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Osmometric Study of Aggregation in Dye Solutions*

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The osmotic coefficient of aqueous solutions of four different dyes was measured as a function of the concentration. From the results the dependence of the mean aggregation number of the dye on the concentration was determined. The calculations were based on the application of the spherical cell model of colloid solutions.

INTRODUCTION

Most dyes constitute a class of electrolytes displaying peculiar properties in their relationship with water. There is a great deal of evidence that dye ions aggregate in aqueous solutions.¹⁻⁵ Several methods have been proposed for the study of this phenomenon. Although very promising, vapour pressure osmometry has been almost completely neglected. Miličević and Eigenmann⁶ reported the values of activity coefficients of two simple acid dyes obtained by this method. Supposing that there is no specific counterion binding and using the Debye-Hückel limiting law, they have shown that Orange II, in contrast to its isomer Orange VIII, is not appreciably dimerized. In our work, the method was applied for the determination of the extent of aggregation in solutions of two direct and two acid dyes, where higher aggregates were also expected. Using the spherical cell model of colloid solutions,⁷⁻¹⁰ we were able to estimate the mean aggregation numbers of the four dyes studied.

EXPERIMENTAL

The dyes C. I. Direct Red 28, C. I. Direct Blue 1, C. I. Acid Red 18, and C. I. Acid Red 88 were purified by crystallization two or more times from 50% by volume aqueous ethanol solution. The stock aqueous dye solutions were prepared and their concentrations were determined spectrophotometrically. The osmotic coefficient of the solutions was measured at 37 ± 0.02 °C by vapour pressure osmometry.¹¹ The instrument used was a Knauer vapour pressure osmometer, calibrated using aqueous KCl solutions whose osmotic coefficients are available in the literature.¹²

THEORETICAL

Consider a dye which dissociates in solution into ν monovalent counterions, each carrying the elementary charge e_0 , and the dye anion of charge $-\nu e_0$. At

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a given dye concentration, c_D , and the corresponding basemolar concentration, $c = \nu c_D$, equal to the concentration of the counterions, the ideal osmotic pressure, Π_{id} , is given by

$$\Pi_{id} = c_D RT (\nu + 1) = c RT (1 + \nu^{-1}) \quad (1)$$

where the first term corresponds to the contribution of the counterions and the second to the contribution of the dye anions, R is the gas constant and T the absolute temperature. The real osmotic pressure, Π , is lower owing to the aggregation of the dye and the coulombic interaction among ions. At the average aggregation number $n = z/\nu$, where $-e_o z$ is the average charge of an aggregate, the contribution of the dye anions is reduced to $c RT/z$. In addition, the decrease of the osmotic pressure due to the atmospheric binding of counterions to the aggregates has to be taken into account. In simple electrolyte solutions, the effect is usually analysed in terms of the Debye-Hückel or related theories. Bearing in mind the pronounced assymetry between the behavior of the aggregates and the counterions due to the considerable difference in charge and in magnitude of the two species, the application of the cell model⁷⁻¹⁰ of colloid solutions is suggested. According to the model, the solution is represented as an ensemble of equal spherical cells of radius R and volume $V_c = 4\pi R^3/3 = z/(N_A c)$, where N_A is Avogadro's number. Each aggregate, approximated by a sphere of radius $a \ll R$, is located in the centre of a cell, and its charge $-ze_o$ is spread uniformly over its surface. The small ions of the net charge opposite and equal to that of an aggregate are distributed throughout the cell according to the Boltzmann distribution. The potential of the mean force, acting on a small ion, is approximated by the mean electrostatic potential, ψ , which satisfies the nonlinear Poisson-Boltzmann equation

$$\frac{1}{r^2} \frac{d}{dr} \left(\varepsilon r \frac{d\psi}{dr} \right) = -F c_b \exp \{ -e_o/kT [\psi(r) - \psi(R)] \} \quad (2)$$

subject to the conditions

$$\left(\frac{d\psi}{dr} \right)_a = \frac{z e_o}{4\pi \varepsilon a^2}, \quad \left(\frac{d\psi}{dr} \right)_R = 0 \quad (3)$$

Here, r is the distance from the centre of a cell, ε is the permittivity, c_b is the concentration of the counterions at the cell boundary ($r = R$), F is the Faraday and k the Boltzmann constant. The radius of the aggregate, a , is, in the first approximation, related to the aggregate charge $z = n\nu$ according to the cube root rule:¹³ $a \approx (3zV_b/4\pi)^{1/3}$, where V_b is the volume per basemole unit of the dye.

As shown previously under the Poisson-Boltzmann approximation¹⁴⁻¹⁸ or by direct differentiation of the partition function,⁹ the contribution of the small ions to the osmotic pressure equals $c_b RT$. At the same time, the contribution of the aggregates is considered to remain virtually unchanged.¹⁶ The overall osmotic pressure is then given by

$$\Pi = RT (c_b + cz^{-1}) \quad (4)$$

while the expression for the osmotic coefficient φ , defined as the ratio of actual to ideal osmotic pressure reads

$$\varphi = (c_b c^{-1} + z^{-1}) (1 + \nu^{-1})^{-1} \quad (5)$$

where c_b is related to z via eqs. (2,3). An implicit equation for z , expressed in terms of φ , is thus obtained, which was used for the determination of the mean aggregation number $n = z/\nu$. Since no tractable analytical solution to eq. (2) has been proposed as yet, the numerical solution, obtained by the fourth order Runge-Kutta method¹⁹ was applied in calculations of the electric field and of the concentration profiles of the small ions.

