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Concentrated salt effects on solvolysis rates in 1,4-dioxane–H_2O mixed solvent and the expansion of the use of the Hammett equation for salt effects

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In the mixed solvent system 50 vol% 1,4-dioxane and H_2O, the concentrated salt effects of alkali metal (M^+) and alkaline earth metal (M^{2+}) perchlorates on the solvolysis rates of aliphatic halides (RX) and related compounds were investigated. The "pseudo" first-order reaction rates (k/s^{-1}) of typical S_N1 substrates, 1-adamantyl chloride and bromide and *tert*-butyl chloride, increased exponentially with increasing concentration of metal salt. The effects of M^{2+} on the reaction rates were larger than those of M^+: Na^+, $Li^+ < Ba^{2+} < Mg^{2+}$. A non-metallic salt, Et_4NBr, at concentrations of ≥1.0 mol dm^{-3} caused the log k value to decrease, although the log k was slightly increased by lower concentrations of the salt (<1.0 mol dm^{-3}). Raman spectra of D_2O containing high concentrations of Et_4NBr suggested a complete distortion of the solvent structure. The increase in log k values in the presence of metal ions was explained by direct "chemical" interaction between halide ions and metal ions with the concentrated salts in the modified media: $X^- \cdots M^+$ or $X^- \cdots M^{2+}$. The solvolysis rates of typical S_N2 substrates, ethyl bromide and methyl tosylate, were much decreased by the addition of concentrated $LiClO_4$. The log k values of borderline S_N1–S_N2 reacting substrates, isopropyl bromide and benzyl halides, remained almost constant, however, more positive slopes in log k in the presence of $LiClO_4$ were caused by the introduction of methyl substituents on benzyl halides; negative slopes were observed upon the introduction of strong electron-withdrawing substituents, such as NO_2 and CN. We observed a correlation (of two different slopes) between the σ^+ values in the Hammett equation and the Δlog k for substituted benzyl halides upon the addition of 1.0 mol dm^{-3} $LiClO_4$, as well as between the log (k_x/k_H) values themselves. We propose here an expansion of the use of the Hammett equation for the concentrated salt effect.

Introduction

Increased reactivities upon the addition of concentrated salts have often been observed in organic reactions in solution.[1] Some salt effects at lower concentrations in aqueous solutions have been evaluated by electrostatic models.[2] In nonaqueous solvents, such as acetic acid[3] and diethyl ether,[4] abnormally high reactivities, even at lower salt concentrations, have been reported. It is known that the rates of S_N1 solvolysis of alkyl halides and related compounds are subject to positive salt effects.[5] Bunton *et al.*[6] reported an exponential increase in the solvolysis rate of *tert*-butyl bromide with increasing 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 effect of the anions is $ClO_4^- > OTs^- \sim NO_3^- \sim Br^- > Cl^- \sim$ no salt $> F^- > OH^-$. However, Allen *et al.*[7] have reported a great difference in the salt effects of $LiClO_4$ and Bu_4NClO_4 on the solvolysis of 4-methoxybenzyl chloride in 85% (v/v) aqueous dioxane.

In previous studies,[8,9] we have observed that, for a typical S_N1 substrate, such as 1-adamantyl halides or *tert*-butyl chloride, cation effects increase as $Et_4N^+ \ll Li^+$, $Na^+ < Mg^{2+}$, Ba^{2+} as perchlorate salts, in methanol–H_2O and acetone–H_2O mixed solvents. We have pointed out that the cation effect proposed by Bunton *et al.*[6] would have been reduced by the interaction between M^+ (the metal ions) and the anions (except for ClO_4^-) in modified media in the presence of concentrated salts. For the incredibly strong interaction between the metal ions and simple anions in "aqueous" solutions, we have proposed a model for water containing highly concentrated salts (*cf.*, ref. 8). This model can be outlined as follows: in a highly concentrated salt solution (>*ca.* 5 mol dm^{-3}), too many ions are present to be fully solvated by H_2O molecules. Under such extreme conditions, the network of hydrogen bonding by the solvent is almost destroyed. Isolated molecules of H_2O are very different from bulk water (H–O–H); they could behave just as ethers (R–O–R).

