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The Polarographic Reduction of Acids in Pyridine. The Cause of the Differences in Half-Wave Potentials with Various Supporting Electrolytes

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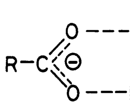
The polarographic reductions of acetic, benzoic, *p*-toluenesulfonic, and perchloric acids have been examined in pyridine solutions with tetrabutylammonium, tetraethylammonium, sodium, and lithium perchlorate as the supporting electrolytes. The difference in the half-wave potentials of the acids was explained in terms of the difference in the degree of interaction between the pyridinium ion and the conjugate bases (e.g., CH_3COO^-) made of the acids. The alkali-metal ions interact with the acetate or benzoate ion to form $RCOO^-(M^+)_2$ (M=Li and Na). The formation constants of $RCOO^-(M^+)_2$ were evaluated by means of the positive shift in the half-wave potential of the pyridinium ion in the presence of a large excess of the alkali metal ions. Substituted acetic and benzoic acids and phenols were also examined so as to ascertain the effect of the substituent groups.

Hickey et al.[1)] reported very interesting behavior in the polarographic reduction of some acids in pyridine: the pyridinium ion produced in 0.1 M[†] $LiClO_4$ is reduced at a more positive potential than that of the wave produced in 0.1 M Et_4NClO_4. The half-wave potential ($E_{1/2}$) of the pyridinium wave in Et_4NClO_4 depends on the acids from which the pyridinium ion is produced, whereas that in $LiClO_4$ is essentially independent of the acids (leveling effect). In spite of their great efforts to clarify the cause of the difference in $E_{1/2}$ between Et_4NClO_4 and $LiClO_4$, they were not able to reach the conclusion, probably because they not only lacked knowledge about the key chemical species but had also failed in preparing the compound ($C_6H_5COONEt_4$) essential for the study in a pure form. Tsuji and Elving[2)] explained the leveling effect qualitatively in terms of the ion-association and ion-exchange reactions.

We have developed a polarographic method[3,4)] to obtain a complex formation constant using the anodic (mercury dissolution) wave induced from a base. By the method, we have confirmed some new species, including the $RCOO^-(M^+)_2$ (M=Li and Na)-type species for the acetate and benzoate ions in acetonitrile.[4)]



The formation of the $[CH_3COOLi_2]^+$ species in acetonitrile was first proposed by Itabashi in 1972.[5)]

In the present investigation, the polarographic behavior of acetic, benzoic, *p*-toluenesulfonic, and perchloric acids in pyridine is examined using several supporting electrolytes. The leveling effect of the acids caused by Li^+ and Na^+ will be accounted for by the formation of the $RCOO^-(M^+)_2$ species. Methyl- and chloro-substituted acetic acids, and chloro-substituted benzoic acids and phenols will also be examined.

The reduction of the hydrogen ion at the dropping mercury electrode is usually accompanied by a high overvoltage in aqueous solutions. Mairanovskii,[6)] however, assumed that some protonated bases (e.g., protonated pyridine) might be reduced reversibly, and he confirmed a normal reversible process for the catalytic hydrogen wave caused by pyridine in a 0.1 M borate buffer containing tetraethylammonium phenylmethanesulfonate.

Experimental

Pyridine from Wako Pure Chemicals (GR grade) was dried with molecular sieves 4A.[7,8)] The method of preparing pure tetraethylammonium benzoate was described in a previous paper.[4)] The supporting electrolytes were prepared and dried by the methods described elsewhere.[9)] Benzoic and *p*-toluenesulfonic acids were dried as has been described previously.[10)] Commercial acetic acid (Wako, GR grade) and perchloric acid (Wako, GR grade, 60%) were used as received. The other acids and phenols, commercially obtained GR or EP grade, were used without further purification.

