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Distribution of oxacyanine dyes between water and nitrobenzene:  
Determination of the partition constants, association and  
potentials of transfer of the dye cations on  
liquid/liquid interfaces

by

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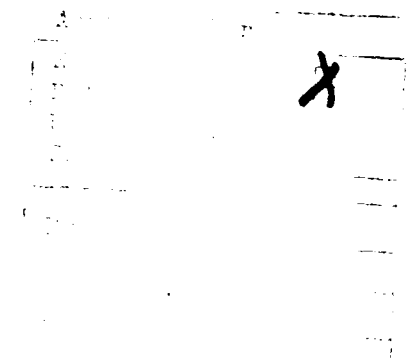
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## Abstract

Partition constants for the oxacyanine dyes between water and nitrobenzene were determined using their absorbance and fluorescence properties. From these values the standard potential of transfer for a group of oxacyanine dye cations was calculated. Several effects, which can cause a variation of observed distribution ratio with dye concentration, are examined. In particular, association of the dyes in the aqueous phase is determined conductometrically and is used in the correction. The effect of dye concentration and acidity of the solvent on the dye distribution ratio is also examined. The standard potential of transfer for these ions is quite negative so that the dyes are more suitable as supporting electrolytes, or must be studied on liquid/liquid interfaces without supporting electrolytes.

## Introduction

The study of charge transport processes occurring on interfaces between two immiscible electrolytes is a developing area in electrochemistry (1-3) with particular emphasis on the exploration of new ion transfer systems. Among the benefits of studying these systems are improvement in our understanding of the processes occurring on the interfaces, collection of kinetic and thermodynamic data for the transfer, development of new electroanalytical tools (4) and improvement in our understanding of the liquid-liquid (L/L) extraction processes (5). Many of the newly studied compounds are also dyes (6-8). A few of the dyes used in L/L electrochemistry have, in addition to their electrochemical properties, the benefit of exhibiting optical phenomena of their own. Of interest in this paper are oxacyanine dyes, which fluoresce, with their fluorescence intensity depending on the solvent. Oxacyanine dyes are used quite often as optical probes to measure biological membrane potentials (9). As the membrane potential changes, the distribution of the dye cation between the extracellular fluid and the cell also changes. Because the fluorescence intensity of the dye inside and outside the cell is different, the change in distribution causes a change in the measured fluorescent intensity of the dye. Thus the fluorescent intensity of the dye can be measured and calibrated to the membrane potential.

For further study of the electrochemical properties of these dyes in a simple interfacial system (water/nitrobenzene), the distribution ratio between nitrobenzene and water was determined for each dye cation. From these ratios, the Gibbs free energy of transfer and the standard potential of transfer for each dye were determined.

## Materials and methods

The oxacyanine dyes were obtained from Molecular Probes, Inc., Eugene, OR. Fisher certified A.C.S. nitrobenzene was purified by filtering through a basic alumina column before use. Water redistilled from glass was used in all experiments. Absorbance measurements were done using a Varian 2290 Spectrophotometer and fluorescence measurements were done using an SLM Model 4800 Spectrofluorometer. The studied dyes are oxacarbocyanines (3 carbons in the connecting conjugated chain) and oxadycarbocyanines (5 carbons in the chain). A generic structural formula for the compounds  $[\text{DiOC}_m(2n+1)]$  is shown in Figure 1, which also illustrates creation of the abbreviated names. Di in the name stands for the two heterocycles, O stands for oxygen in benzoxazole.

The distribution ratios were determined using two methods: (a) by measuring the absorbance of the dye in the nitrobenzene layer before and after mixing with water and (b) by measuring the fluorescence intensity of the water layer after shaking and equilibrating with nitrobenzene containing the dye. Absorbance and fluorescence spectra of the dyes and molar absorptivities have been determined previously (10). Both the water and nitrobenzene were saturated with the other solvent before use in the determination. Temperature was 25 °C.

A Hewlett-Packard 4192A frequency analyzer was used for conductivity measurements. Although frequencies between 10 kHz to 100 Hz were used, only the 100 Hz results were used in the actual calculations since at this frequency the phase shift was small and was not affecting the real impedance reading. The cell used was equipped with parallel platinized platinum electrodes of about 1 cm<sup>2</sup> area and a 3 mm gap. The cell constant was determined both with 1 *m* KCl and 10<sup>-5</sup> mol/l NaI

to be  $0.155 \text{ cm}^{-1}$ . The applied alternating potential was 30 mV. The water used was freshly distilled from glass. Its conductivity was determined before and after the experiment and was subtracted from the actual data. The temperature during the conductivity measurements was maintained at  $25.00 \pm 0.03 \text{ }^\circ\text{C}$ .