For almost 20 years, we have devoted our research to demonstrating that alkali metal ions (Li^+ and Na^+) and alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) have chemical (*i.e.*, covalent bonding or coordinating) as well as Coulombic interactions with many simple anions, not only in low permittivity media,[10] but also in protophobic aprotic solvents of higher permittivities ($20 < \varepsilon_r < 65$). Our studies have used the techniques of voltammetry,[11] conductometry,[12] and UV-visible[13] and NMR spectroscopy.[14] We have explained the large salt effects on the indicator acidity (or Hammett acidity function) using *p*-(dimethylamino)azobenzene[15] and on the proton transfer from tropolone[16] or nitrophenols[17] to amine bases in acetonitrile in terms of the chemical interaction between the anions and M^+ or M^{2+}, and not merely as ion-exchange reactions or the alternation between the contact ion pair (CIP) and the solvent-separated ion pair (SSIP). The formation of trityl (Ph_3C^+) and 4-methoxy-substituted trityl cations from the corresponding halide compounds in acetonitrile solution has been demonstrated, and this formation is attributed to the chemical interaction between M^+ or M^{2+} and the halide ions ($X^- = Cl^-$ and Br^-): $Ph_3CX + 2Li^+ \rightleftharpoons Ph_3C^+ + (Li^+)_2X^-$; $Ph_3CX + M^{2+} \rightleftharpoons Ph_3C^+ + MX^+$.[18,19] In addition, the quantitative formation of the 4-methoxy-substituted trityl cations brought about by the addition of $Ba(ClO_4)_2$ to a solution of $(4\text{-}MeOC_6H_4)Ph_2CCl$ in acetonitrile was found to be mainly due to

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the precipitation of a mixed-anion salt, $BaCl(ClO_4)$.[20] The weak covalent bond, C^+–Cl^-, definitely seems to be cleaved by the chemical interaction as well as the Coulombic interaction between Cl^- and M^+ or M^{2+}. We have found that the ^1H NMR spectra of mixtures of $(4\text{-}MeOC_6H_4)Ph_2CCl$ and $(4\text{-}MeOC_6H_4)$-$Ph_2C^+ClO_4^-$ gave broadened signals even at 90% of the perchlorate salt in CD_3CN.[18b] The C^+–O^- bond in γ-lactone and γ-sultone rings of Rhodamine B base[18a] and Sulfonephthaleins, such as Thymol Blue or Bromothymol Blue,[21] in acetonitrile have been also cleaved by alkali metal and alkaline earth metal perchlorates.

The main points proposed in our previous solvolytic studies[8,9] of MeOH–H_2O and acetone–H_2O systems are as follows. (1) Highly concentrated salts deform 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 ($\geq$1.0 mol dm^{-3}), the exponential increases in solvolysis rates of S_N1 substrates are caused by the formation of "stable" carbocations through direct "chemical" interaction between metal ions and anions (X^-, from the substrates 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)[22] of the substrate. (5) One could easily distinguish S_N1 from S_N2 reactions by observing the substantial increase in the solvolysis rate constant at 1.0 mol dm^{-3} $LiClO_4$ in aqueous mixed solvents.

The purpose of the present study is to support the above proposals with results from another solvent system, a mixed solvent of 50 vol% 1,4-dioxane and H_2O with a permittivity, ε_r = *ca.* 44[23] at room temperature. We can compare the permittivity of the solvent with those of 80 vol% MeOH–H_2O (ε_r = *ca.* 49)[23] and 50 vol% acetone–H_2O (ε_r = *ca.* 55),[23] previously used. The substituent effects on the solvolysis rates of benzyl halides in the presence of $LiClO_4$ are newly examined in the present study; we observed an unexpectedly good correlation between the σ^+ values[24] of the Hammett equation[25] and the increase in solvolysis rates of substituted benzyl halides brought about by the addition of the salt. It is well known that, without salts, the solvolysis rates of substituted benzyl tosylates†[26,27] have been correlated with the Hammett–Brown σ^+ values[24] or related constants.[28] We present here Raman spectra as concrete evidence of the distortion of water structure in the presence of concentrated salts.

Experimental

The solvolysis rates were determined by titration with standard aqueous NaOH using phenolphthalein as the indicator. We used 1,4-dioxane (of a special grade for nonaqueous titration) as received from Wako Pure Chemical Industries. Substituted benzyl halides from TCI were used without further purification. Details for the other reagents and the procedure have been described previously.[8,9] Raman spectra of D_2O (99.9 atom% D from Isotec, Inc.) were recorded with a Jobin Yvon spectrophotometer, model Ramanor U-1000. The argon line at 488 nm was used for excitation. The Raman intensity was standardized with the CD stretching band of 5 vol% CD_3OD–D_2O as an internal intensity standard;[29] CD_3OD, 99.8 atom% D from Aldrich was used.

