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Interaction between halide anions and lithium and substituted-ammonium cations or acids in acetonitrile by direct current polarography

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adsorption effects serve to alter the peak current-concentration relation at higher concentrations. Last, but perhaps most significantly, the operating principles and therefore the selectivities of the various approaches are different. Specifically, the metallic electrodes provide considerably more general detection responding not only to carbohydrates but also to numerous alcohols, amines, and sulfur compounds as well. Interestingly, the CoPC CMEs, operating by an entirely different mechanism, have shown response only to α -keto acids and mercaptans in addition to carbohydrates.

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Interaction between Halide Anions and Lithium and Substituted-Ammonium Cations or Acids in Acetonitrile by Direct Current Polarography

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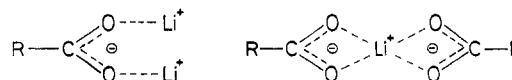
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A polarographic method to study complex formation has been applied to the anodic (mercury dissolution) waves of halide ions in acetonitrile. The formation constants of complexes, such as $(\text{Li}^+)_2\text{Cl}^-$, $(\text{HR})_2\text{Cl}^-$ ($\text{HR} = p$ -bromophenol), and $(\text{HA})_2\text{Cl}^-$ ($\text{HA} = \text{acetic or benzoic acid}$) were obtained by the positive shift in the half-wave potential ($E_{1/2}$) of one of the anodic waves of Cl^- upon the addition of a large excess of (Lewis) acid. Cation acids (alkyl-substituted ammonium, pyridinium, and anilinium) gave similar species, $(\text{R}_n\text{NH}_{4-n}^+)_2\text{Cl}^-$ ($n = 1-3$), etc. The coexistence of Li^+ and HR in a Cl^- solution produced the $(\text{Li}^+)(\text{HR})\text{Cl}^-$ species. On the other hand, the coexistence of Li^+ and HA caused the formation of $(\text{Li}^+)_2(\text{HA})\text{Cl}^-$, in which, one lithium ion seemed to be bound to Cl^- and the other lithium ion to the oxygen atom of the carboxylic acid. As for the bromide ion, the (overall) formation constants of $(\text{HR})\text{Br}^-$ and $(\text{HR})_2\text{Br}^-$ and $(\text{R}_n\text{NH}_{4-n}^+)\text{Br}^-$ and $(\text{R}_n\text{NH}_{4-n}^+)_2\text{Br}^-$ were obtained. However, apparently only a strong cation acid (N,N -dimethylanilinium) could make the $(\text{R}_3\text{NH}^+)_2\text{I}^-$ -type species for the iodide ion.

Many inconsistent phenomena have been reported for alkali halides, especially for LiCl , in nonaqueous solvents (1-5). For instance, Brookes et al. (1) reported that the value of the ion-pair contact distance ($\alpha = 2.15 \text{ \AA}$) for LiCl in acetone deduced from conductivity measurements was practically impossible because the sum of the crystallographic radii is 2.41 \AA . These problems have not been solved yet, although some

suggestions have been made on the possibility of triple-ion formation or of strong solvation.

In previous studies (6-10), we have developed a polarographic method to obtain complex formation constants. The method makes use of the positive potential shift in the anodic (mercury dissolution) wave of a base in the presence of a large excess of (Lewis) acid. A number of new species in nonaqueous solvents have been discovered (6-10) by this method. The identification of the $[\text{Li}_2\text{A}]^+$ and $[\text{LiA}_2]^-$ ($\text{A} = \text{the acetate or benzoate ion}$) complexes (6) made it possible to understand the inconsistency between experimental and calculated values of conductivity of lithium trifluoroacetate in propylene carbonate by Jansen and Yeager (11). Jansen has discussed the formation of the triple ions (12).



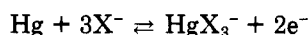
The formation of the $[\text{CH}_3\text{COOLi}_2]^+$ species in acetonitrile was first proposed by Itabashi (13).

We have indicated (6) some limitation of the solubility method of measuring the formation constants of the homo- or heteroconjugation reaction (formation of $\text{A}^-(\text{HA})_n$ or $\text{A}^-(\text{HX})_n$) for simple carboxylates, such as the acetate or benzoate because such a simple carboxylate readily forms the $[\text{Li}_2\text{A}]^+$ type species in acetonitrile.