The implicit functions were solved by iteration using TK-Solver Plus software by Universal Technical Systems, Rockford, IL.

## Results

Before further consideration of the liquid-liquid distribution we shall examine how the distribution relates to properties of an electrified system. The purpose is to emphasize that the partition constant of a charged species is a function of interfacial potential, an aspect not often recognized.

A substance without a charge, A, in a single definite state is distributed between immiscible or only partially immiscible liquids  $\alpha$  and  $\beta$  in a constant ratio, and at equilibrium

$$K_{D(p,T,\text{system})} = \frac{[A]_{\beta}}{[A]_{\alpha}} \quad [1]$$

Constant temperature, pressure and defined system are required. The prerequisite for this definition is that substance A has the same form in both phases (i.e. no association, dissociation or side reactions take place). It is often stressed that  $K_D$  is invariable (11). For charged species, however, this is true only in the absence of extraneous electrical potential. A system without electrical charge at the chemical equilibrium requires that chemical potentials of each component present in either phase be equal:

$$\mu_A^\alpha = \mu_A^\beta \quad [2]$$

and since

$$\mu_A^\alpha = \mu_A^{0,\alpha} + RT \ln a_A^\alpha \quad [3]$$

and

$$\mu_A^\beta = \mu_A^{0,\beta} + RT \ln a_A^\beta \quad [4]$$

where  $\mu^0$  is a standard chemical potential, it is possible to write:

$$\frac{a_A^\beta}{a_A^\alpha} = \exp\left(-\frac{\Delta G_{tr, A}^{0, \alpha \rightarrow \beta}}{RT}\right). \quad [5]$$

$\Delta G_{tr, A}^{0, \alpha \rightarrow \beta} = \mu_A^{0\beta} - \mu_A^{0\alpha}$  is the standard Gibbs energy of transfer for solute A from  $\alpha$  to  $\beta$ , which is a thermodynamic constant. With the usual allowance for activity

coefficients being equal in both phases, the ratio  $\frac{a_A^\beta}{a_A^\alpha}$  becomes  $\frac{[A]_\beta}{[A]_\alpha}$  and  $K_D$

from equation [1] is indeed a constant.

For charged particles,  $A'$ , at equilibrium the equivalence of electrochemical potential:  $\tilde{\mu}$  has to be used in the calculation. It holds that

$$\tilde{\mu}_{A'}^\alpha = \tilde{\mu}_{A'}^\beta \quad [6]$$

where

$$\tilde{\mu}_{A'}^\alpha = \mu_{A'}^{0\alpha} + RT \ln a_{A'}^\alpha + z_i F \varphi_\alpha \quad [7]$$

and

$$\tilde{\mu}_{A'}^\beta = \mu_{A'}^{0\beta} + RT \ln a_{A'}^\beta + z_i F \varphi_\beta \quad [8]$$

By inserting [7] and [8] in [6] we obtain



$$\frac{a_{A'}^{\beta}}{a_{A'}^{\alpha}} = \exp \{ (\Delta\varphi_{\beta}^{\alpha} - \Delta_{\beta}^{\alpha} \varphi_{A'}^0) (z_1 F / RT) \}, \quad [9]$$

where  $\Delta\varphi_{\beta}^{\alpha} = \varphi^{\alpha} - \varphi^{\beta}$  is the difference between the electrical potentials of the two phases, which is the electric potential drop on the interface (12) and  $\Delta_{\beta}^{\alpha} \varphi_{A'}^0 = \Delta G_{tr, A'}^{0, \alpha \rightarrow \beta} / nF$  is the standard potential of transfer of ion  $A'$  from  $\alpha$  to  $\beta$ . The corresponding standard Gibbs energy is not a true thermodynamic value because it requires adoption of an extrathermodynamic model (13), nevertheless, it is a constant. Similarly as in [5], the left side of equation [9] is a form of the partition constant. The partition constant of a charged species is here a function of the interfacial potential,  $\Delta\varphi_{\beta}^{\alpha}$ . If the interfacial potential is affected in an unknown or uncontrollable manner, an error in determining the partition constant will result.

