The Effect of Water on the Reduction Potentials of Some Aromatic Compounds in the DMF-Water System

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From the viewpoint of the interaction between the oxidized or the reduced form of a depolarizer and solvents, the solvent effect on the half-wave potentials was studied. Another factor affecting the $E_{1/2}$, *i.e.*, pH or ion-pair formation, was also examined. The correction for the liquid junction potential was carried out by the use of the ferrocene standard. The reduction products, radical anions or dianions, were found to be stabilized by the hydrogen-bonding with water where the hydrogen-bond interaction of the dianion was stronger than that of the monoanion. Aromatic hydrocarbon radical anions, whose charges are dispersed over the molecule, were less susceptible to this solvent transfer than were the anthraquinone radical anion and the dianion, whose charges are strongly localized.

In a previous paper,[1] a study of the rate of the protonation reaction of aromatic hydrocarbon radical anions with water has been reported; the rates were found to be greatly accelerated by the increase in the water content in DMF-water mixtures. This behavior was interpreted in terms of the hydrogen-bond interaction of radical anions or transition states with water.

The present work will deal with the interaction of the radical anions of several aromatic compounds with solvents.

Experimental

Materials. All the organic reagents except *p*-dinitrobenzene were obtained commercially. E.P.-grade anthraquinone was purified by recrystallization from ethanol, and E.P.-grade *p*-benzoquinone, by sublimation. G.R.-grade ferrocene, methylviologen, azulene, and fluoranthene were used without further purification. *p*-Dinitrobenzene was prepared and purified according to the method of Starkey[2] (mp. 173°C). The tetraethylammonium perchlorate (TEAP) and tetraethylammonium bromide (TEAB) were the same as have been described previously.[3] G.R.-grade lithium perchlorate was trihydrate and was dehydrated by heating it to a constant weight before preparing the DMF solution. G.R.-grade lithium hydroxide and a tetraethylammonium hydroxide aqueous solution were used without further purification. The solvents used were purified in the usual manner. The dimethylformamide (DMF) was the same as has been described previously.[3] The acetonitrile was dried over phosphorus pentoxide and then fractionally distilled; its water content was below 0.01%. G.R.-grade ethanol and acetone were used without further purification; their water contents were 0.3% and 0.2% respectively. These water contents were measured by Karl Fischer titration.

Polarography. A saturated calomel electrode was connected to the cell by a 1 N KNO_3-agar bridge,[3,4] which outlet was positioned just above the dropping mercury electrode. The use of a conventional aqueous potassium chloride agar salt bridge for precise work in non-aqueous solvents has been criticised.[5] Therefore, the use of the 1 N KNO_3 aqueous agar bridge must be checked; the effect of the dipping or aging time of the bridge was studied by the following experiments.

One end of the bridge was dipped in DMF-water solutions containing the same quantities of methylviologen and TEAP as the solution for polarographic measurements, while the other end was dipped in a 1 N KNO_3 aqueous solution. From one half-wave potential measurement with the bridge to another, the aging solution was renewed, because the dissolution of the bridge components contaminates the aging solution.

In the studies of other reducible substances, the 1 N KNO_3 agar bridges were aged in depolarizer free basic solutions. Each solution was deaerated by bubbling pure nitrogen[3] for 15—20 min. In the case of the solution which contained a small amount of water, the water content was determined by Karl Fisher titration just after recording a polarogram.

The pH-dependence of the half-wave potential was studied in Britton-Robinson buffer solutions. The polarographs used were Yokogawa Denki models POL-11 and POL-21 for recording the D.C. and A.C. polarograms respectively. The pH of the solution was measured with a Toa Denpa PM-5A pH meter. All the measurements were carried out at 25°C.

Results and Discussion

The Reference Electrode. The half-wave potentials of methylviologen in the DMF-water system are presented in Table 1. It is evident that the half-wave potentials are reproducible within ±10 mV independently of the aging time. However, at least 10—15 min are required for the practical setting of bridges. Therefore, the potential drift caused within 10—15 min is not presented. The drift of the potential may be much less with the 1 N KNO_3 aqueous agar bridge in a DMF-water system than with an aqueous agar KCl bridge in acetonitrile.[5] As the water contents in a DMF-water system are comparatively ineffective on the half-wave potentials and the summit potentials of methylviologen (Table 1 and Fig. 8), the existence of water extracted from the aqueous agar salt bridge has practically no influence on the half-wave potentials. In other experiments, however, it is desirable

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[1] S. Hayano and M. Fujihira, This Bulletin, **44**, 2046 (1971).