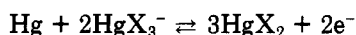
Incidentally, the mechanism of the "leveling effect" in the polarographic reduction of some acids in pyridine containing Li^+ or Na^+ as the supporting electrolyte was also confirmed by the formation of $[\text{Li}_2\text{A}]^+$ or $[\text{Na}_2\text{A}]^+$ (14). Tsuji and Elving

(15) explained the "leveling effect" qualitatively in terms of $[\text{LiA}]$ and not $[\text{Li}_2\text{A}]^+$.

In the present investigation, the anodic waves of halide (Cl^- , Br^- , and I^-) ions are polarographically examined in the presence of alkali metal and substituted ammonium ions, Brøsted acid, etc. The oxidation of mercury in the presence of halide ions (X^-) in nonaqueous solvents can occur via two steps (16–20).



(the first wave, i.e., the more negative wave)



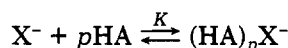
(the second wave, i.e., the more positive wave)

The half-wave potential ($E_{1/2}$) of the wave is a function of concentration (or activity) of X^- (20) as follows (25 °C):

$$E_{1,1/2} = C_1 - 0.059 \log [\text{X}^-] \quad (\text{the first wave}) \quad (1)$$

$$E_{2,1/2} = C_2 + \frac{0.059}{2} \log [\text{X}^-] \quad (\text{the second wave}) \quad (2)$$

where C_1 and C_2 are constants. When an acid HA is added, which reacts with X^- (cf. eq 3) to decrease the activity of X^- ,



$$K = [(\text{HA})_p\text{X}^-] / [\text{X}^-][\text{HA}]^p \quad (3)$$

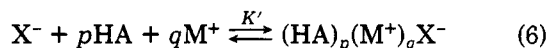
$E_{1,1/2}$ may shift positively and $E_{2,1/2}$ negatively. Combining eq 1 and 3, we have the following equation about the shift in $E_{1/2}$ of the first wave (cf. ref 6):

$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log K + 0.059p \log [\text{HA}] \quad (4)$$

where $(E_{1/2})_c$ and $(E_{1/2})_s$ are the half-wave potentials of X^- in the presence and absence of HA, respectively. Equation 4 can be extended to a more complicated case, in which two kinds of reacting agents, HA and M^+ , are present at the same time:

$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log K' + 0.059p \log [\text{HA}] + 0.059q \log [\text{M}^+] \quad (5)$$

The formation constant (K') for reaction 6 can be obtained if $E_{1/2}$ of X^- in the absence of both HA and M^+ is taken as $(E_{1/2})_s$.



The incomplete dissociation of the added salts (e.g., $\text{Li}^+\text{ClO}_4^-$, $n\text{-Bu}_3\text{NH}^+\text{ClO}_4^-$) in acetonitrile was ignored in this study. The dissociation of acids (HA , R_3NH^+ , etc.) is extremely small in acetonitrile (cf. Table II). The activity coefficients of all the species in the solution were assumed to be unity for simplicity.

EXPERIMENTAL SECTION

Acetonitrile was purified as described previously (21). Tetraethylammonium chloride and iodide, commercially obtained and tetraethylammonium bromide prepared by the method mentioned previously (22) were dried over P_2O_5 under vacuum at room temperature. The preparation methods of lithium, sodium, and tetraethylammonium perchlorates as the supporting electrolyte have been mentioned elsewhere (22).

Caution. Appropriate care should be exercised in the handling of 60% perchloric acid and in the preparation of perchlorate salts.

