Facilitated Ion-Transfer of a Hydrophobic Tetraalkylammonium Ion in Nitrobenzene to Aqueous Phase by Humic Acid

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Ion transfer at an interface of organic nitrobenzene and aqueous phases was polarographically studied in the presence of humic acid using an ascending aqueous electrode. The transfer of hydrophobic tetraheptylammonium cation as a supporting electrolyte ion in nitrobenzene to the aqueous phase was greatly facilitated by the incorporation into the micelle-like humic acid aggregates formed around CMC of humic acid.

Humic substances are the most widely distributed natural organic matters on surface of the earth. They are thought to play an important role in the environment. Interactions of soil humic and fluidic acids with metal ions and organic compounds have been studied.[1] Ion-transfer voltammetry across an interface of immiscible organic and aqueous electrolyte solutions is one of very useful tools for better understanding the solution properties of ions. We describe here ion-transfer polarographic behaviors of a hydrophobic cationic compound in nitrobenzene in the presence of humic acid using an ascending aqueous electrode, in relation to the solubilizing property of humic acid.

Humic acid was prepared from sodium humate (Aldrich). The concentrated aqueous solution of the Na salt was filtered to remove insoluble materials and the filtrate was acidified with HCl to pH 2 to obtain the precipitate as the acid form. The resultant precipitate was washed thoroughly with distilled water, centrifuged, and freeze-dried. The contents of carboxyl group and phenolic hydroxy group in the humic acid[2] were determined by nonaqueous neutralization titration[3] to be 4.0 mmol/g and 1.4 mmol/g, respectively.

The four-electrode cell for ion transfer was shown in Figure 1. The ion-transfer voltammetric measurements were conducted by current-scan polarography using an ascending aqueous phase electrode.[4] The organic phase of nitrobenzene contained 0.04 M tetraheptylammonium tetraphenylborate (Hep_4NBPh_4) as a supporting electrolyte. The ion-transfer polarographic half-wave potential of tetraethylammonium ion from aqueous phase to nitrobenzene, $\Delta\varphi_{1/2}(NEt_4^+)$, was -344 mV in this cell construction.

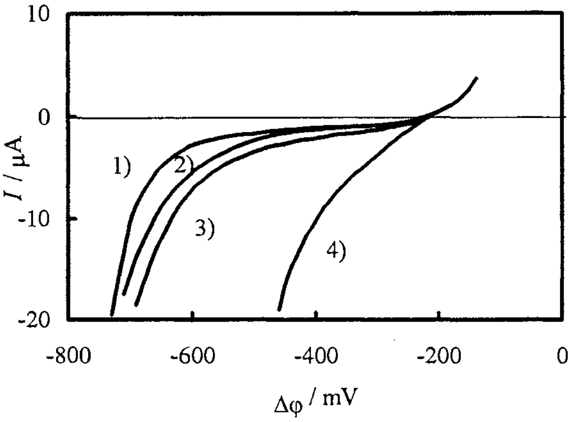

Figure 2. Effect of humic acid concentration on ion transfer polarograms of tetraheptylammonium ion. Concentration of humic acid in aqueous phase: 1) 0, 2) 500 mg/L, 3) 800 mg/L, 4) 1000 mg/L. Concentration of Hep_4NBPh_4 in nitrobenzene: 0.04 M.

Figure 2 shows ion transfer polarograms when the concentration of humic acid was varied. Under the pH condition carboxylic acid in humic acid dissociate completely to give the humate anion. At the concentration less than 100 mg/L, the polarograms are the same as the background current. This indicates that no appreciable ion transfer including humate anion transfer from aqueous phase to organic nitrobenzene phase occurs although alkyl carboxylates and benzoate derivatives showed a distinct polarographic wave corresponding to the anion transfer from aqueous to organic phases.[5] At the concentration more than 100 mg/L the negative current increasing monotonically without limiting current appears and the rising potential shifts to more positive potential with increasing in the humic acid concentration in aqueous phase. Moreover, the rising potential shifts also positively with the concentration of Hep_4NBPh_4 in organic nitrobenzene phase at the humic acid concentration of 800 mg/L

