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PARTITIONING OF ORGANIC SOLUTES BETWEEN THE MICELLAR AND THE AQUEOUS PHASE AS STUDIED WITH AN ARTIFICIAL KIDNEY

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Summary. The partitioning of p-nitrophenyl acetate and of p-methylphenylsulfonylmethyl methanesulfonate into CTAB micelles in aqueous solution has been quantitatively investigated by means of a Cordis Dow C-Dak 1.3D artificial kidney.

In recent years it has been recognized that the dominant factor determining the efficiency of micellar catalysis of bimolecular and higher order reactions is usually the increased concentration of the reactants incorporated in the micellar pseudophase relative to that in bulk aqueous solution.[1] In extreme cases strong micellar catalysis is observed even if the second or higher-order rate constant for the reaction appears to be substantially decreased in the micellar pseudophase.[2,3] Several kinetic treatments have been devised to analyse these kinetic micellar effects.[1] These theories require reliable data for the distribution of the organic reagents between the bulk and micellar "phases" in terms of a partition constant. At present several techniques are available for the study of this partitioning, but usually the application thereof hinges on the validity of several assumptions involved in the analysis of the data. These assumptions are difficult to verify independently.[3] Recently, considerable progress was made when ultrafiltration, using regenerated cellulose membranes, was successfully applied in the measurement of solubilizate distribution in micellar solutions.[4]

The purpose of this communication is to demonstrate the use of a Cordis Dow C-Dak 1.3D artificial kidney[5] for the separation of organic solutes present in water and in the micellar pseudophase. A major advantage of this method is the high filtration speed as a result of the large membrane surface. The artificial kidney contains about 13.500 hollow fibers of regenerated cellulose with an effective surface area of about 1.3 m^2. A representative procedure is the following. A solution of p-nitrophenyl acetate (PNPA; $1.0.10^{-5}$ M) in aqueous micellar cetyltrimethylammonium bromide (CTAB; seven concentrations in the range

$8.0.10^{-4}$ - $6.0.10^{-3}$ M) with a total volume of 1.2 l is recycled through the kidney at a speed of 6-20 $ml.s^{-1}$ under slight nitrogen pressure (0.3-0.4 atm). After two hours[6] at 25.0 ± 0.1°C, 10 ml samples were collected from both the filtrate (at a speed of 4 $ml.\ min^{-1}$) and the filtrand and were analyzed by means of UV spectroscopy (PNPA, λ_m = 274 nm)[7] and conductivity measurements (CTAB). Variation of pressure and circulation speed had no significant effect on the filtrate composition. Experiments with a solution of PNPA in the presence of CTAB at a concentration below the critical micelle concentration revealed similar transport rates of PNPA and CTAB through the membrane. Finally, it could also be shown[8] that leakage of micelles through the membrane occurred to less than 3%.

If the association constant K is defined for the equilibrium

$$(CTAB)_n + PNPA \overset{K}{\rightleftharpoons} (CTAB)_n.PNPA$$

it can easily be shown[3] that

$$K = \frac{A-A'}{A'} \quad \frac{1}{[CTAB] - cmc} \qquad (1)$$

where A and A' are the optical densities of PNPA (at 274 nm) in filtrand and filtrate, respectively, [CTAB] is the total surfactant concentration and cmc the critical micelle concentration. As required by this treatment, a plot of (A-A')/A' vs. [CTAB] is found to be linear (Figure 1; r = 0.993). From the slope of this plot the value of K (73 ± 5 M^{-1}) is calculated which agrees satisfactorily with the association constants obtained by Almgren and Rydholm[10] (K = 50 ± 5 M^{-1}) and by Funasaki[11] (K = 54 M^{-1}) from solubility experiments.[12] Furthermore, the cmc obtained from Figure 1 ($7.2 . 10^{-4}$ M) agrees excellently with that obtained by using a fluorescence technique (cmc = $8.0.10^{-4}$ M).[13] This provides evidence that the assumed pseudophase model for solubilization in micellar solutions is essentially correct.

