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Diffusion in concentrated micellar and hard sphere solutions

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Résumé. — Cet article présente des résultats expérimentaux obtenus par diffusion quasi-élastique de la lumière pour différentes solutions micellaires chargées. Le comportement du coefficient de diffusion mutuel D_m aux grandes concentrations provient des interactions hydrodynamiques à plusieurs corps. Ces interactions sont prises en compte via l'équation semi empirique Navier-Stokes écrantée. Le tenseur effectif à deux corps a été calculé jusqu'au terme en r^{-7} (r est la distance entre les deux particules), à l'aide du formalisme de Mazur et van Saarloos. Ce tenseur n'est pas « écranté », en ce sens que son comportement aux longues distances est en puissance inverse de r et non pas en exponentielle décroissante. Une constante « d'écrantage » K est proposée ne dépendant de la fraction volumique ϕ que par un seul paramètre ajustable. L'évolution de D_m avec la concentration micellaire est bien reproduite en utilisant la même valeur de K pour les différentes forces ioniques. Aux grandes fractions volumiques les interactions hydrodynamiques sont essentiellement dominées par les répulsions de type sphère dure. Cette observation est confirmée par la simulation du coefficient de diffusion mutuelle et self pour une solution de sphères dures en utilisant la même valeur pour K . Cette constante peut s'écrire : $Ka \simeq \phi$ où a est le rayon des particules, ce qui est en accord avec les conclusions d'Adelman.

Abstract. — We present experimental results of quasi-elastic light scattering for different charged micellar solutions. The characteristic concentration dependence of the mutual diffusion coefficient D_m at large volume fraction arises from the many-body hydrodynamic interactions. These interactions are introduced through the quasi-empirical screened Navier-Stokes equation. The effective pair mobility tensor has been calculated for terms up to r^{-7} (r is the inter-particle distance) with the formalism of Mazur and van Saarloos. The tensor is not « screened » in the sense that its long distance behaviour is as an inverse power of r , rather than exponential. A single « screening » constant K is proposed which is volume fraction dependent with only one adjustable parameter. The evolution of D_m with the micellar concentration has been well reproduced by the same value of K at various ionic strengths. At large volume fraction ϕ the hydrodynamic interactions are essentially dominated by uncharged hard-sphere repulsions. This observation is confirmed by the fit of the dynamics of concentrated hard-sphere solutions. The behaviour of the self and mutual diffusion coefficients is described by using the same « screening » constant. This can be written as $Ka \simeq \phi$ where a is the particle radius, which is in agreement with the results previously derived by Adelman.

1. Introduction.

The dynamic properties of micellar or colloidal solutions, as manifested in the mutual diffusion coefficient, measured by dynamic light scattering experiments, are governed by direct thermodynamic and indirect (particle-solvent-particle) hydrodynamic interactions. The formers are well known, and can be calculated over a large range of concentrations. On the other hand, the hydrodynamic interactions are much more difficult to account for, except for dilute solutions where they are restricted to two-body interactions. The pair mobility tensor was first calculated as a power series of r^{-1} (r is the inter-

particle distance) by Batchelor [1-2] and Felderhof [3-4]. Using a statistical mechanics approach for this tensor and for the pair distribution function we can calculate the mutual and self diffusion coefficients of dilute colloidal solutions.

For more concentrated solutions, the n -particles contributions to the mobility tensor become important and cannot be neglected. Mazur and Van Saarloos [5] have explicitly calculated the three and four-body mobility tensors by developing them as a series in r^{-n} . However, because these tensors require integration with multiple particle distribution functions which are not presently available, they have not been used to calculate the diffusion constants [6, 7]. Even if

these functions are approximated they lead to multiple-integrals which are quickly prohibitive in computation time.

