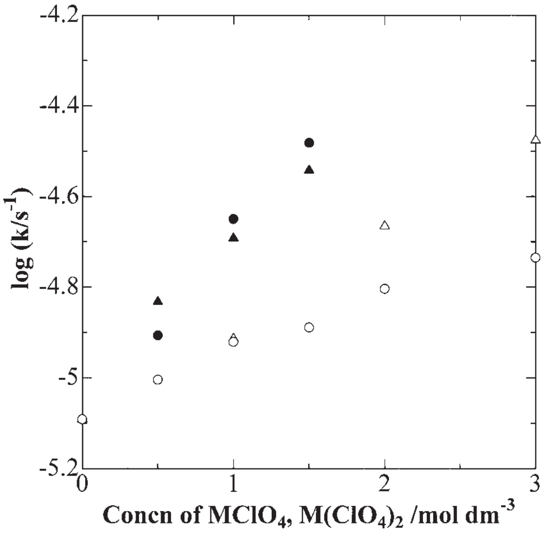


Fig. 4. Changes in the solvolysis rate constants of 2-adamantyl bromide with the addition of various salts in 50 vol % sulfolane–H_2O at 80 °C: (○) $NaClO_4$; (△) $LiClO_4$; (●) $Mg(ClO_4)_2$; (▲) $Ba(ClO_4)_2$.

stant of the substrate was observed to be $k/\text{s}^{-1} = 8.10 \times 10^{-6}$ at 80 °C. The $\log(k/\text{s}^{-1})$ value increased linearly with increasing concentration of $LiClO_4$. However, the salts of the other metal ions, Na^+, Mg^{2+}, and Ba^{2+}, gave convex curves at higher salt concentrations. The acceleration effects by the metal ions increased as $Na^+ < Li^+ < Mg^{2+}$, Ba^{2+}. The metal cations should assist the formation of a stable carbocation from 2-adamantyl bromide in a manner similar to 1-adamantyl chloride. However, the carbocation of a secondary carbon type may be less stable than of a tertiary carbon type. Therefore, the degree of acceleration caused by the metal salts in the solvolysis rate for 2-adamantyl bromide should be less than that for 1-adamantyl chloride, regardless of the difference in the leaving group. For instance, the solvolysis rates of the 1- and 2-derivatives increased with the logarithm factors $[\Delta \log(k/\text{s}^{-1})]$ of +0.85 and +0.62 at 3.0 mol dm^{-3} $LiClO_4$, respectively. Ionization potentials and electron affinities of adamantane (Ad) have been evaluated by Yan et al.;[38] 1-Ad^+ is predicted to lie 47 kJ mol^{-1} below 2-Ad^+. The influence of alkyl substitution on the solvent effects in solvolysis of 1-adamantyl bromide has been examined by Takeuchi et al.[39] In the above discussion, only the stability of the carbocation was taken into account; the role of the leaving group is also important. However, the problem of solvation for anions prevented us from discussing further.

The deceleration effects on 2-adamantyl bromide in the presence of non-metallic salts, Et_4NX, were observed as $ClO_4^- < Br^- < Cl^- < TsO^-$: the $\log(k/\text{s}^{-1})$ values of −5.19, −5.26, −5.40, and −5.48, respectively, for 1.0 mol dm^{-3} salts. The fact that the solvolysis rates of 2-adamantyl bromide and 1-adamantyl chloride were decelerated by the non-metallic salts in the same order of the salt anion indicated that the common ion effect was not much concerned in the solvent system, although the common ion salt effects have been reported in S_N1 solvolyses in acetic acid,[40] phenol,[41] and aqueous acetone.[42]

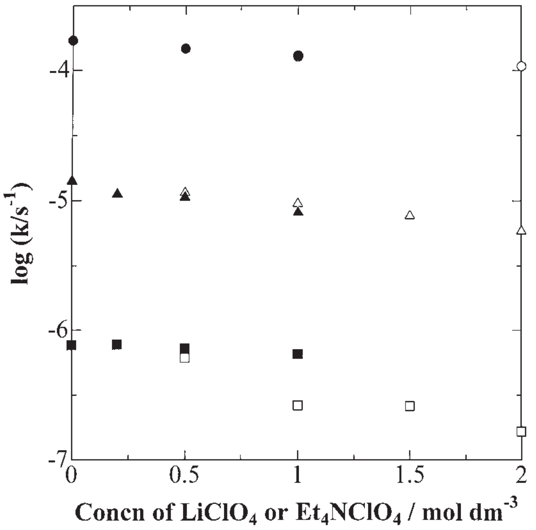


Fig. 5. Changes in the solvolysis rate constants of S_N2 substrates with the addition of $LiClO_4$ or Et_4NClO_4 in 50 vol % sulfolane–H_2O at 80 °C: (circles) hexyl tosylates; (triangles) hexyl bromide; (squares) hexyl chloride. Open and solid symbols are for $LiClO_4$ and Et_4NClO_4, respectively.

