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Polarographic Studies of the Ion-pair Formation and Conjugation Reactions of Acetate and Benzoate Ions in Acetonitrile

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An acetate ion (A^-) formed a homoconjugated species, $A^-(HA)_2$, with 2 molecules of acetic acid (HA) in the presence of a large excess of HA in an acetonitrile solution. In the presence of both acetic acid and $LiClO_4$, one molecule of HA was derived from $A^-(HA)_2$ by means of a lithium ion to from an ion-paired species, HA_2^-Li, as follows: $A^-(HA)_2+Li^+ \overset{K_{ex}}{\rightleftharpoons} HA_2^-Li^+ + HA$. The equilibrium constant, K_{ex}, was evaluated as 1.1×10^4 from the shift in the anodic half-wave potential of the acetate ion. As for the benzoate ion (A'^-) and HA′, similar reactions occured, and the constant of the exchange reaction was evaluated as 6×10^3. The effect of the sodium ion and HA (or HA′) on the A^- (or A'^-) ion was complicated. On the other hand, the presence of $[M(A')_2]^-$ (M=Li, Na, K) was proved by the shift of the cathodic wave of the alkali metal. The addition of water caused the apparent stability constant of $[Li(A')_2]^-$ to decrease extremely.

Polarography has been a powerful means to determine the stability constants of metal complexes. The difference in half-wave potential between a complex and the free metal ion is used in a usual calculation. In some cases,[1)] however, the anodic wave-height was measured in order to evaluate the concentration of the uncomplexed ligand in the solution.

Reilley *et al.*[2)] have reported an interesting method to obtain a stability constant; their method is based on the shift of the anodic wave of the complex-forming agent in the presence of an excess of the metal ions. At the same time, however, they pointed out a limiting feature of that method: the wave-height decreased in the cases of interactions between EDTA and Pb^{2+}, *etc.* in aqueous solutions. Therefore, we have modified the relationship proposed by Reilley *et al.* and successfully applied it to an ion-pair formation reaction in a nonaqueous solvent. Using this method, we have evaluated the equilibrium constants from the shift in the half-wave potential of the anodic wave of acetate or benzoate ions in the presence of an excess of alkali metal ions. This method was also extended to a reaction for not only an ion-pair formation, but also a homo- or heteroconjugation.

Kolthoff *et al.*[3,4)] have reported, based on potentiometric or conductometric measurements, that acetate or benzoate ions associate (homoconjugate) with one molecule of acetic or benzoic acid in acetonitrile. In the same solvent, on the other hand, Pawlak *et al.*[5)] showed the association of acetate and other carboxylate ions with 2 molecules of the corresponding acid. We were much interested in the above inconsistency and the fact that the solubilities of alkali carboxylates are much increased by the addition of a large amount of acetic acid in a protophobic solvent.

In the present paper, we studied, by means of polarography, the conjugation and ion-pair formation reactions for acetate and benzoate ions in the presence of large amounts of acetic and benzoic acids, and alkali metal ions in acetonitrile. In acetonitrile, the acetate ion or its homoconjugated ion gives a well-defined anodic wave,[6)] although the polarographic anodic wave of the acetate ion is difficult to observe in an aqueous solution. On the other hand, the formation of alkali metal dibenzoate complexes were proved by the shift of the cathodic wave of the alkali metal in the presence of a large excess of the benzoate ion. Moreover, the effect of water on the apparent stability constant for the lithium dibenzoate complex was examined in the solvent.

Experimental

The tetraethylammonium acetate and benzoate were prepared according to the procedure of Kolthoff *et al.*[3,7)] The methods of purifying acetonitrile (MeCN) and of preparing Et_4NClO_4, $LiClO_4$, $NaClO_4$, and $KClO_4$ have been described elsewhere.[8)] Benzoic acid of a GR grade was dried in a vacuum at room temperature. The other GR-grade chemicals were used without further purification. Polarograms were recorded with a Yanagimoto Polarograph, Model p-1000, and a Watanabe X-Y recorder, Model WX-4401-L0. The rate of the potential sweep was 2 mV/s. The dropping mercury electrode had the following open-circuit characteristics: $m=1.26$ mg/s and $\tau=3.2$ s in a 0.1 M** Et_4NClO_4–MeCN solution at $h=50$ cm. All the polarographic measurements were carried out in an H-type cell at 25.0+0.2 °C. The reference electrode was a silver-silver perchlorate electrode, Ag/0.1 M $AgClO_4$–MeCN.

