Standard Redox Potentials of R^-/R^+ Reference Redox Couples and Solvent Activity Coefficients

Tadaaki KAKUTANI, Yoshikazu MORIHIRO, Mitsugi SENDA,* Reiji TAKAHASHI,**
and Koichi MATSUMOTO**

Department of Agricultural Chemistry, Kyoto University, Kyoto 606
****Department of Chemistry, Ritsumeikan University, Kyoto 603*

(Received April 20, 1978)

The standard redox potentials of five R^-/R^+ redox couples that can be considered as candidates for the reference redox couple, *i.e.*, the anion/cation couples of tris(2,2′-bipyridine)iron(II), tris(2,2′-bipyridine)ruthenium(II), cobaltocene, perylene, and 9,10-diphenylanthracene, have been determined in acetonitrile, dimethyl sulfoxide, *N,N*-dimethylformamide and propylene carbonate by means of polarography and voltammetry. The results confirmed that the standard potentials of these redox couples are independent of the solvents studied so that they can be used as solvent-independent reference points for potential comparisons. The solvent activity coefficients of the silver ion have been estimated on the basis of these reference redox couples.

The evaluation of single-ion solvent activity coefficients, ${}^{o}\gamma^{s}_{ion}$, for the transfer of ions from a reference solvent (superscript o) to another solvent (superscript s) is one of the most interesting problems of solution chemistry. Since the problem is not accessible to exact thermodynamics, extrathermodynamic procedures must be followed. Thus various extrathermodynamic procedures have been proposed by several authors for the estimation of the solvent activity coefficients of single ions. The current status of this field has been comprehensively reviewed in several recent papers.[1–6)]

In a previous paper,[7)] two of the authors (M.S. and R.T.) proposed that the standard redox potential, $E^{\circ}_{R^-/R^+}$, of the R^-/R^+ redox couple may work as a solvent-independent reference point in various solvents if the R^-/R^+ redox couples, being named the reference redox couples, have the following chemical features: a) the R^+ and R^- ions are very large in size with the charge shielded by large organic groups, and b) the charge distribution in the R^+ ion is the same or very nearly the same as that in the R^- ion. It was also pointed out that the standard redox potentials can be estimated from polarographic reversible half-wave potentials of R/R^+ and R^-/R couples and that this approach should give an accurate and convenient estimation of single-ion solvent activity coefficients.

In this study the standard redox potentials of several R^-/R^+ redox couples that can be considered as candidates[7)] for the reference redox couple (*i.e.*, the anion/cation couples of tris(2,2′-bipyridine)iron(II), tris(2,2′-bipyridine)ruthenium(II), cobaltocene, perylene and 9,10-diphenylanthracene) have been determined in acetonitrile (AN), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and propylene carbonate (PC) by means of polarography and voltammetry. Furthermore the solvent activity coefficients of the silver ion have been estimated on the basis of these R^-/R^+ reference redox couples. An estimation of the absolute electrode potentials of the silver/silver ion electrodes in nonaqueous solvents has been attempted.

Experimental

Chemicals. Commercial PC(a Merk product for synthesis) was dried over molecular sieves 5A for several days and fractionally distilled twice under vacuum. The central 70% fraction of the distillate was collected from each distillation and stored under a nitrogen atmosphere after dry nitrogen gas had been passed through the distillate for several hours. Spectro grade DMF was stirred with molecular sieves 4A overnight and distilled under vacuum. The central 60% fraction was collected and stored under a nitrogen atmosphere after dry nitrogen gas had been passed though the distillate for one hour. Spectro grade DMSO was dried over molecular sieves 5A for two days and twice distilled under vacuum. The central 70% fraction was collected in each distillate and stored under a nitrogen atmosphere. Analytical grade AN was refluxed over phosphorus pentaoxide (5 g/l) for 15 min and distilled at the rate of 100 ml/h. The central 80% fraction of the distillate was refluxed over CaH_2(2 g/l) for half an hour and fractionally distilled through Widmer's fractional distillation column at the rate of 100 ml/h. The central 80% fraction was collected and dried over anhydrous sodium carbonate. Just before use the dried AN was fractionally distilled through a 1 m column packed with stainless steel helices.

Tetraethylammonium perchlorate (TEAP) was prepared and purified by the method previously described.[8)] The salt was vacuum-dried at 100 °C for 24 h and stored in a desiccator. Just before use the salt was again vacuum-dried at 100 °C for two hours. Commercial silver perchlorate was purified by repeated recrystallization with dried thiophene-free benzene[9)] and vacuum-dried at 60 °C, both processes being carried out in the dark. Silver nitrate of analytical grade (a product of Wako Pure Chemicals) was used without further purification. Rubidium perchlorate was prepared by the equimolar addition of perchloric acid to an aqueous solution of rubidium bromide, which was then purified by repeated recrystallization with twice distilled water and vacuum-dried at 100 °C for 24 h. Tris(2,2′-bipyridine)iron(II) perchlorate ($Fe(bpy)_3(ClO_4)_2$) and tris(2,2′-bipyridine)ruthenium(II) bromide ($Ru(bpy)_3Br_2$) were kindly supplied by Dr. T. Matsumura-Inoue of Nara University of Education. Reagent grade perylene was purified by repeated recrystallization with toluene. Analytical grade 9,10-diphenylanthracene (DPA) (a product of Nakarai Chemicals for scintillation use) was used without further purification. Cobalticenium hexafluorophosphate (Cp_2CoPF_6) was prepared according to Wilkinson's procedure[10)] with a slight modification,[11)] and purified by repeated recrystallization from a 2: 1 methanol–acetone mixture.

Electrochemical Measurements. Dc polarograms and cyclic voltammograms were measured with a potentiostat, Yanaco

Model PE-21-TB2S, equipped with a function generator, YHP 3310B. Ac polarographic measurements were performed with a lock-in amplifier, NF LI-572B, equipped with the above potentiostat system. Double potential-step measurements[12] for chemical kinetics following charge transfer were carried out with the same system as the dc polarograph. The data were recorded using both a transient memory, Union Giken System 71-02, and an X-Y recorder, Yokogawa 3077.

All voltammetric measurements were performed in Cell A under potentiostatic conditions. A three electrode system consisting of a working electrode (dropping mercury, platinum plane button, or hanging mercury drop electrode), a coiled platinum wire auxiliary electrode, and a nonaqueous silver/silver ion reference electrode, at room temperature (25±1 °C) under a dry nitrogen atmosphere was used.