Table I lists the partition constant determined by the fluorescence method for nine of the oxacyanine dyes. In order to estimate the Gibbs free energy of transfer and standard potential of transfer for the dye cations, a nonthermodynamic assumption known as the "tetraphenylarsonium tetraphenylborate (TPAsTPB) assumption" (14) was used. According to this assumption, both  $TPAs^{+}$  and  $TPB^{-}$  have, due to their almost identical makeup, equal values of their individual partition constants between any set of arbitrary solvents.

Since it is possible to write for a salt BA

$$\log K_{BA} = \log K_{B^{+}} + \log K_{A^{-}}, \quad [10]$$

one receives for the value of the partition between water and nitrobenzene

$$\log K_{\text{TPAs}^+} = \log K_{\text{TPB}^-} = 6.3, \quad [11]$$

because the experimentally obtained value for  $\log K_{\text{TPAsTPB}}$  is 12.6. From these assumed properties and experimental partition values for various salts it is possible to calculate partition constants for individual ions. A list of individual partition constants for several ions in water/nitrobenzene was first published by Rais (15). From his work, the value for iodide ( $\log K_{\text{I}^-} = -3.3$ ) was used to calculate values for the oxacyanine dyes used in this work, which are all iodide salts:

$$\log K_{\text{dye}^+} = \log K_{\text{Dye}} - \log K_{\text{I}^-}, \quad [12]$$

where  $K_{\text{dye}^+}$  is the partition constant for the dye cation and  $K_{\text{Dye}}$  is the partition constant for the dye-iodide molecule.

It should be noted how the partition constant relates to the observed distribution ratio  $D$ . For a single uni-univalent electrolyte ( $\text{Dye} = \text{dye}^+\text{I}^-$ ) a condition of electroneutrality has to be accomplished, therefore

$$D_{\text{dye}^+} = D_{\text{I}^-} \quad [13]$$

and

$$\log K_{\text{Dye}} = \log D_{\text{dye}^+} + \log D_{\text{I}^-} = \log D_{\text{dye}^+}^2, \quad [14]$$

where  $D_{\text{dye}^+}$  is the experimental distribution ratio for the dye, which is not equal to  $K_{\text{dye}^+}$  from equation [12]. Because  $K_{\text{Dye}}$  is a constant independent of interfacial potential,  $D_{\text{dye}^+}$  will also remain a constant as long as the prerequisite of [14] — the presence of only one kind of electrolyte — is fulfilled.

The standard change of Gibbs energy of transfer of the dye ions from water to nitrobenzene and the corresponding standard potentials of transfer, listed in Table I, easily follow. The change of Gibbs energy of transfer from water to nitrobenzene for an individual dye cation can be calculated from its definition

$$\Delta G_{tr, dye^+}^{w \rightarrow nb} = -RT \ln K_{dye^+} \quad , \quad [15]$$

with the standard value  $\Delta G^0$  calculated at 25 °C. The standard potential of transfer from water (w) to nitrobenzene (nb) ( $\Delta_{nb}^w \varphi^0 = \varphi^w - \varphi^{nb}$ ) for an individual ion is

$$\Delta_{nb}^w \varphi_i^0 = \Delta G_{tr, i}^{0, w \rightarrow nb} / nF \quad . \quad [16]$$

Standard potential of transfer is the most useful value in electrochemical studies of liquid/liquid interfaces since it is conceptually similar to the standard reduction potentials in redox reactions.

To be able to assess the ability to observe transport of dye ions across the liquid/liquid interface during voltammetric experiments, the individual potentials of transport for different dyes from Table I have to be compared to the transport potentials of ions used for supporting electrolytes. The values for the commonly used aqueous electrolyte LiCl are  $\Delta_{nb}^w \varphi_{Li^+}^0 = 395$  mV and  $\Delta_{nb}^w \varphi_{Cl^-}^0 = -324$  mV, and for tetrabutylammonium tetraphenylborate (TBATPB) in nitrobenzene they are  $\Delta_{nb}^w \varphi_{TBA^+}^0 = -248$  mV and  $\Delta_{nb}^w \varphi_{TPB^-}^0 = 372$  mV (16). The positive side of the polarization window (i.e. aqueous side positive) is thus limited by the  $TPB^-$  transport from nitrobenzene and the negative side is limited by  $TBA^+$  transport to water.

The fourth column in Table I demonstrates that all the dyes studied have potentials of transport more negative than  $\text{TBA}^+$  which means that the fluorescent ions will not be transported across the interface without concurrent transport of  $\text{TBA}^+$  if TBATPB were used as a base electrolyte. Cyclic voltammograms obtained on such systems have demonstrated this problem clearly. Only curves typical for a base electrolyte appear. These dyes themselves would, on the other hand, be suitable base electrolyte cations if it were not for their cost.