Results and Discussion

Effects of Acetic Acid and Lithium Ion on Anodic Wave of Acetate Ion. The acetate ion gave an anodic wave at −0.45 V (0.35 mM) in acetonitrile containing 0.1 M Et_4NClO_4 as a supporting electrolyte. The wave height was linear to the concentration of the acetate ion over the range of 0.1—1 mM. The half-wave potential shifted slightly to the negative side with an increase in the concentration of the depolarizer. The anodic wave is certainly based on the dissolution of the mercury(I) ion in an acetonitrile solution, judging from the linearity of the relation of E *vs.* $\log(i_d-i)$ and the extremely small solubility of $Hg_2(CH_3COO)_2$ in the solvent. The variation in the limiting current with the height of the mercury head (h) indicated diffusion control.

When acetic acid (HA) was added to the solution of the acetate ion, the half-wave potential of the anodic wave shifted greatly to the positive potential. Figure 1 shows the shift of the half-wave potential in the presence of acetic acid. The ten-fold increase in the

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** Throughout this paper, $1\ M=1\ mol\ dm^{-3}$.

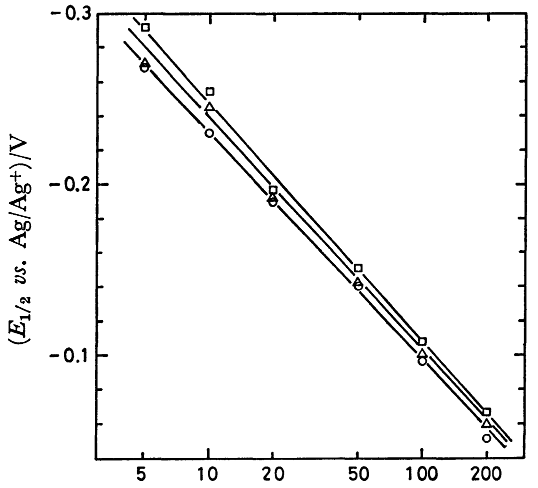


Fig. 1. Effect of acetic acid on the anodic half-wave potential of acetate ion in acetonitrile solutions containing 0.1 M Et_4NClO_4. (○) 0.18, (△) 0.35, (□) 0.70 mM of acetate ion.

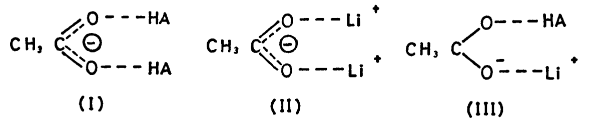
concentration of acetic acid caused the half-wave potential for the acetate ion to shift 120 mV positively. The anodic waves were diffusion-controlled and reversible when 10 mM or more of acetic acid was added to 0.35 mM of the acetate ion. We applied the following equation to the homoconjugation reaction:

$$(E_{1/2})_c = (E_{1/2})_s + \frac{0.059}{n}\log K_{\text{homo}} + \frac{0.059}{n}p\log[\text{HA}], \qquad (1)$$

assuming the activity and diffusion coefficients of A^- and the homoconjugated species to be equal to each other; here, $(E_{1/2})_s$ is the half-wave potential of the acetate ion, $(E_{1/2})_c$ is the $E_{1/2}$ of the homoconjugated species for the acetate ion, and K_{homo} is the formation constant of the homoconjugation reaction. We obtained $p=2.0$ and $K_{\text{homo}}=$*ca.* $5.7\times10^7\ M^{-2}$ from the slope of the graph and the $(E_{1/2})_c-(E_{1/2})_s$ value, since $n=1$ in the case of the formation of the mercury(I) salt.[9] The above results show that the acetate ion forms a very stable homoconjugated species, $A^-(HA)_2$ with 2 molecules of acetic acid (see also Scheme 1):

$$A^- + 2HA \underset{}{\overset{K_{\text{homo}}}{\rightleftarrows}} A^-(HA)_2. \qquad (2)$$