	Hg (or Pt)	0.5—1 mM depolarizer	1 mM $AgNO_3$ or $AgClO_4$	Ag
Cell A:		0.2 M TEAP	(10 mM $AgNO_3$ in DMF)	
		solvent s	0.2 M TEAP	
			solvent s	

The half cells in Cell A were interconnected through sintered glass. The platinum working electrode (area 7.9×10^{-3} cm^2), sealed in glass, was polished with emery paper (#3000) and then immersed in an aqueous iron(II) sulfate solution for approximately half an hour. It was then washed in distilled water, dried, and pre-immersed in the solution to be studied. Good experimental reproducibility was obtained by using this procedure. The hanging mercury drop electrode was a Metrohm mercury drop electrode E 410. As the reference electrode an Ag/1 mM $AgNO_3$(or $AgClO_4$), 0.2 M TEAP, s, electrode was used for the measurements in s=PC, DMSO or AN. The potential of the reference electrode was found to be stable and reproducible for at least 2 h after the electrode's preparation. However, the Ag/1 mM $AgNO_3$ electrode was unstable in DMF and this was most likely due to the reduction of the silver ion by the solvent[13] (the potential of the electrode which was left standing for 4 hours was about 20 mV more negative compared to that of the freshly prepared electrode). Therefore an Ag/10 mM $AgNO_3$, 0.2 M TEAP, DMF electrode was used for the measurements in DMF. This electrode was found to be satisfactorily stable and gave reproducible results for at least 2 h after the preparation. For these reasons the reference electrodes were freshly prepared for each measurement, and the measurements were finished within 2 h after the preparation. The data in DMF obtained with the above reference electrode were converted to those referred to the Ag/1 mM $AgNO_3$, 0.2 M TEAP, DMF electrode by using the emf value of the following freshly prepared cell:

Ag	1 mM $AgNO_3$	10 mM $AgNO_3$	Ag
	0.2 M TEAP	0.2 M TEAP	
	DMF	DMF	

Results

Nonaqueous electrochemistry of Fe(bpy)$_3^{2+}$,[14,15] Ru(bpy)$_3^{2+}$,[15] Cp_2Co^+,[11,16,17] DPA,[18] and perylene[18] has been studied by many authors. These studies have revealed that in aprotic dipolar media these compounds give one-electron reversible reduction or oxidation steps, involving redox couples R/R$^+$ and R$^-$/R, defined by the equations: R$^+$+e=R and R+e=R$^-$. These compounds are also of relatively large size. For these reasons the above compounds were selected as the candidates for the R$^-$/R$^+$ reference redox couple.

Electrochemical Reduction of Fe(bpy)$_3^{2+}$ and Ru(bpy)$_3^{2+}$. These complexes[14,15] gave four reduction waves in aprotic media. The second and third reduction steps were assigned to the redox reactions of M(bpy)$_3^+$+e=M(bpy)$_3$ and M(bpy)$_3$+e=M(bpy)$_3^-$, respectively. In general the behavior of these complexes in the four solvents as investigated in this study was found to agree with data obtained by previous authors. The dc half-wave potentials, $E_{1/2}$, of these reduction steps conformed, within experimental error, to the corresponding ac peak

TABLE 1. ELECTROCHEMICAL DATA OF THE SECOND AND THIRD REDUCTION STEPS OF Fe(bpy)$_3^{2+}$ AND Ru(bpy)$_3^{2+}$ IN NONAQUEOUS SOLVENTS CONTAINING 0.2 M TEAP AT 25 °C

Complex	Step	$-E_{1/2}$/V	ΔE/mV	$-E^{\mathrm{CV}}_{1/2}$/V	$\Delta E^{\mathrm{CV}}_{\mathrm{p}}$/mV	$-E^{\mathrm{AC}}_{\mathrm{p}}$/V	$\Delta E^{\mathrm{AC}}_{\mathrm{p}}$/mV
		(a) Propylene carbonate					
Fe(bpy)$_3^{2+}$	2nd	2.21	55	2.22	60	2.21	90
	3rd	2.44	55	2.45	69	2.45	93
Ru(bpy)$_3^{2+}$	2nd	2.19	56	2.20	59	2.20	95
	3rd	2.42	55	2.43	66	2.43	90
		(b) DMF					
Fe(bpy)$_3^{2+}$	2nd	1.85	55	1.85	62	1.85	97
	3rd	2.10	55	2.11	74	2.11	95
Ru(bpy)$_3^{2+}$	2nd	1.84	55	1.84	60	1.84	92
	3rd	2.09	55	2.09	70	2.09	89
		(c) Acetonitrile					
Fe(bpy)$_3^{2+}$	2nd	1.79	50	1.79	62	1.79	90
	3rd	2.03	50	2.03	64	2.03	100
Ru(bpy)$_3^{2+}$	2nd	1.78	50	1.77	60	1.77	90
	3rd	2.02	50	2.01	60	2.01	88
		(d) DMSO					
Fe(bpy)$_3^{2+}$	2nd	1.68	58	1.68	61	1.68	90
	3rd	1.92	55	1.92	63	1.92	95
Ru(bpy)$_3^{2+}$	2nd	1.66	55	1.66	60	1.66	90
	3rd	1.90	55	1.90	60	1.90	90

potentials, E_p^{AC}, and the half-wave potentials, $E_{1/2}^{CV}$, calculated from the cyclic voltammetric (CV) peak potentials. The conventional criteria of the reversibility, such as the dc polarographic slope, $\Delta E(\equiv E_{1/4}-E_{3/4})$, CV anodic-cathodic peak separation, ΔE_p^{CV}, ac polarographic half-width, ΔE_p^{AC}, *etc.*, showed that the second and third reduction steps are a reversible one-electron process in all the solvents studied. Some experimental results are shown in Table 1.

Electrochemical Reduction of Cp_2Co^+. Previous work[16,17)] has revealed that this compound gives two reduction waves in AN and that the first reduction step corresponds to a simple reversible one-electron reduction from the cobaltocene cation to neutral cobaltocene:

$$Cp_2Co^+ + e \rightleftarrows Cp_2Co \qquad E_1 \qquad (a)$$

Regarding the reduction mechanisms of the second step, there are several points of disagreement between the two previous papers.[16,17)] In contrast to the earlier report by Gubin *et al.*[17)] that the second reduction step is a one-electron irreversible process, Geiger[16)] has recently reported that in AN the neutral cobaltocene formed at the first reduction step is reduced by an ECE mechanism;