Results and discussion

Concentrated salt effects on S_N1 reactions

Fig. 1 shows the effects of alkali metal and alkaline earth metal perchlorates on the solvolysis rate of 1-adamantyl bromide in the mixed solvent of 50 vol% 1,4-dioxane and water at 35 °C. The log (k/s^{-1}) value increased linearly with increasing concentration of $LiClO_4$. The effects of $NaClO_4$ were similar to those of $LiClO_4$. Barium perchlorate also caused a linear increase in the log k with a much larger slope than the alkali metal ions. The "pseudo" first-order rate constants, k/s^{-1}, were 1.60×10^{-4} and 6.57×10^{-4} for 1.0 mol dm^{-3} $LiClO_4$ and $Ba(ClO_4)_2$, respectively. The log k increased almost linearly in the presence of $\leq$0.5 mol dm^{-3} $Mg(ClO_4)_2$; however, the slope bacame more gradual with $\geq$0.75 mol dm^{-3} of the salt. On the other hand, the solvolysis rate constant of 1-adamantyl bromide was decreased markedly by the addition of a non-metallic salt, Et_4NBr, though the k value increased very slightly in the presence of 0.5 mol dm^{-3} Et_4NBr. The remarkable decrease in the rate constant has been attributed to the decrease in solvent activities.[8,9] The solvolysis rate of *tert*-butyl chloride in 90 vol% acetone–H_2O has been found to be considerably accelerated by the addition of metal perchlorates but to be decelerated by Et_4NClO_4.[9] We did not demonstrate a distinct common anion (Br^-) effect for the solvolysis rates in our previous studies,[8,9] although Bunton and Nayak[30] have examined the common ion effect in S_N1 solvolysis of *tert*-butyl chloride in aqueous methanol.

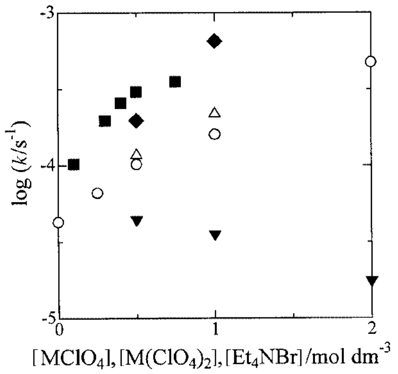

Fig. 1 Changes in the solvolysis rates of 1-adamantyl bromide with the addition of various salts in 50 vol% 1,4-dioxane–H_2O at 35 °C: (○) $LiClO_4$; (△) $NaClO_4$; (■) $Mg(ClO_4)_2$; (◆) $Ba(ClO_4)_2$; (▼) Et_4NBr.

The solvolysis rate constant of 1-adamantyl chloride also increased exponentially with increasing concentration of the alkali metal and alkaline earth metal perchlorates in the same solvent at 35 °C, *cf.* Table 1 for $LiClO_4$. The cation effects increased in the order $Na^+ \leq Li^+ < Ba^{2+} < Mg^{2+}$. The linearity in log k was observed up to at least 3.0, 1.0, 1.5 and 2.0 mol dm^{-3} for $LiClO_4$, $NaClO_4$, $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$, respectively. Substantial increases in the rate constants were caused by the addition of salts, *e.g.*, Δlog k = +1.2 for 3.0 mol dm^{-3} $LiClO_4$ at 50 °C. The activation energies (E_a) for 1-adamantyl chloride and bromide were found to have almost constant values, both *ca.* 80 kJ mol^{-1}, even in the presence of 0–2.0 or 3.0 mol dm^{-3} $LiClO_4$ at 25–50 °C. Judging from the unchanged activation energies with the concentrated salts, the reaction mechanism (S_N1) of the adamantyl halides would seem to be retained regardless of the absence or presence of salts.

$$RX + M^+ \longrightarrow RX\cdots M^+ \longrightarrow R^+ + X^-\cdots M^+ \xrightarrow{2H_2O} ROH + H_3O^+X^- + M^+$$

The exponential increase in solvolysis rate constants of the "limiting" S_N1 substrates (RX) with increasing concentration of the metal ions (M^+, M^{2+}) has been explained by the direct "chemical" interaction between X^- and M^+ or M^{2+}, and not merely by the medium effect.[8,9] In dilute aqueous solutions, such interaction between the anions and the cations would never be possible. The changes in solvent structure, observed by Raman spectroscopy, are discussed in the final section. In S_N1 systems, once carbocations are formed in water-mixed solvents, it is an easy task for the carbocations to react with water

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† Tosylate = toluene-*p*-sulfonate.

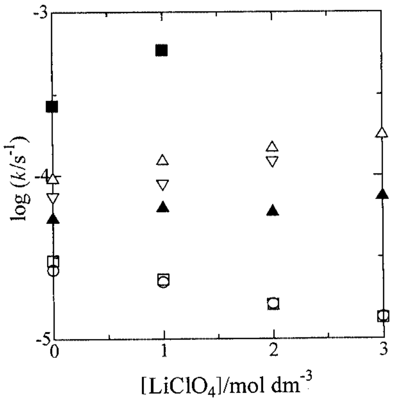


Fig. 2 Variation of solvolysis rates for different substrates with increasing concentration of LiClO$_4$ in 50 vol% 1,4-dioxane–H$_2$O at 75 °C: (▽) benzyl chloride; (△) benzyl bromide at 50 °C; (▲) isopropyl bromide; (□) ethyl bromide; (○) methyl tosylate at 50 °C; (■) *tert*-butyl chloride at 25 °C.