Another approach developed by Beenakker and Mazur [8, 9] consists of evaluating the diffusion coefficient as an expansion of correlation functions of increasing order, and then algebraically resumming the many-sphere hydrodynamic contributions using a special class of correlation functions, known as « ring-selfcorrelations ». This method gives a renormalized tensor which describes the hydrodynamically interacting particles *via* the suspension rather than *via* the solvent. It gives results in relative correct agreement with experiment [8, 9] for hard sphere systems but has the inconvenience that the expression for D is not a virial development and that its extension to charged systems is not immediate.

A further approach, more empirical, consists of directly defining an effective Navier-Stokes equation which describes the solution rather than the solvent : in this paper we have used the well known screened Navier-Stokes equation [10, 11]. This equation is correct for porous media. It has been recently used in the case of Brownian particles but it is important to note that its application to such solution is based on severe approximations [11].

Here, we do not intend to present a new and exact treatment of the hydrodynamic interactions, but rather to try to obtain a quantitative agreement between numerous experimental data in various systems and a simple model using only one adjustable parameter which is independent of the physical parameters. At the moment, such a treatment requires the use of the screened Navier-Stokes equation. The « screened » constant in this equation is obtained in an empirical manner.

The solution of this equation gives an effective pair mobility tensor which describes the particle-solution-particle hydrodynamic interactions. It is important to note that the « screened » term — which supposes that the hydrodynamic interactions decrease rapidly when the inter-particle spacing goes to infinity (typical behaviour in $e^{-\kappa r}$) — is in this case partially inexact, since it is shown that the long range behaviour of the effective mobility tensor is not exponential but in inverse power of r (see expressions (2.10), (2.12)).

The development of the effective pair mobility tensor was first calculated by Adelman [10] at the Oseen level, and then by Snook *et al.* [12] for the dipole-dipole part. The restriction of the whole development at this order is insufficient and does not provide an agreement with the experimental results. Snook *et al.* overcome this difficulty by using semi-empirical effective mobility tensors obtained by mixing the solutions of the unscreened and the screened Navier-Stokes equations with exponential screening factors [12]. Their expressions for the mobility tensor are simple to use but do not correspond to the original « screened » problem.

Thus, we report here the development of the effective tensor (solution of the screened N-S equation) up to the term in r^{-7} using the formalism of Mazur and Van Saarloos [5]. The mobility tensor together with the screened Coulombic hard sphere potential are used to calculate the mutual diffusion coefficient for different micellar solutions. The screening constant which appears in the effective N-S equation is volume fraction dependent and is adjusted with only one parameter (independent of all the physical characteristics of the system) to give the best agreement with experimental data derived from light scattering measurements on cationic micellar solutions (alkyltrimethylammonium bromide). Finally, the mutual and self-diffusion coefficients on concentrated hard sphere solutions are fitted using the same numerical value of the parameter.

Section 2 is devoted to the theoretical development of the mobility tensor and of the mutual diffusion coefficient. This is followed by a short presentation of materials and dynamic light scattering methods (Sect. 3). The measured diffusion coefficient of micellar solutions was studied as a function of surfactant concentration at different salt concentrations and the characteristic parameters of micelles are reported. The interpretation and discussion are presented in section 4. The empirical parameter that describes the effective tensor allows a fit between experiment and theory to be made. The agreement obtained from both charged and uncharged systems at large volume fraction is illustrated by the behaviour of the hydrodynamic effect of charged hard sphere solutions with or without added salt. At last some comments are made on the classical concentrated dispersions of particles stabilized by short chain hydrocarbons [13-15]. These particles are a good approximation to hard spheres which have been extensively studied.

2. Theory.

The colloidal solution is described by a system of hard charged spheres in a continuous solvent, additional ions are treated as point charged. With these assumptions, the classical expression for the mutual diffusion coefficient, defined from the first cumulant of the autocorrelation function of the scattered intensity, is [16, 17] :

$$D_m(q) = \frac{D_0(1 + H(q))}{S(q)}. \quad (2.1)$$

Where $D_0 = k_B T \mu_0$ is the ideal diffusion coefficient. $\mu_0 = \frac{1}{6 \pi \eta a}$ is the ideal mobility for a sphere of radius a and η is the solvent viscosity.