[2] E. B. Starkey, "Organic Synthesis," Coll. Vol. II, (1950) p. 225.

[3] S. Hayano and M. Fujihira, This Bulletin, **44**, 1496 (1971)

[4] M. E. Peover and J. D. Davies, *J. Electroanal. Chem.*, **6**, 46 (1963).

[5] J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **66**, 1708 (1962).

Table 1. Effect of aging-time of 1 n KNO_3 agar bridges on the half-wave potentials of methylviologen in DMF-water system

H_2O	0%		20%		40%		60%		80%		100%	
day$\diagdown -E_{1/2}$	I	II	I	II	I	II	I	II	I	II	I	II
0	0.48	0.87	0.53	0.91	0.56	0.94	0.59	0.97	0.62	1.00	0.67	1.03
1	0.48	0.87	0.53	0.92	0.56	0.94	0.58	0.97	0.62	1.00	0.68	1.03
3	0.47	0.86	0.52	0.92	0.56	0.94	0.58	0.98	0.62	1.00	0.68	1.03
10	0.48	0.87	0.52	0.90	0.56	0.94	0.58	0.98	0.61	1.00	0.67	1.03
20	0.48	0.87	0.51	0.92	0.57	0.94	0.59	0.98	0.62	1.00	0.67	1.03
30	0.48	0.87	0.51	0.91	0.56	0.95	0.58	0.98	0.62	1.00	0.67	1.03
70	0.48	0.88	0.51	0.91	0.57	0.95	0.59	0.98	0.62	1.01	0.67	1.03
120	0.49	0.90	0.52	0.92	0.55	0.94	0.59	0.98	0.62	1.00	0.66	1.03

I and II are $-E_{1/2}$ of the first and the second waves in V *vs.* SCE.

to use the aged bridge to prevent the accidental introduction of water into the solution, because the increase of water may remarkably affect the half-wave potentials or the summit potentials, as in the case of anthraquinone reduction (Fig. 5). The aging time of a week is adopted since such a bridge gives only a small potassium wave in a polarogram.

pH-Dependence of the Half-Wave Potentials. The $E_{1/2}$-pH plot for anthraquinone in water is shown in Fig. 1. The breaks in the curve (or the intersection of extrapolated linear parts) indicate the pK_a-values for the individual degrees of dissociation[6)] in such a reversible system. The pK_a-values of anthrahydroquinone are found to be pK_{a1}=10.9 and pK_{a2}=11.8 from the plot in Fig. 1. Therefore, in the pH-region where the $E_{1/2}$ is pH-independent, the electrode process is a reversible two-electron transfer and the reduction product is the dianion.

The pH-dependence of the electrode process of *p*-dinitrobenzene has been studied by polarography[7)] or by cyclic voltammetry.[8,9)] The $E_{1/2}$-pH plot is similar to that of anthraquinone, and in an alkaline solution the reversible two-electron reduction to the dianion proceeds.

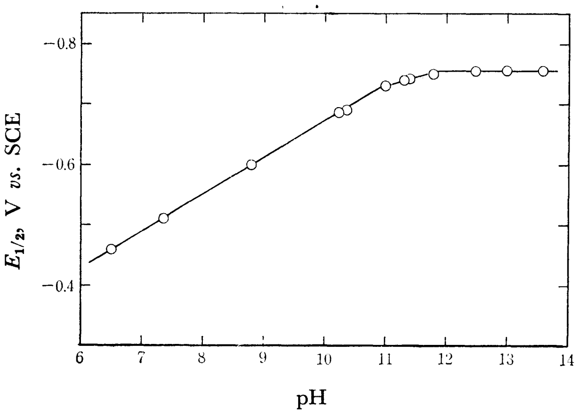

Fig. 1. $E_{1/2}$−pH plot of anthraquinone in water.

