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Homogeneous and Electrochemical Electron-Transfer Reaction of Nitrobenzene Anion Radical Dissolved in Nitrobenzene

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Nitrobenzene anion radical was stably prepared by the electrolytic reduction of nitrobenzene solution containing various kinds and amounts of tetraalkylammonium perchlorates. The rate constants of homogeneous electron-transfer reactions of these nitrobenzene anion radicals with nitrobenzene molecules as a solvent were determined by ESR method at various temperatures. These rate constants at 25 °C were about $10^7\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ and comparable with the rate constant of electron-transfer reation between nitrobenzene and its anion radial in *N,N*-dimethylformamide. The quasi-first order rate constants evaluated from these rate constants were about $10^8\,\mathrm{s^{-1}}$ and were larger than the rate constants of the intramolecular electron-transfer reactions of the anion radical of bis(*p*-nitrophenyl) compounds except for bis(*p*-nitrophenyl)methane. The absorption spectrum of the solution of nitrobenzene anion radical in nitrobenzene containing 0.1 M tetrabutylammonium perchlorate or 0.1 M tetraethylammonium perchlorate showed an additional weak peak at about 800 or 900 nm as well as the ordinary peak. The light energies of these additional peaks were in good agreement with the energy values of the optical electron-transfer reactions evaluated according to the theory of Hush from the activation energies of corresponding thermal electron-transfer reactions. The rate constants of electrochemical electron-transfer reactions and the diffusion coefficients of nitrobenzene anion radical in nitrobenzene were also measured.

Nitrobenzene (NB) is well-known to be reduced to a stable anion radical in an aprotic solvent as *N,N*-dimethylformamide (DMF),[1] and also can be used as a solvent at room temperature. An anion radical molecule dissolved in a solvent composed of its parent molecules such as NB^- in NB, can exchange its electron with contiguous parent molecules. Such an electron-exchange reaction is different from usual electron-exchange reactions in the following points: Anion radical and its parent molecules are always in contact with one another, and therefore do not require their encounter prior to the electron transfer between them. This would be expected to cause the following unique behavior of such a system. According to Hush,[2] electron-transfer reactions can be caused not only by thermal energy but also by optical energy when two reactants are in the immediate neighbourhood of each other. He discussed the relation between the activation energy of a thermal electron-transfer reaction and the light energy of the corresponding optical electron-transfer reaction. In the electron-transfer systems examined by them, however, only one of the values of the electron-transfer rate and the absorption maximum was determined. Therefore, the theory about the relation between them has not yet been proved experimentally. Since NB^- molecules are always in the immediate neighbourhood of NB molecules in the considering NB^-/NB system, the possibility of the occurrence of the optical electron-transfer reaction between them may be very high. Furthermore, the rate constant of thermal electron-transfer reaction between them can be easily determined by ESR.

On the other hand, as suggested by Levich,[3] Dahms,[4] and Ruff and Friedrich,[5] the large increase of the apparent diffusion coefficient of anion radicals due to an electron-hopping mechanism may be expected to occur in these systems.

In this paper, we report the rate constants and the activation energies of homogeneous electron-transfer reactions, the absorption spectra, the rate constants of electrochemical electron-transfer reactions, and the diffusion coefficients of NB^- prepared by electrolytic reduction of NB containing various tetraalkylammonium perchlorates. Furthermore, we will examine the possibility of the occurrence of an optical electron-transfer reaction and the increase of the diffusion coefficients of NB^- in this system by making use of these results.

Experimental

Reagents. Nitrobenzene commercially obtained was purified by passing through a column packed with activated alumina from ICN Pharmaceuticals GmbH & Co. Tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) used as supporting electrolytes were prepared and purified as described in the previous paper.[6]

Cell and Electrodes. Electrolytic cell used for electrochemical measurements was an air-tight Pyrex glass cell composed of three compartments. For voltammetric measurements, a platinum gauze and a platinum sphere were used as the counter and working elctrodes respectively. The reference electrode used for the measurements of cyclic voltammogram (CV) for a NB solution without NB^- was composed of a silver wire dipped in the NB solution which was saturated with $AgNO_3$ and contained the same supporting elctrolyte as the test solution. The reference and the counter electrode used for the measurements of CV for a NB solution containing NB^- was the platinum gauze electrode in the test solution. For bulk electrolysis, the platinum gauze electrode was used as the working electrode, and a platinum spiral wire was used as the counter electrode. Bulk electrolysis was carried out while stirring the solution with a magnetic stirrer.