Solvolyses of S_N2 Substrates, Hexyl Chloride, Bromide, and Tosylate. As typical S_N2 substrates, hexyl halides and tosylate were selected in the present study; aliphatic halides of shorter aliphatic chains, such as methyl or ethyl chloride, are apt to escape from the reaction vessel because of their low boiling points: −23.7, 12.3, 46–47, 78.5, 107.8, and 134 °C for methyl, ethyl, propyl, butyl, pentyl, and hexyl chlorides, respectively.[43] In Fig. 5 are shown the changes in the solvolysis rates, $\log(k/\text{s}^{-1})$ of hexyl chloride, bromide, and tosylate with 0–2.0 mol dm^{-3} $LiClO_4$ in 50 vol % sulfolane–H_2O at 80 °C. As contrasted with the cases of the typical S_N1 substrates, the solvolysis rates of the S_N2 substrates were not accelerated but rather slightly decelerated by the addition of the metal perchlorates. The $\log(k/\text{s}^{-1})$ value of hexyl tosylate decreased linearly with increasing $LiClO_4$ concentration: the decrease in $\log(k/\text{s}^{-1})$, $\Delta \log k = -0.13$ and -0.20 at 1.0 and 2.0 mol dm^{-3} $LiClO_4$. As for the halide substrates, more distinct deceleration appeared to be caused by the addition of $LiClO_4$ of higher concentrations: the decrease for the chloride substrate; $\Delta \log k = -0.46$ and -0.66 at 1.0 and 2.0 mol dm^{-3} $LiClO_4$, respectively (cf. Table 2). The activation energy (E_a) was found to be 94.6 kJ mol^{-1} for the solvolysis of hexyl tosylate without salts in the solvent (50–80 °C). The $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ values at 55 °C were evaluated to be 91.9 kJ mol^{-1}, −58.2 eu, and 110.0 kJ mol^{-1}, respectively, with R = 0.9999.

It goes without saying that in the S_N2 solvolysis (hydroysis) system, the metal cations may have no way to assist to give X^- on the S_N2 transition state ($H_2O\cdots C^{\delta+}H_2R\cdots X^{\delta-}$). The deceleration in the solvolysis in the presence of $LiClO_4$ can be attributed to the decrease in the activity of water, which attacks the substrate in order to initiate the solvolysis reaction. A non-metallic salt, Et_4NClO_4, also caused the deceleration in the solvolysis rates of the S_N2 substrates to a similar extent as $LiClO_4$ (cf. Fig. 5).

Table 2. "Pseudo" First-Order Reaction Rate Constants of the Solvolyses for Typical S_N2 Substrates in the Presence of Various Salts in 50 vol % Sulfolane–H_2O Solvent at 80 °C

Substrate	Temp/°C	Salt[a)]	k/s^{-1}	$\log(k/s^{-1})$	$\Delta\log(k/s^{-1})$[b)]
Hexyl chloride	80	No salt	7.67×10^{-7}	−6.12	—
	80	$LiClO_4$	2.62×10^{-7}	−6.58	−0.46
	80	Et_4NClO_4	6.52×10^{-7}	−6.19	−0.07
	80	Et_4NCl	6.99×10^{-7}	−6.16	−0.04
	80	Et_4NBr[d)]	1.15×10^{-5}	−4.94	+1.18
	80	Et_4NOTs[c),d)]	1.37×10^{-6}	−5.86	+0.26
Hexyl bromide	80	No salt	1.41×10^{-5}	−4.85	—
	80	$LiClO_4$	9.49×10^{-6}	−5.02	−0.17
	80	Et_4NClO_4	8.24×10^{-6}	−5.08	−0.23
	80	Et_4NCl[d)]	4.95×10^{-7}	−6.31	−1.46
	80	Et_4NBr	2.03×10^{-5}	−4.69	+0.16
	80	Et_4NOTs[c),d)]	2.58×10^{-5}	−4.59	+0.26
Hexyl tosylate	80	No salt	1.70×10^{-4}	−3.77	—
	80	$LiClO_4$	1.27×10^{-4}	−3.90	−0.13
	80	Et_4NClO_4	1.30×10^{-4}	−3.89	−0.12
	80	Et_4NCl	5.27×10^{-7}	−6.28	−2.51
	80	Et_4NBr	1.89×10^{-5}	−4.72	−0.95
	80	Et_4NOTs[c)]	1.50×10^{-4}	−3.82	−0.05