To be able to investigate the transport of the fluorescent dyes across the L/L interface, one has to either use a more hydrophobic cation for the base electrolyte such as crystal violet ( $\text{CV}^+$ ), whose  $\Delta_{\text{nb}}^{\text{w}}\varphi_{\text{CV}^+}^0$  is calculated to be  $-410$  mV, or forsake the use of base electrolytes altogether. The second alternative seems to have more merit. It was noted (17) that in unsupported solutions the ion transport across liquid/liquid interfaces exhibits behavior which is not seen at metal/liquid interfaces. It will be these differences, rather than the similarities between the two processes, that will be the scope of our future study.

## Discussion

Table I lists the partition constants obtained by measuring the dye fluorescence change in the water layer. Preceding these measurements, a series of experiments to determine the partitioning by absorption spectroscopy in the nitrobenzene phase was performed. The absorbance measurements are limited by the magnitude of the difference in the absorbance before and after partitioning. The partition equilibrium is shifted strongly towards the nonaqueous phase, thus the comparison of concentrations in the nonaqueous phase before and after partition

between two liquids gives a small difference between two large numbers. This results in large relative error, particularly at low initial concentrations.

Since the fluorometric measurements have a lower detection limit than the absorbance measurements, the distribution ratios calculated from fluorescence measurements should be more accurate. An added benefit of fluorescence measurement is that by measuring fluorescence in the aqueous phase the complication arising from a small difference between two large numbers is removed. An experimental noise still, however, arises from monitoring very low concentrations of dyes. The results obtained from fluorescence measurements follow more closely the partitioning values estimated from previous solubility data for the dyes (10) in water, than do the results calculated from absorbance measurements. However, even with the better detection limit, the fluorometric technique is not capable of giving reliable results for the more hydrophobic dyes, hence the uncertain values in Table I.

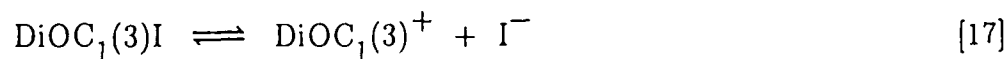
The distribution ratio for  $\text{DiOC}_1(3)$  was determined over the range of initial concentration in nitrobenzene of  $2 \times 10^{-3}$  to  $4 \times 10^{-6}$  mol/l. Below this range the determination is limited by the low concentration of the dye in the water phase (approximately  $10^{-7}$  mol/l), which is below the detection limit of our technique. At concentrations above this level the results for distribution ratio still varied from 38 to 250, increasing with decreasing initial concentrations of the dye in the nitrobenzene phase. Using these values to calculate the standard potential of transfer gives  $\Delta_n^w \phi_{\text{dye}^+}^0$  for  $\text{DiOC}_1(3)$  between  $-289$  mV and  $-338$  mV for the concentration range  $10^{-3}$  to  $10^{-5}$  mol/l dye in nitrobenzene. The values reported in Table I are based on  $10^{-4}$  mol/l concentration. Inspection of Eq. [14] applied for the dye

cation and its counter ion iodide in the absence of other ions will reveal that the distribution ratio should not depend on concentration of the dye. There are several possible causes for the deviation. In the light of the relevance of these findings to the electrochemical studies on interfaces between two immiscible electrolytes, we shall discuss two possible reasons – ionic association and the influence of minority ions on distribution.

*Conductivity and ion association in aqueous phase.*

Association of the dye in water was determined by conductometric measurements. Only  $\text{DiOC}_1(3)$ , the most soluble of the dye series, was investigated. Figure 2 shows its molar conductivity as determined from the experimental data. Solutions in the concentration range from  $10^{-6}$  to  $3 \cdot 10^{-5}$  mol/l in water were measured in a cell with a 3 mm electrode gap. The uncertainty associated with measurements at the low concentrations is such that  $\Lambda_0$  (at infinite dilution) for the iodide salt  $\text{DiOC}_1(3)$  had to be estimated.  $\Lambda_0$  for  $\text{DiOC}_1(3)^+$  is not known, but we estimate it to be  $\approx 40 \text{ S} \cdot \text{cm}^2 \text{ mol}^{-1}$ , a value comparable to other organic cations of similar properties. Since the value  $\Lambda_0(\text{I}^-)$  is  $76.8 \text{ S} \cdot \text{cm}^2 \text{ mol}^{-1}$ , value for the salt was estimated at  $115 \text{ S} \cdot \text{cm}^2 \text{ mol}^{-1}$ .