$$Cp_2Co + e \rightleftarrows Cp_2Co^- \qquad E_2 \qquad (b)$$

$$Cp_2Co^- \longrightarrow Z \qquad (c)$$

$$Z + e = Z^- \qquad E_3 \qquad (d)$$

where the intermediate Z is more reducible than the cobaltocene. He also showed that the rate of the chemical reaction (c) was relatively slow ($k\approx 0.1\ s^{-1}$ in AN). In addition the redox reaction (b) was shown to be highly reversible in AN.[11)] The polarographic data on this compound in AN, DMF, and PC found here were consistent with the reduction mechanism proposed by Geiger.[16)] The polarographic limiting current of the second reduction step, $i_l^{(2)}$, was slightly larger than that of the first reduction step, $i_l^{(1)}$, and the ratio, $i_l^{(2)}/i_l^{(1)}$, when corrected for drop time, decreased and approached unity with increasing mercury column height, as shown in Table 2. A plot of log $[i/(i_l-i)]$ *vs.* E for the second wave gave a straight line with a slope of 59 mV. On CV, the cathodic peak height of the second reduction step, $i_{cp}^{(2)}$, was not proportional to the square root of the scan rate, in contrast to the behavior of the first reduction step. As the scan rate increased the ratio $i_{cp}^{(2)}/i_{cp}^{(1)}$, $i_{cp}^{(1)}$ being the cathodic peak height of the first step, decreased and approached unity ($i_{cp}^{(2)}/i_{cp}^{(1)}\approx 1$ at $v\geq 0.5$ V/s). The peak potential of the second cathodic peak was practically invariant with the change in the scan rate. These results can be interpreted by assuming the ECE mechanism[19-22)] with a slow chemical reaction (c). The rate constant of the chemical reaction (c) was estimated from the polarographic limiting currents[20,22)] as given in Table 2. Analysis of the CV data yielded a rate constant of the same order of magnitude; $k=0.1$ to $0.2\ s^{-1}$ in these solvents. The dc polarographic theory[22)] for the ECE mechanism predicts that, for $k=0.2\ s^{-1}$ or less, the observed half-wave potential of the second step will agree with the reversible half-wave potential of the Cp_2Co/Cp_2Co^- couple within a few millivolts when $E_3\geq E_2$. Thus it can be concluded that the deviation of the observed half-wave potential from the true reversible half-wave potential of this redox couple (b) will be negligibly small in AN, DMF, and PC. It was also found that the ac peak potential of the second step agreed with the corresponding dc half-wave potential. On the other hand, this compound gave three reduction waves in DMSO. The first reduction step was found to represent a one-electron reversible reduction from the cobaltocene cation to cobaltocene. The second and third reduction steps appeared irreversible, showing no corresponding anodic peaks on the CV curves at $v=1$ V/s. Thus, the reversible half-wave potential of the Cp_2Co/Cp_2Co^- couple in DMSO could not be determined.

TABLE 2. POLAROGRAPHIC RESULTS OF COBALTICENIUM HEXAFLUOROPHOSPHATE IN APROTIC MEDIA CONTAINING 0.2 M TEAP AT 25 °C

h/cm[a)]	τ/s[b)]	$i_l^{(2)}/i_l^{(1)}$ [c)]	k/s^{-1} [d)]
	(a) AN		
40	2.47	1.199	0.19
50	1.96	1.169	0.20
60	1.66	1.125	0.17
70	1.40	1.117	0.18
	(b) DMF		
40	2.71	1.124	0.10
50	2.19	1.100	0.10
60	1.82	1.063	0.07
70	1.56	1.038	0.05
	(c) PC		
40	2.56	1.124	0.11
50	2.05	1.075	0.08
60	1.70	1.108	0.14
70	1.45	1.092	0.14

a) Mercury column height. b) Drop time at the potential where $i_l^{(2)}$ was measured. c) Instantaneous current ratio, corrected for drop time. d) Calculated by the table in Ref. 20.

Electrochemical Oxidation and Reduction of DPA and Perylene. It has been reported that DPA and perylene undergo reversible one-electron oxidations and reductions to produce reasonably stable cation and anion radicals,[18)] respectively. For this reason these compounds were also selected as candidates for the R$^-$/R$^+$ reference redox couple. All polarographic and voltammetric data obtained in this study indicated that the first reduction steps of these compounds are reversible one-electron reductions to anion radicals, which are highly stable in all four solvents studied. On the other hand, these compounds were found to undergo reversible one-electron oxidations to produce stable cation radicals in AN and PC only. In DMSO, DPA gave no oxidation wave within the limits of anodic potential range, whereas perylene gave an irreversible oxidation wave in this solvent, showing no corresponding cathodic peak on the CV curves at $v=1$ V/s. In DMF, DPA gave an oxidation wave, which was most likely complicated by a succeeding chemical reaction of the cation radical. Thus in CV, the ratio of cathodic to anodic peak current, i_{cp}/i_{ap}, increased with the increasing voltage scan rate. Also the anodic to cathodic peak

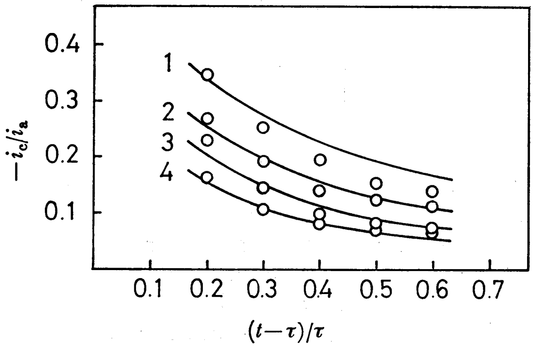

Fig. 1. Plots of $-i_c/i_a$ *vs.* $(t-\tau)/\tau$ for the oxidation step of DPA in DMF containing 0.2 M TEAP at 25 °C. Solid lines represent theoretical curves for $k=3.7\ \mathrm{s}^{-1}$ and points are experimental results;
(1) $\tau=0.192$ s; (2) $\tau=0.295$ s; (3) $\tau=0.384$ s; (4) $\tau=0.491$ s.

separation increased as the voltage scan rate was increased. These results indicate that this oxidation step is a quasi-reversible one-electron oxidation succeeded by a chemical reaction. To estimate the reversible half-wave potential of the DPA/DPA$^+$ couple in this solvent, an attempt was made to determine the rate constant of the succeeding chemical reaction, using the double potential step method developed by Shwarz and Shain.[12] The initial dc potential was set at 0.49 V *vs.* the Ag/10 mM $AgNO_3$ electrode, and the anodic polarization step of 0.99 V was applied for a given interval, τ, followed by the cathodic polarization at 0.49 V. Typical results, corrected for the base current, for different intervals are shown in Fig. 1. The points represent the experimental results and the solid lines represent the theoretical curves for $k=3.7\ \mathrm{s}^{-1}$. Therefore, based on the theory,[23] in CV the deviation of the observed anodic peak potential of this compound from the supposed anodic peak potential of a hypothetical redox couple, either reversible or quasi-reversible, without succeeding chemical reaction should be less than 1 mV at $v=1$ V/s. Thus the reversible half-wave potential was estimated from the CV data at $v\geq 1$ V/s, as follows. According to Matsuda and Ayabe,[24] the anodic peak potential, E_p(quasi), of a quasi-reversible oxidation step can be written as

$$E_p(\text{quasi}) = E^r_{1/2} + (RT/nF)\Xi(\Lambda),$$

where $E^r_{1/2}$ is the reversible half-wave potential and Λ is a function of the electrochemical kinetic parameters, k_s and α, and the voltage scan rate, v. The parameter Λ can be estimated from the CV peak separation, ΔE_p, by using a working curve of $\Psi(\equiv\Lambda/\sqrt{\pi})$ *vs.* ΔE_p calculated by Nicholson.[25] Using this Λ value, the $\Xi(\Lambda)$ value can be obtained and consequently the $E^r_{1/2}$ value.[24] The results are summarized in Table 3, assuming $\alpha=0.5$. The values of $E^r_{1/2}$ estimated at various scan rates were constant, indicating that the value of $E^r_{1/2}$ estimated by this method is reliable. In DMF, perylene gave an oxidation wave, however the oxidation appeared irreversible and showed no corresponding cathodic peak on the CV curves.