a) The salt concentration of 1.0 mol dm^{-3}. b) $\Delta\log(k/s^{-1}) = \log(k_1/s^{-1})$[with salt] − $\log(k_0/s^{-1})$[no salt] for each substrate. c) p-Toluenesulfonate (tosylate) salt. d) Only the linear parts in the ln[S] vs t plot were evaluated because there is a leaving group exchange reaction.

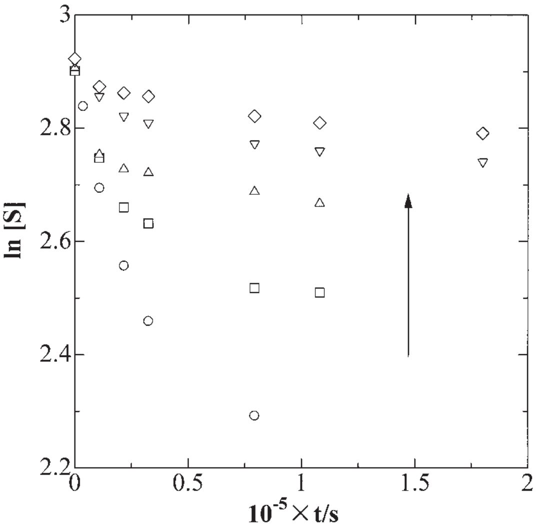


Fig. 6. The (apparent) substrate concentration changes for hexyl bromide with time during solvolysis in the presence of Et_4NCl in 50 vol % sulfolane–H_2O at 80 °C: (○) 0; (□) 0.1; (△) 0.2; (▽) 0.5; (◇) 1.0 mol dm^{-3} Et_4NCl.

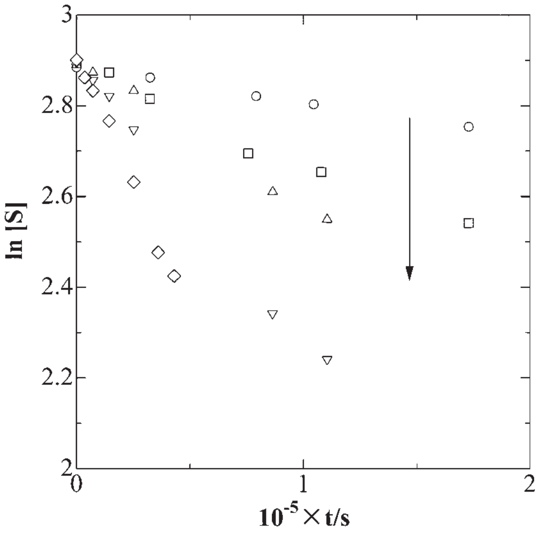


Fig. 7. The (apparent) substrate concentration changes for hexyl chloride with time during solvolysis in the presence of Et_4NBr in 50 vol % sulfolane–H_2O at 80 °C: (○) 0; (□) 0.1; (△) 0.2; (▽) 0.5; (◇) 1.0 mol dm^{-3} Et_4NBr.

Solvolyses Accompanied by "Ion Exchange" Reactions of S_N2 Substrates. It must be noticed that the effects by tetraethylammonium salts other than the perchlorate on the solvolysis rates of the S_N2 substrates were completely different from those of Et_4NClO_4.

Figure 6 shows the plots of ln[S] vs t during the solvolysis of hexyl bromide in the presence of various concentrations of Et_4NCl, where the amount of substrate, [S], is expressed by the titration volume (mL) with NaOH ($[V_\infty - V_t]$). The plots can demonstrate the drastic decreases in (apparent) solvolysis rates of hexyl bromide by the addition of Et_4NCl. Oppositely, the plots in Fig. 7 demonstrate the drastic increases of the (apparent) solvolysis rates of hexyl chloride by the addition of Et_4NBr. The relatively slow solvolysis reaction, compared with the exchange between Cl^- and Br^-, may cause the curved lines for the whole observed period. With a careful examination of the plots of ln[S] vs t in Fig. 6, we found that, in the very early stage of the reaction, the ln[S] value decreased following that for hexyl bromide itself even in the presence of Et_4NCl (e.g., 0.2 mol dm^{-3}); however, the plots formed linear

