CHEMISTRY LETTERS, pp. 449-452, 1987.

The Polarographic Study on the Interaction between Halide Anions and Lithium Cation or Acids in Acetonitrile

Masashi HOJO,* Hironori NAGAI, Minoru HAGIWARA, and Yoshihiko IMAI
Department of Chemistry, Faculty of Science, Kochi University,
Kochi 780

A new polarographic method to study complex formation has been applied to the anodic waves of halide ions in acetonitrile. The formation of complexes, such as $(Li^+)_2Cl^-$, $(HR)_2Cl^-$ (HR = p-bromophenol), $(Li^+)(HR)Cl^-$, $(Li^+)_2(HA)Cl^-$ (HA = benzoic acid) was clarified.

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 ion-pair contact distance (a = 2.15 Å) for LiCl in acetone deduced from conductivity measurements was practically impossible because the sum of the crystallographic radii is 2.41 Å. These problems have not been solved, 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 new polarographic method to obtain complex formation constants. The method makes use of the positive potential shift of the anodic (mercury dissolution) wave of a base in the presence of a large excess of (Lewis) acids. A number of new species in nonaqueous solvents have been discovered[6-10] by this method.

In the present investigation, the anodic waves of halide ions are examined in the presence of cations and Brønsted acids. The oxidation of mercury in the presence of halide ions (X^-) in nonaqueous solvents can occur via two steps.[11,12]

$$Hg + 3X^- \rightleftharpoons HgX_3^- + 2e^- \quad \text{(the first wave, i.e. more negative wave)}$$

$$Hg + 2HgX_3^- \rightleftharpoons 3HgX_2 + 2e^- \quad \text{(the second wave, i.e. more positive wave)}$$

The half-wave potential ($E_{1/2}$) of the wave is a function of concentration (or activity) of X^- [12] as follows (at 25 °C):

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

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

where C_1 and C_2 are constants. When an acid HA is added, which reacts with X^- (see Eq. 3) to decrease the activity of X^-, $E_{1,1/2}$ may shift positively and $E_{2,1/2}$ negatively.

$$X^- + p\,HA \xrightleftharpoons{K} (HA)_pX^- \qquad K = [(HA)_pX^-]/[X^-][HA]^p \tag{3}$$

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

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

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

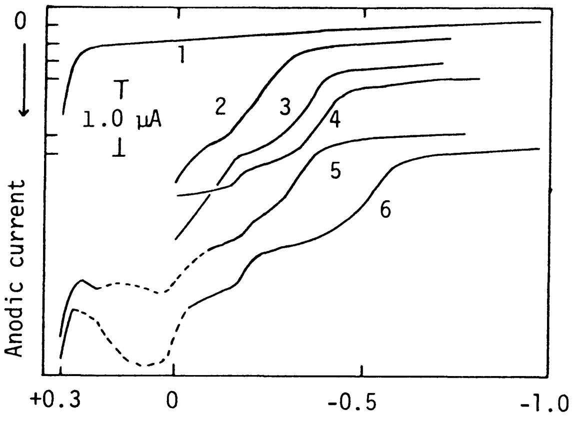


Fig. 1. D.c. polarograms of Cl^- in acetonitrile containing various supporting electrolytes and acids. $[Et_4NCl]$ = 0.5 mM. (1) Base current of 0.1 M Et_4NClO_4; (2) 0.1 M n-Bu_3NHClO_4; (3) 0.1 M p-bromophenol, 0.1 M Et_4NClO_4; (4) 0.1 M benzoic acid, 0.1 M Et_4NClO_4; (5) 0.1 M $LiClO_4$; (6) 0.1 M Et_4NClO_4.

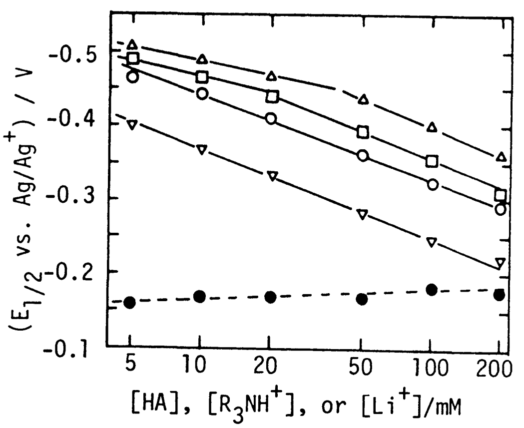


Fig. 2. Shift in $E_{1/2}$ of the first wave of Cl^- with changing concentration of acids and Li^+. $[Et_4NCl]$ = 0.5 mM. (△) Benzoic acid; (□) p-bromophenol; (○) $LiClO_4$; (▽) n-Bu_3NHClO_4; (●) the second wave, $LiClO_4$. Et_4NClO_4 was added to adjust the ionic strength to 0.1 M.

case, in which two kinds of reacting agents, HA and M^+, are present at the same time (Eq. 5).

