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EFFETS DES INTERACTIONS ELECTROSTATIQUES SUR LES REACTIONS DE
TRANSFERT D'ELECTRONS

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Effets des interactions électrostatiques sur
les réactions de transfert d'électrons

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Les réactions rapides de transfert d'électrons ont été étudiées par radiolyse pulsée. Cette technique permet de créer dans un temps de l'ordre de 10^{-8} s et de façon homogène dans la masse de la solution, des radicaux et ions radicaux ayant des potentiels redox élevés. Dans le cas de l'électron solvaté, l'effet des interactions électrostatiques sur la constante de vitesse des réactions limitées par la diffusion est décrit avec une bonne approximation par l'équation de Debye lorsque la mobilité des ions est connue. Un certain nombre de déviations par rapport à la théorie sont dues à la formation de paires d'ions. Ceci peut être mis expérimentalement en évidence pour les réactions entre anions en complexant les cations avec un cryptate.

Les réactions relativement lentes $k < 10^8 \text{ M}^{-1}\text{s}^{-1}$ sont plus sensibles aux interactions électrostatiques que les réactions limitées par la diffusion. Dans les cas où il n'y a pas formation de paires d'ions, la constante de vitesse dépend de la constante diélectrique du solvant et du rayon de réaction.

Le cas plus complexe des réactions presque limitées par la diffusion c'est-à-dire où l'étape physique et l'étape chimique ont des vitesses voisines sera discuté brièvement.

EFFECT OF ELECTROSTATIC INTERACTIONS ON ELECTRON-TRANSFER REACTIONS.

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INTRODUCTION

Electrostatic interactions play an important role in the rate of ionic reactions, not only through the activity coefficients which depend of the ionic strength of the medium (1) but more directly the coulombic forces between the ionic reactants change the collision frequency. The first treatment of the effect of electrostatic interactions was given by Christansen and Scatchard (2) (equation I)

$$(I) \quad k = k_0 e^{-Q} \quad Q = \frac{NZ_A Z_B e^2}{\epsilon d R T}$$

where N is the Avogadro number, Z_A and Z_B the charge of the reacting species e the electronic charge, ϵ the dielectric constant of the solvent and d the reaction distances k_0 would be the rate in a medium of infinite dielectric constant. This equation predicts that a plot of $\log k$ against $\frac{1}{\epsilon}$ is a straight line and the slope gives d the reaction distance.

When the reaction is diffusion controlled equation I is no longer valid and is replaced by the Debye equation (3) (equation II).

$$k = k_d \times \frac{e^Q}{e^{Q-1}} \quad \text{where } k_d = \frac{4 \pi N}{1000} (D_A + D_B) d$$

is the Smoluchowski equation for diffusion controlled reactions in absence of electrostatic interactions (4) and the second member of equation II is a correction factor which accounts for the effect of electrostatic interactions. D_A and D_B are the diffusion coefficients of the ions. The comparison between the two equations for the same reaction distance is given in figure 1.