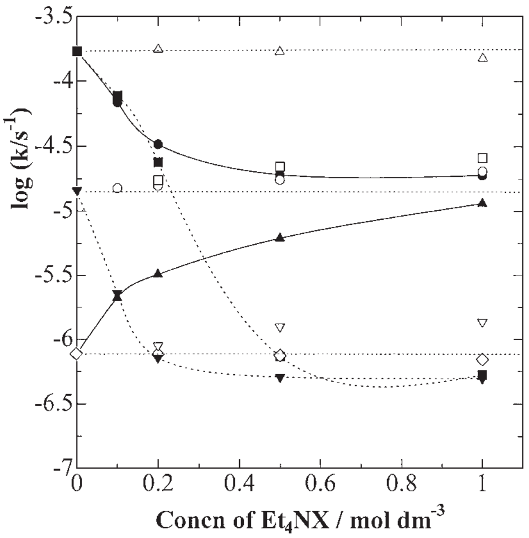
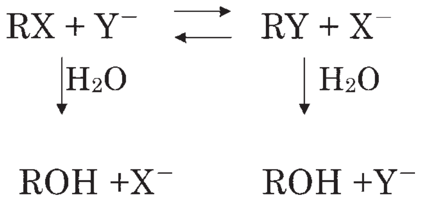


Fig. 8. Changes in the solvolysis rate constants of S_N2 substrates with the addition of various salts in 50 vol % sulfolane–H_2O at 80 °C: (●) Et_4NBr; (■) Et_4NCl; (△) Et_4NOTs for hexyl tosylate; (○) Et_4NBr; (▼) Et_4NCl; (□) Et_4NOTs for hexyl bromide; (▲) Et_4NBr; (◇) Et_4NCl; (▽) Et_4NOTs for hexyl chloride.

curves parallel to the plot curve for hexyl chloride afterward (cf. Figs. 6 and 7). The linear parts in the plots of ln[S] vs t were utilized for evaluating the k values.

Figure 8 shows the changes in the solvolysis rates of hexyl chloride, bromide, and tosylate in the presence of 0–1.0 mol dm^{-3} $Et_4N^+X^-$ ($X^- = Cl^-$, Br^-, and TsO^-). The solvolysis rate of hexyl bromide was remarkably decelerated with increasing concentration of Et_4NCl and approached that of the chloro-substrate (the intrinsic value) at 0.2 mol dm^{-3} Et_4NCl; further addition of the salt caused slightly further deceleration of the solvolysis rate. However, Et_4NBr or Et_4NOTs caused no or minor acceleration in the hexyl bromide solvolysis. On the other hand, the solvolysis rate of hexyl chloride was remarkably accelerated with increasing the concentration of Et_4NBr; at 1.0 mol dm^{-3} Et_4NBr, the rate approached that of hexyl bromide (the intrinsic value). The salts of Cl^- and TsO^- caused no and a minor acceleration effect, respectively, on the solvolysis rate of the chloro-substrate. The acceleration and deceleration effects with the addition of different anions may suggest that "ion exchange" reactions occur prior to or in parallel to the solvolysis reaction.

The addition of 0.5 mol dm^{-3} Et_4NBr and Et_4NCl to hexyl tosylate caused deceleration in the solvolysis rates towards those of (as if) hexyl bromide and chloride, respectively. The addition of Et_4NOTs caused no change in the solvolysis rate of hexyl tosylate as well as of the halide substrates. The above results may verify that the tosylate ion in the added salt has a weak ability to substitute (or exchange) the anions from the substrates, i.e., hexyl bromide and chloride. However, the bromide and chloride ions can substitute anions easily from all the substrates. It is well known that the nucleophilicity order of halide ions in aprotic solvents, such as acetone, is $Cl^- > Br^- > I^-$, whereas it is $Cl^- < Br^- < I^-$ in aqueous solution.[44] Harris et al.[45] have noted the attack of nucleophiles on methyl esters in water as follows: the log k value for $CH_3OSO_2C_6H_5$ was increased by factors of 2.0 and 2.6 with Cl^- and Br^-, respectively, compared with H_2O at 25 °C.



Scheme 2. The "anion exchange" and solvolysis (hydrolysis) reactions in the presence of sufficient amounts of different anions.