The addition of another acid, such as propionic and benzoic acid or phenol, to a solution of the acetate ion also gave a slope of *ca.* 120 mV, which indicated that heteroconjugated species, $A^-(HX)_2$ were formed.



(I) (II) (III)

Scheme 1.

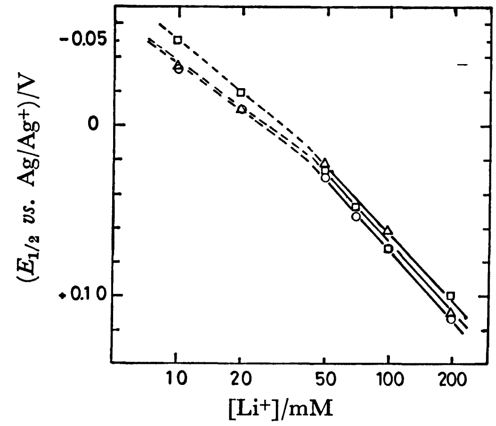


Fig. 2. Effect of Li^+ on the $E_{1/2}$ of acetate ion. (○) 0.18, (△) 0.35, (□) 0.70 mM of acetate ion. Total ionic strength was kept formally 0.1 M with Et_4NClO_4, except 0.2 $LiClO_4$ solution.

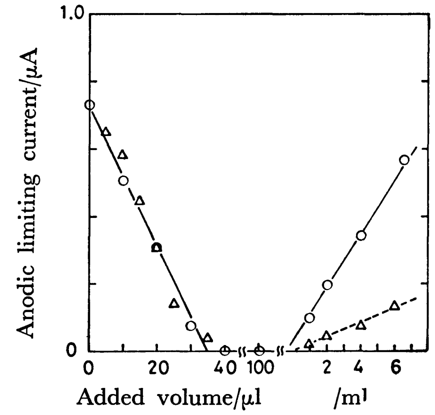


Fig. 3. Amperometric titration curves for 0.35 mM acetate ion of 20 ml by 0.2 M $LiClO_4$ and $NaClO_4$. (○) $LiClO_4$, (△) $NaClO_4$. The changes of total volume were corrected.

Acetate ion gave an anodic wave in a 0.1 M $LiClO_4$–MeCN solution at an extremely positive potential (+0.06 V) compared with that in an Et_4NClO_4 solution. The shift of $E_{1/2}$ to the positive potential was considered to be caused by ion-pair (or complex) formation between Li^+ and the acetate ion. The effect of the Li^+ concentration on the half-wave potential for the acetate ion was also examined, as shown in Fig. 2. However, when the concentration of $LiClO_4$ was low (1—20 mM) for the 0.35 mM acetate ion, the wave-height of the acetate ion was extremely depressed. The decrease in the anodic wave-height would be caused by the precipitation of CH_3COOLi. This strange phenomenon was clearly exhibited when 20 ml of a 0.35 mM acetate-ion solution was titrated by a 0.2 M $LiClO_4$–MeCN solution, as shown in Fig. 3. The anodic wave (−0.45 V) of the acetate ion disappeared at the 1:1 equivalent point. Again, an anodic wave from the acetate ion appeared at −0.05—+0.06 V for the addition of a large excess of Li^+. From an analysis similar to that above, with 50—200 mM of $LiClO_4$, we concluded that, in the presence of a large excess of Li^+, the acetate ion exists in the form of $CH_3COO^-(Li^+)_2$, which is electrochemically active. We had the formation constant of $K_f=1\times10^{11}\ M^{-2}$ for the following reaction:

$$CH_3COO^- + 2Li^+ \overset{K_f}{\rightleftarrows} CH_3COO^-(Li^+)_2. \qquad (3)$$

When 0.1 M $NaClO_4$ was used as the supporting electrolyte, the solution of the acetate ion formed a white precipitate (CH_3COONa, $pK_{sp}=9.1$ by Kolthoff and Chantooni[10]) and showed only a very small anodic wave at −0.1 V. A titration curve for the 0.35 mM acetate ion obtained by the use of 0.2 M $NaClO_4$ is also shown in Fig. 3.

