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A NOVEL ELECTROCHEMICAL SOLVENT PARAMETER AND ITS APPLICATIONS TO MICELLAR SYSTEMS

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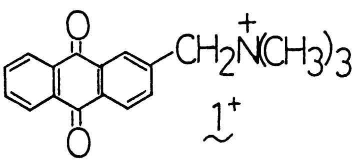
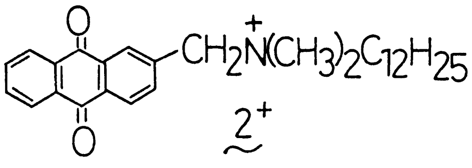
The peak-to-peak potential of cyclic voltammogram of (2-anthraquinonylmethyl)trimethylammonium bromide was linear in Kosower's Z value over a wide range of DMF-water mixtures. Using this relationship, the anthraquinone moiety of (2-anthraquinonylmethyl)-dodecyldimethylammonium bromide solubilized in cationic micelles was found to reside at the Stern layer.

Some spectroscopic solvent parameters, e.g. Kosower's Z value,1) Nakajima's Py value,2) and the $E_T(30)$ value,3) are now widely used in investigating the polarity of a number of solvents. However, there are no solvent parameters based on the physicochemical properties measured by electrochemical method. The purpose of this paper is to present a new solvent parameter obtained by cyclic voltammetry of an anthraquinone derivative and to apply it to some micellar systems. The redox potential of anthraquinone (AQ) is reported to be very solvent sensitive4) and AQ derivatives are supposed to play important roles in biological membrane and in solar energy storage,5-8) so that it is important to investigate quantitatively their redox potential dependence on the polarity of their surroundings. In addition, the obtained microenvironment features of the micellar interfacial region is of general importance for colloidal and interfacial systems and membranes.

The AQ derivatives used are (2-anthraquinonylmethyl)trimethylammonium bromide ($\underset{\sim}{1}^{+}$)9) and (2-anthraquinonylmethyl)dodecyldimethylammonium bromide ($\underset{\sim}{2}^{+}$).



$\underset{\sim}{1}^{+}$



$\underset{\sim}{2}^{+}$

Spectroscopic and electrochemical measurements were carried out at 25 °C, by using the test solutions containing LiOH and tetraethylammonium perchrolate as the supporting electrolytes. A gold disk or glassy carbon disk electrode from BAS and a saturated calomel electrode (SCE) were used respectively as the working and the reference electrodes.

Figure 1 shows representative cyclic voltammograms for $\underset{\sim}{1}^{+}$ in DMF-alkaline water systems with water contents of (A) 100 vol% and (B) 20 vol%. The addition of DMF has separated one wave on the voltammogram with 100% water into two waves.10) The difference between the most cathodic peak potential on the forward scan (E_{pc}) and the most anodic peak potential on the reversal scan (E_{pa}), $\Delta E_p(\mathbf{1}^+)$, were determined to be 65 mV for (A) and 268 mV for (B), respectively.

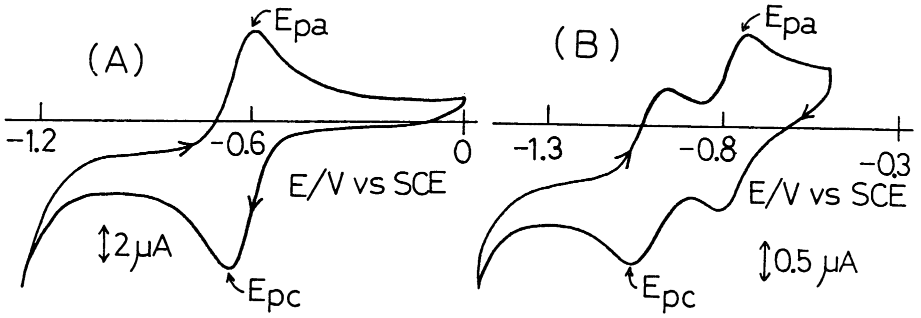


Fig. 1. Cyclic voltammograms for $\mathbf{1}^+$ in DMF-alkaline water systems at Au disk electrode at 25 °C: (A) 0.99 mM (mM = mmol dm^{-3}) $\mathbf{1}^+$, water 100 vol%; (B) 0.47 mM $\mathbf{1}^+$, water 20 vol%. Scan rate: 50 mV s^{-1}. Working electrode area: 0.021 cm^2.