Judging from the symmetrical feature (cf. Fig. 8) of the changes in the solvolysis rates of hexyl bromide and chloride with increasing concentrations of Et_4NCl and Et_4NBr, respectively, we may suppose that the nucleophilicities of Cl^- and Br^- are at the same level in a 50 vol % sulfolane–H_2O solution at 80 °C. The proposed mechanisms of the "anion exchange" and hydrolysis reactions are illustrated in Scheme 2.

In the series of studies, we have realized that, in the coexistence of Et_4NCl, some substrates possessing much higher boiling points than the reaction temperatures, such as ethyl tosylate ($bp_{15} = 173$ °C)[43] or butyl bromide ($bp_{760} = 101.3$ °C),[43] have been lost in reaction vessels easily and no substrates remain to be solvolized; this suggests some parts of the substrates have been already converted into more volatile compounds (eg., EtCl, the boiling point of 12.3 °C) while solvolysis reactions are occurring.

The technique of adding a strong nucleophile (e.g., lyate ions or the azide ion) has been often used so as to examine the tendency of a substrate to react through either the S_N1 or S_N2 pathway.[46,47] In 75% aqueous dioxane, the addition of 0.1 mol dm^{-3} NaN_3 to 1-adamantyl bromide (a typical S_N1 substrate, at 100 °C) and 2-propyl tosylate (an S_N1–S_N2 borderline substrate, at 50 °C) caused the formation of RN_3 in 6 and 87%, respectively.[46]

Raman Spectral Changes of Water OD Stretching with Adding Organic Solvents and Salts, or with Increasing Temperature. Figure 9 shows the Raman spectra of water (D_2O) containing sulfolane at room temperature. The pure D_2O gives an OD stretching band with two peaks at 2380 and 2520 cm^{-1}; these peaks are assigned to strongly hydrogen-bonded D_2O and weakly (or non-) hydrogen-bonded D_2O, respectively.[48] Upon the addition of sulfolane to D_2O, the peak at 2520 increased at the expense of the intensity at 2380 cm^{-1}. The increasing content of sulfolane caused further decreases in the intensity at 2380 cm^{-1} and an increase in the intensity of the peak at 2520 cm^{-1} or at higher wavenumbers. At 90 vol % sulfolane, the wavenumber of weakly (or non-) hydrogen-bonded D_2O seemed to approach that of the D_2O monomer ($\nu_1 = 2671$ cm^{-1}) in the gas phase.[49] It has been suggested that the bulk water, in which the H_2O molecules may highly associate through hydrogen bonding, would be altered into rather isolated water molecules by the addition of aprotic solvents.[14]

Further distortion of the water structure was brought by the addition of salts into water–organic solvent mixtures.

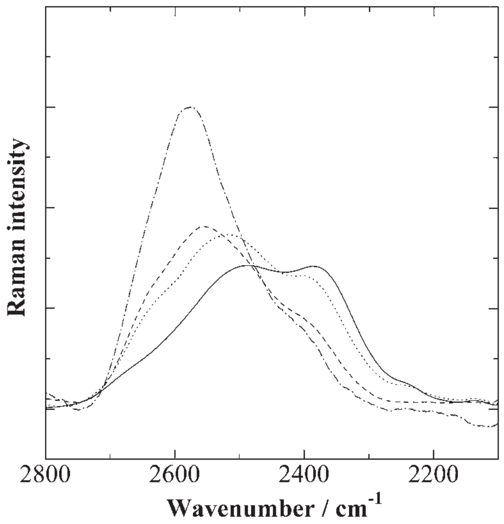


Fig. 9. The Raman spectra of D_2O containing sulfolane at room temperature: (——) 0; (- - - -) 50; (– – –) 75; (– - –) 90 vol % of sulfolane.

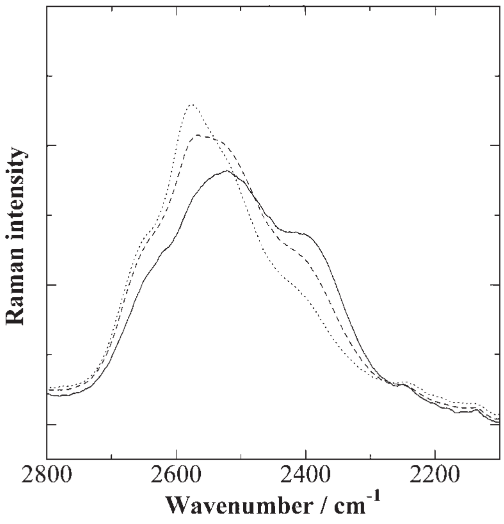


Fig. 10. The Raman spectra of 50 vol % sulfolane–D_2O mixed solvent in the presence of concentrated $LiClO_4$ at room temperature: (——) R = ∞ (no salt); (– – –) R = 20; (- - - -) R = 10; where R = [sulfolane + D_2O]/[$LiClO_4$].