Trimethylammonium perchlorate ($\text{Me}_3\text{NHClO}_4$) was prepared by neutralizing 30 mL of trimethylamine (ca. 30% aqueous solution) in 50 mL of acetone with 60% perchloric acid. This solution was evaporated to dryness under reduced pressure at less than 50 °C. The salt was recrystallized from acetone and was washed with ethyl ether. The crystals were dried under vacuum

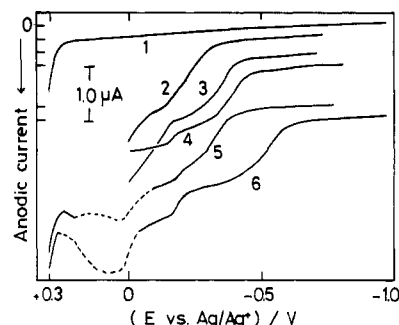


Figure 1. dc polarograms of Cl^- in acetonitrile containing various supporting electrolytes and acids, $[\text{Et}_4\text{NCl}] = 0.5 \text{ mM}$: (1) base current in $0.1 \text{ M Et}_4\text{NClO}_4$ (without Cl^-); (2) $0.1 \text{ M } n\text{-Bu}_3\text{NHClO}_4$; (3) $0.1 \text{ M } p\text{-bromophenol} + 0.1 \text{ M Et}_4\text{NClO}_4$; (4) $0.1 \text{ M benzoic acid} + 0.1 \text{ M Et}_4\text{NClO}_4$; (5) 0.1 M LiClO_4 ; (6) $0.1 \text{ M Et}_4\text{NClO}_4$.

at room temperature. Triethylammonium perchlorate ($\text{Et}_3\text{NHClO}_4$) was prepared from 10 mL of triethylamine in 50 mL of acetone. The salt was dissolved in ethanol and precipitated with ethyl ether. Diethylammonium perchlorate ($\text{Et}_2\text{NH}_2\text{ClO}_4$) was also prepared by the method similar to the triethylammonium salt. Ethylammonium perchlorate ($\text{EtNH}_3\text{ClO}_4$) was prepared from ethylamine (ca. 70% aqueous solution) in acetone. The resultant salt was dissolved in ethanol and precipitated with ethyl ether. The crystals were dried at 60 °C. Tributylammonium perchlorate ($n\text{-Bu}_3\text{NHClO}_4$) similarly prepared was dissolved in ethyl ether and precipitated with water. Pyridinium perchlorate ($\text{C}_5\text{H}_5\text{NHClO}_4$) was prepared from pyridine and perchloric acid and recrystallized twice from an acetone and ethanol mixture. Anilinium and N,N -dimethylanilinium perchlorates ($\text{PhNH}_3\text{ClO}_4$ and $\text{PhNMe}_2\text{HClO}_4$) were prepared in a similar way and washed with ethyl ether. All the salts were dried over P_2O_5 under vacuum at room temperature unless otherwise stated. Other GR grade chemicals were used as received or after being dried under vacuum.

Polarograms were recorded with a Yanagimoto polarograph, Model P-1000, and a Watanabe X-Y recorder, Model WX-4410-L0. The rate of the potential sweep was 5 mV/s. The dropping mercury electrode had the following open-circuit characteristics: $m = 1.28 \text{ mg/s}$ and $\tau = 2.9 \text{ s}$ in a $0.1 \text{ M Et}_4\text{NClO}_4\text{-MeCN}$ solution at $h = 50 \text{ cm}$. The drop time was regulated to be 1.0 s by means of a Yanagimoto P-1000-ST drop-timer. The reference electrode was a $\text{Ag}/0.1 \text{ M AgClO}_4\text{-MeCN}$ electrode. All the polarographic measurements were carried out at 25 ± 0.2 °C.

RESULTS AND DISCUSSION

Anodic Waves of the Chloride Ion. Tetraethylammonium chloride gave two anodic waves (ca. 2:1 in wave heights) in acetonitrile containing $0.1 \text{ M Et}_4\text{NClO}_4$ as the supporting electrolyte, as is shown in Figure 1 and Table I. The wave height of the first wave (more negative wave) was proportional to the concentration of Cl^- over the range of 0.1–1.0 mM. Whereas, the second wave (more positive one) was not observed until the concentration of Cl^- became more than 0.3 mM. Over the range of 0.3–1.0 mM, the second wave height was also proportional to the concentration of Cl^- . The half-wave potential ($E_{1/2}$) of the first wave shifted negatively with increasing concentration of Cl^- ($\Delta E_{1/2} / \Delta \log [\text{Cl}^-] = \text{ca. } -59 \text{ mV}$), as predicted by eq 1. The first wave seemed to be a reversible two-electron process, judging from the slope in the wave analysis (E vs. $\log [i/(i_d - i)^3]$). Both waves were diffusion controlled ($i_1 \propto h^{1/2}$).