RESULTS AND DISCUSSION

Table I lists the osmotic coefficients, φ , measured in solutions of the four dyes over a broad concentration range. In Figure 1, the mean aggregation

TABLE I

The Measured Osmotic Coefficients of Different Aqueous Dye Solutions at 37 °C

C. I. Direct Red 28 ($\nu=2$)

$c/(\text{basemol dm}^{-3})$	φ
0.00275	0.898
0.00412	0.864
0.00598	0.811
0.00786	0.742
0.00958	0.708
0.01164	0.684
0.01359	0.656
0.01590	0.637
0.01814	0.620
0.0200	0.616
0.0273	0.602
0.0776	0.535

C. I. Direct Blue 1 ($\nu=4$)

$c/(\text{basemol dm}^{-3})$	φ
0.00198	0.864
0.00385	0.824
0.00596	0.798
0.00796	0.769
0.00996	0.708
0.0138	0.596
0.0298	0.560
0.0659	0.489

C. I. Acid Red 18 ($\nu=3$)

$c/(\text{basemol dm}^{-3})$	φ
0.01032	0.823
0.01854	0.735
0.0240	0.696
0.0304	0.683
0.0456	0.671
0.0601	0.662
0.0767	0.644
0.0924	0.634
0.1245	0.609

C. I. Acid Red 88 ($\nu=1$)

$c/(\text{basemol dm}^{-3})$	φ
0.00222	0.965
0.00419	0.934
0.00636	0.881
0.00838	0.836
0.0106	0.806
0.0127	0.781
0.0148	0.760
0.0171	0.729
0.0193	0.700
0.0215	0.688

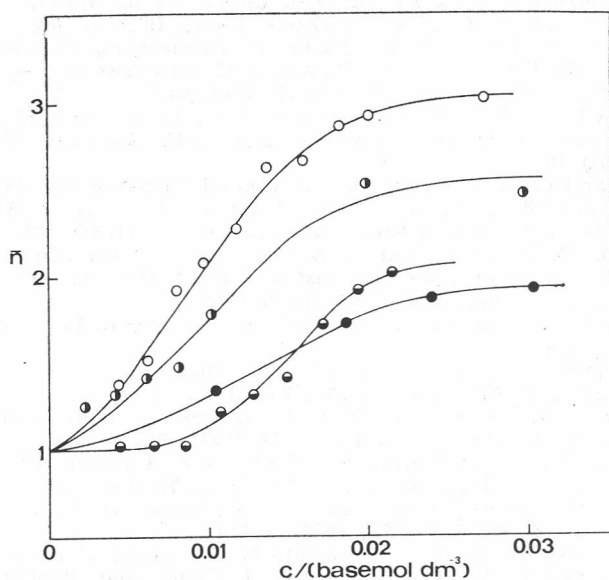


Figure 1. The mean aggregation number of the dyes: C. I. Direct Red 28 (○), C. I. Direct Blue 1 (●), C. I. Acid Red 18 (●), and C. I. Acid Red 88 (●).

numbers, n , obtained by eq. (5) from measured osmotic coefficients are presented as functions of the dye concentration. Here, the effective aggregate radii, a , were determined by using the approximate value $V_b \sim 0.5 \text{ nm}^3$, estimated from the molecular model of the dyes studied. As shown, n increases appreciably with concentration in dilute solutions. At concentrations above $\sim 2 \cdot 10^{-2}$ basemol dm^{-3} this increase is slowed down. The plateau values of n indicate that dimers and trimers dominate in concentrated solutions, while higher aggregates are less expected. Actually, the calculations were restricted to concentrations below $3.5 \cdot 10^{-2}$ basemol dm^{-3} , where the condition $a \ll R$ is still satisfied and the errors due to inexact estimate of the aggregate size and geometry are of minor importance. This was verified in additional calculations applying the original model with different values of a , and the modified cell model with aggregates represented as charged prolate ellipsoids of revolution.²⁰ In order to evaluate the influence of the approximations inherent in the Poisson-Boltzmann treatment a few calculations were also carried out by using the modified Poisson-Boltzmann equation²¹ with the small ion-small ion correlation being considered as proposed in a previous paper.²² The improved values of n , obtained in this way, agree within $\pm 5\text{--}10\%$ with these presented in Figure 1. According to the simplifications of the model and calculation, and the fact, that eq. (5) does not yield the arithmetic average of n in inhomogeneous systems, the values shown in Figure 1 represent only the first estimate of actual degrees of aggregation. It is considered, however, that more accurate numerical data would not essentially alter the conclusions of our study.

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IZVLEČEK**Osmometrična raziskava agregacije v raztopinah barvil**

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Izmerjeni so bili osmozni koeficienti vodnih raztopin štirih različnih barvil v odvisnosti od koncentracije. Iz merskih rezultatov je bila določena koncentracijska odvisnost stopnje agregacije opazovanih barvil. Računi so bili osnovani na uporabi sfernega celičnega modela koloidnih raztopin.