Figure 10 shows the changes in Raman spectra of a 50 vol % sulfolane–D_2O mixed solvent containing concentrated $LiClO_4$. The concentration of $LiClO_4$ is represented by the ratio of the sum of moles of sulfolane and D_2O ([sulfolane] + [D_2O]) to the moles of $LiClO_4$ ([$LiClO_4$]). With increasing the concentration of $LiClO_4$, i.e., decreasing the R value, the intensity around 2400 cm^{-1} decreased, indicating that hydrogen-bonded water molecules were altered into non-hydrogen bonded, i.e., isolated water molecules. The addition of Et_4NBr caused effects similar to those by $LiClO_4$; however, the wavenumber of the ca. 2520 cm^{-1} peak remained almost constant with increasing concentration of Et_4NBr. The changes of Raman spectra of D_2O containing Et_4NBr or LiBr have been discussed.[14]

Temperature effects on the Raman spectra of 50 vol % sulfolane–D_2O were also examined over the range of 5–75 °C. At higher temperatures, the intensity around 2400 nm decreased, and the peak intensity at ca. 2520 cm^{-1} slightly increased: The distortion of hydrogen-bonding structure at higher temperature was demonstrated. It can be concluded that the hydrogen-bonding structure of bulk water is distorted not only by the addition of good amounts of organic solvents and concentrated salts but also by increasing temperature, admitting that D_2O is a more structural liquid than H_2O.[50] Recently, Raman spectra of water monomers were observed in highly supersaturated droplets of $NaClO_4$, $LiClO_4$, and $Mg(ClO_4)_2$; where the hydrogen-bonding network of water molecules were broken.[51] The water structure has been widely discussed for water–organic solvent mixtures.[52]

Now, we may conclude that the properties of the sulfolane–H_2O solution containing concentrated salts are approaching those of "dihydrogen ether." In "dihydrogen ether" or a modified "aqueous" solution, direct chemical interaction should operate between alkali metal or alkaline earth metal ions (M^+ or M^{2+}) and anions from substrates (RX).

Experimental

Sulfolane as the solvent, purchased from Nacalai Tesque and Wako were used as received. The substrates from Tokyo Kasei (TCI) were used without further purification: 1-adamantyl chloride (>98%) and bromide (>97%), 2-adamantyl bromide (>97%), *t*-butyl chloride (>98%), hexyl chloride (>95%), bromide (>98%), and *p*-toluenesulfonate (tosylate) (>98%). Salts of $NaClO_4$, Et_4NBr, Et_4NOTs, and Pr_4NBr from Aldrich as well as $LiClO_4$ and Et_4NCl from Wako, and *n*-Bu_4NCl from TCI were used. Tetraethylammonium perchlorate (Et_4NClO_4) was prepared by adding an equivalent amount of $HClO_4$ to Et_4NBr in water. The precipitates were filtered, washed with cold water and were recrystallized from water several times, followed by drying at 70 °C in vacuo. Tetrabutylammonium bromide was prepared as follows: tributylamine and butyl bromide in acetonitrile solvent were reflaxed for 36 h, followed by evaporation of the solvent to dryness; the *n*-Bu_4NBr precipitates were recrystallized from ethyl acetate twice and dried at 70 °C in vacuo. Commercially obtained transition-metal salts, $Ni(ClO_4)_2 \cdot 6H_2O$ (Aldrich), $Co(ClO_4)_2 \cdot 6H_2O$ (Alfa), $NiCl_2 \cdot 6H_2O$, $NiBr_2$, $CoCl_2 \cdot 6H_2O$, and $CoBr_2$ (Wako), were used as received.

The initial concentrations of the substrates were all kept at 0.010 mol dm^{-3} in the reaction vessels. In principle, 0–90% consumption of a substrate was followed for evaluating the rate constant (relative error of <±1.0%), except for some cases; in S_N2 substrates containing Et_4NX salts, only the linear parts in the ln[S] vs *t* curve were utilized. Details for the other reagents and the procedure for the kinetic experiments have been described previously.[12–14] Raman spectra of D_2O (99.9 atom % D from Aldrich) were recorded with a Horiba-Jobin Yvon LabRam Spectrograph HR-800. The Raman intensity was standardized with the CD stretching band of 5 vol % CD_3OD–D_2O as an internal intensity standard; CD_3OD, 99.8 atom % D, from Aldrich was used. The temperature of the sample was regulated by circulating water of constant temperature (5–75 °C).