When the solvent effect on $E_{1/2}$ is discussed from the viewpoint of the solvation-energy difference between oxidized and reduced species before and after electron transfer, these pH-independent half-wave potentials to the dianion should be compared with those in other solvents in which also only the electron transfer occurs.

Ion-pair Formation. Ion-pair formation is another factor which exerts an influence on the value of the half-wave potential. In order to discuss the solvent effect on the half-wave potential, this factor must be eliminated as much as possible.

The formation of complexes between the radical anions or dianions and the cations of the supporting electrolyte in solvents with moderate dielectric constants, such as dimethylformamide and acetonitrile, has been studied,[4,10)] and it has been found that the half-wave potentials for the production of dianions are shifted to the positive side of the potential to a much greater extent than those for the monoanions, and that this positive shift tendency is in the order of $Li^+ > Na^+ > K^+ > NEt_4^+ > NBu_4^+$ in respect to the cation. The difference between NEt_4^+ and NBu_4^+ is small. In the present study, tetraethylammonium salts were used in order to eliminate the effects of ion-pair formation on the half-wave potential.

The effect of increasing the lithium-ion concentration on the half-wave potentials of *p*-dinitrobenzene in DMF, while the total salt concentration is kept constant with tetraethylammonium perchlorate, is shown in Fig. 2. The shifts are greater for the dianion than for the monoanion, and the behavior is similar to that of anthraquinone.[4)] One *p*-dinitrobenzene dianion is associated with two lithium cations above a 1.2×10^{-2} M lithium cation concentration. As the concentration of the lithium cation should be much higher than that of *p*-dinitrobenzene,[6)] the dependence of $E_{1/2}$ on the lithium concentration could not be measured in the low-concentration range of lithium. As the $E_{1/2}$ values with TEAP are known, the intersections of the left-hand side of the straight line with the linear part, which is independent of the lithium-ion

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[6)] J. Heyrovsky and J. Kuta, "Principle of Polarography," Academic Press, New York, N.Y. (1966), pp. 147, 161, and 181.

[7)] L. Holleck and H. J. Exner, *Z. Elektrochem.*, **56**, 677 (1952); L. Holleck and H. Schmidt, *ibid.*, **59**, 56 (1955).

[8)] W. Kemula, Z. Kublik, and R. Cyranski, *Roczniki Chem.*, **36**, 1349 (1962).

[9)] S. Hayano and M. Fujihira, presented at the 14th Symposium of Polarography, Hiroshima, Oct., 1968.

[10)] L. Holleck and D. Becher, *J. Electroanal. Chem.*, **4**, 321 (1962).

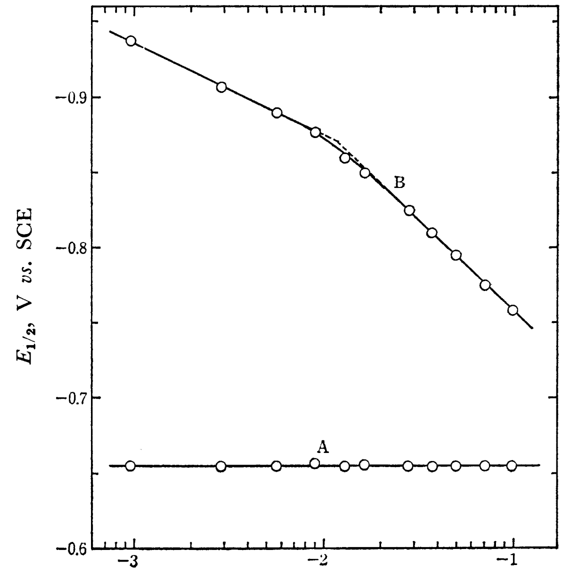

Fig. 2. Dependence of $E_{1/2}$ of *p*-dinitrobenzene on lithium ion concentration in DMF, A, *p*-DNB + e $\rightleftharpoons$ *p*-DNB$^{\dot{-}}$; B, *p*-DNB$^{\dot{-}}$ + e $\rightleftharpoons$ *p*-DNB^{2-}.

concentration, may be estimated to be about 6×10^{-4} M. Therefore, a *p*-dinitrobenzene dianion forms a 1 : 1 complex with a lithium cation in the lithium concentration range of 6×10^{-4}—1.2×10^{-2} M. On the other hand, monoanions are not associated with lithium in the lithium-concentration range measured.