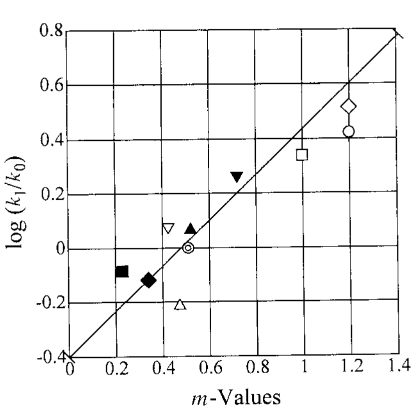


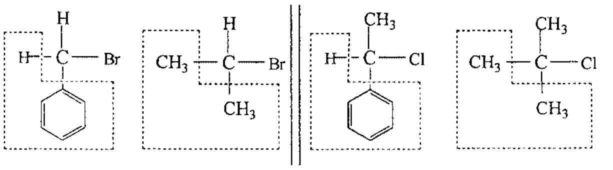
Fig. 3 The relation between log (k_1/k_0) and the Grunwald–Winstein m-value of RX: (○) 1-adamantyl chloride; (◇) 1-adamantyl bromide; (□) *tert*-butyl chloride; (▽) benzyl chloride; (▲) isopropyl bromide; (◆) ethyl bromide; (■) methyl tosylate; (△) 4-nitrobenzyl bromide; (▼) 3-methylbenzyl chloride; (◎) 3-chlorobenzyl bromide.

molecules immediately, even if the activities of the water molecules are decreased by concentrated salts. The rate constant of the reaction between the trityl cation (Ph_3C^+) and water in acetonitrile solvent has been measured using the ^1H NMR line broadening technique.[31]

Borderline S_N1–S_N2 and typical S_N2 substrates

The concentrated salt effects of LiClO$_4$ on the solvolysis rate constants ("k/s^{-1}") of borderline S_N1–S_N2 reacting substrates and typical S_N2 substrates in the 50 vol% 1,4-dioxane–H$_2$O mixture were examined. Fig. 2 shows the log (k/s^{-1}) values at 75 °C of the borderline S_N1–S_N2 reacting substrates, *i.e.*, benzyl chloride and bromide ($PhCH_2X$) and isopropyl bromide (Me_2CHBr), in the solvent. The rate constants for the benzyl halides increased just slightly with increasing concentration of LiClO$_4$; there was almost no increase for isopropyl bromide, compared with the S_N1 substrate, *tert*-BuCl (Me_3CCl). However, the log k values of the typical S_N2 substrates, ethyl bromide ($MeCH_2Br$) and methyl tosylate (CH_3OTs), decreased linearly with increasing concentration of LiClO$_4$.

The activity of the water in a mixed solvent may be much decreased by the addition of ≥1.0 mol dm^{-3} LiClO$_4$; therefore, the "k/s^{-1}" values of S_N2 substrates are expected to be depressed. The log k value of isopropyl bromide (a borderline S_N1–S_N2 substrate) was almost constant, even when the concentration of the salt was increased, probably because the increased concentration of the carbocation (Me_2CH^+ for S_N1) is cancelled by the decrease in the water activity, which causes considerable depression in the S_N2 reaction path. We think that even a very minor increase in the equilibrium concentration (of an active state) can cause an observable increase in the kinetic constant. In the case of benzyl halides, the partially preferable S_N1 reaction may owe much to the stabilization of the benzyl cation ($PhCH_2^+$) by delocalization of the positive charge into the benzene ring. The substituent effects on the rate constants of benzyl halides in the presence of LiClO$_4$ are discussed in the next section. Roughly speaking, the log (k_1/k_0) values of benzyl chloride or bromide and isopropyl bromide are regarded as being close each other, that is, increases in k values caused by the addition of 1.0 mol dm^{-3} LiClO$_4$ are all small values. This fact may indicate that a phenyl group acts just as two methyl groups would on the carbon center. The log (k_1/k_0) values for 1-phenylethyl chloride and *tert*-BuCl have also been found to be similar,[8] *cf.* Scheme 1.