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References

1 G. A. Clarke, R. W. Taft, *J. Am. Chem. Soc.* **1962**, *84*, 2295.

2 Z. Abbas, M. Gunnarsson, E. Ahlberg, S. Nordholm, *J. Phys. Chem. B* **2002**, *106*, 1403.

3 J. E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley, New York, **1975**; *Ions and Ion Pairs in Organic Reactions*, ed. by M. Szwarc, Wiley-Interscience, New York, **1972**, Vol. 1; **1974**, Vol. 2; A. Loupy, B. Tchoubar, *Salt Effects in Organic and Organometallic Chemistry*, VCH, Weinheim, **1992**.

4 S. Winstein, E. Clippinger, A. H. Fainberg, G. C. Robinson, *J. Am. Chem. Soc.* **1954**, *76*, 2597; A. H. Fainberg, S. Winstein, *J. Am. Chem. Soc.* **1956**, *78*, 2767; S. Winstein, P. E. Klinedinst, Jr., G. C. Robinson, *J. Am. Chem. Soc.* **1961**, *83*, 885; S. Winstein, P. E. Klinedinst, Jr., E. Clippinger, *J. Am. Chem. Soc.* **1961**, *83*, 4986.

5 J. Catalan, C. Diaz, F. Garcia-Blanco, *J. Org. Chem.* **1999**, *64*, 6512.

6 E. Grunwald, S. Winstein, *J. Am. Chem. Soc.* **1948**, *70*, 846.

7 A. A. Frost, R. G. Pearson, *Kinetics and Mechanisms*, 2nd ed., John Wiley & Sons, New York, **1961**, p. 152.

8 C. A. Bunton, S. K. Huang, *J. Am. Chem. Soc.* **1972**, *94*, 3536; C. A. Bunton, T. W. D. Pesco, A. M. Dunlop, K.-U. Yang, *J. Org. Chem.* **1971**, *36*, 887.

9 A. D. Allen, T. T. Tidwell, O. S. Tee, *J. Am. Chem. Soc.* **1993**, *115*, 10091.

10 A. Kumar, U. D. Phalgune, S. S. Pawar, *J. Phys. Org. Chem.* **2001**, *14*, 577.

11 A. Kumar, *Chem. Rev.* **2001**, *101*, 1.

12 L. C. Manege, T. Ueda, M. Hojo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 589.

13 L. C. Manege, T. Ueda, M. Hojo, M. Fujio, *J. Chem. Soc., Perkin Trans. 2* **1998**, 1961.

14 M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1735.

15 V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, **1978**, p. 20.

16 R. H. Erlich, E. Roach, A. I. Popov, *J. Am. Chem. Soc.* **1970**, *92*, 4989.

17 Y. Marcus, *J. Solution Chem.* **1984**, *13*, 599.

18 S. Winstein, E. Grunwald, H. W. Jones, *J. Am. Chem. Soc.* **1951**, *73*, 2700.

19 M. Hojo, Y. Imai, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1963.

20 M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai, *J. Phys. Chem.* **1989**, *93*, 955; M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, *Electrochim. Acta* **1994**, *39*, 629; M. Hojo, H. Hasegawa, N. Hiura, *J. Phys. Chem.* **1996**, *100*, 891; M. Hojo, H. Hasegawa, Y. Morimoto, *Anal. Sci.* **1996**, *12*, 521; M. Hojo, T. Ueda, M. Nishimura, H. Hamada, *J. Phys. Chem. B* **1999**, *103*, 8965.

21 Z. Chen, M. Hojo, *J. Phys. Chem. B* **1997**, *101*, 10896; M. Hojo, T. Ueda, Z. Chen, M. Nishimura, *J. Electroanal. Chem.* **1999**, *468*, 110.

22 M. Hojo, H. Hasegawa, H. Tsurui, K. Kawamura, S. Minami, A. Mizobe, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1619.