All the polarograms were recorded with a Yanagimoto polarograph, Model P-1000 and a Watanabe X-Y recorder, Model WX-4401-L0, with the potential sweep rate of 5 mV s^{-1}, at (25±0.2)°C. Two dropping mercury electrodes were used: the open-circuit characteristics of the electrodes at h=50 cm were m=2.02 mg s^{-1} and τ= ca. 4 s (capillary A), and m=1.79 mg s^{-1} and τ=4.0 s (capillary B), in 0.1 M Et_4NClO_4-pyridine. The drop time was regulated at 1.0 s for all the polarographic measurements. The reference electrode was a silver-silver perchlorate electrode, Ag/0.1 M $AgClO_4$-pyridine. Pure nitrogen was used for the deoxygenation of polarographic solutions.

Results and Discussion

Acetic, Benzoic, *p*-Toluenesulfonic, and Perchloric Acids. Benzoic acid gave a single cathodic wave at ca. −1.57 V in pyridine containing 0.1 M Et_4NClO_4 as the supporting electrolyte, as is shown in Fig. 1. The wave height was linear to the concentration of benzoic acid over the range of 0.1—1 mM. The wave was found to be diffusion-controlled, as is indicated by the relation of $i_l \propto \sqrt{h}$. With 0.1 M n-Bu_4NClO_4, a similar wave was observed at almost the same potential. With 0.1 M

[†] 1 M=1 mol dm^{-3}.

Table 1. The d.c. Polarographic Data of Perchloric, p-Toluenesulfonic, Benzoic, and Acetic Acids in Pyridine with Various Supporting Electrolytes

Supporting electrolyte$^{a)}$	$E_{1/2}$$^{b)}$/V (Prewave)	i_l/μA (Prewave)	$E_{1/2}$/V (Main wave)	i_l/μA (Main wave)	Slope$^{c)}$/mV
$[\mathrm{HClO_4}]=1.0\,\mathrm{mM}$					
n-Bu$_4$N$^+$	−1.0	0.15	−1.20	2.6	59
Et$_4$N$^+$	−1.07	0.2	−1.235	2.8	63
Na$^+$	−0.97	0.25	−1.215	2.75	56
Li$^+$	−1.01	0.2	−1.23	2.85	58
$[p\text{-TOs}]=1.0\,\mathrm{mM}$					
n-Bu$_4$N$^+$	−1.07	0.2	−1.21	2.3	74
Et$_4$N$^+$	−1.05	0.15	−1.245	2.1	58
Na$^+$	−0.98	0.2	−1.23	2.0	54
Li$^+$	−1.04	0.3	−1.24	2.35	47
$[\mathrm{C_6H_5COOH}]=1.0\,\mathrm{mM}$					
n-Bu$_4$N$^+$	—		−1.585	2.5	80
Et$_4$N$^+$	—		−1.57	2.6	73
Na$^+$	−1.06	0.3	−1.30	2.5	75
Li$^+$	−1.03	0.3	−1.24	2.5	53
$[\mathrm{CH_3COOH}]=0.96\,\mathrm{mM}$					
n-Bu$_4$N$^+$	—		−1.75	2.85	110
Et$_4$N$^+$	—		−1.69	2.95	100
Na$^+$	−1.125	0.25	−1.37	2.6	79
Li$^+$	−1.08	0.3	−1.285	2.4	63

a) 0.1 M perchlorate salts. b) vs. Ag/0.1 M AgClO$_4$-pyridine. c) $-E$ vs. $\log[i/(i_d-i)]$. Capillary A was used for measuring the data in Table 1.