Electrochemical Measurements. The anion radical of NB

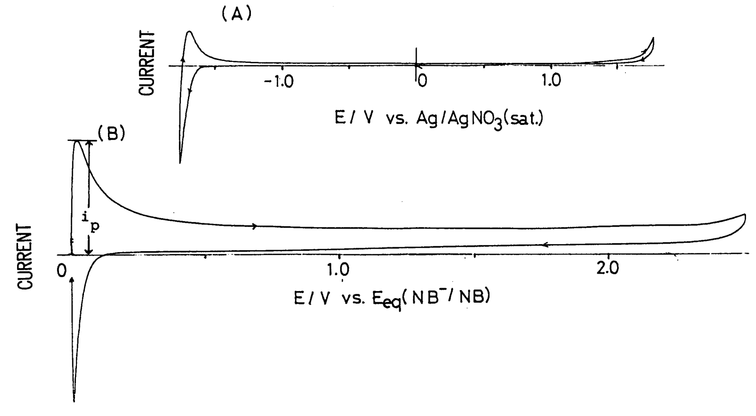


Fig. 1. Cyclic voltammograms of NB containing 0.1 M TEAP; (A) without NB$^-$, (B) with 0.8 mM NB$^-$. Scan rate: 0.1 V s^{-1}.

was prepared by electrochemical reduction. The concentration of NB$^-$ was determined by the quantity of electricity passed during the electrolysis. Diffusion coefficients were determined by potential step chronoamperometry. Standard rate constants of the electrochemical electron transfer reactions were determined by the galvanostatic double pulse (gdp) method. A conventional potentiostat and function generators assembled from operational amplifiers were used for linear sweep voltammetry. Galvanostatic double pulse measurements were performed on an apparatus devised in this laboratory.[7]

ESR Measurements. ESR spectra were measured with a JEOL JES3BSX ESR spectrometer equipped with a variable temperature adapter.

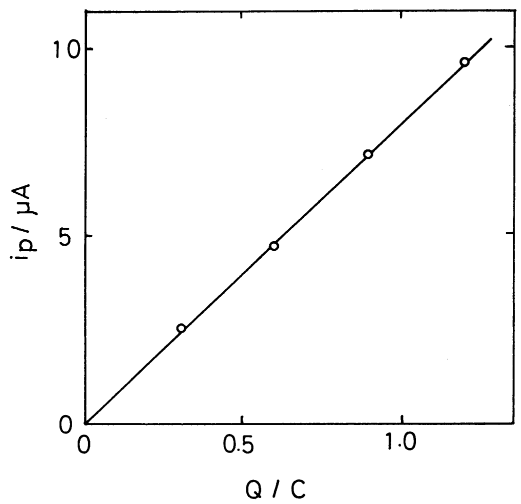


Fig. 2. Dependence of peak current, i_p, on the quantity of electricity, Q, consumed during the electrolytic reduction of NB containing 0.1 M TEAP.

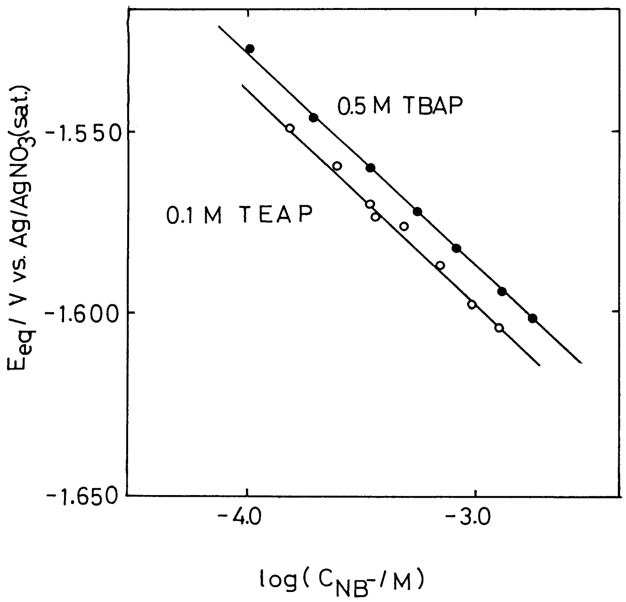


Fig. 3. Nernst plots for the NB$^-$/NB systems in NB containing 0.1 M TEAP and 0.5 M TBAP.