When benzoic acid (HA) was added to a 0.5 mM Cl^- solution, the $E_{1/2}$ of the first wave shifted positively. The $E_{1/2}$ of the second wave was not affected since the HgX_3^- species may not interact with HA. The shifts of the half-wave potentials are shown in Figure 2. The slope, $\Delta E_{1/2} / \Delta \log [\text{HA}]$, for the first wave changed from 59 mV (5–20 mM HA) to 124 mV (50–200 mM). The presence of benzoic acid did not affect the wave height, reversibility, and diffusion control character of the Cl^- wave. The formation of $(\text{HA})\text{Cl}^-$ and $(\text{HA})_2\text{Cl}^-$

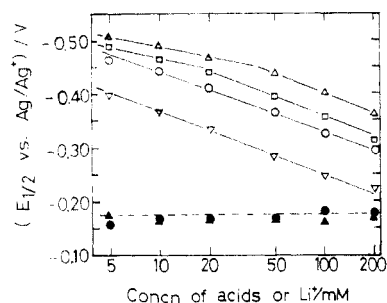


Figure 2. Shift in $E_{1/2}$ of the first wave of Cl^- with changing concentration of acids and Li^+ , $[\text{Et}_4\text{NCl}] = 0.5 \text{ mM}$: (Δ) benzoic acid; (\square) p -bromophenol; (\circ) LiClO_4 ; (∇) $n\text{-Bu}_3\text{NHClO}_4$; (\bullet) the second wave, LiClO_4 ; (\blacktriangle) the second wave, benzoic acid. Et_4NClO_4 was added when the ionic strength was less than 0.1 M.

Table I. dc Polarographic Data for Anodic Waves of Halide Ions in Acetonitrile Containing Various Supporting Electrolyte Cations at 25 °C

supporting electrolyte ^c	first wave ^a		second wave ^b	
	$E_{1/2}/\text{V}$	$I_1/\mu\text{A}$	$E_{1/2}/\text{V}$	$I_1/\mu\text{A}$
[Et_4NCl] = 0.50 mM				
Et_4NClO_4	-0.53 ₄	0.87	-0.18	0.3
NaClO_4	— ^e			
LiClO_4	-0.32 ₅	0.8	-0.18	0.15
$\text{C}_5\text{H}_5\text{NHClO}_4$ ^f	-0.25 ₂	0.8	-0.15	0.3
$n\text{-Bu}_3\text{NHClO}_4$	-0.24 ₈	0.8	-0.15	0.16
[Et_4NBr] = 0.50 mM				
Et_4NClO_4	-0.56 ₂	1.07	-0.14	0.32
NaClO_4	-0.52	1.0	-0.16	0.35
LiClO_4	-0.49	1.9	-0.15	0.25
[Et_4NI] = 0.50 mM				
Et_4NClO_4	-0.64	1.05	-0.20	0.2
NaClO_4	-0.63	1.05	-0.18	0.2
LiClO_4	-0.63 ₅	1.0	-0.20	0.2

^a The more negative wave. ^b The more positive wave. ^c Concentrations of the supporting electrolytes are all 0.1 M. ^d vs. $\text{Ag}/0.1 \text{ M AgClO}_4\text{-MeCN}$ electrode. ^e No wave was observed because of precipitation of NaCl . ^f Pyridinium perchlorate.

(heteroconjugated species) was shown by the slope of 59 mV ($p = 1$) and ca. 120 mV ($p = 2$), respectively. In Table II are listed the formation constants obtained by eq 4. The effect of p -bromophenol was similar to that of benzoic acid. Kolthoff and Chantooni have reported the formation of these hetero-

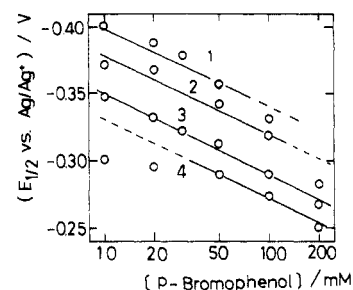
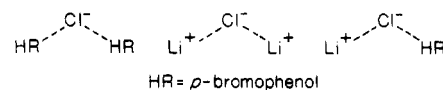


Figure 3. Shift in $E_{1/2}$ of the first wave of Cl^- with changing concentrations of both Li^+ and p -bromophenol, $[\text{Et}_4\text{NCl}] = 0.5 \text{ mM}$: (1) 10; (2) 20; (3) 50; (4) 100 mM of LiClO_4 . Et_4NClO_4 was added when the ionic strength was less than 0.1 M.

conjugated species, based on the solubility method (23–25).