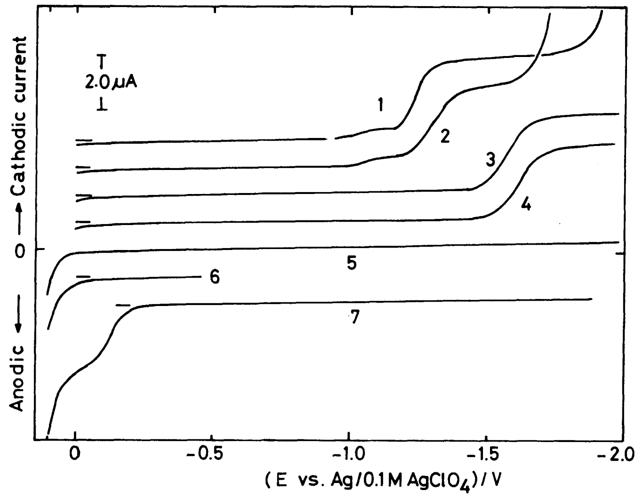


Fig. 1. D.c. polarograms of benzoic acid and the benzoate ion in pyridine containing various supporting electrolytes at 25°C.
[Benzoic acid]=1.0 mM for 1—4.
1: 0.1 M LiClO$_4$, 2: 0.1 M NaClO$_4$, 3: 0.1 M Et$_4$NClO$_4$, 4: 0.1 M Bu$_4$NClO$_4$, 5: the base current with 0.1 M Et$_4$NClO$_4$, 6: [C$_6$H$_5$COOEt$_4$N]=0.99 mM, 0.1 M LiClO$_4$ or NaClO$_4$, 7: [C$_6$H$_5$COOEt$_4$N]=0.99 mM, 0.1 M Et$_4$ClO$_4$.

LiClO$_4$ and NaClO$_4$, however, the wave was shifted to more positive potentials and the wave was accompanied by a prewave (Table 1). Similar behavior has been reported by Hickey et al.:[1] they attributed the main wave to the reduction of the pyridinium ion formed from benzoic acid and pyridine. Acetic acid gave a less reversible cathodic wave at a more negative potential than benzoic acid. The half-wave potential of the wave depended on the supporting electrolyte cation. On the other hand, the main waves for perchloric or p-toluenesulfonic acid (p-TOs) were observed at more positive potentials (−1.20—−1.245 V), being almost indifferent to the kind of supporting electrolyte cations.

The half-wave potentials of the main wave for the acids in the presence of the tetraalkylammonium ions are in this order: $\mathrm{HClO_4} \simeq p$-TOs>benzoic acid>acetic acid. The negative shift for the weaker acids may be accounted for by the interaction between the pyridinium ion and the conjugate-base anion ($\mathrm{PyH^+}$ ∧∧ $\mathrm{RCOO^-}$). Therefore, the effect of the benzoate ion on the $E_{1/2}$ for benzoic acid was examined. A ten-fold concentration increase (from 10 to 100 mM) of tetraethylammonium benzoate shifted the $E_{1/2}$ for benzoic acid (1 mM) ca. 120 mV negatively and decreased the wave height linearly down to half of the initial height at 100 mM of the salt. This shows a strong interaction between the pyridinium cation and the benzoate anion. The potential shift of ca. 120 mV with a 10-fold increase in the benzoate concentration suggested that the compound formed by the pyridinium ion and a large excess of the benzoate ion might be a 1 : 2 complex (pyridinium dibenzoate; cf. $[\mathrm{Li^+(C_6H_5COO^-)_2}]$ in Ref. 4). At any rate, the benzoate and acetate ions seemed to be bound to the pyridinium ion so tightly because neither pyridinium benzoate nor acetate gave any anodic wave, although tetraethylammonium benzoate gave a well-defined anodic wave at −0.12 V with 0.1 M Et$_4$NClO$_4$ (Fig. 1).