Scheme 1

Fig. 3 shows a linear relationship between the m-values (by Grunwald and Winstein)[22] and the log (k_1/k_0) values of RX, where the k_1 and k_0 stand for the solvolysis rate constants in the presence and the absence of 1.0 mol dm^{-3} LiClO$_4$, respectively. The m-value may suggest the extent of S_N1 for a substrate. The typical S_N1 substrates gave large positive log (k_1/k_0) values, however, the S_N2 substrates gave negative log (k_1/k_0) values. 3-Chlorobenzyl bromide, whose m-value can be regarded to be 0.51,[35] gave ±0 for the log (k_1/k_0) in the mixed solvent of 50 vol% 1,4-dioxane and H$_2$O. We have proposed, as mentioned in our introduction, that an S_N1 reaction can be easily distinguished from others merely by observing a substantial positive log (k_1/k_0) value in the water–mixed solvents. We have to admit that the most appropriate m-value for each substrate in the present solvent system (50 vol% 1,4-dioxane–H$_2$O) was not always cited because of a lack of data, at least according to our survey of literature. Nevertheless, the present results are consistent with our proposal.

It might be expected that a very strong interaction between X^- and some transition metal ions (M^{n+}) would cause a substantial positive slope in the relationship between log (k/s^{-1}) *vs.* [M^{n+}], even for borderline S_N1–S_N2 substrates, such as benzyl halides ($PhCH_2X$). Note that the interaction between X^- and Li^+ is not so strong as that between X^- and M^{n+} and also that the presence of concentrated salts causes deceleration of the S_N2 reaction because of the decrease in the water activity. Roberts and Hammett[36] have shown that the solvolysis rates of benzyl chloride in dioxane–H$_2$O mixed solvents are accelerated by the mercury ion at much lower concentrations (*e.g.*, 0.025 mol dm^{-3}): $R–Cl\cdots Hg^{2+} \rightarrow R^+ + HgCl^+$, $R^+ + H_2O \rightarrow ROH + H^+$. Rudakov and Kozhevnikov[37] have reported that C–X bond heterolysis (mechanism S_N1) due to the reaction $RX + M^+ \rightarrow R^+ + MX$ is accelerated by metal ions M^+ (Lewis acids) which form stable halide complexes MX with the anion, X^-. Transition metal ions, Ag^+, Bi^{3+}, Cd^{2+} and Pb^{2+}, cause increases in the solvolysis rates of *tert*-BuCl in an EtOH–H$_2$O mixed solvent.

Concentrated salt effects on substituted-benzyl halides

In this section, the effects of concentrated LiClO$_4$ on substituted-benzyl halides are discussed in detail. Figs. 4 and 5 show the solvolysis rates of substituted-benzyl halides with increasing concentration of LiClO$_4$. The introduction of a methyl-substituent into benzyl chloride at the *o*- and *p*-positions caused the rate constant to increase substantially compared with the unsubstituted benzyl chloride (*cf.* Figs. 2

Table 1 (Apparent) first-order reaction rates of solvolysis for organic halides (RX) in 50 vol% 1,4-dioxane–H_2O in the absence and the presence of $LiClO_4$

Substrate	Temp/°C	$k_0{}^a$/s^{-1}	$k_1{}^a$/s^{-1}	$k_2{}^a$/s^{-1}	log (k_1/k_0)	log (k_2/k_1)	*m*-value[b]
1-Adamantyl chloride	35	2.78×10^{-6}	7.37×10^{-6}	1.86×10^{-5}	0.423	0.402	1.20 (25 °C)[c]
	50	8.60×10^{-6}	3.17×10^{-5}	7.51×10^{-5}	0.567	0.354	—
1-Adamantyl bromide	25	1.61×10^{-5}	5.27×10^{-5}	9.24×10^{-5}	0.515	0.244	1.20 (25 °C)[c]
	35	4.05×10^{-5}	1.60×10^{-4}	4.76×10^{-4}	0.597	0.474	—
	50	2.55×10^{-4}	7.76×10^{-4}	—	0.483	—	—
tert-Butyl chloride	25	2.69×10^{-4}	5.87×10^{-4}	—	0.339	—	1.0 (25 °C)[b]
Isopropyl bromide	75	5.47×10^{-5}	6.37×10^{-5}	5.99×10^{-5}	0.066	−0.027	0.52 (50 °C)[d]
Benzyl chloride	75	7.48×10^{-5}	8.95×10^{-5}	1.23×10^{-4}	0.078	0.140	0.425 (50 °C)[e]
Benzyl bromide	50	9.52×10^{-5}	1.23×10^{-4}	1.48×10^{-4}	0.112	0.078	—
Ethyl bromide	75	3.02×10^{-5}	2.31×10^{-5}	1.62×10^{-5}	−0.117	−0.153	0.34 (55 °C)[c]
Methyl tosylate	50	2.65×10^{-5}	2.23×10^{-5}	1.64×10^{-5}	−0.084	−0.135	0.23 (75 °C)[f]
2-Methylbenzyl chloride	75	1.79×10^{-4}	3.03×10^{-4}	4.13×10^{-4}	0.228	0.134	—
3-Methylbenzyl chloride	75	8.27×10^{-5}	1.09×10^{-4}	1.74×10^{-4}	0.120	0.203	0.72[g]
4-Methylbenzyl chloride	50	3.52×10^{-5}	8.61×10^{-5}	1.96×10^{-4}	0.388	0.358	—
4-(*tert*-Butyl)benzyl chloride	50	1.59×10^{-5}	3.73×10^{-5}	7.87×10^{-5}	0.37	0.325	—
3-Chlorobenzyl bromide	75	2.42×10^{-4}	2.42×10^{-4}	1.86×10^{-4}	0	−0.113	0.51[g]
4-Chlorobenzyl bromide	50	5.82×10^{-5}	6.49×10^{-5}	7.66×10^{-5}	0.065	0.072	—
4-Nitrobenzyl bromide	75	1.15×10^{-4}	7.05×10^{-5}	5.05×10^{-5}	−0.214	−0.145	0.472 (60 °C)[h]
4-Cyanobenzyl bromide	75	1.12×10^{-4}	1.09×10^{-4}	8.09×10^{-5}	−0.015	−0.127	—