For a cation acid ($n\text{-Bu}_3\text{NH}^+$), the $E_{1/2}$ of the Cl^- wave was shifted 120 mV positively by a 10-fold increase of the concentration of $n\text{-Bu}_3\text{NHClO}_4$ (over the range of 5–200 mM). Even Et_2NH_2^+ and EtNH_3^+ caused the $E_{1/2}$ of the Cl^- wave to shift 120 mV positively with a 10-fold increase of the substituted ammonium ions, over the range of 10–200 and 10–100 mM, respectively. The value of 120 mV ($p = 2$) indicated the formation of the $(\text{R}_n\text{NH}_{4-n})_2\text{Cl}^-$ ($n = 1\text{--}3$)-type species. Pyridinium and anilinium ions gave similar results. The formation constants of these species are listed in Table II. As for Li^+ , the slope ($\Delta E_{1/2}/\Delta \log [\text{Li}^+]$) of 115 mV was observed over the range of 5–200 mM Li^+ . The formation of $(\text{Li}^+)_2\text{Cl}^-$ was proposed with the formation constant of $10^{5.5}$ (M^{-2}).



Wojciechowski and Osteryoung (29) have reported the positive shift in the first wave of Cl^- with increasing concentration of LiClO_4 in acetonitrile. They suggested that the formation of ion pairs between Li^+ and Cl^- in the bulk affected the anodic process of Cl^- .

Figure 3 shows the effect of the coexistence of LiClO_4 and p -bromophenol (HR) on the $E_{1/2}$ of Cl^- . In the presence of 50 mM Li^+ , the $E_{1/2}$ shifted 60 mV (and not 120 mV) to the positive upon a 10-fold increase in the concentration of HR. Similar potential shift was observed with other concentrations of Li^+ . On the other hand, the $E_{1/2}$ was also shifted ca. 60 mV positive by a 10-fold increase of the Li^+ concentration in the presence of a fixed concentration of p -bromophenol (e.g.,

Table II. Overall Formation Constants (log K) of Halide "Complexes" ($(\text{HA})_p\text{Cl}^-$, $(\text{R}_3\text{NH}^+)_p\text{Cl}^-$, $(\text{Li}^+)_p\text{Cl}^-$, etc.) by the Analysis of the First Anodic Wave of Halide Ions

(Lewis) acid ^a	dissociation const of acid in MeCN ^b	Cl^-		Br^-		I^-	
		$p = 1$	$p = 2$	$p = 1$	$p = 2$	$p = 1$	$p = 2$
CH_3COOH	22.3	2.3	3.7				
$\text{C}_6\text{H}_5\text{COOH}$	20.7	2.6	4.1	(1.7)			
$p\text{-BrC}_6\text{H}_4\text{OH}$	25.6	3.1	5.0	2.1	3.2	— ^c	
Me_3NH^+	17.6		6.2	— ^d	4.8	2.0	— ^d
Et_3NH^+	18.5		6.7	3.2	4.8	2.2	— ^d
Et_2NH_2^+	18.8		6.5	3.1	4.8	2.1	— ^d
EtNH_3^+	18.4		6.0	2.7	4.4	— ^c	— ^d
$n\text{-Bu}_3\text{NH}^+$	18.1		6.6	3.1	4.9	2.0	— ^d
$\text{C}_5\text{H}_5\text{NH}^+$ ^e	12.3		6.5	3.0	4.7	(1.8)	
PhNMe_2H^+ ^f			8.0	— ^d	5.8	2.5	3.8
PhNH_3^+	10.6		7.5	3.4	5.2	— ^c	— ^d
Li^+			5.5	2.0	— ^d	—	

^a For the cation acids and Li^+ , the anion was ClO_4^- . ^b The pK_a or pK_{BH^+} values were cited from the following literature: acetic and benzoic acid, ref 26; p -bromophenol, ref 27; trimethylammonium, ref 28; triethylammonium, diethylammonium, ethylammonium, tributylammonium, pyridinium, and anilinium, ref 26. ^c The slope of $\Delta E_{1/2}/\Delta \log [(\text{Lewis acid})]$ was 40–45 mV. ^d The slope of $\Delta E_{1/2}/\Delta \log [(\text{Lewis acid})]$ was 71–92 mV. ^e Pyridinium ion. ^f N,N -Dimethylanilinium ion.