Results and Discussion

Electrochemical Preparation of NB$^-$ in NB. Figure 1 (a) shows the CV of a solution of NB containing 0.1 M TEAP (1 M=1 mol dm^{-3}). This CV showed a sharp cathodic current rise corresponding to the reduction of NB to NB$^-$, and an anodic peak corresponding to the oxidation of NB$^-$ at about −1.6 V. During the bulk electrolysis with constant current, the solution gradually became brown coloured. Figure 1 (b) shows the CV of a solution of NB$^-$ in NB containing 0.1 M TEAP prepared by the eletrolytic reduction as described above. This CV was obtained by scanning from the equilibrium potential of NB$^-$/NB. It shows an anodic peak current (illustrated as i_p in Fig. 1 (b)) corresponding to the oxidation of NB$^-$ existing in the test solution, at the potential about 25 mV positive from the equilibrium potential.

Figure 2 shows the dependence of i_p for such solution on the quantity of electricity (Q) consumed during the electrolytic preparation of the solution. Good linearity was attained between i_p and Q. Moreover, the values of i_p, which are proportional to the concentration of NB$^-$ in NB containing various tetraalkylammonium perchlorates, decreased only 10—20% after a period of one night from the end of the preparation. These results show that NB$^-$ in NB prepared electrolytically is fairly stable.

Table 1. Standard Redox Potentials, $E°$, of NB^-/NB Systems in NB Containing Various Kinds and Amounts of Tetraalkylammonium Perchlorates

Supporting electrolyte	$E°(NB^-/NB)/V$ vs. $Ag/AgNO_3$(sat.)	
	Potentiometry	Potential sweep method
0.1 M TEAP	−1.782	−1.782
0.17 M TEAP	−1.778	−1.757
0.1 M TBAP	−1.775	−1.757
0.5 M TBAP	−1.764	−1.783

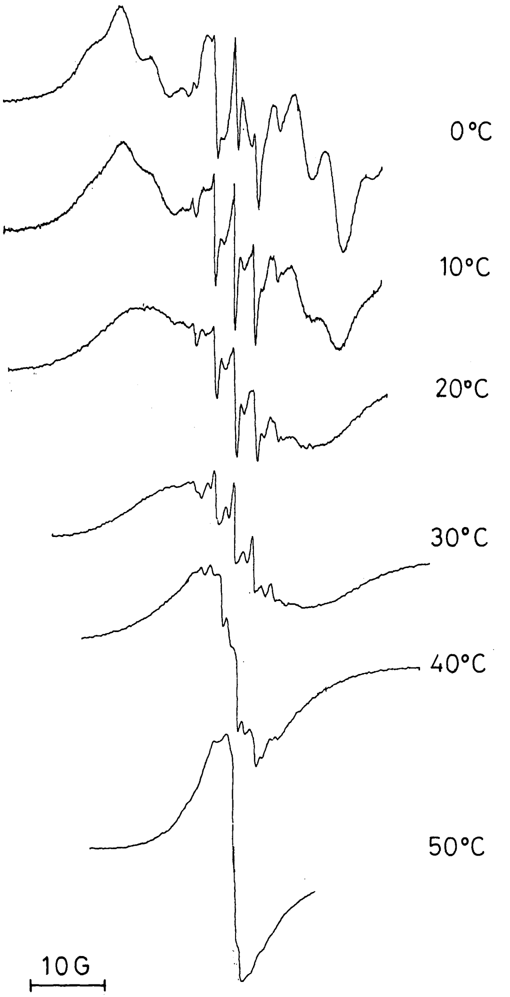


Fig. 4. ESR spectra of NB^- prepared by the electrolytic reduction of NB containing 0.5 M TBAP at various temperatures. Concentration of NB^- is about 1 mM.

