Observation of Intermolecular Charge-Transfer Spectra for Propyl Viologen Dihalides in a Series of Polyether Media

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(Received September 13, 1995)

1,1- Dipropyl- 4,4- bipyridinium diiodide($PV^{2+} \cdot 2I^-$) in a series of polyethers (PEOs, HO- $(-CH_2CH_2O-)_n$ -H, $n = 1 \sim 14$)[1] gave an intermolecular charge- transfer spectrum, which shifted to longer wavelength with larger absorbance in less polar medium, in the visible region. An increase in temperature resulted in an increase in absorbance as a result of an ion- dipole interaction between PV^{2+} cation and polyether solvent.

Polyethers such as poly(ethylene oxide) and poly-(propylene oxide) have recently received a great deal of attention as polymer solvents because of their potential applications to solid- state batteries and other solid- state ionic devices as well as because of the many unanswered fundamental questions and interesting observations on ion solvation and ion transport in these polymers.[2]

In this communication, we first report on intermolecular charge-transfer(CT) spectra of 1,1'-dipropyl-4,4'-bipyridinium salts ($PV^{2+} \cdot 2X^-$, $X^- = I^-$, Br^-, Cl^- and ClO_4^-) in a series of PEOs. The dependences of the CT spectra on the anion (X^-) as well as the number (n) of the $-CH_2CH_2O-$ unit are demonstrated on the basis of the observed correlationships between absorption maximum wavelength λ_{max} (and absorbance Abs (λ_{max})) and molar fraction (f_{OH}) of terminal hydroxyl (OH) groups.

10 mM(1 M = 1 mol dm^{-3}) $PV^{2+} \cdot 2X^-$ was dissolved in each of PEOs in a closed drybox flushed with N_2 gas dried over silica gel and P_2O_5 powder, and then the solutions were dried under reduced pressure at 50-60 ℃ for 24 h. The UV- vis spectra of the prepared PEO solutions were measured using the closed quartz cell with light- path length of 1 mm.

Figure 1 shows typical spectra for the PEO_{400} solutions. The CT band position shifted to shorter wavelengths ("blue shift") by changing the anion of the $PV^{2+} \cdot 2X^-$ salts from I^- to Br^-, Cl^-, and ClO_4^-. The $PV^{2+} \cdot 2I^-$ solution gave a well-defined absorption peak at 428 nm (a). The absorption for the $PV^{2+} \cdot 2Br^-$ solution was only partially visible (b), due to occultation by the absorption of the bipyridinium ring. For the $PV^{2+} \cdot 2X^-$ ($X^- = Cl^-$ and ClO_4^-), no absorption peak was observed in the visible region (c, d). These facts can be expected, since the oxidation potential of the anion donor increases in the order of I^-, Br^-, Cl^- and ClO_4^-,[3] and a CT is essentially dependent on the oxidation potential of the donor.[4] At the same time such a donor- dependence of CT band position means that the observed CT is an intermolecualr process. This type of CT absorption has also been previously observed for CT complexes of 4, 4'- bipyridinium ions with ionic (or neutral) organic compounds or inorganic ions.[5-9] Another direct evidence that electron is transferred from I^- ion to the PV^{2+} ring is a red shift of the CT peak for $PV^{2+} \cdot 2I^-$ compared with that for KI (the inset in Figure 1), showing that PV^{2+} ion greatly enhances electron excitation of iodide anion. The absorption maxima at 295 and 375 nm are considered to correspond to an electron- transfer process: $I^- \rightarrow I + e^-$ as in the case of KI in water (λ_{max} = 193.7 and 225.9 nm).[10, 11] The different λ_{max} values (i.e., ca. 360 and 428 nm) for $PV^{2+} \cdot 2I^-$ in H_2O and PEO_{400} are also remarkable (a,e). Such differences in λ_{max} in PEO_{400} and H_2O are due to the different polarity of both solvents.

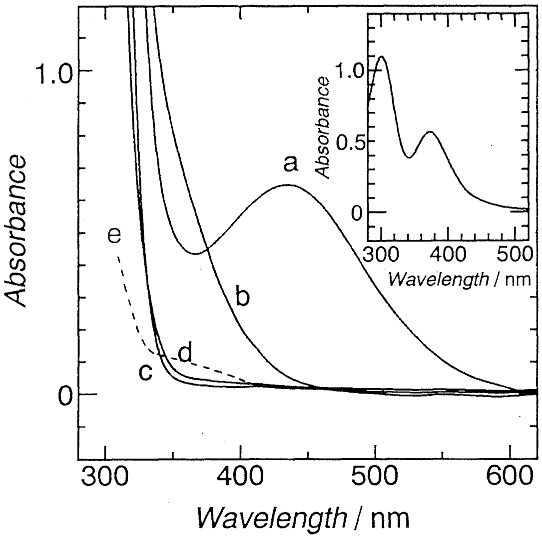

Figure 1. UV- vis spectra of 10 mM $PV^{2+} \cdot 2X^-$ (X^- : (a) I^-, (b) Br^-, (c) Cl^- and (d) ClO_4^-) in PEO_{400} and (X^- :(e) I^- in H_2O at 25 ℃. The inset represents a CT spectrum of 1 mM KI in PEO_{400}.