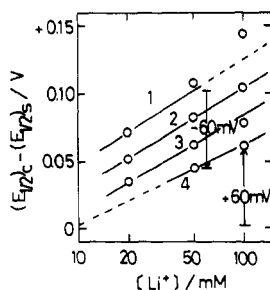
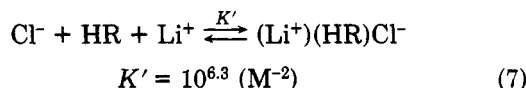
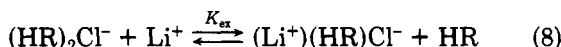


Figure 4. Shift in $E_{1/2}$ of the first wave of Cl^- with changing concentrations of both Li^+ and p -bromophenol (HR): (1) 20; (2) 50; (3) 100; (4) 200 mM of HR. ($E_{1/2}$)_s is the $E_{1/2}$ of $(\text{HR})_2\text{Cl}^-$ at the corresponding concentration of HR; see the text. Other conditions are identical with those in Figure 3.

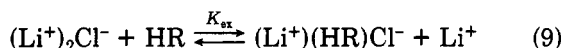
50 mM). The values of $p = 1$ and $q = 1$ in eq 5 indicate the formation of $(\text{Li}^+)(\text{HR})\text{Cl}^-$.



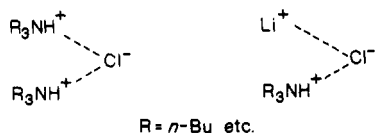
The data in Figure 3 can be rearranged to make Figure 4: each $E_{1/2}$ value in Figure 3 was standardized by subtracting the $E_{1/2}$ value of $(\text{HR})_2\text{Cl}^-$. As the $E_{1/2}$ of $(\text{HR})_2\text{Cl}^-$ (20–200 mM of HR), each value given in Figure 2 was used. Figure 4 indicates that the $(E_{1/2})_c - (E_{1/2})_s$ value at a fixed concentration of HR (e.g., 200 mM) changes ca. 60 mV in the positive direction with a 10-fold increase of Li^+ concentration, while the value at the fixed concentration of Li^+ (e.g., 50 mM) shifts ca. 60 mV in the opposite direction (negatively) with a 10-fold increase of the HR concentration. These data show that $p = -1$ and $q = 1$ in eq 5. Thus, the following reaction occurs upon the addition of Li^+ in the presence of HR:



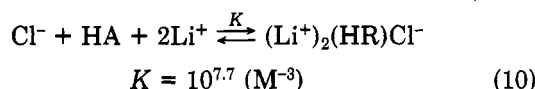
The equilibrium constant of the exchange reaction (K_{ex}) can be obtained easily: the last two terms in eq 5 will be cancelled by equalizing the concentrations of HR and M^+ (cf. $-p = q = 1$). Thus, we obtained $\log K_{\text{ex}} = 1.3_6$ for eq 8. For the exchange reaction of eq 9, $\log K_{\text{ex}}$ is given to be 0.8_5 . The



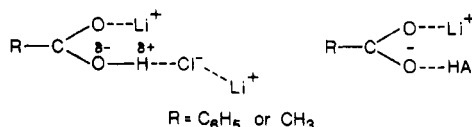
coexistence of Li^+ and $n\text{-Bu}_3\text{NH}^+$ (instead of p -bromophenol) also gave results similar to those shown in Figure 3 or 4. The exchange constants were found to be $\log K_{\text{ex}} = 0.1_7$ and 1.3 for $(n\text{-Bu}_3\text{NH}^+)_2\text{Cl}^-$ and $(\text{Li}^+)_2\text{Cl}^-$, respectively.