In Fig. 3, we show the Nernstian plots between equilibrium potentials and the logarithm of the concentrations of NB^- determined from Q for the solution of NB^- in NB containing 0.1 M TEAP or 0.5 M TBAP. These plots showed good linearity. The solutions of NB^- in NB containing other supporting electrolyte also showed linear Nernstian plots. All of the slopes of these Nernstian plots were close to 60 mV per decade of concentration. This result shows that the electrode reactions of NB^- in NB containing several tetraalkylammonium perchlorates are the reversible ones accompanying the transfer of one electron. Table 1 shows the value of the standard redox potentials for NB^-/NB couples determined from these Nernstian plots in NB containing several kinds and amounts of tetraalkylammonium perchlorates, together with those determined by the potential sweep method according to the literatures.[8] The values determined by both methods agreed well with each other.

Homogeneous Electron-Transfer Reaction of NB^- in NB. Figure 4 shows the ESR spectra of the solutions of NB containing about 1 mM of NB^- and 0.5 M TBAP at various temperatures. Each spectrum was composed of one group of intense broad lines corresponding to NB^- superposed by another group of weak and sharp lines corresponding to a small amount of paramagnetic impurity probably formed by the decomposition of NB^-. The ESR signal due to NB^- at low temperature has a hyperfine structure, but this hyperfine structure disappeared and the ESR lines changed to a single broad one at higher temperature. ESR spectra of the solutions of NB containing NB^- and other tetraalkylammonium perchlorates are similar to these spectra.

These ESR signals due to NB^- can be well reproduced by computer simulation by the use of a modified Bloch equation. By these simualations we can determine the rate constant (k) of the homogeneous electron-exchange reactions between NB^- and NB. In these simulations we have used the values of hyperfine coupling constants for NB^- produced electrolytically in *N,N*-dimethylformamide (DMF) containing TEAP.[1] Figure 5 shows the Arrhenius plots for the rate constants of homogeneous electron-exchange reactions between NB^- and NB in the solutions containing 0.1 M TEAP or 0.5 M TBAP determined as described above. The respective rate constants at the same temperature are different from each other, and their activation energies are equal to 31 and 35 kJ mol^{-1} for the solutions containing 0.1 M TEAP or 0.5 M TBAP, respectively. This difference may be due to the ion pairing of NB^- with the different tetraalkylammonium ions as well as in the case of anthracene anion radical.[6]

Table 2 shows the homogeneous rate constants for the electron-exchange reactions at 25 °C between NB^- and NB determined in this experiment together with the value determined in DMF by Malachesky et al.[9] It is noteworthy that the values in this experiment are nearly equal to that in DMF. In this experiment, the molecule of NB^- is always in contact with NB molecules, but such a situation did not affect the rate of the electron-exchange reaction. The reason for this result may be based on the fact that these reactions are slow and not diffusion limited.

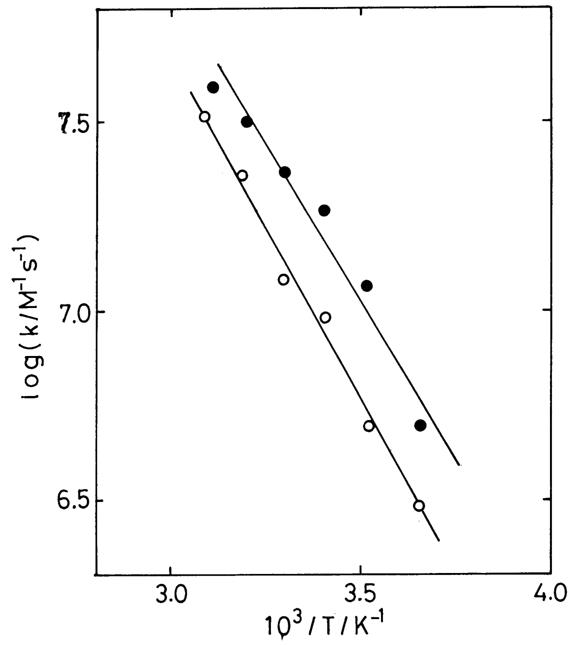


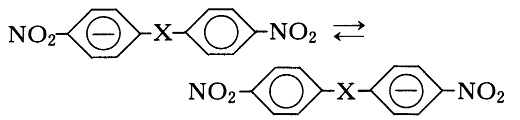
Fig. 5. Arrhenius plots for homogeneous electron-transfer reactions of NB^-/NB systems in NB containing (—○—) 0.5 M TBAP or (—●—) 0.1 M TEAP.