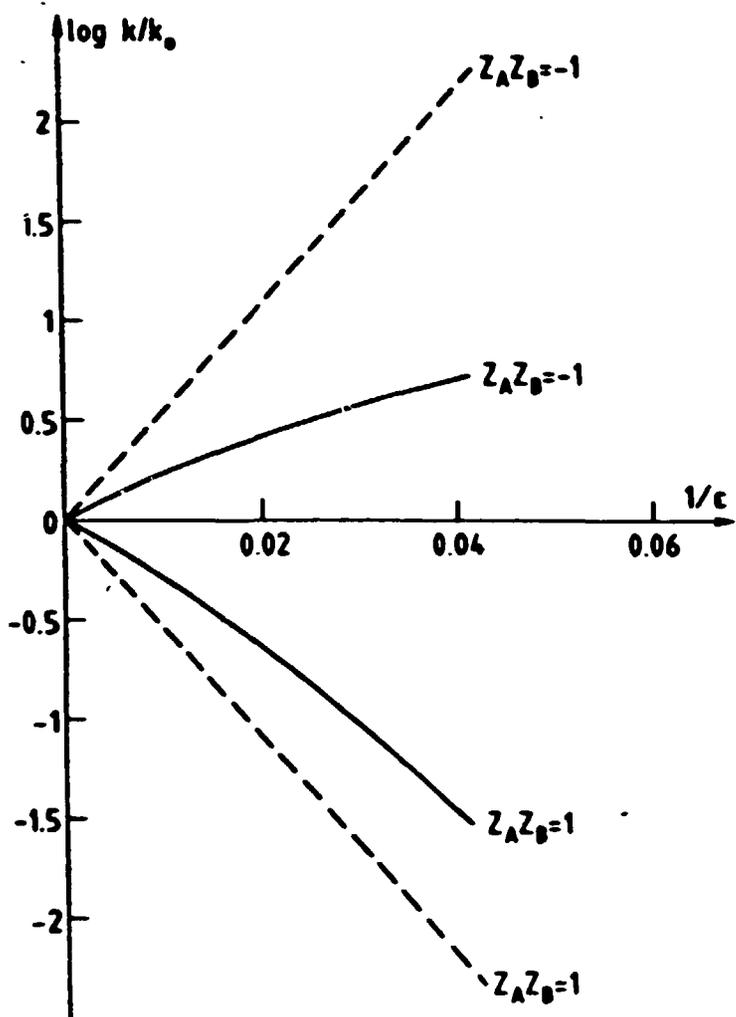


FIGURE 1

---- Equation I
 ——— Equation II
 $d = 4.3 \text{ \AA}$

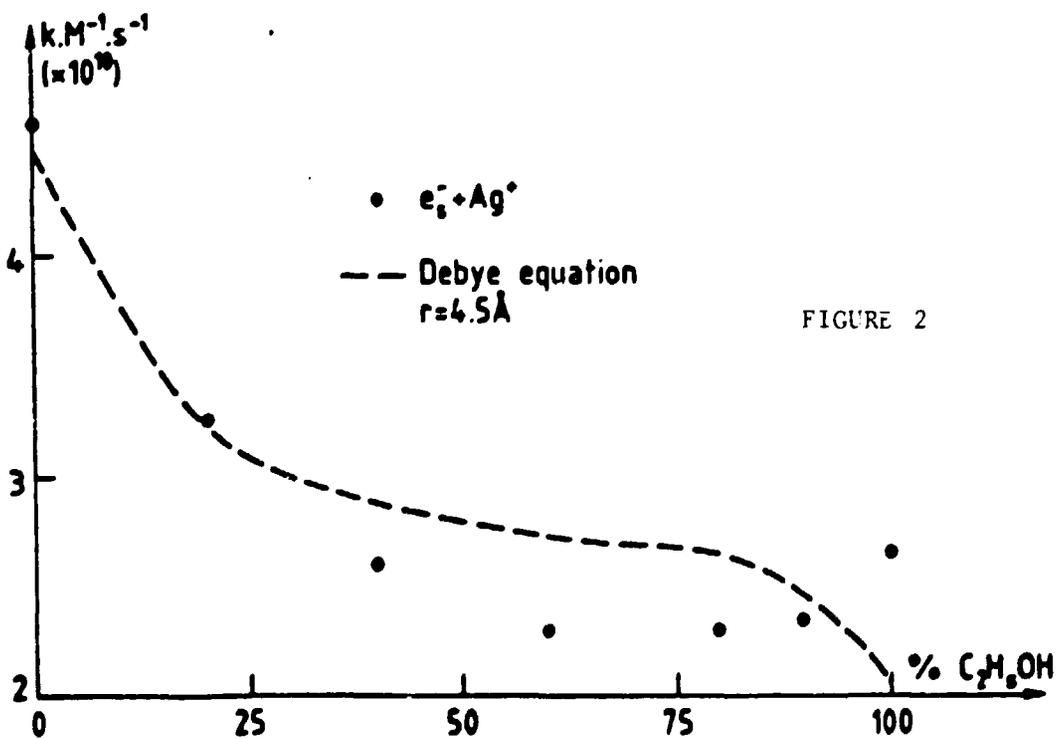


FIGURE 2

We have studied the effect of electrostatic interaction on the rate constants of solvated electrons with anions and cations in water-ethanol mixtures where the dielectric constant change from 80 to 25 at room temperature. Water-ethanol mixtures have two advantages : first the diffusion coefficients of solvated electron are known (5) and the diffusion coefficients of other ions are often available from conductivity measurements. Secondly the absorption spectra of the solvated electron change very little with the composition of the mixture (6) . This means that the solvation energy of the electron, which can play an important role in the rate, (7) remains approximately constant for the whole range of composition.

EXPERIMENTAL SECTION

Solvated electrons were produced by pulse radiolysis of the solution using a modified Febetron 707 delivering single pulses of electrons in the energy range 1.6 - 1.8 MeV. The total duration of the electron pulse is less than 20 ns. The irradiation cell of high purity silica was rectangular and the optical path was 2.2 cm. Experimental details on the fast spectrophotometric detection system are given in previous publications (8) (9) . The dose determined from the initial absorption of the solvated electron varied from 5 to 15 krads.