The Half-wave Potential of Some Organic Compounds in a Mixed Solvent System. The present work is intended to consider the effects of solvents on the reduction potential of organic compounds. Quinones and *p*-dinitrobenzene are reduced reversibly to the dianions in alkaline aqueous solutions, as has been described above. On the other hand, these compounds give two one-electron reversible waves in aprotic solvents.[11–13]

Then, the changes of half-wave potentials in the DMF-alkaline water system were measured.[15] The results with *p*-dinitrobenzene are shown in Fig. 3. The logarithms of the volume percent of water are used as the abscissa, because it is desirable to know in detail the change in the region which contains small amounts of water. The half-wave potentials of some organic compounds in DMF can be found in the literature, but usually the water contents, which are essentially more or less involved in the solvents, have not been described. As is shown in Fig. 3, however, the half-wave potentials were found to be constant in the region of water content below 0.1%. These values can be practically regarded as the half-wave potentials in DMF.

When the lithium salt is used as the supporting electrolyte in DMF, the $E_{1/2}$ values of the second wave are affected and shift to more positive potentials, as has been described above. This tendency continues until the water contents reach 20—30% (Fig. 3); that is, the dianion is stabilized by water without breaking the ion-pair with the lithium cation when small amounts of water are added.

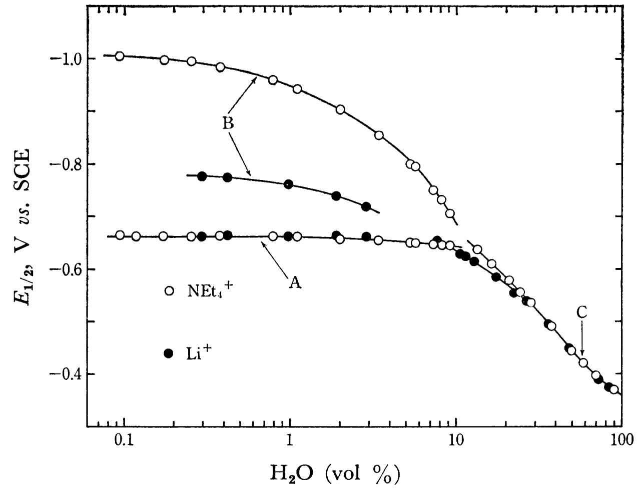

Fig. 3. Dependence of $E_{1/2}$ of *p*-dinitrobenzene on the alkaline water content in DMF-alkaline water system,[15] A, neutral → monoanion; B, monoanion → dianion; C, neutral → dianion.

In Figs. 4—8 can be seen the variation in the A.C. summit potentials of *p*-dinitrobenzene, anthraquinone, and some other organic compounds with the composition of the solvent medium, where no correction for the liquid junction potential is taken into account. As the half-wave potential reading of the very close waves is difficult, the A.C. summit potentials are shown instead of the half-wave potentials.[16] The variation in anthraquinone is similar to that in *p*-dinitrobenzene. In DMF, the difference in the summit potentials of anthraquinone is larger than that in *p*-dinitrobenzene; thus, the variations in the summit potentials of the first and the second waves of anthraquinone could be obtained over a wide range of composition in the DMF-alkaline water system. These compounds showed similar behavior in DMF-ethanol systems (Figs. 4, 5, and 7). On the other hand, anthraquinone showed little change in the summit potentials in DMF-ace-

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11) M. E. Peover, *J. Chem. Soc.*, **1962**, 4540.

12) M. E. Peover, *Trans. Faraday Soc.*, **60**, 479 (1964).

13) Strictly speaking, the semiquinone formation constants

$$K=\frac{[\mathrm{S}]^2}{[\mathrm{Ox}][\mathrm{Red}]}$$

of these compounds are small[14] in alkaline water and are large in aprotic solvents. The semiquinone formation constant is obtained by[6,14]

$$E_1-E_m=E_m-E_2=\frac{RT}{2F}\ln K$$

where E_1 is the reduction potential of the oxidized form to the semiquinone, E_2 is the reduction potential of the semiquinone to the reduced form, and E_m is the mid point potential.