Table 2. Rate Constants of Homogeneous Electron-Transfer Reactions between NB^- and NB at 25 °C

Solvent	Supporting electrolyte	$k/M^{-1}\,s^{-1}$
NB	0.1 M TEAP	1.9×10^{7} a)
NB	0.5 M TBAP	1.5×10^{7} a)
DMF	0.01 M TEAP	3.0×10^{7} b)

a) This experiments. b) Ref. 9.

However, such a situation is interesting from another view point. Since the NB^- molecule are always in contact with NB molecules, the quasi-first order rate constant, $k_1=k[NB]$, may be closely related to the rate constants of the following intramolecular electron-transfer reactions,



(1)

where X represents some bifunctional groups. Table 3 shows the quasi-first order rate constant, k_1, determined in this experiment and the rate constants of intramolecular electron-transfer reactions of such compounds measured by Harriman and Maki.[10] The fact that the quasi-first order rate constant is larger than the rate constants of intramolecular electron-transfer reactions except bis(*p*-nitrophenyl)methane is based on the follwing points: (a) A molecule of NB^- in this experiment is surrounded by several NB molecules, (b) the overlap of the orbitals of NB^- and NB in which the transfering electrons exist or will exist, is larger than those for the intramolecular electron-transfer reactions.

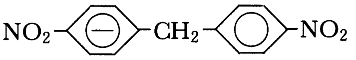
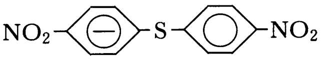
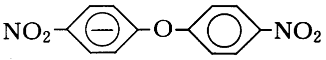
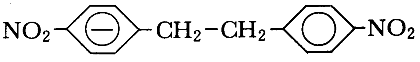
Examination of the Optical Electron-Transfer Reaction of NB^- in NB. Hush discussed the intervalence-transfer absorption of mixed valent compounds.[2] In his papers, he derived the relations between the light energy of such optical electron-transfer reaction, E_{op}, and the activation energy of the corresponding thermal electron-transfer reaction, E_{th} and between the wavenumber of the intervalence-transfer absorption maximum, $\bar{\nu}_{max}$, and the half width of the absorption band, $\Delta\bar{\nu}_{1/2}$, according to the theory of Kubo and Toyozawa.[11] When the Gibbs energy of the thermal

Table 3. Comparison between the Quasi-First Order Rate Constant of Electron-Transfer Reaction of NB^- in NB and the Rate Constants of Intramolecular Electron-Transfer Reactions of Bis(*p*-nitrophenyl) Compounds

A. Quasi-First Order Rate Constant (This Experiment)

System	$k_1=k[NB]/s^{-1}$
NB^-/NB	$1-2\times10^{8}$

B. Rate Constants of Intramolecular Electron-Transfer Reactions a)

Reactant	k_1/s^{-1}	
	In acetonitrile	In dimethyl sulfoxide
	$>10^{8}$	$>10^{8}$
	2×10^{6}	9×10^{6}
	1×10^{6}	3×10^{6}
	1×10^{6}	2×10^{6}

a) Ref. 10.

electron-transfer reaction, ΔG°, is zero as in the NB^-/NB system, these relations are represented by the following equations.

$$E_{op}=4E_{th} \tag{2}$$

$$\bar{\nu}_{max}=(\bar{\nu}_{1/2})^2/2310 \ (\bar{\nu} \text{ in cm}^{-1}) \tag{3}$$