Table 3. Cyclic voltammetric results of DPA in DMF containing 0.2 M TEAP at 25 °C

v/V s^{-1}	1	4.7	9.7
E_p/V	0.96	0.98	1.00
ΔE_p/mV	115	150	199
$\Lambda/\sqrt{\pi}$	0.39	0.20	0.12
Ξ (Λ)	2.33	3.21	4.05
$E^r_{1/2}$/V	0.90	0.90	0.90

Table 4. Polarographic reversible half-wave potential of R/R$^+$, R$^-$/R, and R$^-$/R$^+$ redox couples measured against Ag/1 mM Ag$^+$, 0.2 M TEAP electrode in various solvents at 25 °C

	$-E^r_{1/2}$· (R/R$^+$)/V	$-E^r_{1/2}$· (R$^-$/R)/V	$-E^r_{1/2}$· (R$^-$/R$^+$)/V
(a) Propylene carbonate			
DPA	−0.51	2.56	1.03
Perylene	−0.30	2.37	1.04
Cobaltocene	1.63	2.55	2.09
Fe(bpy)$_3$	2.21	2.45	2.33
Ru(bpy)$_3$	2.20	2.43	2.32
Rb$^+$	2.63	—	—
(b) DMF			
DPA	−0.90	2.23	0.67
Perylene	irr	2.03	irr
Cobaltocene	1.27	2.21	1.74
Fe(bpy)$_3$	1.85	2.11	1.98
Ru(bpy)$_3$	1.84	2.09	1.97
Rb$^+$	2.42	—	—
(c) Acetonitrile			
DPA	−0.96	2.16	0.60
Perylene	−0.75	1.96	0.61
Cobaltocene	1.19	2.12	1.66
Fe(bpy)$_3$	1.79	2.03	1.91
Ru(bpy)$_3$	1.77	2.01	1.89
Rb$^+$	2.21	—	—
(d) DMSO			
DPA	n.w.	2.01	—
Perylene	irr	1.82	irr
Cobaltocene	1.11	irr	irr
Fe(bpy)$_3$	1.68	1.92	1.80
Ru(bpy)$_3$	1.66	1.90	1.78
Rb$^+$	2.26	—	—

Table 4 summarizes the reversible half-wave potentials of R/R$^+$ and R$^-$/R redox couples of the five compounds studied and of the rubidium ions in PC, DMF, AN and DMSO. In addition the corresponding reversible half-wave potentials of the five R$^-$/R$^+$ redox couples, $E^r_{1/2}$(R$^-$/R$^+$), which were calculated by

$$E^r_{1/2}(\mathrm{R^-/R^+}) = (E^r_{1/2}(\mathrm{R/R^+})+E^r_{1/2}(\mathrm{R^-/R}))/2,$$

are illustrated.

Discussion

As described previously,[7] the standard redox potential of the R$^-$/R$^+$ redox couple, $E^\circ_{\mathrm{R^-/R^+}}$, measured against a silver/silver ion reference electrode can be expressed by

$$E^\circ_{\mathrm{R^-/R^+}}:\ \mathrm{R^+ + 2e = R^-}, \tag{1}$$

$$\begin{aligned} E^{\circ}_{\mathrm{R^-/R^+}} &= (E^{\circ}_{\mathrm{R/R^+}}+E^{\circ}_{\mathrm{R^-/R}})/2 \\ &= (A+I)/2F-(G^{\mathrm{s}}(\mathrm{R^-})-G^{\mathrm{s}}(\mathrm{R^+}))/2F \\ &\quad + \Delta G^{\mathrm{s}}(\mathrm{Ag/Ag^+})/F, \end{aligned} \tag{2}$$

where $E^{\circ}_{\mathrm{R/R^+}}$ and $E^{\circ}_{\mathrm{R^-/R}}$ are the standard redox potentials of the redox couples, $\mathrm{R/R^+}$ and $\mathrm{R^-/R}$, respectively, as defined by

$$E^{\circ}_{\mathrm{R/R^+}}\colon\ \mathrm{R^+} + \mathrm{e} = \mathrm{R}, \tag{3a}$$

$$E^{\circ}_{\mathrm{R^-/R}}\colon\ \mathrm{R} + \mathrm{e} = \mathrm{R^-}. \tag{3b}$$

In Eq. 2, A and I respectively represent the electron affinity and ionization potential of the neutral molecule R derived from $\mathrm{R^+}$ or $\mathrm{R^-}$ by the above redox reaction (3a) or (3b), $G^{\mathrm{s}}(\mathrm{R}^i)$ $(i=+, -)$ is the solvation energy of the ion R^i, and $\Delta G^{\mathrm{s}}(\mathrm{Ag/Ag^+})$ is the free energy change of the reference electrode reaction,

$$\mathrm{Ag^+} + \mathrm{e} = \mathrm{Ag} \tag{3c}$$

in solvent, s. When $\mathrm{R^+}$ and $\mathrm{R^-}$ are very large in size with the charge shielded by large organic groups and the charge distribution in the $\mathrm{R^+}$ ion is the same or nearly the same as that in the $\mathrm{R^-}$ ion, it can be assumed that

$$\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}} = G^{\mathrm{s}}(\mathrm{R^-}) - G^{\mathrm{s}}(\mathrm{R^+}) = 0. \tag{4}$$

Then $E^{\circ}_{\mathrm{R^-/R^+}}$ should be solvent-independent;

$$E^{\circ}_{\mathrm{R^-/R^+}} = (A+I)/2F + \Delta G^{\mathrm{s}}(\mathrm{Ag/Ag^+})/F. \tag{5}$$

The half-wave potential $E^{\mathrm{r}}_{1/2}(\mathrm{R^-/R^+})$ is related to the standard potential $E^{\circ}_{\mathrm{R^-/R^+}}$ by

$$E^{\mathrm{r}}_{1/2}(\mathrm{R^-/R^+}) = E^{\circ}_{\mathrm{R^-/R^+}} + (RT/2F)\ln(f_+\sqrt{D_-}/f_-\sqrt{D_+}),$$

where f_+ and f_- are the activity coefficients and D_+ and D_- the diffusion coefficients of $\mathrm{R^+}$ and $\mathrm{R^-}$, respectively. It is quite reasonable to assume $f_+=f_-$ and $D_+=D_-$ for the $\mathrm{R^-/R^+}$ couple, so that $E^{\mathrm{r}}_{1/2}(\mathrm{R^-/R^+})$ equated to $E^{\circ}_{\mathrm{R^-/R^+}}$ is a very good approximation (see Table 4).