[a] The k_0, k_1, and k_2 values are the solvolysis rate constants at 0, 1.0, and 2.0 mol dm^{-3} $LiClO_4$, respectively. [b] The *m*-values in EtOH–H_2O mixed solvent system by the Grunwald–Winstein equation (*cf.* ref. 22), unless otherwise noted. [c] Ref. 32. [d] Ref. 33. [e] Ref. 22(*b*). [f] Ref. 34. [g] Ref. 35; the value of 3-methylbenzyl tosylate in EtOH–H_2O mixed solvents and other solvent systems using an extended Grunwald–Winstein equation. [h] Ref. 22(*c*); in 50–90 wt% dioxane–H_2O mixed solvents.

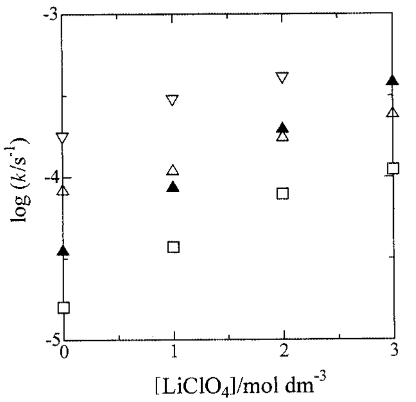


Fig. 4 Variation of solvolysis rates for substituted-benzyl chlorides with increasing concentration of $LiClO_4$ at 75 °C: (▽) 2-Me; (△) 3-Me; (▲) 4-Me at 50 °C; (□) 4-(*tert*-butyl)benzyl chloride at 50 °C.

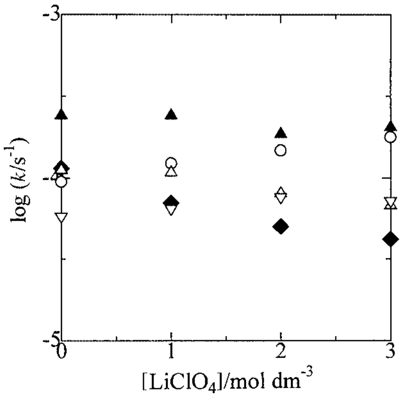


Fig. 5 Variation of solvolysis rates for substituted-benzyl bromides with increasing concentration of $LiClO_4$ at 75 °C: (○) unsubstituted benzyl bromide; (▲) 3-Cl; (▽) 4-Cl at 50 °C; (◆) 4-NO_2; (△) 4-CN.

and 4). The enhanced increased solvolysis rate of, especially, 4-methylbenzyl chloride in the presence of $LiClO_4$ is as remarkable as that of *tert*-BuCl, a typical S_N1 substrate. We have to mention that, without the salt, the rate constants of the benzyl chlorides at 75 °C increased as follows: unsubstituted ("k/s^{-1}" = 7.48×10^{-5}) < 3-methyl (8.27×10^{-5}) < 2-methyl (1.79×10^{-4}) < 4-methyl (3.48×10^{-4}, roughly estimated from the value at 50 °C). On the other hand, strong electron-withdrawing substituents, such as NO_2 and CN, caused remarkable decreases in the solvolysis rates; the order of "k/s^{-1}" values of substituted-benzyl bromides with electron-withdrawing substituents at 75 °C were 4-NO_2 (1.15×10^{-4}) ~ 4-CN (1.12×10^{-4}) < 3-Cl (2.42×10^{-4}) < 4-Cl (5.75×10^{-4}, roughly estimated from the data at 50 °C). It is quite natural that the log k values for the *m*- and *p*-positions of the substituted-benzyl chlorides and bromides seem to obey the Hammett equation, log (k_X/k_H) = $\rho\sigma^+$, where ρ is the reaction constant, −1.88 for the solvolysis of $ArCH_2Cl$ (in aqueous acetone at 69.8 °C)[25] and σ^+ is the substituent constant by Brown and Okamoto.[24]