Next, we shall consider the interaction between $A^-(HA)_2$ and Li^+. We added both acetic acid and the Li^+ ion in various concentrations to solutions of the acetate ion, and then recorded the half-wave potentials. The waves were diffusion-controlled and were reversible when sufficient amounts of acetic acid and Li^+ were added. If the $E_{1/2}$ of $A^-(HA)_2$ is taken as the standard,[11] we obtain the following equation by assuming conditions similar to Eq. 1:

$$(E_{1/2})_c = (E_{1/2})_s + 0.059 \log K_{ex} + 0.059 p \log[HA] + 0.059 q \log[Li^+], \quad (4)$$

where $(E_{1/2})_s$[12] is the half-wave potential of $A^-(HA)_2$ and $(E_{1/2})_c$ is the $E_{1/2}$ of the resultant species. From the data in Fig. 4, we obtained $p=-1$ and $q=1$. If the value of p were zero ($p=0$), the following equation would be realized. $A^-(HA)_2+Li^+ \rightleftarrows A^-(HA)_2Li^+$. However, in practice, $p=-1$, which shows that one HA is present on the right-hand side of the reaction equation. Also, the fact that $q=1$ shows that one Li^+ ion reacts with $A^-(HA)_2$ as follows:

$$A^-(HA)_2 + Li^+ \overset{K_{ex}}{\rightleftarrows} HA_2^- Li^+ + HA. \quad (5)$$

The above equation shows the formation of the species $HA_2^-\ Li^+$, which consists of an acetate ion, an acetic acid, and a lithium ion. In Eq. 4, if we take $[HA]=[Li^+]$, the value of K_{ex} can be easily obtained from the value of $(E_{1/2})_c-(E_{1/2})_s$, since $-p=q=1$. The experimental results are shown in Table 1. The obtained values coincide well with one another for 0.18—0.7 mM) of the acetate ion containing 20—200 mM of the acid and the Li^+ ion (*e.g.*, $[HA]=[Li^+]=50$ mM). As an average, we obtain the equilibrium constant of the exchange reaction (the formation constant of the species) $K_{ex}=1.1\times10^4$. Therefore, when the acetate ion is present with both acetic acid and the Li^+ ion in acetonitrile, $HA_2^-Li^+$ is the predominant species and the concentration of $A^-(HA)_2$ becomes negligibly small.

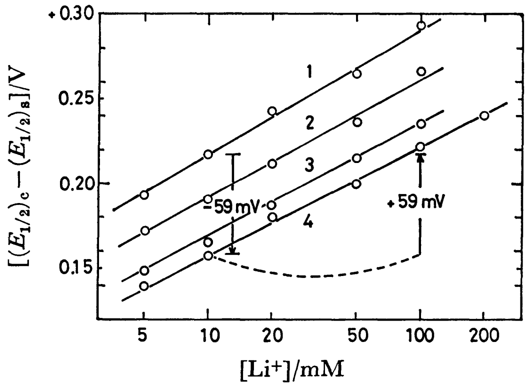


Fig. 4. Shift in $E_{1/2}$ of acetate ion by the presence of both acetic acid and Li^+ ion. (1) 20, (2) 50, (3) 100, (4) 200 mM of the acid. $[CH_3COO^-]=0.35$ mM. See the text for $(E_{1/2})_c-(E_{1/2})_s$.