$S(q)$ is the well known structure factor :

$$S(q) = 1 + c \int (g^{(2)}(r) - 1) e^{iq \cdot r} dr \quad (2.2)$$

where $C = N/V$ is the particle concentration and $g^{(2)}(r)$ is the pair distribution function. The latter can be calculated over a large concentration range, with the RMSA integral equation [18, 19] from the screened Coulombic hard sphere potential [20] :

$$V(r) = +\infty \quad r \leq 2a$$

$$= k_B T \frac{z^2 L_B}{r} \frac{e^{-\kappa(r-2a)}}{(1 + \kappa a)^2} \quad r > 2a \quad (2.3)$$

where $L_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}$ is the Bjerrum length (7.19 Å at 298 K in water), Z is the particle charge and $\kappa = [4\pi L_B(2C_s + CZ)]^{1/2}$ is the Debye screening parameter, C_s is the salt concentration.

For simplicity we suppose that the particles are monodisperse and of radius a . We have : $g^{(2)}(r) = 0$ for $r \leq 2a$.

The exact expression for the hydrodynamic term $H(q)$ is :

$$\mu_0(1 + H(q)) = \frac{1}{N} \left\langle \sum_{i,j=1}^N \hat{\mathbf{q}} \cdot \bar{\bar{\boldsymbol{\mu}}}_{ij} \cdot \hat{\mathbf{q}} e^{i\mathbf{q} \cdot \mathbf{r}_{ij}} \right\rangle. \quad (2.4)$$

The sum runs over the N particles present in the solution. \mathbf{r}_{ij} is the vector between the particles i and j . \mathbf{q} is the scattering vector and $\hat{\mathbf{q}} = \mathbf{q}/q$. $\bar{\bar{\boldsymbol{\mu}}}_{ij}$ is the generalized mobility tensor which takes into account the hydrodynamic interactions between the particles. $\bar{\bar{\boldsymbol{\mu}}}_{ij}$ relates simultaneously the velocity \mathbf{u}_i of the particle i to the force \mathbf{F}_j applied to the particle j :

$$\mathbf{u}_i = \sum_{j=1}^N \bar{\bar{\boldsymbol{\mu}}}_{ij} \cdot \mathbf{F}_j. \quad (2.5)$$

In the absence of the hydrodynamic interactions $\bar{\bar{\boldsymbol{\mu}}}_{ij}$ reduces to $\mu_0 \delta_{ij} \bar{\mathbf{1}}$. The difficulties in developing expression (2.4) arise from the fact that the mobility tensor depends on the positions of all the particles and not only on \mathbf{r}_{ij} . The total tensor can be decomposed into a sum of tensors which are themselves functions of 2, 3, 4, ... particle positions. The n body tensor gives a $\phi^{(n-1)}$ contribution to $H(q)$ where $\phi = \frac{4\pi a^3 c}{3}$ is the volume fraction.

Recently, Mazur and Van Saarloos [5] have explicitly calculated the two, three and four body tensors up to order r^{-7} in the interparticle spacing r .

Except for the two-particle integral, the calculation of the integral of the n body tensor with the n distribution function $g^{(n)}$ is difficult ; indeed, the knowledge of the functions $g^{(n)}$ for $n \geq 3$ requires heavy calculations (excepted at infinite dilution). Moreover the multiple integrals of $g^{(n)}$ are quickly prohibitive in computation time.

The approximation of the full mobility tensor to the pair mobility tensor $\bar{\bar{\boldsymbol{\mu}}}$ [2] is exact when one needs the linear behaviour of D_m versus ϕ at small concentrations but does not account for the experimental

mutual diffusion D_m in concentrated solutions [6, 7]. In particular, this leads to negative values of D_m above a certain volume fraction.