14) R. Gill and H. I. Stonehill, *J. Chem. Soc.*, **1952**, 1845.

15) Below 10 percent of water in DMF, hydroxide anion reacts with *p*-dinitrobenzene to give nitrophenol, therefore 0.1 N perchlorate salt aqueous solutions were used instead of 0.1 N hydroxide aqueous solutions below 10 percent of water.

16) As the A. C. summit potentials agreed with the D. C. half-wave potentials within at most 20 mV for the present systems, these potentials may be looked as the same. Methylviologen, however, gave tensammetric peaks in addition to the faradaic peaks in the A. C. polarogram in water.

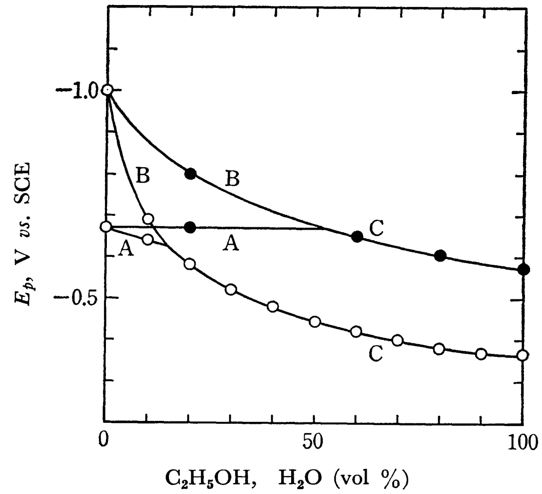

Fig. 4. E_p of *p*-dinitrobenzene in DMF-alkaline water[15] and in DMF-ethanol system, ○, DMF-alkaline water; ●, DMF-ethanol.

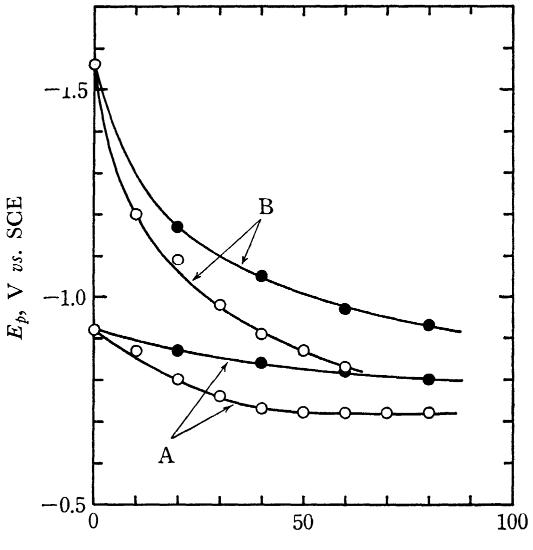

Fig. 5. E_p of anthraquinone in DMF-alkaline water and in DMF-ethanol system, ○, DMF-alkaline water; ●, DMF-ethanol.

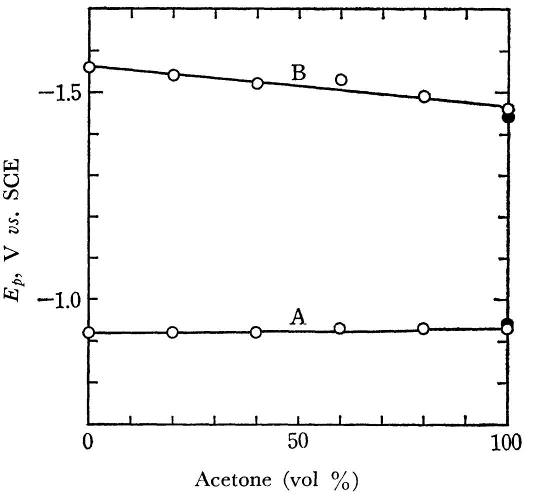

Fig. 6. E_p of anthraquinone in DMF-acetone and in acetonitrile, ○, DMF-acetone; ●, in acetonitrile.