The concentration of solvated electrons was always much lower than the solute concentration to ensure that the bimolecular reaction follows pseudo first order kinetics. The rate constants were determined from the decay of the absorption of the solvated electron in solutions containing various concentrations of solutes after subtracting the decay arising from the solvent. Extrapolation to zero ionic strength was made according to the Brønsted Bjerrum equation (10).

RESULTS AND DISCUSSION

1/ Reaction with Ag^+

The reaction

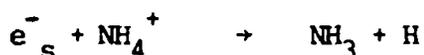


is diffusion controlled in water and in ethanol (11) . In water ethanol mixtures the rate remains diffusion controlled (figure 2) and the deviations from the Debye equation are smaller than 30 %. The reaction radius 4.5 \AA is close to the sum of $(r_{e_s^-} + r_{Ag^+}) = 4 \text{ \AA}$.

The decrease in the rate constant from water to ethanol is not due to the lower thermodynamic activity of Ag^+ in alcohols than in water (12) but to the decrease of the diffusion coefficients of e_s^- and Ag^+ . This effect is stronger than the increase due to the electrostatic interactions (figure 1) and the net effect is a small decrease in the rate. When $Z_A Z_B = 1$ the effect of diffusion coefficients and electrostatic interactions act in the same direction and the rate constant decreases by two orders of magnitude from water to ethanol (13) .

2/ Reaction with NH_4^+

In water the reaction

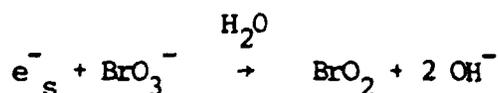


is comparatively slow $k < 10^7 M^{-1}S^{-1}$ and becomes almost diffusion controlled in ethanol (11) .

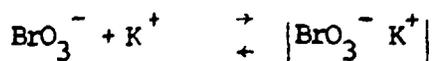
In that part which is not diffusion controlled the rate apparently follows the equation I (figure 3) but the slope gives a reaction radius of 2 \AA which is smaller than the sum of $(r_{e_s^-} + r_{NH_4^+}) = 4.2 \text{ \AA}$. When the concentration of ethanol increases the rate constant is faster than expected. Two experiments were performed in water-methanol mixtures and the rate constants were also faster than expected. This cannot be due to the formation of ions pairs between NH_4^+ and Cl^- which would screen the charge on NH_4^+ and hence decrease the reaction rate.