The half-wave potentials of the reduction waves for

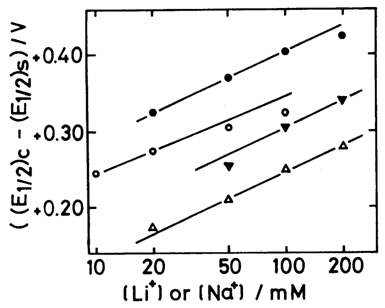


Fig. 2. Shifts of the half-wave potentials of the cathodic waves of acetic and benzoic acids (1 mM) with the addition of alkali metal ions. (●): Acetic acid, Li^+, (○): benzoic acid, Li^+, (▼): acetic acid, Na^+, (△): benzoic acid, Na^+. The total ionic strength is kept to be 0.1 M with Et_4NClO_4, except for 200 mM solutions of Li^+ and Na^+. See the text for $(E_{1/2})_c$ and $(E_{1/2})_s$.

acetic and benzoic acids were shifted positively by the supporting electrolyte cation in this order: $Li^+ > Na^+ > Et_4N^+ \simeq n\text{-}Bu_4N^+$. The positive shift by alkali metal cations suggested that the interaction between the pyridinium ion and the acetate or benzoate ion would be weakened by the interaction between the acetate or benzoate ion and the alkali-metal cations. Figure 2 shows the shifts in the $E_{1/2}$ for acetic and benzoic acids with the concentration changes in Li^+ and Na^+. The $E_{1/2}$ shifted ca. 120 mV positively upon a 10-fold increase in the concentration of the alkali-metal ions, except in the case of benzoic acid with Li^+ (ca. 100 mV). The waves became reversible and diffusion-controlled at higher concentrations of Li^+ or Na^+ ($\gg$ 20 mM) in most cases. However, for acetic acid, more than 50 mM of Na^+ was needed to obtain the reversible and diffusion-controlled wave.

The following equation was used to analyze the above data:

$$(E_{1/2})_c = (E_{1/2})_s + \frac{0.059}{n}\log K + \frac{0.059}{n} p \log [M^+], \qquad (1)$$

where n is the number of electrons and p is the number of M^+ bound to a carboxylate ion. The term of $(E_{1/2})_c$ means the $E_{1/2}$ of an acid in the presence of an alkali-metal ion. As the standard ($(E_{1/2})_s$), the $E_{1/2}$ of the acid in the absence of alkali-metal ions (with 0.1 M Et_4NClO_4) was taken. K stands for the overall formation constant. The other conditions for Eq. 1 are similar to those given in Refs. 3, 4, or 11. In Eq. 1, we get $p=2$, since the pyridinium ion is reduced by one electron ($n=1$)[2,12,13] and the slope of $\Delta E_{1/2}/\Delta\log [M^+]$ is ca. 120 mV, as has been mentioned above.

Thus, the reaction for acetic acid is as follows:

$$PyH^+ \sim\!\sim\!\sim CH_3COO^- + 2\,M^+ \overset{K}{\rightleftarrows} PyH^+ \cdots\cdots CH_3COO^-(M^+)_2. \qquad (2)$$

The formation constants of the ion pair (or complex) between the acetate ion and the lithium and sodium ions were found to be log (K/M^2)=ca. 8.8 and ca. 7.1 respectively. We ignored the irreversibility of the wave for acetic acid in the absence of an alkali-metal ion. For the benzoate ion, the values were log (K/M^2)= ca. 7.8 and ca. 6.2 with Li^+ and Na^+ respectively. In acetonitrile,[4] the formation constants of $CH_3COO^-(Li^+)_2$ and $C_6H_5COO^-(Li^+)_2$ in the reactions between $RCOONEt_4$ and Li^+ were obtained as log (K/M^2)=11.0 and ca. 9.0 respectively. The values of the formation constants are only approximate, however, because of some irreversibility in the waves and an incomplete dissociation of $M^+ClO_4^-$ in pyridine solutions.

