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Osmotic Coefficients of C.I. Acid Orange 7 in Aqueous Solution and in the Presence of Simple Electrolyte

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ABSTRACT

The aggregation of a monoazo acid dye was studied with osmometry. The osmotic coefficients of the dye were measured in aqueous solution and in 0.01 M potassium chloride. The mean aggregation numbers were calculated on the basis of the spherical cell model of dye in the solution. The results showed that the aggregation process is more distinctive in the presence of a simple electrolyte, probably because of the screening effect of the salt ions. © 1997 Elsevier Science Ltd

Keywords: acid dye, aggregation, osmometry, spherical cell model.

INTRODUCTION

Understanding of the aggregation process is of great importance in the analysis of the properties of dyes in solutions, and aggregation has been the subject of numerous investigations. A variety of methods have been used to investigate this phenomenon. We decided to study the aggregation of the monoazo acid dye C.I. Acid Orange 7 by means of osmometry, since this has been shown to be an efficient and sufficiently accurate method [1]. In order to estimate the influence of a simple electrolyte on aggregation, osmotic coefficients of the dye in aqueous solution, and in the solution of 0.01 M potassium chloride, were measured. Using the spherical cell model, we were able to estimate the mean aggregation number of the dye in aqueous solution, as well as in the potassium chloride solution.

EXPERIMENTAL

The dye C.I. Acid Orange 7 (Fig. 1) was synthesized by coupling diazotized sulfanilic acid to 2-naphtholate [2]. It was recrystallized three times from methanol:water (2:1). After ionic exchange (Amberlite IR 120, in Na^+ form), crystallization from aqueous methanol was repeated. The dye was finally recrystallized three times from non-aqueous medium (benzene:N,N-dimethylformamide = 2:1) and finally dried at 80°C in vacuum.

The measurements were made at 25°C using a Knauer Vapour Pressure Osmometer. The instrument was calibrated using aqueous KCl solutions, whose osmotic coefficients are available in the literature [3].

RESULTS AND DISCUSSION

In Fig. 2, the measured osmotic coefficients of the dye in aqueous solution and in 0.01 M KCl are presented as a function of the dye concentration.

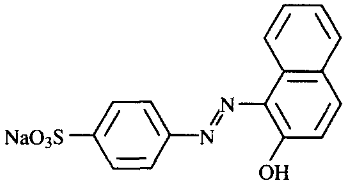

Fig. 1. C.I. Acid Orange 7.

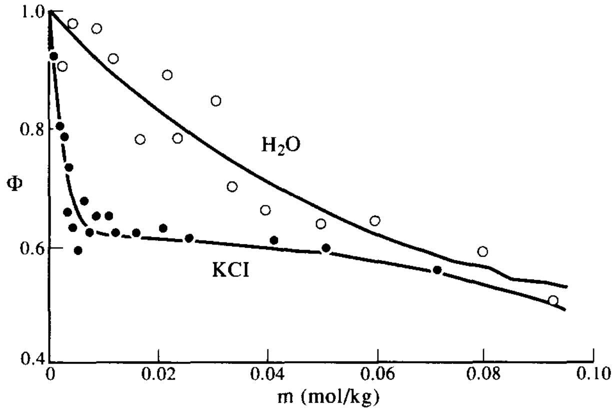

Fig. 2. Osmotic coefficients as a function of dye concentration in aqueous solution and in 0.01 M potassium chloride solution.

The measured osmotic coefficients were compared to those obtained by the spherical cell model [1, 4] for different degrees of aggregation. According to the model, the solution is represented as a system of spherical cells of volume $V_c = zN_A/c$, where N_A is the Avogadro number and c is the concentration of ionogenic groups in basemol dm^{-3}. An aggregate approximated by a sphere of volume zV_b and radius $a = (3zV_b/4\pi)^{1/3}$ is located in each cell, carrying the charge $-ze_o$ and surrounded by simple ions of total charge ze_o [1]. The volume $V_b = 0.5$ nm^3 was estimated [1, 5, 6] on the basis of the molecular model of the investigated dyes. The calculations were made within the limits of low concentrations, where the condition $zV_b \ll V_c$ is satisfied, and therefore inaccurate estimation of V_b and deviations from the spherical model have no essential influence. The distribution in the cell was calculated using the nonlinear Poisson–Boltzmann equation.