Figure 2A shows a plot of $\Delta E_p(\mathbf{1}^+)$ thus determined vs. the composition of water (vol%). The $\Delta E_p(\mathbf{1}^+)$ value increases as the water content decreases, while the plot of $\Delta E_p(\mathbf{1}^+)$ against Kosower's Z value11) shows a good linear dependence (Fig. 2B), indicating that the value of $\Delta E_p(\mathbf{1}^+)$ also can be used as a solvent parameter.

The average microenvironment of the anthraquinone moiety of $\mathbf{2}^+$ 12) in normal micellar systems could be numerically expressed in terms of the Z value under the following assumption: the microenvironment of the anthraquinone moiety of $\mathbf{2}^+$ in the micelle has the same polarity in the Z value as that of $\mathbf{1}^+$ in a mixed solvent, when $\Delta E_p(\mathbf{2}^+)$ is equal to $\Delta E_p(\mathbf{1}^+)$.

Figure 3 shows a cyclic voltammogram for 0.79 mM $\mathbf{2}^+$ in 0.1 M (M = mol dm^{-3}) dodecyltrimethylammonium bromide (DTAB) aqueous solution containing 0.2 M LiOH. The peak-to-peak potential $\Delta E_p(\mathbf{2}^+)$, $E_{pa} - E_{pc}$, determined was 140 mV and the corresponding Z value is 89 from Fig. 2B. The $\Delta E_p(\mathbf{2}^+)$ measured and the corresponding Z values of $\mathbf{2}^+$ in cetyltrimethylammonium bromide (CTAB) aqueous solution were 160 mV and 88, respectively. These values of Z indicate that the anthraquinone moiety of $\mathbf{2}^+$ resides at the interfacial region of the micelle, i.e. "the Stern layer" where the value of Z is 80-90.13)

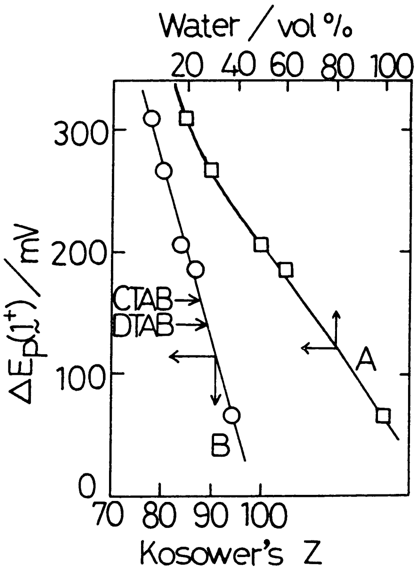


Fig. 2. Plots of $\Delta E_p(\mathbf{1}^+)$ vs. (A) the composition of water (vol%) and (B) Kosower's Z value.

As described above, the ΔE_p values reflect the solvent polarity of the environment as successfuly as the Z value. This is because the change in solvation energy of the dianion of anthraquinone moiety, AQ^{2-}, is more sensitive to the change in solvent polarity than that of the monoanion radical, $AQ^{\cdot-}$; that is, the half-wave potential for the second wave, $E_{1/2}(2)$, shifts more to a positive potential than that for the first wave, $E_{1/2}(1)$, as a result of more stabilization of AQ^{2-} than $AQ^{\cdot-}$ with increasing solvent polarity.

$$AQ + e \rightleftarrows AQ^{\cdot-} ;\ E_{1/2}(1) \qquad (1)$$

$$AQ^{\cdot-} + e \rightleftarrows AQ^{2-} ;\ E_{1/2}(2) \qquad (2)$$

The relation of the concentration of AQ and AQ^{2-} to $AQ^{\cdot-}$ at equilibrium is expressed by the comproportionation constant K,[14)]

$$2AQ^{\cdot-} \overset{K}{\rightleftarrows} AQ + AQ^{2-} \qquad (3)$$

and accordingly, the ΔE_p value corresponds to a physicochemical parameter reflecting the K value. The ΔE_p measured was converted to $(E_{1/2}(1) - E_{1/2}(2))$ by using a working curve for ΔE_p vs. $(E_{1/2}(1) - E_{1/2}(2))$ given by Taube et al.[14)] and then the K value was calculated from Eq. 4.[4,15)]

$$E_{1/2}(1) - E_{1/2}(2) = -(RT/F)\ln K \qquad (4)$$

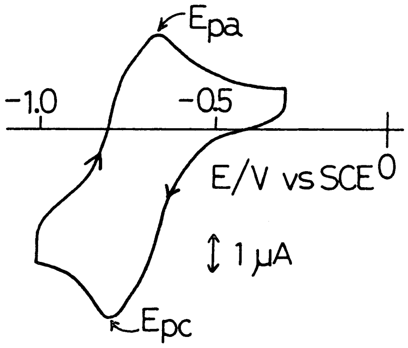


Fig. 3. Cyclic voltammogram for 0.79 mM $\mathbf{2}^+$ in 0.1 M DTAB aqueous solution containing 0.2 M LiOH at 25 °C. Scan rate: 50 mV s^{-1}. Working electrode area: 0.071 cm^2.