Thus, not only the logarithm of the relative rate constant, log (k_X/k_H), without the salt, but also the extent of the increase in k (or log (k_1/k_0)) in the presence of 1.0 mol dm^{-3} $LiClO_4$, is enhanced by the introduction of the electron-donating group to benzyl chloride. The possible formation of a stable carbocation center at the benzene-ring carbon by resonance effects for the *p*-substituted compound in the presence of concentrated $LiClO_4$ may promote an S_N1 mechanism for the solvolysis. Therefore, the enhanced increase in the k value caused by the salt is observed for 4-methylbenzyl chloride (Δlog k = 0.388 upon addition of 1.0 mol dm^{-3} $LiClO_4$), which is as high as that observed for *tert*-butyl chloride (Δlog k = 0.339, *cf.* Table 1).

Fig. 6 shows the relationship between the σ^+ value[24] in the Hammett equation and the increase in log k for the substituted-benzyl halides caused by the addition of 1.0 mol dm^{-3} $LiClO_4$ (in fact, the average value between log (k_1/k_0) and log (k_2/k_1)); unexpectedly, a good correlation is observed. This observed correlation suggests that use of the Hammett equation can be possibly expanded even to concentrated salt effects. In a similar way, two different slopes have been reported in the correlation between the σ^+ values and log (k_X/k_H) in the solvolysis of substituted benzyl tosylates in aqueous acetone[26] and in acetic acid.[27] An application of the Yukawa and Tsuno LArSR equation[28] might improve the linearity. The observed correlation strongly supports the idea that the extent of the concentrated salt effect is dependent on the stability of the carbocation as the solvolysis intermediate species. In an acetonitrile–water mixed solvent, a similar good correlation between the σ^+ and

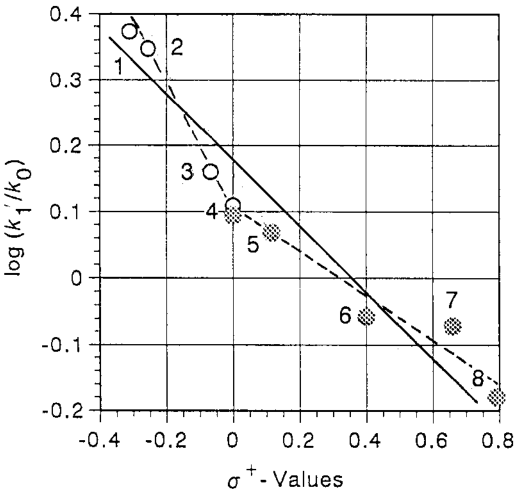


Fig. 6 The relationship between the σ^+ value in the Hammett equation and the increase in log *k* caused by the addition of 1.0 mol dm^{-3} $LiClO_4$ for substituted benzyl halides: (1) 4-Me; (2) 4-(*tert*-Bu); (3) 3-Me; (4) unsubstituted (H); (5) 4-Cl; (6) 3-Cl; (7) 4-CN; (8) 4-NO_2. The open and solid symbols represent the benzyl chlorides and benzyl bromides, respectively.

log(k_1/k_0) values has also been observed.[38] Recently, Kevill *et al.*[39] reported satisfactory correlations of the solvolysis rate constants of benzyl toluene-*p*-sulfonate and substituted derivatives using an extended Grunwald–Winstein equation.

Richard and Yeary[40] have observed a four-fold increase in k_{obsd} by the addition of 0–6.0 mol dm^{-3} $NaClO_4$ in H_2O for the solvolysis of 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl iodide (4-MeOArCH(CF_3)I), and have mentioned that these reactions are subject to a large positive perchlorate salt effect, which may be attributed to stabilization of the carbocation-like transition state for the solvolysis reaction by ClO_4^-. Judging from the positive effect caused by the salt, it may be a partial S_N1 reaction. However, we have discussed the weakness of the interaction between ClO_4^- and carbocations in acetonitrile.[9] The ClO_4^-, which is not hydrated strongly, may also effectively distort the solvent structure. Cox and Maskill[41] have reported a large enhancement in the solvolysis rate of *tert*-alkyl iodide in EtOH–H_2O mixed solvents by the addition of I_2. The chemical interaction between I^- and I_2 should promote the formation of the carbocation in solution: $RI + I_2 \rightarrow R^+ + I_3^-$.