The coexistence effect of Li^+ and benzoic acid on the Cl^- wave was also examined. In this case, however, we obtained $p = 1$ and $q = 2$ in eq 5, which indicated the following reaction:



The $(\text{Li}^+)_2(\text{HA})\text{Cl}^-$ species seems to be very probable in the light of $\text{A}^-(\text{HA})\text{Li}^+$ ($\text{A}^- = \text{C}_6\text{H}_5\text{COO}^-$ or CH_3COO^-) which was reported previously (6).



The coexistence of acetic acid and Li^+ in the Cl^- solution also

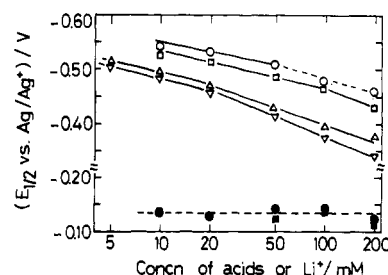


Figure 5. Shift in $E_{1/2}$ of the first wave of Br^- with the concentration of acids and Li^+ , $[\text{Et}_4\text{NBr}] = 0.5$ mM: (O) LiClO_4 ; (\square) p -bromophenol; (\blacktriangle) $\text{Et}_3\text{NHClO}_4$; (∇) $\text{PhNH}_3\text{ClO}_4$; (\bullet) the second wave, LiClO_4 ; (\blacksquare) the second wave, p -bromophenol. Et_4NClO_4 was added when the ionic strength was less than 0.1 M.

gave $p = 1$ and $q = \text{ca. } 2$ in eq 5, and the formation constant of $(\text{Li}^+)_2(\text{HA})\text{Cl}^-$ was obtained as $\log K = \text{ca. } 7.2$.

Anodic Waves of Bromide and Iodide Ions. The polarographic data of Br^- and I^- with various supporting electrolytes are also listed in Table I. With 0.1 M Et_4NClO_4 as the supporting electrolyte, the first anodic wave of Br^- occurred at a more negative potential than that of Cl^- at a same concentration of the depolarizers (0.5 mM). The log plot (E vs. $\log [i/(i_d - i)^3]$) of the wave gave a straight line with the slope of 34 mV. The wave showed the diffusion control character of $i_1 \propto h^{1/2}$.

The presence of 5–20 mM benzoic acid in a 0.5 mM Br^- solution containing 0.1 M Et_4NClO_4 gave only a minor effect on the $E_{1/2}$ of the first wave of Br^- . For 50–400 mM of benzoic acid, the slope, $\Delta E_{1/2}/\Delta \log [\text{HA}]$, was ca. 75 mV. In Figure 5, the effect of p -bromophenol on the anodic waves of Br^- is shown. The $E_{1/2}$ of the first wave was affected by the addition of p -bromophenol, while, that of the second wave was not affected. The slope, $\Delta E_{1/2}/\Delta \log [\text{HR}]$ of the first wave was 60 mV over the range of 10–100 mM of p -bromophenol. The slope changed to 120 mV at more than 100 mM of p -bromophenol. The formation of two heteroconjugated species, i.e., $(\text{HR})\text{Br}^-$ and $(\text{HR})_2\text{Br}^-$ was shown with the (overall) formation constants of 2.1 and 3.1, respectively. Substituted-ammonium ions, pyridinium ion, and N,N -dimethylanilinium ion gave both mono- and dicoordinated “complexes” with the bromide ion, e.g., $(\text{Et}_3\text{NH}^+)\text{Br}^-$ and $(\text{Et}_3\text{NH}^+)_2\text{Br}^-$. However, the formation constants of $(\text{Me}_3\text{NH}^+)\text{Br}^-$ and $(\text{PhNMe}_2\text{NH}^+)\text{Br}^-$ were not obtained polarographically because the slopes, $\Delta E_{1/2}/\Delta \log [\text{cation acid}]$, were both more than 60 mV (~ 80 mV) even at lower concentrations of the acids (5–20 mM). The positive shift in $E_{1/2}$ of the first wave of Br^- with 0.1 M Na^+ or Li^+ , as is shown in Table I, suggested the interaction between Br^- and Na^+ or Li^+ . The (ion-pair) formation constant of Li^+Br^- could be obtained as $10^{2.0}$ since the slope, $\Delta E_{1/2}/\Delta \log [\text{Li}^+]$ was 56 mV for 20–50 of Li^+ . The slope was 91 mV for 50–200 mM of Li^+ . The interaction between Na^+ and Br^- was too small to obtain the ion-pair formation constant polarographically.