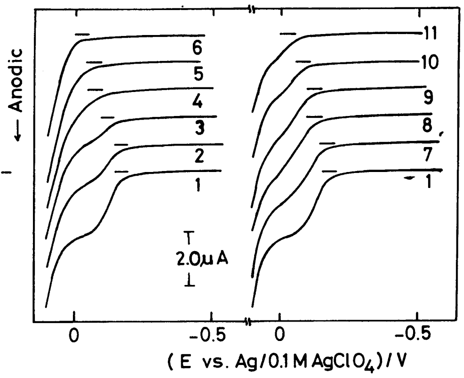
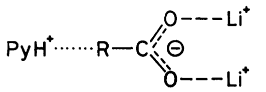


Fig. 3. Changes in the anodic wave from the benzoate ion in 0.1 M Et_4NClO_4–pyridine with the addition of $LiClO_4$ and $NaClO_4$.
$[C_6H_5COOEt_4N]$=0.99 mM.
1: Li^+ and Na^+ free, 2: 0.4, 3: 0.6, 4: 0.8, 5: 1.0, 6: 2.0 mM of Li^+, 7: 0.4, 8: 0.8, 9: 1.0, 10: 1.4, 11: 2.0 mM of Na^+.

In this study, the cathodic wave of the pyridinium ion was used as the indicator. The pyridinium ion is not bound to the alkali-metal ion directly, but through the acetate (or benzoate) ion.



The relatively positive and constant values of the $E_{1/2}$ of $HClO_4$ and p-TOs with various supporting electrolytes indicate that the perchlorate and p-toluenesulfonate ions should interact only weakly with the pyridinium ion ($PyH^+ \cdots\cdots ClO_4^-$). If the interaction between the pyridinium ion and the conjugate base anion (from acetic or benzic acid) were completely removed by any interaction, the reduction potential of the weak acid would approach the positive value of $HClO_4$ or p-TOs.

Figure 3 shows the change in the anodic (mercury dissolution) wave from the benzoate ion (1 mM) in pyridine-0.1 M Et_4NClO_4 upon the addition of Li^+ and Na^+. The wave height of the anodic wave from the benzoate ion decreased linearly with the increase in the concentration of Li^+, and the wave disappeared completely at 1 mM of Li^+. Upon the addition of Na^+, a positive shift of the anodic wave was observed because

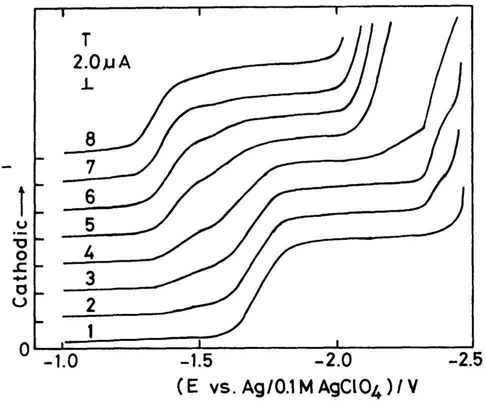


Fig. 4. Changes in the polarographic wave of 1 mM acetic acid (10 ml) with the addition of 0.1 M $LiClO_4$. The supporting electrolyte is 0.1 M Et_4NClO_4. 1: Li^+ free, 2: 40, 3: 100, 4: 200, 5: 500 μl, 6: 1, 7: 2, 8: 5 ml of 0.1 M $LiClO_4$ added. The total volume changes are not corrected.

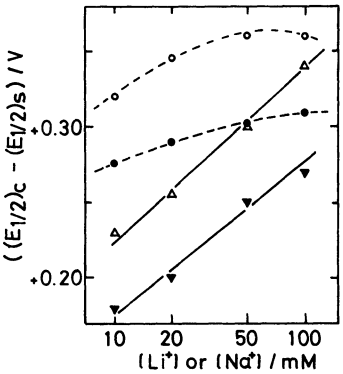


Fig. 5. Shifts in the half-wave potentials of cathodic waves of chloro-substituted benzoic acids (1 mM) with the addition of alkali metal ions.
(○): *p*-Chlorobenzoic, Li^+, (△): *p*-chlorobenzoic, Na^+, (●): 2,4-dichlorobenzoic, Li^+, (▼): 2,4-dichlorobenzoic acid, Na^+. The total ionic strength is kept to be 0.1 M with Et_4NClO_4. See Fig. 2 for $(E_{1/2})_c$ and $(E_{1/2})_s$.