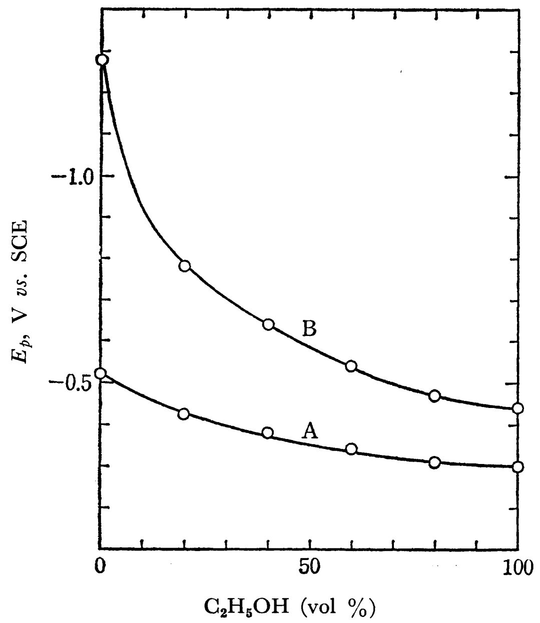

Fig. 7. E_p of *p*-benzoquinone in DMF-ethanol system.

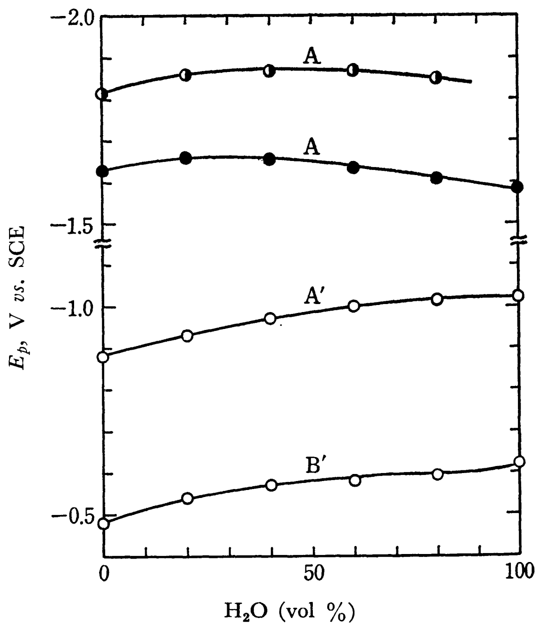

Fig. 8. E_p of methylviologen in DMF-water and E_p of azulene and fluoranthene in DMF-alkaline water system, ○, methylviologen; ●, azulene; ◑, fluoranthene. A′, monocation → neutral; B′, dication → monocation.

tone[17] and may similarly show little change in DMF-acetonitrile (Fig. 6).

The dielectric constants of the solvents used are given in Table 2. A comparison of the values of ε with the variation in the summit potentials described above leads to the conclusion that the solvent effect on the half-wave potentials cannot be explained by the Born equation only:

$$-\Delta G_{el}^{\circ} = \frac{Nz^2e^2}{2r}\left(1-\frac{1}{\varepsilon}\right)$$

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[17] As the supporting electrolyte, tetra-*n*-propylammonium perchlorate (Nakarai Chemicals reagent for polarography) was used, because of low solubilities of tetraethylammonium salts in acetone.

where e is the electronic charge, ε is the dielectric constant of the medium, N is Avogadro's number, and r is the radius of the ion. The Born equation predicts that the reduction potential of the neutral molecule to the anion shifts to a more positive potential in the solvent with the higher dielectric constant. In view of this, the remarkable positive shift of the half-wave potentials (or summit potentials) with an increase in the ethanol content in the DMF-ethanol system cannot be interpreted. The positive shift of the half-wave potentials with an increase in the water or alcohol content can be interpreted preferably by the hydrogen-bond interaction[11] of the produced anions with water or alcohol. As is shown in Figs. 4, 5, and 7, the summit potentials of the second waves, which correspond to the reductions from the monoanion to the dianion, shifted remarkably to a positive potential with an increase in the water or alcohol content. This may be due to the stronger hydrogen-bond interaction of the dianion than that of the monoanion. In the case of methylviologen, it is predicted that such a positive shift will not be observed, because two one-electron waves of methylviologen correspond to the reductions from the dication to the monocation and from the monocation to the neutral molecule, and generally the cation and the neutral molecule are much poorer acceptors of a hydrogen bond than the anion is. In fact, the behavior (Table 1 or Fig. 8) is different from that of *p*-dinitrobenzene or anthraquinone. The half-wave potentials show a rather negative shift with an increase in the amount of water. These shifts are not caused by the change in solvation, but by the liquid junction potential, for the half-wave potentials of ferrocene, which were assumed to give the same potentials in various solvents, also showed a negative shift in the DMF-water system as the water content increased. The half-wave potentials of ferrocene, measured by cyclic voltammetry with the Pt anode, are shown in Table 3. According to the assumption that ferrocene-ferricinium couple has the same potential in various solvents, the variation of $E_{1/2}$ in Table 3 is equal to the change in the liquid junction potential with the composition of the DMF-water system.