Table 1 summarizes ΔE_p, $(E_{1/2}(1) - E_{1/2}(2))$, and K values for some anthraquinone derivatives in 0.2 M LiOH aqueous solution at 25 °C. It can be seen from Table 1 that the equilibrium represented by Eq. 3 for $\mathbf{2}^+$ solubilized in normal micelles is shifted to the left-hand side compared with that for the anthraquinone derivatives in non-micellar aqueous system.

Table 1. Peak-to-peak potential, ΔE_p, half-wave potential difference, $E_{1/2}(1) - E_{1/2}(2)$, and the disproportionation constant, K, of some AQ derivatives in 0.2 M LiOH aqueous solution at 25 °C

Substrate	ΔE_p/mV	$\{E_{1/2}(1) - E_{1/2}(2)\}$/mV	10^2K
AQS^- a)	60	40	21
1^+	65	45	17
2^+ + DTAB	140	100	2.0
2^+ + CTAB	160	120	0.94

a) AQS^- is sodium 9,10-anthraquinone-2-sulfonate.

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References

1) E.M. Kosower, J. Am. Chem. Soc., **80**, 3253 (1958).
2) A. Nakajima, Bull. Chem. Soc. Jpn., **44**, 3272 (1971).
3) C. Reichardt, Angew. Chem., Int. Ed. Engl., **18**, 98 (1979).
4) a) "Electroanalytical Chemistry," ed by A.J. Bard, Marcel Dekker, INC., New York (1967), Vol. 2, p.11;
   b) S. Hayano and M. Fujihira, Bull. Chem. Soc. Jpn., **44**, 2051 (1971).
5) M. Fujihira, J. Electroanal. Chem., **130**, 351 (1981).
6) J.M. Bobbitt and J.P. Willis, J. Org. Chem., **42**, 2347 (1977).
7) M. Fujihira, S. Tasaki, T. Osa, and T. Kuwana, J. Electroanal. Chem., **137**, 163 (1982); **150**, 665 (1983).
8) M. Fujihira, H. Yoneyama, and S. Aoyagui, J. Chem. Soc., Chem. Commun., submitted for publication.
9) **2**$^+$ and (2-bromomethyl)anthraquinone (**3**) were prepared according to the procedures described in reference [8]. **1**$^+$ was prepared according to the following procedures: 0.51 g of **3** was added to a solution of 0.4 M $N(CH_3)_3$ in 150 ml of ethanol. Then the mixture was filtered off and washed with hexane. The crude product was purified by recrystallization from 70 ml of ethanol. Yield 88%. Found: C, 57.12; H, 4.82; N, 3.71%. Calcd for $C_{18}H_{18}NO_2Br + H_2O$: C, 57.14; H, 4.76; N, 3.70%. ^{1}H-NMR(DMSO-d_6) and IR(KBr) spectra were consistent with the assigned structure.
10) M. Fujihira and S. Hayano, Bull. Chem. Soc. Jpn., **45**, 644 (1972).
11) The band-shape matching technique was used to estimate the band position of 1-ethyl-4-carbomethoxypyridinium iodide when the band are only partially accesible owing to high polarity: A. Ray and P. Mukerjee, J. Phys. Chem., **70**, 2138 (1966).
12) **2**$^+$ itself formed micelles. The micellar weight of **2**$^+$ in 0.2 M LiOH was determined to be 1.4×10^4 by the quasielastic light scattering method. The CMC value of **2**$^+$ in 0.2 M LiOH was determined to be 0.073 mM by the UV method: K. Hoshino, T. Saji, M. Fujihira, and S. Aoyagui, to be submitted.
13) K.S. Scanze, T.F. Mattox, and D.G. Whitten, J. Am. Chem. Soc., **104**, 1733 (1982).
14) D.E. Richardson and H. Taube, Inorg. Chem., **20**, 1278 (1981).
15) J. Heyrovsky and J. Kuta, "Principle of Polarography," Academic Press, New York (1966).

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