3/ Reaction with BrO_3^-

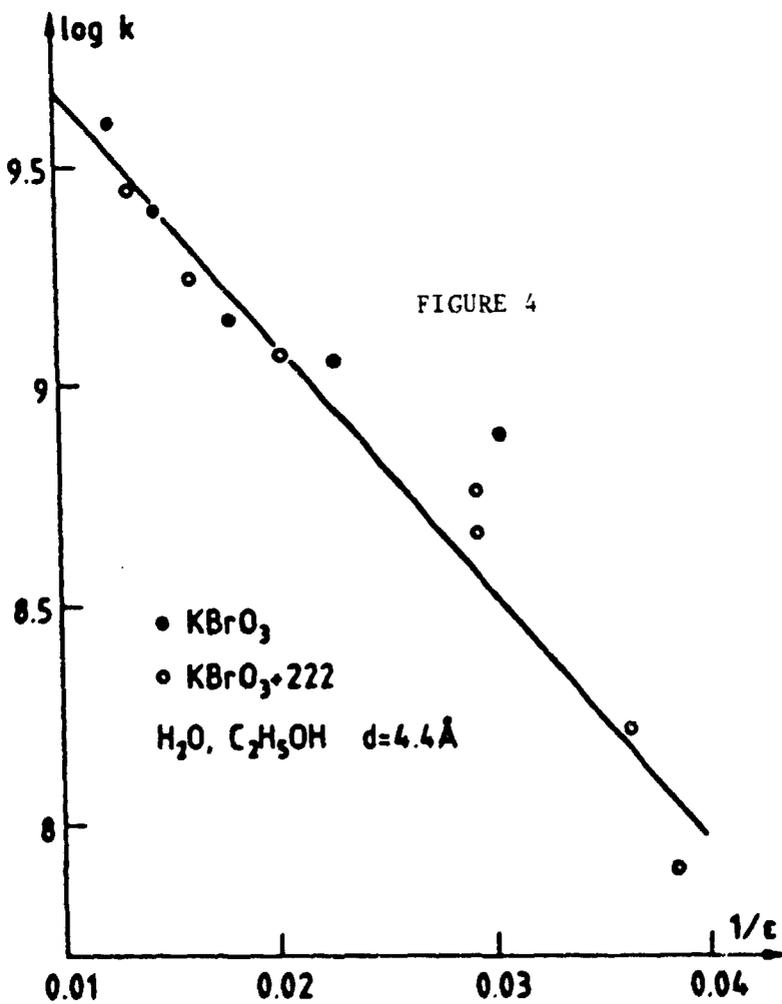
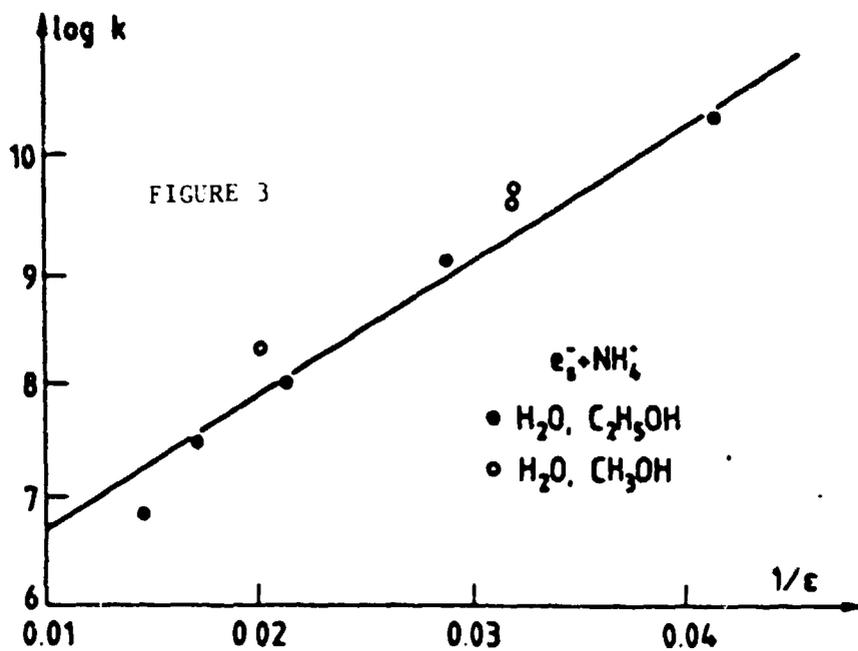
The reaction



is fast but not diffusion controlled in water. When $KBrO_3$ is used deviations from equation I are observed when the dielectric constant is lower than 40. The rate constants are faster than expected. But in this case formation of ion pairs



would increase the rate of reaction with the solvated electron (8) . To check this hypothesis cryptand 222 was added to the solutions. The cryptand 222 has a three-dimensionnal cavity of 1.4 \AA and complexes strongly K^+ (14) . The complex which is nearly spherical has a radius of about 5 \AA and does not easily form ion pairs with anions (15) .



The cryptand 222 does not react with e_s^- (16) . In the region of high dielectric constant addition of 222 does not change the rate constant between e_s^- and BrO_3^- (figure 4) , but for $\epsilon < 40$ the rate is slower than in absence of 222. A plot of $\log k$ against $\frac{1}{\epsilon}$ gives a reasonably straight line with a reaction distance of 4.4 Å .

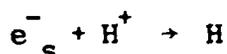
NEAR DIFFUSION CONTROLLED REACTIONS

When the rate of diffusion and the rate of the chemical reaction are of the same magnitude the rate constant k is given by the equation

$$(III) \quad \frac{1}{k} = \frac{1}{k_d} + \frac{1}{k_c}$$

where k_d and k_c are the rate constants respectively for the diffusion controlled reaction and for the chemical reaction (17) . For ionic reaction k_c and k_d are given by equations I and II respectively.

An example is given by the reaction



which is not truly diffusion controlled in water. In water-ethanol mixtures the rate is almost independant of the dielectric constant until the mixture is 99 % in weight of ethanol (13) . In this range the proton remains bonded to a water molecule and the apparent lack of electrostatic effect is due to a compensation between k_c and k_d (Table I) .

wt % C ₂ H ₅ OH	0	50	80	99
k_d in $10^{10} M^{-1}S^{-1}$	9,5	4	3,4	3,1
k_c in $10^{10} M^{-1}S^{-1}$	3,2	8,36	32,3	122
k equation III	2,4	2,4	3,1	3
k exp. (ref. 13)	2,4	2,5	2,9	2,8

$$r_{e_s^-} + r_{H^+} = 4,3 \text{ \AA}$$

$$k_0 = 6.1 \cdot 10^9 M^{-1}S^{-1}$$

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