The osmotic pressure π is determined by the concentration of aggregates (c/z) and the concentrations of simple ions at the cell boundary ($c_i(R)$) [5] [eqn (1)].

$$\pi = RT\left[c/z + \sum c_i(R)\right] \tag{1}$$

where R is the gas constant and T is absolute temperature.

In the presence of a simple monovalent salt in the solution, eqn (1) reads as eqn (2):

$$\pi = RT[c/z + c_+(R) + c_-(R)] \tag{2}$$

in which $c_+(R)$ and $c_-(R)$ are the concentrations of cations and anions at the cell boundary, respectively.

The corresponding nonlinear Poisson–Boltzmann equation is, for the first case, shown in eqn (3)

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}y}{\mathrm{d}r}\right) = \frac{F^2}{\varepsilon_o\varepsilon RT}c_+\Phi_+e^y \tag{3}$$

and for the latter case in eqn (4)

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}y}{\mathrm{d}r}\right) = \frac{F^2}{\varepsilon_o\varepsilon RT}(c_+\Phi_+e^y - c_-\Phi_-e^y) \tag{4}$$

The boundary conditions are

$$y(R) = 0 \qquad \left(\frac{\mathrm{d}y}{\mathrm{d}r}\right)_{r=a} = -\frac{ze_oF}{4\pi\varepsilon_o\varepsilon RTa^2} \qquad \left(\frac{\mathrm{d}y}{\mathrm{d}r}\right)_{r=R} = 0$$

where $y = -\psi F/RT$, $c_+ = c_+(R)/\Phi_+$, $c_- = c_-(R)/\Phi_-$, c_+ and c_- are the average concentrations of cations and anions, respectively, ψ is the potential of the mean force, acting on a small ion, approximated by the mean electrostatic potential, r is the distance from the center of the polyion, ε is dielectric constant of the solvent and ε_0 permittivity of the vacuum.

Numerical solution of the Poisson–Boltzmann equation in the system of spherical symmetry and in the presence of a simple electrolyte was analogous to that of the system of cylindrical symmetry [7]. The calculated osmotic pressure greatly depends on the average charge of the aggregate z, as well as on the c/z part, as also on all $c_i(R)$. Osmotic pressures π, calculated with eqn (3), were compared to those measured for dye in the aqueous solutions, whereas osmotic pressures, calculated using eqn (4) and diminished for the osmotic pressure of the reference solution KCl, were compared to the measured difference of osmotic pressures of dye in the electrolyte solution. The value z, which gave the best agreement between the calculated and measured values, was adopted to estimate the mean aggregation number $n = z/v$, where v is the dye valency.

The mean aggregation numbers, obtained in this way, are shown in Fig. 3. As is evident, at relatively low concentrations in aqueous solutions only a slight dimerization of the dye occurs. In the presence of a simple electrolyte, the situation changes completely. In this case, the mean aggregation number abruptly increases with concentration already at low concentrations. It is interesting that at higher dye concentrations the presence of a simple electrolyte only slightly increases the aggregation number at a given dye

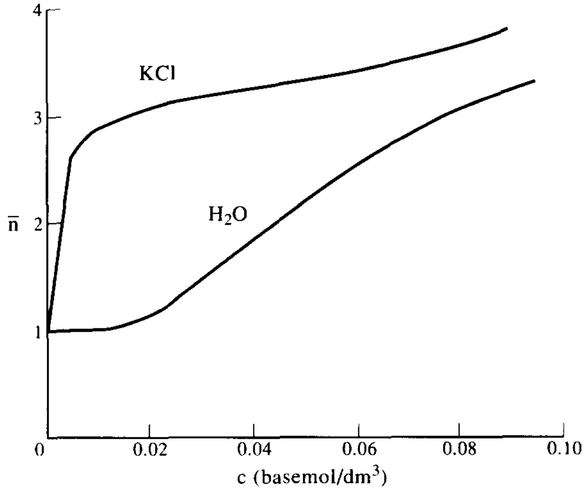

Fig. 3. Mean aggregation number as a function of dye concentration in aqueous solution and in 0.01 M potassium chloride solution.

concentration. The rapid increase of the mean aggregation number at low concentrations of dye in the presence of a simple electrolyte can be ascribed to screening of the charged groups on the dye due to the simple salt ions.

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