Table 1. The difference in half-wave potential for acetate ion in solutions containing the same concentration of acetic acid and Li^+

Concn of HA and Li^+/mM	$[(E_{1/2})_c-(E_{1/2})_s{}^{a)}]$/V		
	0.18	0.35	0.70 mM of acetate ion
20	0.247	0.243	0.232
50	0.246	0.238	0.240
100	0.241	0.235	0.240
200	0.237	0.238	0.236
Av.	0.243	0.238	0.237
$\log K_{ex}$	4.10	4.02	4.01
	$K_{ex}=1.1\times10^4$		

a) See the text.

Kolthoff *et al.*[3] reported $K_{homo}=5\times10^3\ M^{-1}$ as the homoconjugation reaction of the acetate ion ($A^- + HA \overset{K_{homo}}{\rightleftarrows} HA_2^-$) in acetonitrile. With the help of the value given by them, we obtained the ion-pair formation constant $K_{ion}=$ *ca.* $1\times10^8\ M^{-1}$ for the following reaction: $HA_2^- + Li^+ \overset{K_{ion}}{\rightleftarrows} HA_2^-\ Li^+$.

Effects of Benzoic Acid and Lithium Ion on Anodic Wave of Benzoate Ion. The benzoate ion gave an anodic wave at a slightly more positive potential (−0.36 V at 0.3 mM) than the acetate ion in an acetonitrile solution containing 0.1 M Et_4NClO_4 as the supporting electrolyte. The wave-height was linear to the concentration of the benzoate ion over the range of 0.2—1 mM. The other behavior of the anodic wave of the benzoate ion was similar to that of the acetate ion.

The addition of benzoic acid (HA′) to the benzoate solution caused the half-wave potential of the anodic wave to shift positively. From the analysis of Eq. 1, we obtained $p=2.0$ and $K_{homo}=$ *ca.* $1\times10^7\ M^{-2}$ with 0.2—0.4 mM of the benzoate ion and 20—200 mM of benzoic acid. Here, the formation of homoconjugated species, $A'^-(HA')_2$, with 2 molecules of benzoic acid (HA′) was proved to be present, as in the case of the acetate ion.

In a 0.1 M $LiClO_4$–MeCN solution, the anodic wave from the benzoate ion appeared at *ca.* +0.085 V. However, the calibration curve did not show a linearity, for the solution formed a white precipitate (C_6H_5COOLi) at higher concentrations of benzoate (more than 0.4 mM). Despite this, the formation constant of $C_6H_5COO^-(Li^+)_2$ was evaluated to be *ca.* $1\times10^9\ M^{-2}$ with 0.2 mM benzoate and 100—200 mM $LiClO_4$.

When both benzoic acid and Li^+ were present with the benzoate ion, the half-wave potential of the benzoate ion shifted in a manner similar to that in the case of the acetate ion, shown in Fig. 4. From the same analysis as Eq. 4, we obtained the equilibrium constant of 6×10^3 for the following exchange reaction:

$$A'^-(HA')_2 + Li^+ \overset{K_{ex}}{\rightleftarrows} HA'^-_2 Li^+ + HA'. \quad (6)$$

The addition of benzoic acid and Na^+ instead of Li^+

to a benzoate solution caused the half-wave potential of the benzoate ion to shift in a strange manner: the value of $q=1$, but $p=ca.\ -0.5$, so the results could not be explained well. Incidentally, the behavior of the acetate ion in the presence of acetic acid and Na^+ was much more complicated.