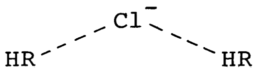
$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log K' + 0.059\, p \log [HA] + 0.059\, q \log [M^+] \quad (5)$$

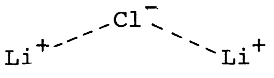
The formation constant(K') for Reaction 6 can be obtained if $E_{1/2}$ of X^- in the absence of both HA and M^+ is taken as $(E_{1/2})_s$.

$$X^- + p\,HA + q\,M^+ \xrightleftharpoons{K'} (HA)_p(M^+)_qX^- \quad (6)$$

The incomplete dissociation of the added salts (e.g., $LiClO_4$, n-Bu_3NHClO_4) in acetonitrile was ignored in this study. All the anodic waves were reversible.

Tetraethylammonium chloride gave two anodic waves (ca. 2:1 in wave heights) in acetonitrile containing 0.1 M (1 M = 1 mol dm^{-3}) Et_4NClO_4 as the supporting electrolyte, as is shown in Fig. 1 and Table 1. When benzoic acid (HA) was added to the Cl^- solution, the $E_{1/2}$ of the first wave (more negative wave) shifted positively. The $E_{1/2}$ of the second wave (more positive one) was not affected, as the HgX_3^- species may not interact with HA. The shifts of the half-wave potentials are shown in Fig. 2. The slope, $\Delta E_{1/2}/\Delta \log[HA]$, for the first wave changed from 59 mV (5 - 20 mM of HA) to 124 mV (50 - 200 mM). The presence of benzoic acid affected none of the wave height, reversibility, and diffusion control character of the Cl^- wave. The formation of $(HA)Cl^-$ and $(HA)_2Cl^-$ (heteroconjugated species) was shown by the slope of 59 mV (p = 1) and ca. 120 mV (p = 2), respectively. In Table 2 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 heteroconjugated species.[13,14] The slope of 115 mV was observed for Li^+, and the formation of $(Li^+)_2Cl^-$ was proposed with the formation constant of $10^{5.5}$ (M^{-2}).





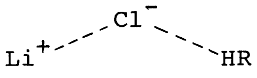


Figure 3 shows the effect of the coexistence of $LiClO_4$ and p-bromophenol (HR)

Table 1. D.c. polarographic data for anodic waves of halide ions in acetonitrile containing various supporting electrolyte cations at 25 °C

Supporting electrolyte[b)]	Et_4NCl[a)]				Et_4NBr[a)]		Et_4NI[a)]	
	First wave		Second wave		First wave[c)]		First wave[c)]	
	$E_{1/2}$[d)]/V,	$I_l/\mu A$	$E_{1/2}$/V,	$I_l/\mu A$	$E_{1/2}$/ V,	$I_l/\mu A$	$E_{1/2}$/ V,	$I_l/\mu A$
Et_4N^+	-0.53_4	0.87	-0.18_4	0.3	-0.56_2	1.07	−0.64	1.05
Na^+	___e)				−0.52	1.0	-0.63_5	1.05
Li^+	-0.32_5	0.8	-0.18_2	0.15	−0.49	0.95	-0.63_5	1.0
$C_5H_5NH^+$ f)	-0.25_2	0.8	−0.15	0.3				
$n\text{-}Bu_3NH^+$	-0.24_8	0.8	-0.15_2	0.16	−0.37	0.6	−0.55	1.22

a) Concentrations of halides are all 0.5 mM. b) Supporting electrolytes are 0.1 M perchlorates. c) The values of the second waves are not shown here. d) vs. Ag/0.1 M $AgClO_4$-MeCN electrode. e) No wave was observed by precipitation. f) Pyridinium ion. (m = 1.28 mg/s, τ = 1.0 s)

Table 2. The overall formation constants (log K) of chloride "complexes"($(HA)_pCl^-$, $(R_3NH^+)_pCl^-$, $(Li^+)_pCl^-$, etc.) by the analysis of the anodic wave of Cl^-

	Benzoic acid	p-Bromophenol	$C_5H_5NH^+$	$n\text{-}Bu_3NH^+$	Li^+
P = 1	2.6	3.1	—	—	—
P = 2	4.1	5.0	6.5	6.6	5.5

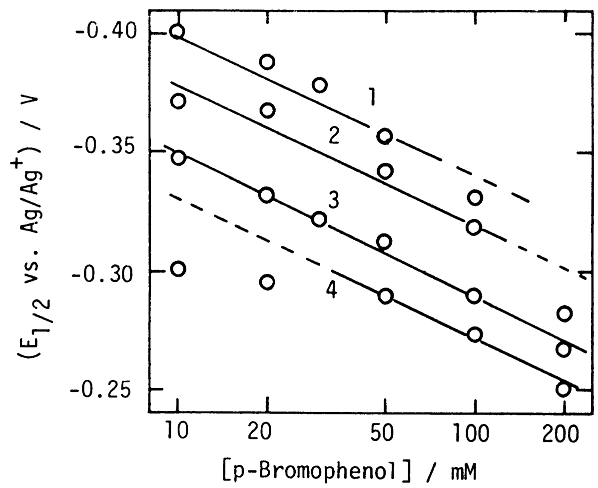


Fig. 3. Shift in $E_{1/2}$ of the first wave of Cl^- with changing concentrations of both Li^+ and p-bromophenol. $[Et_4NCl]$ = 0.5 mM. (1) 10; (2) 20; (3) 50; (4) 100 mM of $LiClO_4$. Et_4NClO_4 was added to adjust the ionic strength to 0.1 M.