Table 2. Dielectric constants of solvents at 25°C

H_2O	DMF	CH_3CN	Ethanol	Acetone
78.5	36.7	36.7	24.3	20.7

Table 3. $E_{1/2}$ of ferrocene

DMF %	100	90	80	70	60	50	40	30	20	10	0
$E_{1/2}$	0.421	0.370	0.331	0.296	0.265	0.242	0.221	0.206	0.193	0.175	0.160

In Fig. 9, the variations in $E_{1/2}$ (or E_p) *versus* the $E_{1/2}$ of the ferrocene with the composition of the DMF-water (or DMF-alkaline water) systems for several organic compounds are shown. As has been described above, methylviologen shows almost constant half-wave potentials in the DMF-water system. On the other hand, anthraquinone shows a much grater positive shift of the summit potentials by the correction for the liquid junction potentials in the DMF-alkaline water system (*cf.* Fig. 5).

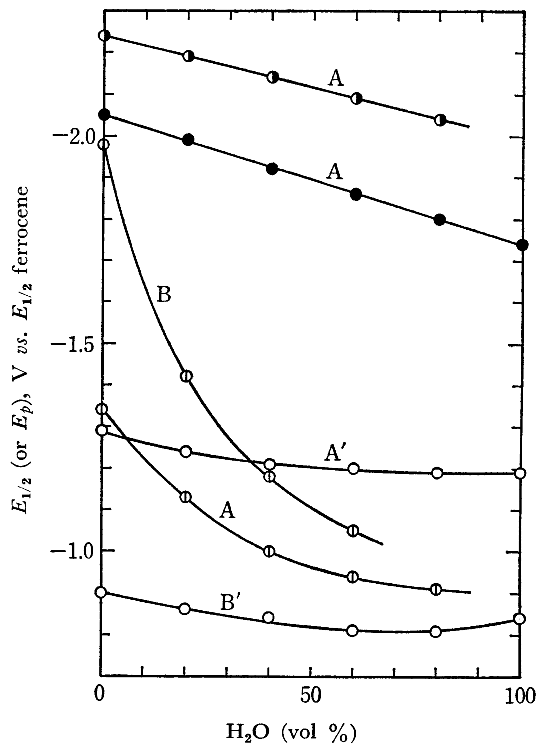

Fig. 9. $E_{1/2}$ of methylviologen, azulene, and fluoranthene, and E_p of anthraquinone *versus* $E_{1/2}$ of ferrocene, ○, methylviologen; ●, azulene; ◑, fluoranthene; ⦶, anthraquinone.

In the case of aromatic hydrocarbons, protonations occur even in the DMF-alkaline water system and affect the half-wave potentials. However, azulene and fluoranthene are known to show a reversible one-electron reduction even in protic media.[18] The variations in their half-wave potentials in the DMF-alkaline water system are also shown in Fig. 9. The positive shift of the potentials with an increase in the water content in the DMF-alkaline water system is much less in the reduction of hydrocarbons than in the reduction of anthraquinone. In the case of aromatic hydrocarbons, the reduction products, radical anions, are known from ESR measurements to have a delocalized negative charge. On the other hand, anthraquinone anions have localized negative charges on the oxygen atoms. Therefore, the hydrogen-bond interaction of anions with water in the DMF-alkaline water system is much less in aromatic hydrocarbon anions than in anthraquinone or *p*-dinitrobenzene anions.

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[18] L. H. Chopard-dit-Jean and E. Heilbronner, *Helv. Chim. Acta*, **36**, 144 (1953).