According to the molecular orbital theory the sum of A and I should be constant for alternant aromatic hydrocarbons. Thus Eq. 5 predicts that for a given solvent $E^{\circ}_{\mathrm{R^-/R^+}}$ of alternant aromatic hydrocarbons should be constant independent of the species of alternant aromatic hydrocarbon. Results in Table 4 show this is the case with perylene and DPA in PC and AN, indicating the validity of Eq. 4 for alternant aromatic hydrocarbons in nonaqueous solvents.[49)]

From Eq. 2 the difference $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$ between the $E^{\circ}_{\mathrm{R^-/R^+}}$'s of two couples, I and II, in a solvent, s, is given by

$$\begin{aligned} \Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s}) &= E^{\circ}_{\mathrm{R^-/R^+}}(\mathrm{I, s}) - E^{\circ}_{\mathrm{R^-/R^+}}(\mathrm{II, s}) \\ &= (A_{\mathrm{I}}+I_{\mathrm{I}})/2F - (A_{\mathrm{II}}+I_{\mathrm{II}})/2F \\ &\quad - (\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{I})-\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{II}))/2F. \end{aligned} \tag{6a}$$

Accordingly, if $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$ were found to be independent of the solvent s for any pair of redox couples, I and II, it must hold that $\Delta\Delta^{\mathrm{I}}G^{\mathrm{II}}(\mathrm{s})=\Delta G^{\mathrm{s'}}_{\mathrm{R^-/R^+}}(\mathrm{I})-\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{II})\approx 0$, because $\Delta\Delta^{\mathrm{I}}G^{\mathrm{II}}(\mathrm{s})$, if appreciable, should be dependent on the solvent s. The last condition means that $\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{I})\approx\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{II})\approx\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{III})\approx\cdots$, which in turn implies that all these $\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}$'s are negligibly small or that Eq. 4 is valid, because $\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{I})$, $\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{II})$, $\Delta G^{\mathrm{s}}_{\mathrm{R^-/R^+}}(\mathrm{III}),\cdots$, if appreciable, should be dependent on the redox couples I, II, III, $\cdots$, respectively. In conclusion, if $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$ is independent of the solvent s, Eq. 4 is valid, so that

$$\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s}) = (A_{\mathrm{I}}+I_{\mathrm{I}})/2F - (A_{\mathrm{II}}+I_{\mathrm{II}})/2F. \tag{6b}$$

A similar argument leads to the conclusion that if the difference $\Delta^{\mathrm{s'}}E^{\mathrm{s''}}(\mathrm{I})$ between the $E^{\circ}_{\mathrm{R^-/R^+}}(\mathrm{I})$'s of a redox couple, I, in any two solvents, s′ and s″, is independent of the redox couple I, Eq. 4 is valid, so that $\Delta^{\mathrm{s'}}E^{\mathrm{s''}}(\mathrm{I})$ should indicate the solvent activity coefficient, ${}^{\mathrm{s'}}\gamma^{\mathrm{s''}}$, of the ion involved in the reference electrode reaction, as shown by

$$\begin{aligned} \Delta^{\mathrm{s'}}E^{\mathrm{s''}}(\mathrm{I}) &= E^{\circ}_{\mathrm{R^-/R^+}}(\mathrm{I, s'}) - E^{\circ}_{\mathrm{R^-/R^+}}(\mathrm{I, s''}) \\ &= (\Delta G^{\mathrm{s'}}(\mathrm{Ag/Ag^+}) - \Delta G^{\mathrm{s''}}(\mathrm{Ag/Ag^+}))/F \\ &= (RT/F)\ln {}^{\mathrm{s'}}\gamma^{\mathrm{s''}}_{\mathrm{Ag^+}}. \end{aligned} \tag{7}$$

Thus the validity of the five $\mathrm{R^-/R^+}$ redox couples employed here as the reference $\mathrm{R^-/R^+}$ redox couple can be checked. Table 5 shows the values of $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$ obtained with pairs of the five redox couples in the solvents studied. Table 6 summarizes the $\Delta^{\mathrm{s'}}E^{\mathrm{s''}}(\mathrm{I})$ values for various solvent pairs measured against the silver/silver ion electrode. These results show that the theoretical predictions (6b) and (7) are satisfied within experimental error by all the five $\mathrm{R^-/R^+}$ redox couples. In particular, it is noteworthy that the hydrocarbon and metal complex systems give practically the same

TABLE 5. $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$ IN VARIOUS SOLVENTS AT 25 °C

I	II	$\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$/V			
		PC	DMF	AN	DMSO
DPA	$\mathrm{Fe(bpy)_3}$	1.30	1.31	1.31	
DPA	$\mathrm{Ru(bpy)_3}$	1.29	1.30	1.29	
DPA	Perylene	0.01		0.01	
DPA	Cobaltocene	1.06	1.07	1.06	
Perylene	Cobaltocene	1.05		1.05	
Perylene	$\mathrm{Fe(bpy)_3}$	1.29		1.30	
Perylene	$\mathrm{Ru(bpy)_3}$	1.28		1.28	
$\mathrm{Ru(bpy)_3}$	Cobaltocene	−0.23	−0.23	−0.23	
$\mathrm{Ru(bpy)_3}$	$\mathrm{Fe(bpy)_3}$	0.01	0.01	0.02	0.02
$\mathrm{Fe(bpy)_3}$	Cobaltocene	−0.24	−0.24	−0.25	

TABLE 6. $\Delta^{\mathrm{s'}}E^{\mathrm{s''}}$ (I) FOR VARIOUS REDOX COUPLES AT 25 °C

s′	s″	$\Delta^{\mathrm{s'}}E^{\mathrm{s''}}(\mathrm{I})$/V					
		DPA	Perylene	$\mathrm{Fe(bpy)_3}$	$\mathrm{Ru(bpy)_3}$	Cobaltocene	Average
DMF	PC	0.36		0.35	0.35	0.35	0.35
AN	PC	0.43	0.43	0.42	0.43	0.43	0.43
DMSO	PC			0.53	0.54		0.54
AN	DMF	0.07		0.07	0.08	0.08	0.08
DMSO	DMF			0.18	0.19		0.19
DMSO	AN			0.11	0.11		0.11

results although they are quite different in their chemical structures.