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 shifts were observed with other concentrations of Li^+. On the other hand, the $E_{1/2}$ was shifted ca. 60 mV positively by a 10-fold increase of the Li^+ concentration in the presence of a fixed concentration of p-bromophenol (e.g. 50 mM). The values of p = 1 and q = 1 in Eq. 5 indicate the formation of $(Li^+)(HR)Cl^-$.

$$Cl^- + HR + Li^+ \xrightleftharpoons{K'} (Li^+)(HR)Cl^-$$
$$K' = 10^{6.3}\ (M^{-2}) \qquad (7)$$

The data in Fig. 3 can be rearranged: each $E_{1/2}$ value in Fig. 3 was standardized by subtracting the $E_{1/2}$ value of $(HR)_2Cl^-$. As the $E_{1/2}$ of $(HR)_2Cl^-$ (20 - 200 mM of HR), the values given in Fig. 2 were used. The rearranged figure 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 the Li^+ concentration. While, that 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 with the addition of Li^+ in the presence of HR.

$$(HR)_2Cl^- + Li^+ \xrightleftharpoons{K_{ex}} (Li^+)(HR)Cl^- + HR \tag{8}$$

The equilibrium constant of the exchange reaction 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 $\log K_{ex} = 1.3_6$ for Eq. 8. For the exchange reaction of Eq. 9, $\log K_{ex}$ is given to be 0.8_5.

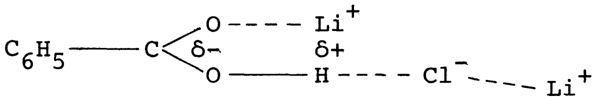
$$(Li^+)_2Cl^- + HR \xrightleftharpoons{K_{ex}} (Li^+)(HR)Cl^- + Li^+ \tag{9}$$

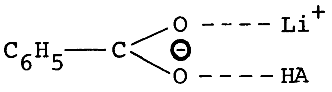
The coexistence of Li^+ and $n\text{-}Bu_3NH^+$ (instead of p-bromophenol) also gave results similar to those shown in Fig. 3. The exchange constants were obtained to be $\log K_{ex} = 0.1_7$ and 1.3 for $(n\text{-}Bu_3NH^+)_2Cl^-$ and $(Li^+)_2Cl^-$, respectively.

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

$$Cl^- + HA + 2\,Li^+ \xrightleftharpoons{K} (Li^+)_2(HA)Cl^- \qquad K = 10^{7.7}\ (M^{-3}) \tag{10}$$

The $(Li^+)_2(HA)Cl^-$ species seems to be very probable in the light of $A^-(HA)Li^+$ ($A^- = C_6H_5COO^-$) which was reported previously.[6]





The polarographic data for Br^- and I^- are also listed in Table 1.

This paper was kindly looked over by Professor Kosuke Izutsu of Shinshu University.

References

1) H. C. Brookes, M. C. B. Hotz, and A. H. Spong, J. Chem. Soc., A, 1971, 2415.
2) J. N. Butler and J. C. Synnott, J. Am. Chem. Soc., 92, 2602 (1970).
3) M. Salomon, J. Phys. Chem., 73, 3299 (1969).
4) L. G. Savedoff, J. Am. Chem. Soc., 88, 664 (1966).
5) J. E. Prue and P. J. Sherrington, Trans. Faraday Soc., 57, 1795 (1961).
6) M. Hojo and Y. Imai, Bull. Chem. Soc. Jpn., 56, 1963 (1983).
7) M. Hojo and Y. Imai, Anal. Chem., 57, 509 (1985).
8) M. Hojo and Y. Imai, Anal. Sci., 1, 185 (1985).
9) M. Hojo and Y. Imai, J. Electroanal. Chem. Interfacial Electrochem., 209, 297 (1986).
10) M. Hojo and Y. Imai, Bunseki Kagaku, 32, E77 (1983).
11) "Encyclopedia of Electrochemistry of the Elements," ed by A. J. Bard, Marcel Dekker, New York (1982), Vol. 9(a), p. 58.
12) A. M. Bond, "Modern Polarographic Methods in Analytical Chemistry," Marcel Dekker, New York (1980), p. 101.
13) I. M. Kolthoff and M. K. Chantooni, Jr., J. Am. Chem. Soc., 91, 4621 (1969).
14) M. K. Chantooni, Jr., and I. M. Kolthoff, J. Am. Chem. Soc., 92, 7025 (1970).

(Received November 21, 1986)