Assuming partial dissociation of the salt



described by an apparent dissociation constant  $K'$  and a degree of dissociation  $\alpha$ , it is within the realm of experimental uncertainty valid to write

$$\alpha \approx \frac{\Lambda}{\Lambda_0}, \quad [18]$$

where  $\Lambda_0$  is the limiting molar conductivity and  $\Lambda$  is the molar conductivity at a given concentration. For a uni-univalent electrolyte it holds for an apparent dissociation constant that (c.f. (18))

$$K' = \frac{\alpha^2 c}{1-\alpha} \approx \frac{\Lambda^2 c}{\Lambda_0(\Lambda_0 - \Lambda)}. \quad [19]$$

The logarithm of  $K'$  is relatively insensitive to the correct estimate of  $\Lambda_0$ . Table II lists  $\log K'$  for  $\Lambda_0$  between 100 and 150.  $\text{S} \cdot \text{cm}^2 \text{mol}^{-1}$ . The previously estimated  $\Lambda_0 = 115 \text{ S} \cdot \text{cm}^2 \text{mol}^{-1}$  yields an apparent dissociation constant with an experimental uncertainty of  $\log K' = -4.8 \pm 0.2$ .

*Effect of dye association on its apparent partition constant.*

We shall express the formula of the dye as BA and we shall also assume that both the dissociated cation  $B^+$  and the solvated molecule BA provide indistinguishable optical signals (absorption, fluorescence).

Association in both phases  $\alpha, \beta$  with corresponding association constants  $K_\alpha$  and  $K_\beta$  can be written as





The partition constant for the individual ion  $B^{+}$  is defined as

$$K_D = \frac{[B_{\beta}^{+}]}{[B_{\alpha}^{+}]}, \quad [22]$$

whereas the apparent distribution ratio  $D$ , accessible from the partition experiment is

$$D = \frac{c - [B_{\alpha}^{+}] - [BA_{\alpha}]}{[B_{\alpha}^{+}] + [BA_{\alpha}]}, \quad [23]$$

where the total concentration  $c$  is

$$c = [B_{\alpha}^{+}] + [BA_{\alpha}] + [B_{\beta}^{+}] + [BA_{\beta}]. \quad [24]$$

After using [20] through [22] and [24] in [23], we obtain

$$D = K_D \left( \frac{1 + K_{\beta} K_D [B_{\alpha}^{+}]}{1 + K_{\alpha} [B_{\alpha}^{+}]} \right), \quad [25]$$

where  $[B_{\alpha}^{+}]$  is, from the introduction of [20], [21] and [22] into [24] and from solving the resulting quadratic equation:

$$[B_{\alpha}^{+}] = \frac{-(1 + K_D) + \sqrt{(1 + K_D)^2 + 4(K_{\alpha} + K_{\beta} K_D^2) \cdot c}}{2(K_{\alpha} + K_{\beta} K_D^2)}. \quad [26]$$



If the values for  $K_\alpha$  and  $K_\beta$  are known,  $K_D$  can be obtained, although not as an analytical expression, from [25] and [26]. Study of the above relationships reveals, that in order to observe a decrease in  $D$  with increasing concentration (in accord with the experiment),  $K_\alpha > 1$  (association in water) and  $K_\alpha > K_\beta$ . From the conductivity measurements the estimate for  $K_\alpha = (1/K') = 10^5$ . For the organic salt in the nonaqueous phase we assume  $K_\beta = 0$ .

The computer simulation plot in Figure 3 shows the dependence of apparent  $D$  on the concentration of  $\text{DiOC}_1(3)$  at various values of  $K_\alpha$ . Values of  $K_D$  were chosen such that the value  $D$  at the highest concentration ( $2.1 \times 10^{-3}$  mol/l) would be 38, in accordance with experimental data. Overlay of experimental points shows that although the model describes the observed trend, it does not sufficiently explain the quantitative values of the experiment.

*Deviation of apparent partition constant caused by presence of ionic impurities.*

Since the partition constant for a charged species is a function of interfacial potential (Eq. [9]), any effect causing changes in interfacial potential will contribute to the deviation in the observed partition constant. The presence of ionic impurity would have the same effect as would an imposed potential from an outside electrical source. The inevitable sources of ionic "impurity" in water are its autoprotolysis and, under normal conditions, its dissolution of  $\text{CO}_2$ .