Figure 6 shows the absorption spectra of NB^- prepared by the electrolytic reduction of NB containing 0.1 M TBAP (A) and 0.1 M TEAP (B), together with that of NB^- in DMF containing 0.1 M TEAP (C). The absorption spectrum (A) has a large peak at about 460 nm and an additional small peak at about 790 nm. The spectrum (B) has a large peak at about 580 nm and an additional small peak at about 930 nm. The spectrum (C), however, has only one peak at about 460 nm in the visible range. Chambers and Adams reported that the absorption spectrum of NB^- in DMF containing 0.1 M TEAP has a single peak at 465 nm.[12] Lyons and Mackie reported that the absorption spectrum of NB^- in DMF containing 0.2 M $NaNO_3$ has two adjacent peaks at 435 and 465 nm.[13] However, Ishitani et al. reported that the absorption spectrum of NB^- prepared by potassium reduction in 1,2-dimethoxyethane has a peak at 560 nm.[14] Therfore, the absorption peak of the spectra (A) and (C) at 460 nm can be attributed to the NB^-. Although the reason of the shift of the peak is not clear, the peak of the spectrum (B) at 580 nm may also be attributed to NB^-. If the additional small peak of (A) at 790 nm and that of (B) at 930 nm, which do not exist in the spectrum (C), were the peak due to an optical electron-transfer reaction, there must be a relation represented by Eq. 3. From the values of the activation energies of homogeneous thermal electron-transfer reactions between NB^- and NB described above, we can estimate the values of E_{op} as 140 and 125 kJ mol^{-1} for 0.5 M TBAP and 0.1 M TEAP solutions, respectively. The values of these energies correspond to wavelengths of 850 and 960 nm, respectively. These values are in good agreement with the experimental wavelengths of the additional small peaks of the spectra (A) and (B). This result suggests that these absorption peaks may be attributable to the optical electron-transfer reactions between NB^- molecules and adjacent NB molecules.

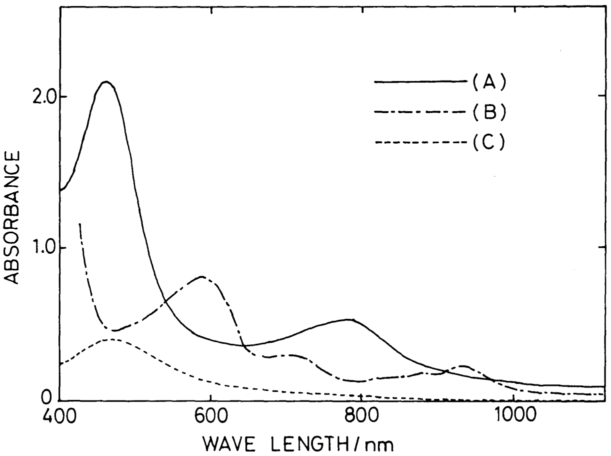


Fig. 6. Absorption spectra of solutions containing NB^- prepared by the electrolytic reduction of (A) NB containing 0.1 M TBAP; (B) NB containing 0.1 M TEAP; (C) DMF solution of NB containing 0.1 M TEAP.

On the other hand, the half width of these additional peaks were smaller than the half values of those predicted by the Eq. 3. This discrepancy may be attributed to the limitation of the applicability of Eq. 3 to this system, or the disturbance of the exact determination of $\Delta\bar{\nu}_{1/2}$ by the impurity formed by the decomposition of NB^-. Therefore, a more carefull experimental and theoretical examination is required for the complete confirmation of the occurence of optical electron-transfer reaction in this system.

Electrochemical Electron-Transfer Reaction Rates of NB^- in NB. Figure 7 shows the plots of log (I_o/Fc_O/cm s^{-1}) vs. log (c_R/c_O) for NB^-/NB couples in NB containing various kinds and amounts of tetraalkylammonium perchlorates determined by the gdp method, where I_o, F, c_O, and c_R are the exchange current density, the Faraday constant, the concentration of oxidant, and the concentration of reductant, respectively. I_o/Fc_O corresponds to the rate constant of electrochemical electron-transfer reaction at various reductant/oxidant ratios. The standard rate constants were determined by the extrapolation of these plots to the zero value of the abscissa. These rate constants in various solutions are different from each other, but even the largest value in 0.17 M TEAP, 7×10^{-3} cm s^{-1}, is smaller by about two orders than that in a DMF solu-