Breakdown of the solvent structure by highly concentrated salts

According to Frank and Wen,[42] the hydration of a salt causes the formation of three different regions around the ions as follows: A: region of immobilization of water molecules; B: region of structure breaking; and C: structurally "normal" water, *i.e.*, the bulk water. The difference in the development of regions A and B determines whether an ion is of the *structure-making* or *structure-breaking* type. For instance, the Li^+ ion causes the development of A over B; therefore, Li^+ is classified as a structure-making ion. The development of region A by Cs^+ is small because of its weak hydration; Cs^+ is therefore a structure breaking ion. This argument may be limited to low or moderate concentrations of a salt. However, we have proposed,[8] as mentioned previously, that the presence of highly concentrated salts in water or water–mixed solvents may cause the depression or disappearance of region C (of "ice-like-ness"). In such extreme conditions, only B (the broken-structure part) in the above model may be effective in the solvent function; the property of the aqueous solvent may be modified to be that of, as we term it, a "dihydrogen ether," [R](H)–O–(H)[R].

Fig. 7 shows the Raman spectra of D_2O containing various concentrations of Et_4NBr at room temperature. The band at around 2510 cm^{-1} developed as the amount of water decreased ($R = [D_2O]/[\text{salt}]$) at the expense of the band at 2390 cm^{-1}.

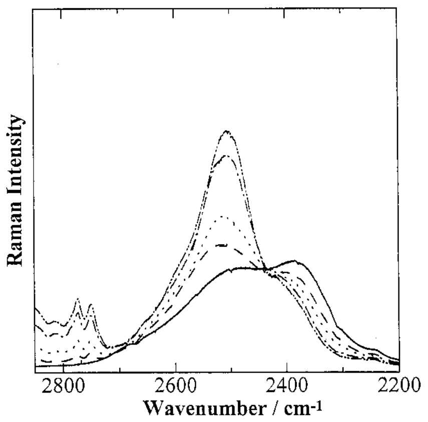


Fig. 7 The Raman spectra of D_2O containing various amounts of Et_4NBr at room temperature: (——) no salt; (— — —) $R = 20$; (-----) $R = 10$; (—-—) $R = 5$; (—--—) $R = 3.75$ where $R = [D_2O]/[Et_4NBr]$.

It has been reported[29] that the Raman OD stretching spectrum of liquid D_2O spans from *ca.* 2200 to 2800 cm^{-1} with a peak wavenumber of *ca.* 2510 cm^{-1}. Our spectrum at $R = 20$ of Et_4NBr is similar to that at $R = 16$ of Et_4NCl in D_2O, measured by Yoshimura and Kanno.[29] Scherer *et al.*[43] have reported Raman spectra of liquid D_2O from −10 to 90 °C; the (isotropic) spectra show the development of a band around 2500 cm^{-1} at the expense of the band around 2400 cm^{-1} with increasing temperature. These bands have been attributed to the OD stretching vibration of the symmetrically hydrogen-bonded complex (2400 cm^{-1}) and of the single-handed complex (2500 cm^{-1}). At any rate, the (partial) breaking or cleavage of hydrogen bond of liquid D_2O with increasing temperature caused the development of the band around 2500 cm^{-1}. Therefore, the spectrum changes caused by increasing concentration of Et_4NBr can be attributed to the cleavage of hydrogen bonding; that is, the large clusters of D_2O are destroyed and turned into smaller clusters by the addition of the highly concentrated salt. Brink and Falk[44] have reported the OD stretching band (in IR spectra) of HDO in aqueous solutions of $NaClO_4$ and $Mg(ClO_4)_2$ of varying concentrations at 28 °C. A band at 2500 cm^{-1} (OD stretching of hydrogen-bonded HDO) in the absence of the salts was overtaken by a high-frequency band (*ca.* 2620–2630 cm^{-1}) with increasing concentration of the salts. Regarding their observations, Verrall[45] has commented that the high-frequency component is due to the extensive breakdown of hydrogen-bonded water structure by ClO_4^-, an effect similar to that of increasing temperature.

Tetraalkylammonium (R_4N^+) salts are usually regarded as having structure-making properties, based on their "hydrophobic effects", larger than expected from their cationic sizes. However, Et_4NBr appears to be one of the most suitable salts for observing the vibration spectra of the solvent part (regions B and C) and not the hydration part (region A), since neither the Et_4N^+ ion nor Br^- is strongly hydrated in aqueous solutions and also its solubility in water is very high at room temperature. Verrall also has mentioned that the R_4NBr series appears to offer a better basis for rationalizing purely structural effects.[45] While admitting that D_2O is a more structured liquid than H_2O,[46] we feel that the whole argument for D_2O could basically be applied to H_2O and H_2O–mixed solvents. In addition, the Raman spectra of D_2O with concentrated LiBr showed great increases in the intensity around 2530 cm^{-1} at the expense of the band at *ca.* 2390 cm^{-1}.[47]

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