Other Interactions between Benzoate Ion and Alkali-metal Cations. When a benzoate-ion solution was amperometrically titrated by $LiClO_4$, the height of the anodic wave of the benzoate ion decreased and the wave disappeared at 1:1 equivalent point. Then, again, with a large excess of $LiClO_4$ an anodic wave from the benzoate ion appeared at a much more positive potential (+0.05—0.08 V) than the initial potential (−0.36 V), in a manner similar to that in the case of the acetate ion, shown in Fig. 3. However, the decrease in the benzoate wave-height was completely different from that in the case of the acetate ion: the wave of the acetate ion decreased linearly with the addition of $LiClO_4$. On the other hand, the total wave of the benzoate ion did not decreased so much with the addition of $LiClO_4$, at first, but then it suddenly disappeared at the equivalent point (see Fig. 5). By a detailed examination of the wave, the anodic wave of benzoate could be divided into two parts, that is, the first wave of *ca.* −0.36 V and the second wave of around −0.16 V. The first wave disappeared at a half of the 1:1 equivalent point. The second wave gradually became large and reached its maximum at the half-equivalent point. The composition ratio of Li^+ to the benzoate ion is 1:2 at the maximum point. Therefore, the formation of the lithium dibenzoate complex, $[Li(C_6H_5COO)_2]^-$, was suggested in the presence of an excess of benzoate ions. Therefore, the following experiments were performed in order to prove the formation of the complex. The cathodic wave of the lithium ion (0.5 mM) being used as the indicator, the shift of the wave was measured in the presence of a large amount of benzoate ions (5—20 mM). The half-wave potential of lithium shifted greatly to a negative potential, *e.g.*, 0.75 V at 10 mM of benzoate, and the presence of more than 50 mM of benzoate caused a wave shift behind the cut-off. The analysis of the results proved the presence of a 1:2 complex and gave the formation constant, K_f, of $10^{16.7}\ M^{-2}$;

$$Li^+ + 2C_6H_5COO^- \overset{K_f}{\rightleftarrows} [Li(C_6H_5COO)_2]^-. \qquad (7)$$

When 0.48 mM of the benzoate ion was titrated by the use of 0.2 M $NaClO_4$, the anodic wave of the benzoate ion did not decrease linearly; therefore, the formation of the sodium dibenzoate complex was suggested. Similar experiments for 0.5 mM of sodium ions with 50—100 mM of benzoate ions gave the formation constant, K_f, of $10^{8.4}\ M^{-2}$ for $[Na(C_6H_5COO)_2]^-$. Even the potassium ion was complexed by the benzoate ion in an acetonitrile solution. The formation constant for $[K(C_6H_5COO)_2]^-$ was given as $10^{4.2}\ M^{-2}$ by experiments with 0.5 mM K^+ and 30—100 mM benzoate ions. When the 0.48 mM benzoate ion was titrated by $KClO_4$, however, the anodic wave of the benzoate ion did not completely disappear, even in the presence of a large excess of $KClO_4$. This phenomenon is probably the result of the large solubility of C_6H_5COOK in acetonitrile. The value of the solubility products for potassium benzoate could not easily be found in the literature, although the values for lithium and sodium benzoates in acetonitrile have been reported to be $pK_{sp}=10.5$[4] and 8.7[10] respectively.

The effect of water on the stability constant of the lithium dibenzoate complex was also examined. As is shown in Fig. 6, the apparent stability constant of the lithium dibenzoate complex decreased extremely with an increase in the concentration of water. In the calculation of the constant, the shift of the half-wave potential of the free lithium ion was corrected because the half-wave potential of the lithium ion was negatively shifted by the addition of water to an acetonitrile solution without a benzoate ion. The shift in the half-wave potential might be caused by the difference in the liquid-junction potential or solvation. By extrapolation, the formation constant of the lithium dibenzoate complex was estimated to be $\log K_f \approx 0$ for 100% water. This fact suggests that the lithium dibenzoate complex does not actually form in an aqueous

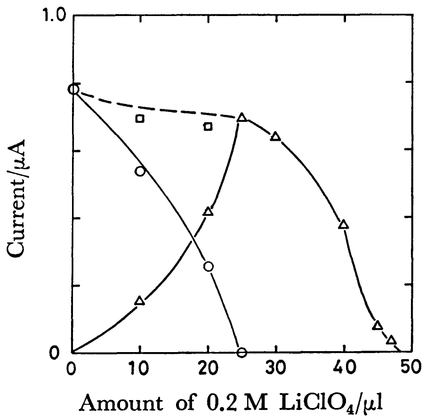


Fig. 5. Amperometric titration curves for 0.48 mM benzoate ion of 20 ml by 0.2 M $LiClO_4$. (○) the first wave of ca. −0.36 V, (△) the second wave of around −0.16 V, (□) total of the two waves.