Regarding the charge distribution in the hydrocarbon ions, it can be confidently assumed that the π-electron spin-density distributions are the same for the monocation and monoanion of an alternant aromatic hydrocarbon. The pairing theorem[26,27] predicts that the π-electron spin-density distributions should be the same for the cation and anion of an alternant aromatic hydrocarbon. Some experimental results[28,29] seem to show that this theorem holds to a high degree of approximation for alternant hydrocarbon ions. Significant differences observed between the ESR spectra of the positive and negative hydrocarbon ions have been interpreted[30,31] in terms of the variation of the σ-π parameter, $Q_{\mathrm{CH}}^{\mathrm{H}}$, in McConnell's relation. Therefore it is quite reasonable to assume that[7] the charge distributions in the cation and anion radicals of perylene and DPA are very nearly the same. In fact, this assumption has been adopted by Case and his coworkers[32] in their estimation of the surface potential of acetonitrile. Parker,[33] in his studies on the energetics of electrode reactions of aromatic hydrocarbons, has also proceeded on this assumption. On the other hand the charge distributions in the cations of the bipyridine complexes seem somewhat different from those in the corresponding anions, since in the first three one-electron reduction steps of the bipyridine complexes each added electron may occupy one of the three vacant π^*-orbitals localized mainly in the ligand molecules.[15] This difference in charge distribution between the R^+ and R^- ions fortunately seems to result in a small effect (probably less than 0.01 eV)[7] on the difference of solvation energy, as indicated by the above $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$- and $\Delta^{\mathrm{s}'}E^{\mathrm{s}''}(\mathrm{I})$-tests. Recently Ogata, Fujisawa, and Tanaka[50] have proposed a $\mathrm{Co(bipy)_3^-}$/$\mathrm{Co(bipy)_3^+}$ couple as a candidate for the reference redox couple.

The Born equation for the free energy of ion solvation was first modified by Latimer, Pitzer, and Slansky[34] and later by numerous other authors.[3,6] This was done by introducing the empirical radius corrections specific to the solvent s, $R_+(\mathrm{s})$ and $R_-(\mathrm{s})$ for cations and anions, respectively. This correction should imply supplemental energies of ion solvation which are not involved in the simple Born equation. These supplemental energies may consist of a part of electrostatic energy of solvation due to ion-multipole interactions, as discussed by Buckingham,[35] and a part of non-electrostatic (or van der Waals') interaction energy of solvation. The latter is dependent on the orientation of solvent molecules in the first solvation sheath. Thus, in the modified Born equation the difference in the solvation free energy between two oppositely charged ions having the same radius should be reflected in the difference between $R_+(\mathrm{s})$ and $R_-(\mathrm{s})$. According to Strehlow,[6] $R_+(\mathrm{AN})=0.072$ and $R_-(\mathrm{AN})=0.061$ nm, which will result, for example, in $\Delta G_{\mathrm{R^-/R^+}}^{\mathrm{AN}}=0.02$ eV for the metal bipyridine complex redox couples.[7] Although Tanaka and Ogata[51] and Nedermeijer-Denessen, de Ligny, and Remijnse[36] have recently shown that the existence of $R_+(\mathrm{s})$ and $R_-(\mathrm{s})$ which are valid for *all* kinds of ions in a specified solvent, s, is questionable, this estimation of $\Delta G_{\mathrm{R^-/R^+}}^{\mathrm{S}}$ based on the empirical radius corrections as well as the discussion on the $\Delta^{\mathrm{I}}E^{\mathrm{II}}(\mathrm{s})$- and $\Delta^{\mathrm{s}'}E^{\mathrm{s}''}(\mathrm{I})$-test described above shows that the error, introduced by assuming $\Delta G_{\mathrm{R^-/R^+}}^{\mathrm{S}}=0$ (Eq. 4) for the redox couples investigated here, is probably not larger than ±0.01 eV. Thus it may be concluded that the standard potentials of the $\mathrm{R^-/R^+}$ redox couples studied here are solvent-independent within an error of ±0.01 V.

To estimate the solvent activity coefficient of an ion at $\mu=0$, μ being the ionic strength, it is necessary to know the dependence of the activity coefficient on the ionic strength in each solvent. Table 7 shows $\Delta E_{1/2}^{\mathrm{r}}$(exptl) as the difference of two experimental values of $E_{1/2}^{\mathrm{r}}(\mathrm{R^-/R^+})$ at two different concentrations of the supporting electrolyte, *i.e.*, 0.05 and 0.2 M TEAP, referred to Ag/1 mM $\mathrm{Ag^+}$ in 0.05 and 0.2 M TEAP, s, electrodes, respectively. Since $E_{1/2}^{\mathrm{r}}(\mathrm{R^-/R^+})\approx E_{\mathrm{R^-/R^+}}^{\circ}$ the difference $\Delta E_{1/2}^{\mathrm{r}}$(exptl) should be equated to the difference of the two reference electrodes, which is expressed by $\Delta E_{1/2}^{\mathrm{r}}=(RT/F)\ln[f_{\mathrm{Ag}}^{+}(0.05\ \mathrm{M})/f_{\mathrm{Ag}}^{+}(0.2\mathrm{M})]$. Table 7 shows $\Delta E_{1/2}^{\mathrm{r}}$(calcd) as the difference calculated by this equation with the Davies equation, $\log f=-A[\sqrt{\mu}/(1+\sqrt{\mu})-0.3\ \mu]$.[37] Good agreement between $\Delta E_{1/2}^{\mathrm{r}}$(exptl) and $\Delta E_{1/2}^{\mathrm{r}}$(calcd) indicates that the Davies equation is applicable to estimate the ionic activity coefficients of the silver ion in the solvents studied. Thus the solvent activity coefficients of the silver ion were corrected for $\mu=0$ using the Davies equation. Table 8 gives the solvent activity coefficients of the silver ion at $\mu=0$, $(RT/F)\ln{}^{\mathrm{S}'}\gamma_{\mathrm{Ag^+}(\mu=0)}^{\mathrm{S}''}$, in molality scale, as obtained by this procedure. Table 8 also gives for comparison the solvent activity coefficients estimated on the basis of other extrathermodynamic assumptions by other authors.[41,46–48] The $(RT/F)\ln{}^{\mathrm{S}'}\gamma_{\mathrm{Ag^+}(\mu=0)}^{\mathrm{S}''}$ values in molarity scale[47,48] were conventionally converted to the values in molality scale by

Table 7. Reversible half-wave potentials of $\mathrm{R^-/R^+}$ redox couples at different concentrations of supporting electrolyte in AN and PC

Solvent	$\mathrm{R^-/R^+}$ couple	$-E_{1/2}^{\mathrm{r}}(\mathrm{R^-/R^+})$/V 0.2 M TEAP[a]	 0.05 M TEAP[b]	$\Delta E_{1/2}^{\mathrm{r}}$(exptl)/mV	$\Delta E_{1/2}^{\mathrm{r}}$(calcd)/mV[c]
AN	DPA	0.603	0.607	4±2	7
	Cobaltocene	1.658	1.663	5±2	7
	$\mathrm{Fe(bpy)_3}$	1.911	1.918	7±2	7
PC	DPA	1.025	1.028	3±2	3

a) V *vs.* Ag/1 mM $\mathrm{Ag^+}$, 0.2 M TEAP. b) V *vs.* Ag/1 mM $\mathrm{Ag^+}$, 0.05 M TEAP.
c) Calculated by Davies equation.

