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Effect of Molecular Size on the Association of *p*-Quinone Anion and Lithium Ion in *N,N*-Dimethylformamide

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Synopsis. Ion pair formation effects of metal ions on the electro-reduction of *p*-quinones in *N,N*-dimethylformamide were studied systematically by polarography. The formation constants of 1 : 1 and 1 : 2 associates, as evaluated by the $1/F_0^2$-weighted least squares method, decrease with increase in the anion size.

In a previous paper,[1] the authors presented effects of the carbonyl group geometry on ion association of several types of carbonyl compound anions and metal cations. The degree of the half-wave potential shifts due to the ion pair formation was observed in the order of *p*-quinones<ketones<*o*-quinones with various uni- and bivalent metal cations. The interaction between the anion and cation can be considered to occur mainly near the carbonyl oxygen of the anion. Taking into consideration the probability of two ions to come into contact, stronger association is expected for the *p*-quinone ion pairs than for the ketone ones. However, the experimental results showed the contrary and, therefore, it was concluded that the factor affecting the ion pair formation of these compounds is not the number of carbonyl groups but their geometry (*i.e.*, charge localization).

In the present paper, we will discuss another factor affecting the association behavior of carbonyl compound anions, *i.e.*, their anion size, studied by polarography. *p*-Quinones were studied because their half-wave potential shifts due to ion pair formation are not large and, therefore, the above effect could be expected to be predominant compared to the geometry effect. In these systems, however, formation of 1 : 2 associates as well as 1 : 1 ones must be taken into consideration.

Experimental

Reagent grade *p*-quinones were used without further purification except for 9,10-anthraquinone which was recrystalized twice from ethanol. Reagent grade *N,N*-dimethylformamide (DMF, Nakarai Chemicals Co.) was distilled by the method described previously.[2] Polarographic measurements were made with a PAR model 173 and a Yanaco P-1000 at 25 °C. The potential scan rate used was 0.5 mV/s and the initial potential was measured to 0.1 mV with a Digital Multimeter TR-6854 (Takeda Riken Co.). The measured value of potential gave a precision of about 0.5 mV. Numerical calculation was carried out on a FACOM M-200 computer at the data processing center of Kyoto University with time sharing services.

Results and Discussion

All *p*-quinones studied underwent 2 one-electron reductions and generated stable mono- and dianions. In the presence of excess alkali metal ion, it is known from ESR studies in ether that 1 : 2 associates as well as 1 : 1 ones are formed.[3] In a previous study,[1] their presence was confirmed by polarography even in the dipolar solvent of DMF, provided the metal ion was present in large excess.

The polarographic half-wave potential shift, $\Delta E_{1/2}$, due to ion pair formation can be explained by the following mechanism: after the first one-electron reversible reduction, the following equiliblium formulas are possible:

$$Q^{-\cdot} + M^+ \rightleftharpoons Q^{-\cdot}M^+, \qquad (1)$$

$$Q^{-\cdot}M^+ + M^+ \rightleftharpoons Q^{-\cdot}(M^+)_2, \qquad (2)$$

where $Q^{-\cdot}$, M^+, $Q^{-\cdot}M^+$, and $Q^{-\cdot}(M^+)_2$ represent a *p*-quinone anion, a metal cation, 1 : 1 associates and 1 : 2 associates, respectively. Accordingly, 59 and 118 mV potential shifts should be observed at 25 °C for the quantitative formation of 1 : 1 and 1 : 2 associates with tenfold increase in the metal ion concentration, respectively. For the evaluation of association constants from the polarographic results, the $1/F_0^2$-weighted least squares method described by Momoki *et al.* was applied.[1,4] The variation in the junction potential between a reference electrode and the solution with the metal ion concentration was found to be negligible from the following experimental result: the half-wave potential due to the reduction of potassium or sodium perchlorate remained constant with various concentrations of lithium perchlorate where the ionic strength of the solution was adjusted to 0.3 M (1 M = 1 mol dm^{-3}) with tetraethylammonium perchlorate. As seen from Fig. 1, $\Delta E_{1/2}$ was largest for 1,4-benzoquinone and