23 M. Hojo, T. Ueda, M. Yamasaki, *J. Org. Chem.* **1999**, *64*, 4939.

24 M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1569.

25 M. Hojo, H. Hasegawa, H. Yoneda, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 971.

26 M. Hojo, H. Hasegawa, H. Yoneda, *J. Chem. Soc., Perkin Trans. 2* **1994**, 1855.

27 M. Hojo, H. Hasegawa, A. Mizobe, Y. Ohkawa, Y. Miimi, *J. Phys. Chem.* **1995**, *99*, 16609.

28 U. Olsher, R. M. Izatt, J. S. Bradshaw, N. K. Dalley, *Chem. Rev.* **1991**, *91*, 137.

29 C. H. Rochester, *Acidity Functions*, Academic Press, London, **1970**.

30 D. A. Binder, M. M. Kreevoy, *J. Phys. Chem.* **1994**, *98*, 10008.

31 M. Hojo, T. Ueda, T. Inoue, M. Ike, to be published.

32 M. Hojo, *Bunseki Kagaku* **2004**, *53*, 1279; M. Hojo, *Kharkov University Bulletin (Ukraine), No. 626, Chemical Series*, **2004**, Vol. 11, pp. 47–64.

33 R. M. Fuoss, C. A. Kraus, *J. Am. Chem. Soc.* **1933**, *55*, 2387; R. M. Fuoss, *Chem. Rev.* **1935**, *17*, 27; C. A. Kraus, *Science* **1939**, *90*, 281.

34 E. S. Rudakov, I. V. Kozhevnikov, *Tetrahedron Lett.* **1971**, *12*, 1333.

35 B. G. Cox, H. Maskill, *J. Chem. Soc., Perkin Trans. 2* **1983**, 1901.

36 R. B. Heslop, P. L. Robinson, *Inorganic Chemistry, A. Guide to Advanced Study*, 3rd ed., Elsevier, **1967**, p. 527.

37 E. Hogfeldt, *Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands*, IUPAC Chemical Data Series, No. 21, Pergamon, Oxford, **1982**.

38 G. Yan, N. R. Brinkmann, H. F. Schaefer, III, *J. Phys. Chem. A* **2003**, *107*, 9479.

39 K. Takeuchi, T. Okazaki, T. Kitagawa, T. Ushino, K. Ueda, T. Endo, R. Notario, *J. Org. Chem.* **2001**, *66*, 2034.

40 S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, G. C. Robinson, *J. Am. Chem. Soc.* **1956**, *78*, 328.

41 T. Kinoshita, M. Itoh, K. Shibayama, K. Takeuchi, *J. Phys. Org. Chem.* **1994**, *7*, 234.

42 L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, N. A. Taher, *J. Chem. Soc.* **1940**, 979.

43 The boiling points are cited from: *The Merck Index*, 11th ed., Merck, Rahway, **1989**; except for pentyl chloride [*Encyclopedic Dictionary of Chemistry (in Japanese)*, ed. by M. Oki, T. Ohsawa, M. Tanaka, H. Chihara, Tokyo Kagaku Dozin, Tokyo, **1989**].

44 S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, J. S. Gall, *Tetrahedron Lett.* **1960**, *1*, 24.

45 J. M. Harris, D. C. Clark, A. Becker, J. F. Fagan, *J. Am. Chem. Soc.* **1974**, *96*, 4478.

46 D. J. Raber, J. M. Harris, R. E. Hall, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1971**, *93*, 4821.

47 J. P. Richard, P. E. Yeary, *J. Am. Chem. Soc.* **1993**, *115*, 1739.

48 J. R. Scherer, M. K. Go, S. Kint, *J. Phys. Chem.* **1974**, *78*, 1304; D. E. Irish, M. H. Brooker, Raman and Infrared Spectral Studies of Electrolytes, in *Advences in Infrared and Raman Spectroscopy*, ed. by R. J. H. Clark, R. E. Hester, Heyden, London, **1976**, Vol. 2, Chap. 5, p. 239.

49 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry*, 5th ed., Wiley-Interscience, New York, **1997**, p. 170.

50 J. E. Gordon, *The Organic Chemistry of Electrolyte Solutions*, Wiley, New York, **1975**, p. 167.

51 Y.-H. Zhang, C. K. Chan, *J. Phys. Chem. A* **2003**, *107*, 5956.

52 F. N. Keutsch, R. J. Saykally, *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 10533; S. Dixit, J. Crain, W. C. K. Poon, J. L. Finney, A. K. Soper, *Science* **2002**, *416*, 829; D. N. Shin, J. W. Wijnen, J. B. F. N. Engberts, A. Wakisaka, *J. Phys. Chem. B* **2002**, *106*, 6014; A. Nose, M. Hojo, T. Ueda, *J. Phys. Chem. B* **2004**, *108*, 798; A. Nose, T. Hamasaki, M. Hojo, R. Kato, K. Uehara, T. Ueda, *J. Agric. Food Chem.* **2005**, *53*, 7074.