A typical pH value of the distilled water used was 6, indicating the presence of  $10^{-6}$  mol/l  $\text{H}^+$  and a corresponding concentration of anions (presumably carbonates). These ions will contribute to the complex equilibrium established between the two

phases, which will subsequently affect the partition of the dye. This effect will be more pronounced as the absolute concentration of the dye becomes smaller.

To evaluate the effect of pH on the distribution ratio of the dye, the presence of hydronium ion can be included in the calculations in the same manner as any other accompanying ion. To calculate the interfacial potential of a system containing an arbitrary number  $j$  of ions  $i$ , the equation, first derived by Hung (19), was used:

$$\sum_{i=1}^j z_i m_i / \left\{ V_\alpha + V_\beta \frac{\gamma_i^\alpha}{\gamma_i^\beta} \exp\left[\frac{z_i F}{RT} (\Delta_\beta^\alpha \varphi - \Delta_\beta^\alpha \varphi_i^0)\right] \right\} = 0, \quad [27]$$

where  $z_i$  is the charge of the ion;  $m_i$ , the total number of moles of the ion in both phases;  $V_\alpha$ , the volume of the  $\alpha$  ( $\text{H}_2\text{O}$ ) phase;  $V_\beta$ , the volume of the  $\beta$  (nitrobenzene) phase;  $\gamma_i^\alpha$  and  $\gamma_i^\beta$ , the activity coefficients of the ion in the  $\alpha$  and  $\beta$  phases, respectively;  $\Delta_\beta^\alpha \varphi$ , the Galvani potential of the interface; and  $\Delta_\beta^\alpha \varphi_i^0$ , the standard potential of transfer of the ion from phase  $\alpha$  to phase  $\beta$ , defined as  $\Delta\varphi = \varphi^\alpha - \varphi^\beta$ . It is assumed here that the activity coefficient of each ion is the same in both phases and that the temperature is  $25^\circ \text{C}$ , so  $\frac{\gamma_i^\alpha}{\gamma_i^\beta} = 1$  and  $\frac{F}{RT} = 38.9 \text{ V}^{-1}$ . Equation [27] can be derived from Eq. [9] if the requirement of electroneutrality in either phase is inserted.

The partition constant of the dye molecule is independent of the interfacial potential changes as  $K_D$  is expressed only by values independent of potential as:

$$\ln K_{\text{Dye}} = F/RT (\Delta_{\beta}^{\alpha} \varphi_{\text{I}^{-}}^{\circ} - \Delta_{\beta}^{\alpha} \varphi_{\text{dye}^{+}}^{\circ}) , \quad [28]$$

which follows from Eq. [10]. As long as only the dye ion and iodide are present in the equilibrated system, the dye concentration in either phase will be equal to the concentration of the dye ion, which is the species observed by our techniques. The partitioning of the dye cation (apparent partition constant of individual ion) is dependent upon the interfacial potential and will change with it, whether the potential is changed by an outside electric circuit or from within the system by presence of other partitioning ions (c.f. Eq. [9]):

$$\ln D_{\text{dye}^{+}} = F/RT (\Delta_{\text{nb}}^{\text{w}} \varphi - \Delta_{\text{nb}}^{\text{w}} \varphi_{\text{dye}^{+}}^{\circ}) . \quad [29]$$

An experiment verifying the effect of an additional partitioning species on the dye distribution was performed using HCl. The results suggest that below  $10^{-5}$  mol/l HCl the effect is negligible. Computer simulation (Figure 4) illustrates the effect. The standard potentials of transfer used for the ions other than  $\text{DiOC}_1(3)^+$  are literature values based on partition constants for those ions;  $\Delta_{\text{nb}}^{\text{w}} \varphi_{\text{I}^{-}}^{\circ} = -195$  mV,  $\Delta_{\text{nb}}^{\text{w}} \varphi_{\text{H}^{+}}^{\circ} = 337$  mV,  $\Delta_{\text{nb}}^{\text{w}} \varphi_{\text{Cl}^{-}}^{\circ} = -324$  mV (15,18). In a series of calculations on a system of equal volumes of water and nitrobenzene containing  $\text{DiOC}_1(3)\text{I}$  and hydrochloric acid, the dye concentration was held constant while the HCl concentration varied from  $10^{-9}$  to 1 mol/l. Calculations were done for the dye concentration  $10^{-4}$  to  $10^{-7}$  mol/l. With increasing HCl concentration the interfacial potential increases and so does the corresponding distribution ratio of dye in nitrobenzene to dye in water. The distribution ratio remains constant at HCl concentrations below  $10^{-5}$  mol/l in agreement with the experiment. Therefore  $\text{H}^{+}$  of water at pH = 6 cannot account for the observed change in the distribution ratio.