TABLE 8. SOLVENT ACTIVITY COEFFICIENTS OF SILVER ION AT ZERO IONIC STRENGTH, $(RT/F)\ \ln^{PC}\gamma^{s}_{Ag^+(\mu=0)}$, IN MOLALITY SCALE ESTIMATED ON VARIOUS ASSUMPTIONS AT 25 °C

The assumptions, as numbered in the table, are (1) $\ln {}^{o}\gamma^{s}_{Ph_4As^+} = \ln {}^{o}\gamma^{s}_{Ph_4B^-}$;[48] (2) ferrocene scale;[47] (3) negligible liquid junction;[47] (4) modified Born equation.[41,46]

s	$-(RT/F)\ \ln^{PC}\gamma^{s}_{Ag^+(\mu=0)}/V$				
	This work	(1)	(2)	(3)	(4)
AN	0.43	0.40	0.47	0.43	0.39
DMF	0.35	0.35	0.40	0.38	0.36
DMSO	0.53	0.51	0.56	0.57	0.53
Water	(0.23)[a]	0.17	0.09	0.24	0.23

a) Calculated by Eq. 8 (see text).

$$\ln {}^{s'}\gamma^{s''}_{Ag^+(\mu=0)}(\text{molal}) + \ln (d_o^{s'}/d_o^{s''}) = \ln {}^{s'}\gamma^{s''}_{Ag^+(\mu=0)}(\text{molar}),$$

where $d_o^{S'}$ and $d_o^{S''}$ are the densities of pure solvents, s′ and s″, respectively. Assumption 1, the reference electrolyte method,[38] equates the solvent activity coefficients of tetraphenylarsonium cation and tetraphenylboride anion, $\log {}^{o}\gamma^{S}_{ph_4As^+} = \log {}^{o}\gamma^{S}_{ph_4B^-}$. Assumption 2, based on Strehlow's ferrocene scale, equates the solvent activity coefficients of ferrocene and ferricinium cation.[39] Assumption 3 neglects the liquid junction potential in a cell composed of a nonaqueous salt bridge of tetraethylammonium picrate.[40] Assumption 4 is based on the solvent activity coefficient of rubidium ion calculated by a modified Born equation.[41] The internal coherency of the solvent activity coefficient of the silver ion estimated by these assumptions seems generally satisfactory in these four solvents. In particular, good agreement is seen between the results reported here and those based on assumptions 1 or 4. Such a correspondence, considering the similarities between assumption 1 and ours, would be expected. The modified Born equation with appropriate empirical parameters seems to give a reasonable estimation to the differences in the solvation free energies of large alkali ions between two solvents.

When electron affinity and ionization potential data are available for the neutral compounds R, the free energy change of the reference electrode reaction, $\Delta G^{s}(Ag/Ag^+)$, by Eq. 5 can be calculated. At present the experimental data are not available, but theoretical values of the electron affinity and ionization potential for perylene are available: $(A+I)_{\text{perylene}}=8.23$ eV[42] or 8.68 eV.[43] Alternatively, for the $(A+I)$ value of perylene, the average value of the experimental data of $(A+I)$ for several other alternant aromatic hydrocarbons can be used, since the molecular orbital theory[44] predicts that the $(A+I)$ for alternant aromatic hydrocarbons should be constant, and available experimental results support this relationship: $(A+I)^{ex}_{av}=8.22$ eV.[32] Assuming 8.22 eV for the $(A+I)$ of perylene, $\Delta G^{s}(Ag/Ag^+)$ by Eq. 5 was calculated and the results are summarized in Table 9. Table 9 also gives the values of the standard free energy change (in molality scale) of the reference electrode reaction, $\Delta G^{os}(Ag/Ag^+)$, conventionally calculated by

$$\Delta G^{os}(Ag/Ag^+) = \Delta G^{s}(Ag/Ag^+) + RT \ln [f_{Ag^+}C_{Ag^+}/d_o],$$

where d_o is the density of the pure solvent and C_{Ag^+} the molar concentration of the silver ion involved in the reference electrode. In the calculations it was also assumed that 1 mM silver salt contained in the reference electrode solution was perfectly dissociated in all the solvents studied. Table 10 shows the values of $(A+I)$ of the compounds used here as the R^-/R^+ reference redox couple which were calculated from Eq. 5 by taking 8.22 eV for the $(A+I)$ of perylene.

TABLE 9. STANDARD FREE ENERGY CHANGES OF REFERENCE ELECTRODE REACTIONS (Ag/Ag^+, s) AND SOLVENT ACTIVITY COEFFICIENTS OF SILVER ION AT 25 °C

s	$(1/F)\Delta G^{s}\cdot$ $(Ag/Ag^+)/V$	$(1/F)\Delta G^{os}\cdot$ $(Ag/Ag^+)/V$	$(RT/F)\cdot$ $\ln^{w}\gamma^{s}_{Ag^+(\mu=0)}/V$
PC	−5.15	−5.34	0.23
AN	−4.72	−4.92	−0.19
DMF	−4.79	−4.99	−0.12
DMSO	−4.62	−4.82	−0.29

TABLE 10. SUM OF ELECTRON AFFINITY AND IONIZATION POTENTIAL FOR FIVE REFERENCE REDOX COUPLES STUDIED

	$(A+I)$/eV
Perylene	8.22[a]
DPA	8.24
Cobaltocene	6.12
$Fe(bpy)_3$	5.64
$Ru(bpy)_3$	5.66

a) Reference value.