the wave was not completely depressed, even at 2 mM of Na^+. In acetonitrile,[4] although the anodic wave from the benzoate ion disappeared at the equivalence point as a result of the formation of the white precipitate of lithium or sodium benzoate, the anodic wave was recovered again at a much more positive potential by the addition of a large excess of Li^+ or Na^+ (the formation of $C_6H_5COO^-(M^+)_2$). Unfortunately, the reappearance of the anodic wave was not observed, even at 0.1 M Li^+ or Na^+, in the pyridine solution, for the potential of the anodic wave was too close to the positive potential limit in the absence of any complex-forming agent (ca. +0.05 V). Thus, the formation of $C_6H_5COO^-(M^+)_2$ was not directly proved by the anodic wave from the benzoate ion in pyridine, unlike as in acetonitrile.

Figure 4 shows the change in the polarographic wave of acetic acid upon the addition of $LiClO_4$. Upon the addition of a small amount of $LiClO_4$, a small cathodic wave appeared at a more positive potential than that of the initial wave in 0.1 M Et_4NClO_4 as the supporting electrolyte. The wave height of the more positive wave increased with the increase in the concentration of $LiClO_4$. At last, the wave merged into the initial wave at high concentrations of $LiClO_4$. These experimental results suggest the successive formation of $RCOO^-Li^+$ and $RCOO^-(Li^+)_2$ from PyH^+ ∿ $RCOO^-$ and $LiClO_4$.

Hickey et al. described that specific differences in the effects of supporting-electrolyte cations appeared to be due to electrocapillary phenomena and perhaps also to the extent of the solvation of the ions.[1] However, the present study as well as the work by Tsuji and Elving[2] shows that the interaction between the pyridinium ion and the conjugate base from a weak acid plays an important role in the reduction potential of the acid in pyridine solutions.

In conclusion, the leveling effect of the carboxylic acids with Li^+ or Na^+ can be explained quantitatively by the formation of $RCOO^-(M^+)_2$-type species, instead of in terms of simple ion-exchange reactions, i.e., $PyH^+A^-+M^+ClO_4^- \rightleftarrows PyH^+ClO_4^-+M^+A^-$ (A^-=the conjugate base of an acid) proposed by Tsuji and Elving,[2] in pyridine solutions.

Methyl- or Chloro-Substituted Acetic and Benzoic Acids and Phenols. The polarographic data for propionic and pivalic ($(CH_3)_3CCOOH$) acids and for chloro-substituted acetic and benzoic acids in pyridine solutions are listed in Table 2. The polarographic behavior of these compounds was very similar to that of acetic and benzoic acids, except that trichloroacetic acid gave a very large wave (6 μA, cf. 3 μA for 1 mM acetic acid) with Et_4N^+ or n-Bu_4N^+ as the supporting-electrolyte cation. The large wave-height for trichloroacetic acid can be explained by the immediate reduction of a chlorine atom in the substituent group, besides the reduction of the pyridinium ion. Only the reduction of the pyridinium ion with one electron (n=1) occurred for the other acids.

With Et_4N^+ or n-Bu_4N^+ as the supporting-electrolyte cation, the half-wave potential of an acid depends on its acid strength. The linear relation between $E_{1/2}$ and pK_a^{aq} (dissociation constant in water) for acids in pyridine has been reported by Tsuji and Elving.[13] With Li^+ or Na^+ as the supporting-electrolyte cation, however, the half-wave potentials of chloro-substituted acetic and benzoic acids were rather constant in value (−1.2—−1.4 V).