Therefore, it is possible that the accompanying counter ion (presumably carbonate) can influence the partition equilibrium.

To investigate this possibility the dependence of the apparent distribution ratio on the dye concentration due to the presence of a constant amount of  $H^+$  (pH 6) and an associated anion was calculated. Curves of the effect caused by anions with standard potentials of transfer between  $-0.4$  and  $-0.2$  V are shown (Figure 5).

This model describes well the experimentally observed trend and points out how the interfacial potential will be poised by the minority ions present. This observation is also known as Donnan failure (20) or more practically as an interference in ion-selective electrodes.

### Summary

Variation of the apparent distribution constant with the concentration of dye was discussed in the view of experimental data, which show that  $D$  for the dye increases with decreasing concentration. One process, which can cause this effect, is the association of the dye in the aqueous phase. Conductivity measurements reveal an association constant on the order of  $10^5$ . This measurement provides additional information necessary for  $L/L$  charge transport measurements. The association constant  $K_\alpha = 10^5$  translates to about 85% dissociation at  $c=2 \times 10^{-6}$  mol/l, which means a correspondingly lower interfacial current observed in cyclic voltammetry.

The second process which can account for the variation is the influence of additional ions. Whereas association can be reasonably well measured and the

resulting corrections are meaningful, additional correction due to the presence of minority ions poses more difficulties. Especially at low concentrations of the dye, the models do not adequately describe the experimental results. Unless the exact nature and L/L transport properties are known, the approximation leading to the desired correction could obscure some other physical effect. A possible effect, not treated here, is the adsorption of the dye on the walls of the glassware, an effect which would give similar results as an increase in the association constant. Although this would better fit our experimental data, we have no supporting measurements with which to evaluate this effect.

Partition measurements are clearly better when made at higher concentrations, where the relative error is lower. In electrochemical measurements, where work over broad concentration ranges is desirable, the effects of association and the presence of additional ions can be considered using the discussed treatment. In particular, when association in the solvent is determined, it is possible to determine  $K_D$  from experimental values of  $D$  using the described procedure (Eq. [25] and [26]).

In order to proceed with the electrochemical study of oxacyanine dye transport across the water-nitrobenzene interface, it is necessary to determine the standard potentials of transfer for the dyes. One method of determining these standard potentials is to calculate them from the partition coefficients of the dyes between the two solvents. One problem with this method is that the fluorometric measurement technique is limited in its ability to measure the distribution of the more hydrophobic dyes. Another difficulty is that the partition ratio is not constant over a range of dye concentrations. Acknowledging these limitations, the standard potentials of transfer calculated by this method will be useful in studying the more hydrophilic dyes within a limited concentration range.

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- Figure 1 General structural formula of the investigated dyes. For  $m=n=1$  the formula will become  $\text{DiOC}_1(3)$ . Full name for this compound is 3,3'-dimethyloxacarbocyanine iodide.
- Figure 2 Molar conductivity of  $\text{DiOC}_1(3)\text{I}$  in water at different dye concentrations.
- Figure 3 Calculated apparent distribution ratio  $D$  of  $\text{DiOC}_1(3)$  as a function of concentration of the dye for different degree of association. Association constant in water  $K_\alpha$  is 1)  $10^4$ , 2)  $3 \times 10^4$ , 3)  $10^5$ , 4)  $10^6$ , and 5)  $10^7$ . Association content in nitrobenzene  $K_\beta=0$ . Circles are experimental values.
- Figure 4 Calculated interfacial potential between water and nitrobenzene after distribution of  $\text{DiOC}_1(3)$  as a function of the presence of a strong acid (HCl). Concentrations of  $\text{DiOC}_1(3)$  are 1)  $10^{-4}$  mol/l, 2)  $10^{-5}$  mol/l, 3)  $10^{-6}$  mol/l, and 4)  $10^{-7}$  mol/l. The change in potential causes the change in observed distribution ratios.
- Figure 5 Calculated changes in the distribution ratio of  $\text{DiOC}_1(3)$  between water and nitrobenzene as a function of the dye concentration in the presence of a hypothetical strong acid HA. The acid concentration is  $10^{-6}$  mol/l. The potential of transfer for the acid anion  $\text{A}^-$  is : 1)  $-0.4$  V, 2)  $-0.35$  V, 3)  $-0.3$  V, 4)  $-0.25$  V, and 5)  $-0.2$  V respectively. Circles are experimental data.