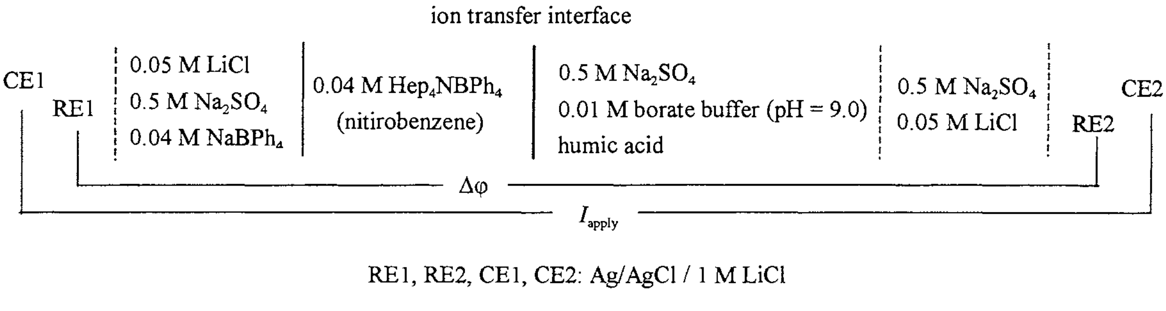

Figure 1. Ion Transfer polarographic cell.

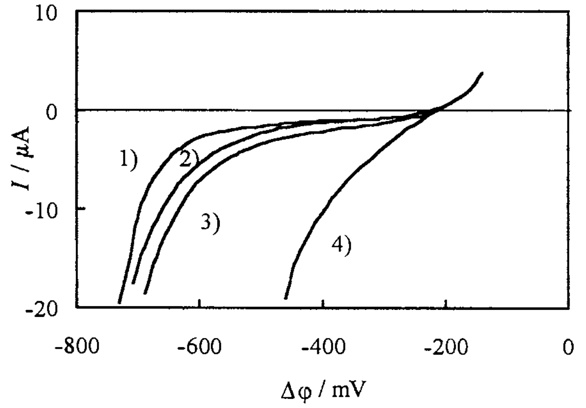

Figure 3. Effect of Hep_4NBPh_4 concentration on ion transfer polarograms of tetraheptylammonium ion. Concentration of humic acid in aqueous phase: 1) 0 mg/L, 2)-4) 800 mg/L. Concentration of Hep_4NBPh_4: 1),4) 0.04 M, 2) 0.01 M, 3) 0.02 M.

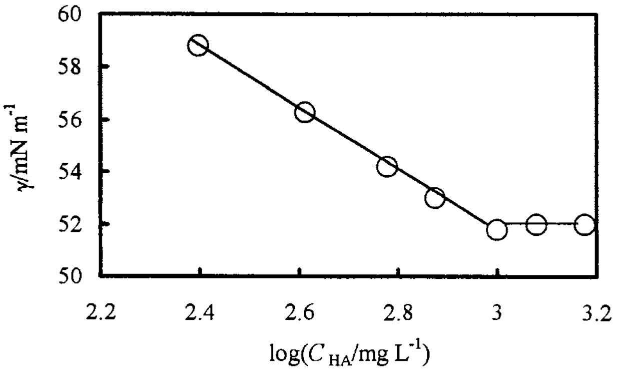

Figure 4. Relation between surface tension and humic acid concentration.

as shown in Figure 3. A negative current is mechanistically caused by an anion transfer from aqueous phase to organic phase or a cation transfer in the opposite direction. The ion-transfer polarographic results in the presence of humic acid suggest that the transfer of a hydrophobic tetraalkylammonium ion of Hep_4N^+ in nitrobenzene is facilitated to the aqueous phase by humate anion rather than the humate anion transfer from aqueous phase to organic nitrobenzene phase.

Figure 4 shows the concentration dependence on the surface tension of humic acid solution containing 0.5 M Na_2SO_4 and 0.01 M borate buffer (pH 9.0).[6] The surface tension decreases with humic acid concentration until the surface tension becomes constant at the concentration of 1000 mg/L, which can be taken as CMC value for the formation of micelle-like aggregates of humate anions similar to that of surfactant systems. Neutral hydrophobic substances such as benzo(a)pyrene[7] and atrazine[8] are solubilized in humate anion aggregates. The concentration range showing the polarographic current due to the Hep_4N^+ cation transfer from organic nitrobenzene phase to aqueous phase is close to the CMC value of humate solution. Thus, the motive force of the hydrophobic Hep_4N^+ cation transfer to aqueous phase is the incorporation of some Hep_4N^+ cations in one of the micelle-like humate aggregates which are formed at the high concentration. The concentration dependence of humic acid in aqueous phase and Hep_4N^+ in nitrobenzene on the rising potential of negative current confirms the incorporation mechanism. Although the both structures of micelle-like humate aggregates and the aggregates incorporated with the hydrophobic cation are not known well, ion transfer voltammetry is useful tool to understand the uptake phenomena of cationic substances of environmentally importance such as methyl viologen by humic acid.

References and Notes

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