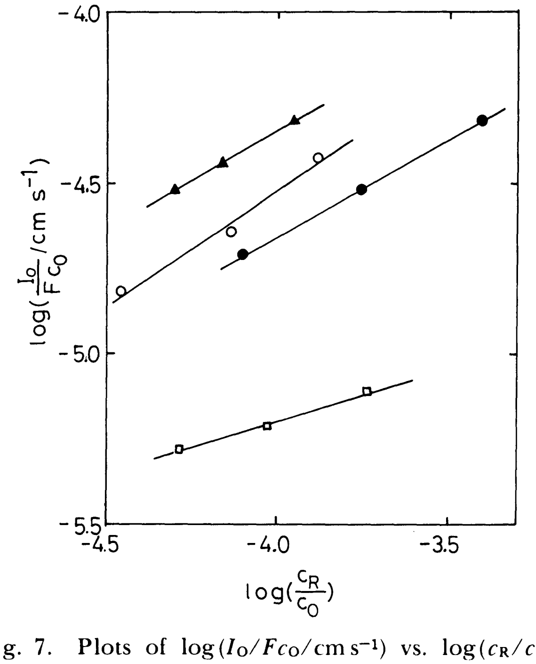


Fig. 7. Plots of log(I_O/Fc_O/cm s^{-1}) vs. log(c_R/c_O) for NB^-/NB systems in NB containing various kinds and amounts of tetraalkylammonium perchlorates determined by gdp method at 25 °C. (—▲—) 0.17 M TEAP; (—○—) 0.1 M TBAP; (—●—) 0.5 M TBAP; (—□—) 0.1 M TAAP.

Table 4. Diffusion Coefficients, D, of NB^- in NB and DMF Containing Various Tetraalkylammonium Perchorates at 25 °C

Supporting electrolyte	Solvent(viscosity/Pa s)	$D/\mathrm{cm^2\,s^{-1}}$
0.1 M TEAP	NB(1.81×10^{-3})	3.6×10^{-6}
0.17 M TEAP	NB(1.81×10^{-3})	3.6×10^{-6}
0.1 M TBAP	NB(1.81×10^{-3})	3.6×10^{-6}
0.5 M TBAP	NB(1.81×10^{-3})	3.2×10^{-6}
0.1 M TEAP	DMF(0.80×10^{-3})	10.8×10^{-6} a)

a) Ref. 15.

tion.[15] NB molecules which have formed compact double layer in contact with the electrode surface may act as oxidants for this electrode reaction. These molecules are considered to be specifically adsorbed oxidants in a sense. The reason for the retardation of the electron-transfer reaction in these system is not clear, but such unique structure of the electrical double layer of these systems as described above may be attributed to these phenomena.

Diffusion Coefficients of NB^- in NB. Dahms,[4] and Ruff and Friedrich[5] derived an expression for the contribution of an exchange reaction to the diffusion coefficient of species which participate in the exchange reaction. When the rate constant of the electron-exchange reaction between NB^- and NB is expressed by k, the apparent diffusion coefficient of NB^- in NB, D_{NB^-}, is represented by the following equation.[5]

$$D_{NB^-}=D^{\circ}_{NB^-}+(\pi\delta^2k/4)c_{NB} \qquad (4)$$

where $D^{\circ}_{NB^-}$ is the intrinsic diffusion coefficient of NB^- in NB when the value of k is assumed to be zero, δ is the jumping distance of an electron from NB^- to NB, and c_{NB} is the concentration of NB. The second term represents the contribution of the electron-exchange reaction.

Table 4 shows the diffusion coefficients of NB^- in NB containing various kinds of tetraalkylammonium perchlorates determined by the potential step method, together with that in DMF. If the contribution of the electron-transfer reaction between NB^- and NB to an apparent diffusion coefficient of NB^- predicted by the Eq. 4 would be larger than the intrinsic diffusion coefficient of NB^-, $D^{\circ}_{NB^-}$, a large apparent diffusion coefficient might be observed. However, this result shows that the diffusion coefficients of NB^- in NB is smaller than the value in DMF, even if we corrected the value considering the difference of the viscosities of these solvents. These results can probably be attributed to the small rate constant of the homogeneous electron-transfer reaction of these systems and ion pairing of NB^- with tetraalkylammonium ions. In fact, although the rate constant of the electron-transfer reaction between anthracene (An) and its anion radical (An^-) is larger by about two orders than these system, its contribution to the electric conductivity of anthracene anion radical is only a few percent.[16] Even when we consider the large concentration of NB in these system compared with that of An, the contribution of the electron-transfer reaction between NB and NB^- may be not so large as to be detectable by this experiment. Moreover, it is considered that NB^- in this system will usually be ion paired with tetraalkylammonium ions, because the odd electrons in free NB^- molecules tend to transfer to NB molecules in the vicinity of tetraalkylammonium ions. In a separate paper, we will report the electrical conductivity of solid NB containing NB^- and tetraalkylammonium salts in order to detect only the contribution of electron hopping to the electric conductivity.

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