The effects of the concentrations of alkali-metal ions on the half-wave potentials of substituted acetic and benzoic acids were also examined. Figure 5 shows the effects of Li^+ and Na^+ on the reduction of *p*-chlorobenzoic and 2,4-dichlorobenzoic acids. The half-wave potential of *p*-chlorobenzoic and 2,4-dichlorobenzoic acids were shifted ca. 120 mV posi-

Table 2. The d.c. Polarographic Data of Other Acids and Phenols in Pyridine with Various Supporting Electrolytes

Supporting electrolyte[a)]	$E_{1/2}$[b)]/V (Prewave)	i_l/μA (Prewave)	$E_{1/2}$/V (Main wave)	i_l/μA (Main wave)	Slope[c)]/mV
$[CH_3CH_2COOH]=1.05$ mM					
n-Bu_4N^+			−1.79	3.0	95
Et_4N^+			−1.72	3.1	95
Na^+	−1.42	0.15	−1.42	2.9	79
Li^+	−1.31	0.2	−1.31	2.8	58
$[(CH_3)_3CCOOH]=0.99$ mM					
n-Bu_4N^+			−1.81	2.9	89
Et_4N^+			−1.74	2.65	82
Na^+	−1.185	0.2	−1.44	2.35	74
Li^+	−1.11	0.25	−1.32	2.45	65
$[ClCH_2COOH]=1.0$ mM					
n-Bu_4N^+			−1.41	2.6	100
Et_4N^+			−1.47	2.65	92
Na^+	−0.965	0.25	−1.205	2.55	66
Li^+	−1.02	0.3	−1.23	2.5	53
$[Cl_2CHCOOH]=1.0$ mM					
n-Bu_4N^+			−1.235	2.5	89
Et_4N^+			−1.30	2.9	82
Na^+	−0.92	0.2	−1.13	2.25	63
Li^+	−1.03	0.2	−1.26	2.4	53
$[Cl_3CCOOH]=0.99$ mM					
n-Bu_4N^+			−1.95	5.9	173
Et_4N^+			−1.72	5.8	205
Na^+	−1.05	0.45	−1.24[d)]	1.6	—
Li^+	−1.07	0.5	−1.25	1.9	58
[p-Chlorobenzoic acid]=1.0 mM					
n-Bu_4N^+			−1.57	2.55	105
Et_4N^+			−1.48	2.65	82
Na^+	−1.04	0.2	−1.31	2.3	68
Li^+	−1.00	0.2	−1.23	2.35	59
[2,4-Dichlorobenzoic acid]=1.0 mM					
n-Bu_4N^+			−1.48	2.35	92
Et_4N^+			−1.48	2.7	87
Na^+	−1.03	0.2	−1.29	2.65	53
Li^+	−1.04	0.25	−1.27	2.6	47
$[C_6H_5OH]=1.0$ mM					
n-Bu_4N^+			−2.065	1.95	142
Et_4N^+			−1.985	2.25	142
Na^+			—[e)]		
Li^+			−1.79	3.1	77
[p-Chlorophenol]=0.93 mM					
n-Bu_4N^+			−1.98	2.1	152
Et_4N^+			−1.91	2.25	126
Na^+			—[e)]		
Li^+			−1.72	2.4	100
[2,4-Dichlorophenol]=1.0 mM					
n-Bu_4N^+			−1.81	2.55	116
Et_4N^+			−1.735	2.6	108
Na^+			−1.555	1.8	84
Li^+			−1.45	2.1	84

a) 0.1 M perchlorate salts. b) vs. Ag/0.1 M $AgClO_4$-pyridine. c) $-E$ vs. $\log[i/(i_d-i)]$. d) A polarographic maximum was accompanied. e) No wave was observed up to the reduction of the Na^+ ion. Capillary B was used for measuring the data in Table 2.

tively by a 10-fold increase in the concentration of $NaClO_4$ ($\Delta E_{1/2}/\Delta\log[Na^+] \simeq 120$ mV). The analyses of the data by means of Eq. 1 gave formation constants of log (K/M^2)=ca. 6.1 and ca. 4.9 for $ClC_6H_4COO^-(Na^+)_2$ and $Cl_2C_6H_3COO^-(Na^+)_2$, respectively. The effect of Li^+ on the waves of both acids is larger than that of Na^+, judging from the potential at each concentration of the aklali-metal ions. However, the