Recently Trasatti[45] has recalculated the absolute potential of the standard hydrogen electrode using the more reliable value of the hydration free energy of protons; $\varepsilon^{\circ}_{abs}=4.31\pm0.04$ V. This value agreed well with those estimated from the calculated absolute potentials of several alkali metal/alkali metal ion electrodes in water. Thus the absolute electrode potential of an Ag/Ag^+ half-cell in water can be calculated; $\Delta G^{ow}(Ag/Ag^+)=-5.11$ eV. From this the solvent activity coefficients for the transfer of the silver ion from water to nonaqueous solvent can be calculated by

$$(RT) \ln {}^{w}\gamma^{s}_{Ag^+(\mu=0)} = \Delta G^{ow}(Ag/Ag^+) - \Delta G^{os}(Ag/Ag^+). \quad (8)$$

The results are given in Tables 8 and 9. These values agree well with those estimated on the basis of the modified Born equation,[41,46] but deviate by about −0.05 V from those estimated by the reference electrolyte method.[48] Note that the determination of solubilities of the reference electrolyte in water is sometimes associated with inaccuracy.[47]

Addendum. After completion of this work,[52] a paper was published by C. Madec and J. Courtot-Coupez,[53] which contains experimental results that confirm that the R^-/R^+ system of alternant aromatic hydrocarbons can be used as a solvent-independent reference for potential comparisons.[7]

We are grateful to Dr. Takeko Matsumura-Inoue of Nara University of Education for her kind gift of bipyridine complexes used in this work. This work was supported by a grant from the Japanese Ministry of Education.

References

1) D. Bauer and M. Breant, "Electroanalytical Chemistry," ed by A. J. Bard, Marcel Dekker, New York (1975), Vol. 8, p. 281.

2) R. G. Bates, "Solute-Solvent Interactions," ed by J. F. Coetzee and C. D. Ritchie, Marcel Dekker, New York (1969), p. 46.

3) O. Popovych, *Crit. Rev. Anal. Chem.*, **1**, 73 (1970).

4) A. J. Parker, *Electrochim. Acta*, **21**, 671 (1976).

5) I. M. Kolthoff, *Pure Appl. Chem.*, **25**, 305 (1971).

6) H. Strehlow, "The Chemistry of Non-Aqueous Solvents," ed by J. J. Lagowski, Academic Press, New York (1966), p. 129.

7) M. Senda and R. Takahashi, *Rev. Polarogr. (Kyoto)*, **20**, 56 (1974).

8) T. Kakutani, S. Totsuka, and M. Senda, *Bull. Chem. Soc. Jpn.*, **46**, 3652 (1973).

9) S. R. Brinkley, Jr. *J. Am. Chem. Soc.*, **62**, 3524 (1940).

10) G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6148 (1952).

11) W. E. Geiger, Jr., and D. E. Smith, *J. Electroanal. Chem. Interfacial Electrochem.*, **50**, 31 (1974).

12) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

13) C. K. Mann, "Electroanalytical Chemistry," ed by A. J. Bard, Marcel Dekker, Vol. 3, New York (1969), p. 57.

14) N. Tanaka and Y. Sato, *Electrochim. Acta*, **13**, 335 (1968).

15) T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, **58**, 401 (1975).

16) W. E. Geiger, Jr., *J. Am. Chem. Soc.*, **96**, 2632 (1974).

17) S. P. Gubin, S. A. Smirnova, and L. I. Denisovich, *J. Organomet. Chem.*, **30**, 257 (1971).

18) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York (1970).

19) I. Tachi and M. Senda, "Advances in Polarography," ed by I. S. Longmuir, Pergamon Press, London (1960), Vol. 2, p. 454.

20) R. S. Nicholson, J. M. Wilson, and M. L. Olmstead, *Anal. Chem.*, **38**, 542 (1966).

21) R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 178 (1965); *ibid.*, **37**, 190 (1965).

22) H. Matsuda, *J. Electroanal. Chem. Interfacial Electrochem.*, **56**, 165 (1974).

23) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

24) H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, **59**, 494 (1955).

25) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).

26) A. D. MacLachlan, *Mol. Phys.*, **2**, 271 (1959).

27) H. M. MacConnell and R. E. Robertson, *J. Chem. Phys.*, **28**, 991 (1958).

28) J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964).

29) G. J. Hoijtink and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, **76**, 836 (1957).

30) J. R. Bolton, "Radical Ions," ed by E. T. Kaiser and L. Kevan, Interscience Publishers, New York (1968), p. 1.

31) G. Vincow, Ref. 30, p. 151.

32) B. Case, N. S. Hush, R. Parsons, and M. E. Peover, *J. Electroanal. Chem. Interfacial Electrochem.*, **10**, 360 (1965).

33) V. D. Parker, *J. Am. Chem. Soc.*, **98**, 98 (1976).

34) W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, **7**, 108 (1939).

35) A. D. Buckingham, *Discuss. Faraday Soc.*, **24**, 151 (1957).

36) H. J. M. Nedermeijer-Denessen, C. L. de Ligny, and A. G. Remijnse, *J. Electroanal. Chem. Interfacial Electrochem.*, **77**, 153 (1977).

37) C. W. Davies, "Ion Association," Butterworths, London (1962).

38) E. Grunwald, G. Baughman, and G. Kohnstam, *J. Am. Chem. Soc.*, **82**, 5801 (1960).

39) H. M. Koepp, H. Wendt, and H. Strehlow, *Z. Elektrochem.*, **64**, 483 (1960).

40) A. J. Parker and R. Alexander, *J. Am. Chem. Soc.*, **90**, 3313 (1968).

41) J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, **89**, 2513 (1967).

42) T. Kunii and H. Kuroda, *Theor. Chim. Acta*, **11**, 97 (1968).

43) M. J. S. Dewar, J. A. Hashmall, and N. Trinajstic, *J. Am. Chem. Soc.*, **92**, 5555 (1970).

44) N. S. Hush and J. A. Pople, *Trans. Faraday Soc.*, **51**, 600 (1955).

45) S. Trasatti, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1752 (1974); *J. Electroanal. Chem. Interfacial Electrochem.*, **52**, 313 (1974).

46) N. Matsuura and K. Umemoto, *Bull. Chem. Soc. Jpn.*, **47**, 1334 (1974).

47) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Am. Chem. Soc.*, **94**, 1148 (1972).

48) B. G. Cox, G. R. Hedwig, A. J. Paker, and D. W. Watts, *Aust. J. Chem.*, **27**, 477 (1974).

49) D. Bauer and J-P. Beck, *Bull. Soc. Chim. Fr.*, **1973**, 1252.

50) T. Ogata, T. Fujisawa, and N. Tanaka, Paper Presented at the Polarographic Meeting, Oct. 7—8, 1976, Nagano; abstract, *Rev. Polarogr. (Kyoto)*, **22**, 124 (1976).

51) N. Tanaka and T. Ogata, *Sci. Rep. Tohoku Univ., Ser. 1*, **57**, 57 (1974).

52) T. Kakutani, Y. Morihiro, M. Senda, R. Takahashi, and K. Matsumoto, Paper presented at the Polarographic Meeting, Nov. 4—5, 1977, Osaka; abstract, *Rev. Polarogr. (Kyoto)*, **23**, 45 (1977).

53) C. Madec and J. Courtot-Coupez, *J. Electroanal. Chem. Interfacial Electrochem.*, **84**, 177 (1977).