We found the correlationships between λ_{max} (and Abs (λ_{max})) and n or f_{OH} in a series of PEOs (Figure 2). The f_{OH} is considered an empirical measure of solvent polarity.[13] Thus, a significant increase in Abs (λ_{max}) with decreasing f_{OH} possibly suggests that solvent polarity is of great importance in solvation of PV^{2+} and I^- ions and the association between them increases as the polarity of the medium decreases. The λ_{max} shifted to longer wavelengths with decreasing f_{OH} ("red shift"), indicating that the CT energy decreases with decreasing solvent polarity (which results in a decrease in solvation energy of PV^{2+} and I^- ions). These observations agree with the expectations for ion- pair CT complexes:[5-9, 14] The CT involves a charged ground state and a neutral excited state. A charged ground state would be more stabilized by solvation in solvent of higher polarity, and

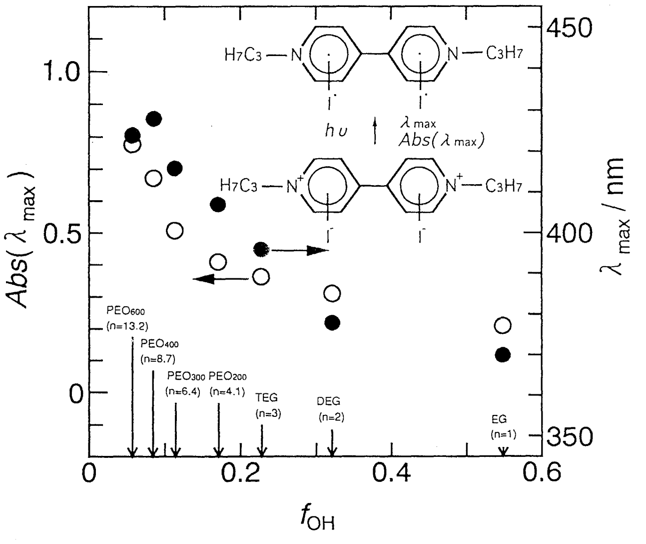

Figure 2. Correlationships between λ_{max} (and *Abs*(λ_{max})) and f_{OH} in a series of PEOs.

CT absorption would be shifted to higher energies as the polarity increases. Here, it should be noted that in the present PEO media, contrary to the CT absorption so far reported for usual media,[5, 6, 14] increasing temperature (T) resulted in an increase in *Abs*(λ_{max}). This is because at higher T an ion-dipole interaction, which is proportional to T^{-1},[15] between PV^{2+} cation and polyether solvent becomes weaker and thus PV^{2+} cation is less favorably solvated, that is, the formation of ion- pair CT complex of PV^{2+} cation with I^- anion becomes more favorable. This is supported by recent electrochmeical studies concerning the dissolution and diffusion of alkyl viologen dihalides in polyethers.[16]

In conclusion, the intermolecular CT spectra of the $PV^{2+} \cdot 2I^-$ complex in PEOs have, for the first time, been observed in the visible region. The results demonstrate that the association between PV^{2+} and I^- ions increases as the solvating power (or polarity) of the medium decreases, resulting in a stronger absorption peak at longer wavelength in less polar medium. Therefore, like "Z - value" proposed by Kosower,[10] who utilized the CT transition energy for 1-ethyl-4-carbomethoxypyridinium iodide as a standard of solvent polarity, the λ_{max} values obtained can be used as a novel, quantitative measure of the polarity and solvating power of polyether media. The detail is now under investigation.

We acknowledge financial support (No. 06226222) of this research, from the Ministry of Education, Science and Culture, Japan, and the Nissan Science Foundation.

References and Notes

1 Ethylene glycol (n = 1,abbreviated as EG); diethylene glycol (n = 2, DEG); trietylene glycol (n = 3, TEG); poly-(ethylene oxide)s with average molecular weight of 200 (n = 4.1), 300 (n = 6.4), 400 (n = 8.7) and 600 (n = 13.2) are abbreviated as PEO_{200}, PEO_{300}, PEO_{400} and PEO_{600}, respectively. These PEOs contained no additives such as anti-oxidants and were gifted from the Nippon Oil and Fat Co. Ltd.

2 For example, J.R.MacCaullum and C.A.Vincent, Polymer Electrolyte Reviews, Elsevier Applied Science, Lonodon (1987), Vo.1; (1989), Vol.2.

3 M.Latimer, *Oxidation Potentials*, 2nd ed., Prentice-HallInc., New York (1952).

4 R.S.Mulliken, *J. Am. Chem. Soc.*, **72**, 600(1950).

5 T.Nagamura and K.Sakai, *Chem. Phys. Lett.*, **141**, 553 (1987);T.Nagamura and K.Sakai, *Ber. Bunsenges. Phys.Chem.*, **92**, 707(1988).

6 J.S.Brinen, J.G.Koren, H.D.Olmstead, and R.C.Hirt, *J.Phys. Chem.*, **69**, 3791(1965).

7 J.P.Kuczynski, B.H.Milosavljevic, A.G.Lappin, and J.K.Thomas, *Chem. Phys. Lett.*, **104**, 149(1984).

8 T.W.Ebbesen and G.Ferraudi, *J. Phys. Chem.*, **87**, 3717 (1983).

9 M.Z.Hoffman, *J. Phys. Chem.*, **88**, 5660(1984).

10 E.M.Kosower, *J. Am. Chem. Soc.*, **80**, 3253(1985).

11 The transition energy difference between two maxima observed for the KI/PEO_{400} system was estimated to be 86.6 kJ mol^{-1}, being in fair agreement with the value predicted for the formation of an iodine atom in the excited state.[12]

12 K.Mirakawa, *Z. Physik.*, **109**, 162(1938).

13 H.Ohno and Y.Ito, *Polym. Adv. Tech.*, **1**, 335(1990).

14 S.F.Manson, *J. Chem. Soc.*, **1960**, 2437.

15 H.Ohno and K.Ito, *Polymer*, **34**, 4171(1993).

16 H.Satoh, H.Ohno, K.Tokuda,and T.Ohsaka, *Electrochim. Acta*, **39**, 2261(1994).