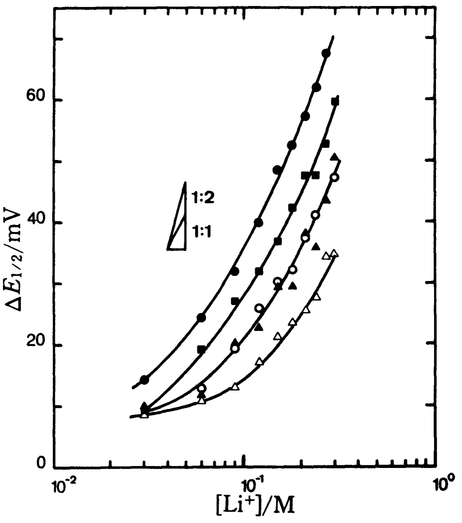

Fig. 1. Relationships between first half-wave potentials of *p*-quinons and lithium ion concentrations.
1,4-Benzoquinone (●), 1,4-naphtoquinone (■), 9,10-anthraquinone (○), 5,12-naphtacenequinone (▲), anthanthrone (△). Slopes for the quantitative formation of 1 : 1 and 1 : 2 associates are also shown in the figure.

TABLE 1. ASSOCIATION CONSTANTS AND CONTACT DISTANCES OF ION PAIRS OF *p*-QUINONE ANIONES WITH LITHIUM IONS AT 25 °C[a)]

Compound	K_1/M^{-1} [b)]	K_2/M^{-2} [b)]	$10^{10}a/\mathrm{m}$
1,4-Benzoquinone	18.9±1.2	108.5±7.0	2.45
1,4-Naphtoquinone	15.6±1.4	41.4±6.5	2.61
9,10-Anthraquinone	11.5±0.8	18.4±3.5	2.95
5,12-Naphthacenequinone	8.1±1.5	20.4±6.0	3.6
Anthanthrone	7.3±1.3	9.8±4 0	4.0

a) Ionic strength was adjusted to 0.3 M with tetraethylammonium perchlorate. b) K_1 and K_2 represent formation constants of 1 : 1 and 1 : 2 associates, respectively.

decreased with increase in molecular size. The associates of 1 : 2 were also formed at higher lithium ion concentrations. Table 1 shows the results of the above calculation together with 95% confidence levels based on Student's T. From this table, it is obvious that the formation constants of both the 1 : 1 and 1 : 2 associates decrease with increase in anion size. Although the 1 : 1 associate has a zero net charge, the second cation can approach it because it constitues an electrostatic dipole.

For the association between two spherical univalent ions, the Fuoss equation can be applied[5)] and the formation constant, K_A (M^{-1}), is expressed by

$$K_\mathrm{A} = (4\pi L a^3 \times 10^{27}/3)\exp(e^2/4\pi\varepsilon_0\varepsilon_\mathrm{r} a k T), \qquad (3)$$

where L, a, and ε_r represent the Avogadro constant, the contact distance between two ions (m), and the relative permittivity of the solvent, respectively, and the other symbols are used with usual meanings. In Table 1, the a-values for 1 : 1 associates calculated from the experimental results are also given. Applying the Fuoss equation, we ignored the solvent dielectric saturation effect, which often makes the ε_r-value decrease in the case of relatively small ions. This will cause relatively large increase in the contact distance a. Although it is also difficult to estimate a-values of actual ion pairs, reasonable correlations were obtained between the calculated a-values and the anion molecular sizes. From the formation constant 1.0×10^4 M^{-1} of Li^+-9, 10-phenanthraquinone$^{-\cdot}$ (PQ$^{-\cdot}$) evaluated in our previous study,[1)] an a-value of 1.0×10^{-10} m was estimated. Since the van der Waals' radius of the oxygen atom is about 1.4×10^{-10} m, the lithium ion appears to interact solely with carbonyl oxygens of PQ$^{-\cdot}$. Therefore, it can be proposed that the association behavior of *o*-quinone anions is not influenced by their size. It was confirmed from the fact that the $\Delta E_{1/2}$'s of 1,2-naphtoquinone and PQ are 197 and 201 mV in the presence of 0.1 M lithium perchlorate in DMF, respectively.[1)] Consequently, for the anions having large formation constants (charge-localized anion), their association constants are determined only by the geometry of carbonyl groups of the anion. On the other hand, for the anions possessing small formation constants (charge-delocalized anion in aprotic polar solvents), the most important factor influencing the association constant can be said to be the molecular size. In the case of the latter, the carbonyl oxygen plays no important role in comparison with the former, and the latter can be considered as being almost spherical in shape. In conclusion, in the *p*-quinone anions their ring portions interact with the cation as well as the carbonyl oxygens, as suggested by the large a-values. This interaction becomes weak as their anion sizes increase, which, of course, cause their formation constants to be small.

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