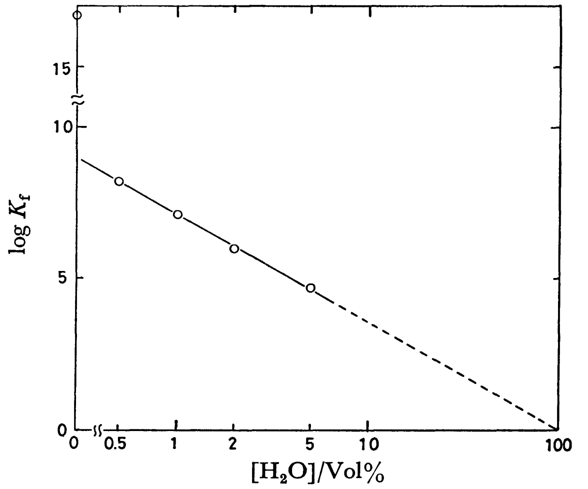


Fig. 6. Effect of water on the apparent stability constant, K_f.

solution. Another experiment showed that a benzoate ion is conjugated by 2 molecules of H_2O in an acetonitrile solution.

The interaction between the acetate ion and alkali metal cations was not fully examined because the behavior of complex reactions for them was complicated, and also because the solubility of tetraethylammonium acetate was much smaller (less than 30 mM) than that of the benzoate ($\approx$200 mM) in acetonitrile.

Conclusion

The results reported in this paper indicate that the formation of homoconjugation for acetate or benzoate is affected by the alkali metal ions in acetonitrile; this is the cause of the difficulty in measuring the precise formation constant of a conjugation reaction by the solubility method.

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9) Because of the formation of the insoluble salt with mercury, $E=E^0_{Hg_2{}^{2+}}+\frac{0.059}{2}\log S-0.059\log[A^-]_0=E^{0\prime}-0.059\log[A^-]_0$, where $S=[Hg_2{}^{2+}]_0[A^-]_0^2$. The diffusion of acetate ions towards the electrode surface is governed by the Ilkovic equation: $-i=\kappa([A^-]-[A^-]_0)=-I_d-\kappa[A^-]_0$. Substituting for $[A^-]_0$ in the former equation leads to: $E=E^{0\prime}-0.059\log\frac{i-I_d}{\kappa}$, $E_{1/2}=E^{0\prime}-0.059\log\frac{(-I_d)}{2\kappa}=E^{0\prime}-0.059\log\frac{[A^-]}{2}$. As for the homoconjugated species; $-i=\kappa'([A^-(HA)_p]-[A^-(HA)_p]_0)=-I_d'-\kappa'[A^-(HA)_p]_0=-I_d'-\kappa'[A^-]_0K[HA]_0{}^p$, $E=E^{0\prime}-0.059\log\frac{i-I_d'}{\kappa'}+0.059\log K[HA]_0{}^p$. As sufficient [HA] is present, $E_{1/2}=E^{0\prime}-0.059\log\frac{(-I_d')}{2\kappa'}+0.059\log K[HA]^p=E^{0\prime}-0.059\log\frac{[A^-(HA)_p]}{2}+0.059\log K[HA]^p$. When $[A^-]\approx[A^-(HA)_p]$, $(E_{1/2})_c-(E_{1/2})_s=0.059\log K+0.059\,p\log[HA]$. Therefore, $n=1$ in Eq. 1.

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11) We can take $A^-(Li^+)_2$ as the standard, and the conclusion is as follows: $A^-(Li^+)_2+HA \overset{K}{\rightleftharpoons} HA_2{}^-Li^++Li^+$, $K=ca.\ 1.4\times10$.

12) For example, when $[HA]=50$ mM and $[Li^+]=100$ mM, $(E_{1/2})_s$ is the $E_{1/2}$ of $A^-(HA)_2$ at $[HA]=50$ mM and Li^+-free.