A second example involves the distribution of p-$CH_3C_6H_4SO_2CH_2OSO_2CH_3$ at 32°C between micelles and water at a constant concentration of CTAB ($43.1.10^{-4}$ M). At seven different filtrand absorbances at 235 nm, K was calculated from eqn. (1) to be 170 ± 15 M^{-1}. Since the temperature dependence of the cmc is small compared with the overall detergent concentration,[14] no correction was applied. The value of K can be fitted with recent results[15] obtained from a

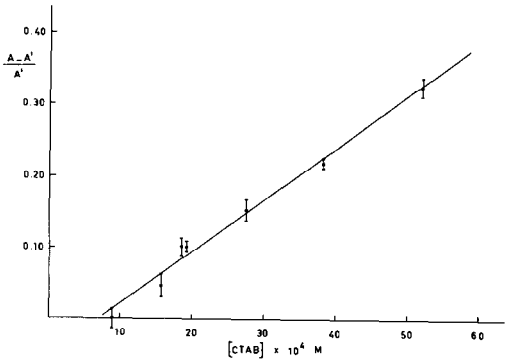

Fig. 1. Plot of (A-A')/A' vs. [CTAB] for the solubilization of PNPA in micellar solutions of CTAB at 25°C.

study of the reaction of the sulfonate with hydroxide ion[16] in the presence of CTAB.

We are continuing to explore the utility of artificial kidneys in the study of the binding of organic solutes to micellar aggregates.

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References and Notes

(1) (a) K. Martinek, A.K. Yatsimirski, A.V. Levashov and I.V. Berezin in "Micellization, Solubilization, and Microemulsions", K.L. Mittal, ed., Vol. 2, Plenum Press, New York, N.Y., 1977, p. 489; (b) L.S. Romsted in Ref. 1a, p. 509.

(2) See, for example, A.A. Bhalekar and J.B.F.N. Engberts, J. Am. Chem. Soc., 100, 5914 (1978).

(3) I.V. Berezin, K. Martinek, and A.K. Yatsimirski, Russ. Chem. Rev., 42, 790 (1973).

(4) S.J. Dougherty and J.C. Berg, J. Colloid Interface Sci., 48, 110 (1974). The filtrate was collected at a speed of 0.5-2 ml. hr^{-1}.

(5) Cordis Dow Corporation, Miami, Florida, USA.

(6) Initially the concentration of PNPA decreased by ca. 15%, apparently because of adsorption to the membrane surface. Within 2 hrs, however, the concentration remained constant and filtrate collection could be started. Adsorption to the membrane may be a drawback of the method when applied to very hydrophobic solutes.

(7) The molar extinction coefficient of PNPA in aqueous solution was equal to that in aqueous CTAB.

(8) In all cases, the CTAB concentration of the filtrate was found to be higher than the cmc, which could be taken to imply that only part of the micelles (ca. 90%) were rejected. However, our experiments with Orange OT solubilized by CTAB clearly revealed that less than 3% of the almost water-insoluble dye[9] had passed the membrane.

(9) (a) R.J. Williams, J.N. Phillips, and K.J. Mysels, Trans. Faraday Soc., 51, 728 (1955); (b) L. Sepulveda and R. Soto, Makromol. Chem., 179, 765 (1978).

(10) M. Almgren and R. Rydholm, J. Phys. Chem., 83, 360 (1979).

(11) N. Funasaki, J. Colloid Interface Sci., 64, 461 (1978).

(12) The somewhat lower K-values reported in ref. (10) and (11) as compared with the present result may well be explained by the higher solute concentrations, which may lead to less efficient binding of part of the solute molecules.[4]

(13) K. Kalyanasundaram and J.K. Thomas, J. Am. Chem. Soc., 99, 2039 (1977).

(14) C. Jolicoeur and P.R. Philip, Can. J. Chem., 52, 1834 (1974).

(15) G.B. van de Langkruis and J.B.F.N. Engberts, to be published.

(16) H.A.J. Holterman and J.B.F.N. Engberts, J. Org. Chem., 42, 2792 (1977).

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