Sodium and lithium ions had almost no effect on the anodic waves of the iodide ion, compared to the data with 0.1 M Et_4NClO_4 as the supporting electrolyte (Table I). The anodic waves of I^- occurred at more negative potentials than those of Br^- . The first wave of I^- was diffusion controlled and the reversible two-electron process: $i_1 \propto h^{1/2}$ and the slope of E vs. $\log [i/(i_d - i)^3]$ was 32 mV. The effect of p -bromophenol and triethylammonium and N,N -dimethylanilinium ions on the first wave is shown in Figure 6. Although the interaction between I^- and p -bromophenol was suggested by the positive shift in $E_{1/2}$ of the I^- wave, the formation constant could not be obtained because of the small slope ($\Delta E_{1/2}/\Delta \log [\text{HR}] = \sim 45$ mV) even at 100–400 mM p -bromophenol. The formation constant of $\text{Et}_3\text{NH}^+\text{I}^-$ from Et_3NH^+ and I^- was obtained to be $\log K = 2.0$. However, the formation of $(\text{Et}_3\text{NH}^+)_2\text{I}^-$ was

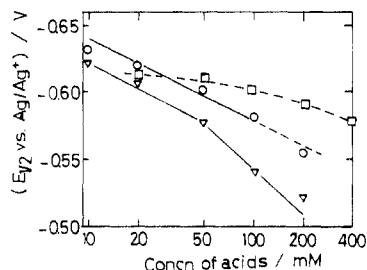


Figure 6. Shift in $E_{1/2}$ of the first wave of I^- with the concentration of acids, $[Et_4NI] = 0.5$ mM: (\square) p -bromophenol; (\circ) Et_3NHClO_4 ; (∇) $PhNMe_2HClO_4$. Et_4NClO_4 was added when the ionic strength was less than 0.1 M.

not confirmed because the slope, $\Delta E_{1/2}/\Delta \log [Et_3NH^+]$, was at most 86 mV even at 100–200 mM Et_3NH^+ . A stronger cation acid, $PhNMe_2H^+$, gave both the $(PhNMe_2H^+)I^-$ and $(PhNMe_2H^+)_2I^-$ species; the slopes $\Delta E_{1/2}/\Delta \log [PhNMe_2H^+]$ were 63 mV (10–50 mM of $PhNMe_2H^+$) and 120 mV (50–200 mM), respectively.

Interaction of Water with Halide Ions. The effect of water on the first waves of the halide ions was examined in acetonitrile containing 0.1 M Et_4NClO_4 . The $E_{1/2}$ of the Cl^- (0.5 mM of Et_4NCl) wave shifted positively with increasing concentration of water. The slope, $\Delta E_{1/2}/\Delta \log [H_2O]$, changed from 88 mV (0.2–1.0 vol % of water in acetonitrile, 1.0 vol % = 0.55 M) to 224 mV (1.0–5.0%). For the bromide ion, the slopes were 72 mV (0.5–1.0%), 95 mV (1.0–2.0%), and 168 mV (2.0–10%). The first wave of the iodide ion was also shifted by the addition of water; the slopes were 20 mV (0.2–1.0%), 80 mV (1.0–5.0%), and 106 mV (2.0–10%). These positive shifts in $E_{1/2}$ of the first waves of halide ions might indicate the formation of $(H_2O)_nCl^-$ ($n =$ up to 4) $(H_2O)_nBr^-$ ($n = 1$ –3), and $(H_2O)_nI^-$ ($n = 1$ and 2) without considering the potential difference in the liquid junction.

By the similar method, we have suggested the formation of $C_6H_5CO_2^-(H_2O)_2$ (6) and $RNO_2^-(H_2O)_2$ ($R = C_6H_5, CH_3$, or $(CH_3)_3C$) (30) in acetonitrile solutions. We believe that these water “complexes” of anions offer some suggestions about the hydration of the anions in aqueous solutions.

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