Table 3. The Values of the $\Delta E_{1/2}/\Delta\log[M^+]$ Slope and the Estimated Values of the Formation Constants of $RCOO^-(M^+)_2$

Acid	Li^+		Na^+	
	Slope/mV	Log$K$[a]	Slope/mV	Log$K$[a]
CH_3COOH	115	8.8	132	7.1
CH_3CH_2COOH	95	9.0	110	7.2
$(CH_3)_3CCOOH$	80	—	—[b]	
$ClCH_2COOH$	25		80	—
$Cl_2CHCOOH$	0		20, 60[c]	
Cl_3CCOOH	—[d]		—[d]	
C_6H_5COOH	100	7.8	120	6.2
p-Chlorobenzoic	≈50[e]		117	6.1
2,4-Dichlorobenzoic	≈40[e]		97	4.9

a) The formation constant, $K(M^{-2})$, in $RCOO^- + 2\,M^+ \rightleftarrows RCOO^-(M^+)_2$. b) The wave height was decreased by the addition of Na^+. c) The curve was separated into two parts, as is shown in Fig. 6. d) Another reaction seems to occur; see the text. e) The slope became smaller at higher concentrations of M^+.

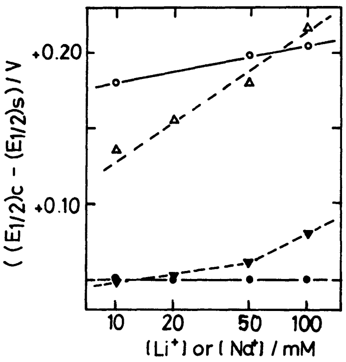


Fig. 6. Shifts in the half-wave potentials of cathodic waves of chloro-substituted acetic acids (1 mM) with the addition of alkali metal ions.
(○): Chloroacetic, Li^+, (△): chloroacetic, Na^+, (●): dichloroacetic, Li^+, (▼): dichloroacetic acid. Na^+. The total ionic strength is kept to be 0.1 M with Et_4NClO_4. See Fig. 2 for $(E_{1/2})_c$ and $(E_{1/2})_s$.

values of $\Delta E_{1/2}/\Delta\log[Li^+]$ are much smaller (40 or 50 mV) than 120 mV. Therefore, the species formed by the reaction between Li^+ and the conjugate base ($RCOO^-$) seems to be, at most, $RCOO^-Li^+$.

The slope of $\Delta E_{1/2}/\Delta\log[M^+]$ (M=Li and Na) were also small in value for chloro-substituted acetic acids, as Table 3 shows. Figure 6 illustrates the effect of Li^+ and Na^+ on the half-wave potentials of chloroacetic and dichloroacetic acids. In the case of dichloroacetic acid, the effect of Li^+ seems to be smaller than that of Na^+, judging from the potential at each concentration of M^+ and from the slope of $\Delta E_{1/2}/\Delta\log[M^+]$. Apparently, the interaction of Na^+ with the dichloroacetate ion is stronger than that of Li^+. This phenomenon may be explained by the difference in the degree of solvation between Li^+ and Na^+, and also by the weakness of the interaction of the dichloroacetate ion with the alkali-metal ions. A lithium ion will be solvated by pyridine more strongly than a sodium ion. We have found interaction between Li^+ and a monoamine as well as acyclic[14] and cyclic[15] polyamines in acetonitrile. The complexing of the lithium ion with pyridine was confirmed in acetonitrile.[16] It seems that the solvation of Li^+ by pyridine is so strong that the dichloroacetate ion cannot interact with Li^+ interact with Li^+ any more, for the basicity of the (dichloro)acetate ion is weakened by the substituted chlorine atoms.

Even the half-wave potentials of phenols were affected by the supporting-electrolyte cations (see Table 2). The interaction between a lithium ion and the anion from substituted phenol has been suggested on the basis of the UV and visible absorption spectra.[13]

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