Table I

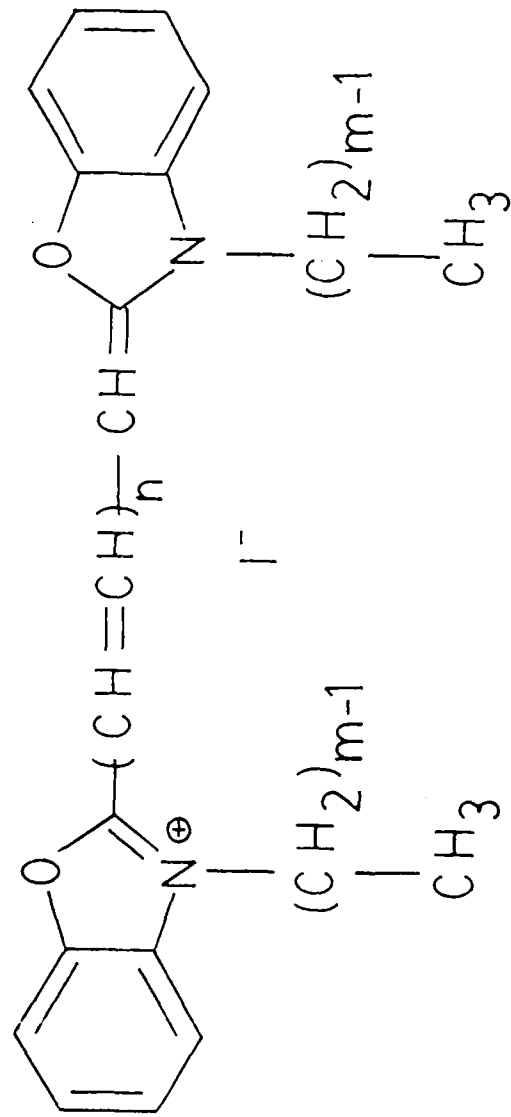
Partition constants of oxacyanine iodide dye salts between nitrobenzene and water, standard Gibbs energies of transfer from water to nitrobenzene and standard potential difference of transfer for individual oxacyanine ions,  $\varphi_w - \varphi_{nb}$ . The values were determined at  $10^{-4}$  mol/l of initial dye concentration and temperature 25 °C.

Dye	$\frac{c_{\text{Dye}}(\text{nb})}{c_{\text{Dye}}(\text{w})}$	$\Delta G_{\text{tr, dye}}^{\circ, \text{w} \rightarrow \text{nb}}$ [ kJ/mol ]	$\Delta_{\text{nb}}^{\text{w}} \varphi_i^{\circ}$ [ mV ]
DiOC <sub>1</sub> (3)	$9.7 \times 10^1$	-30	-310
DiOC <sub>2</sub> (3)	$3.4 \times 10^2$	-33	-350
DiOC <sub>3</sub> (3)	$1.8 \times 10^3$	-37	-390
DiOC <sub>4</sub> (3)	$3.7 \times 10^3$	-39	-410
DiOC <sub>5</sub> (3)	$>1.5 \times 10^4$	< -43	< -440
DiOC <sub>6</sub> (3)	$>2.0 \times 10^5$	< -49	< -510
DiOC <sub>7</sub> (3)	$>2.0 \times 10^5$	< -49	< -510
DiOC <sub>2</sub> (5)	$3.0 \times 10^3$	-39	-400
DiOC <sub>3</sub> (5)	$>4.5 \times 10^3$	< -40	< -420

Table II

Apparent dissociation constant  $K'$  calculated from various estimates of limiting conductivities for  $\text{DiOC}_1(3)\text{I}$ . The average  $K'$  value was calculated between concentrations of  $8.1 \times 10^{-6}$  and  $3.2 \times 10^{-5}$ . Error in  $\log K' \approx 0.2$ .  $\Lambda_0 = 115 \text{ S}\cdot\text{cm}^2\text{mol}^{-1}$  is an estimated value used in further calculations.

$\Lambda_0$ $\text{S}\cdot\text{cm}^2\text{mol}^{-1}$	$\log K'$
100	- 4.6
110	- 4.77
115	- 4.84
120	- 4.9
130	- 5.0
140	- 5.1
150	- 5.2



$DiOC_m(2n+1)$