In order to overcome this difficulty, we want to calculate an effective pair mobility tensor which accounts for the effect of the other particles. The « screening » of the hydrodynamic interactions between particles 1 and 2 by particles 3, 4, 5, ... can be introduced by employing the linearized screened Navier-Stokes equation [11] which governs the solvent motion :

$$\nabla P - \eta \Delta \mathbf{v} + \eta K^2 \mathbf{v} = 0 \quad (2.6)$$

where $\mathbf{v}(\mathbf{r})$ is the solvent velocity and $P(\mathbf{r})$ is the static pressure. Equation (2.6) has been used by many authors [11, 12]. The additional force $(-K^2 \mathbf{v})$ is a simple representation of the « screening » effect. It can be introduced by purely empirical arguments or through more theoretical developments [11].

It is important to note that all interactions between particles and solvent, except the classical excluded volume interactions, have been neglected. This is an approximation for charged systems.

Using a dimensional argument we can write the « screening » constant K as :

$$K = K_0 a^{-1} f(\phi). \quad (2.7)$$

The form of $f(\phi)$ is discussed below.

The problem now consists in calculating the effective pair mobility tensors $\bar{\bar{\boldsymbol{\mu}}}_{11}^{\text{eff}}$ and $\bar{\bar{\boldsymbol{\mu}}}_{12}^{\text{eff}}$ for two spheres immersed in an effective solvent characterized by equation (2.6). This equation must be solved with the conditions :

$$\nabla \cdot \mathbf{v} = 0 = \text{fluid incompressibility} \quad (2.8)$$

$$\mathbf{v}(\mathbf{r}) = \mathbf{u}_i \text{ for } |\mathbf{r} - \mathbf{r}_i| = a = \text{contact condition} \quad (2.9)$$

\mathbf{u}_i is the velocity of the particle i ($i = 1, 2$) centred at $\mathbf{r} = \mathbf{r}_i$.

For simplicity the rotations of the particle have been neglected and the fluid is supposed to be motionless in the absence of particles.

The effective tensor with the screening constant K accounts for the multiple hydrodynamic interactions between particles. Note that the case of one particle immersed in the solvent must be treated with the original unscreened Navier-Stokes equation (then the one-particle tensor remains equal to $\mu_0 \bar{\mathbf{1}}$). Indeed, the slowing down of the motion of one particle by the others is first introduced in the pair tensor. Using this precaution, we are sure that the linear behaviour of $H(q)$ with ϕ at small concentrations $\left(\frac{dH}{d\phi} \Big|_{\phi=0} \right)$ will, as expected, be unperturbed by the screening constant K . Previous calculations [12] using the screened Navier-Stokes equation, did not take this

approach and the theoretical curves of D_m versus ϕ for different values of K do not show the correct behaviour at low concentrations (Fig. 4 of Ref. [12]).

As for the unscreened case, the pair mobility tensor can be expressed as a development of terms whose i th term represents the effect of i hydrodynamic « reflections » between the two particles. Adelman [10] has given the first term (« screened » Oseen tensor) of the development, which reduces to the Oseen tensor (r^{-1}) in the limit $K = 0$. Snook *et al.* [12] have calculated the next term (« screened » dipole-dipole tensor, r^{-3} for $K = 0$). However, the first two terms are not sufficient to provide a good representation of the full development at low or large concentrations. For example, for hard sphere systems, the initial slope value of H versus ϕ is -6.44 , when the development extends to the r^{-7} term, whereas it is -5 if only the Oseen and dipole-dipole terms are used.

Snook *et al.* correct their tensor by using mixed solutions between screened and unscreened mobility tensors. Rather than to use this empirical corrections, we prefer to calculate a more complete development of the effective tensor, where the last term corresponds to the r^{-7} term in the unscreened development.

The « reflection » method associated with Faxen's theorem (which has been used by preceding authors) becomes too complicated for the calculation of the terms from r^{-3} to r^{-7} . Thus, we have used the formalism of Mazur and Van Saarloos' [5]. The development of the mathematical calculation and, particularly, the differences between the screened and the unscreened problem, will be published elsewhere [21].

The following expressions are the final result which is decomposed into two parts associated with self and cross contributions respectively. (P is the tensor $\bar{\mathbf{f}}\bar{\mathbf{f}}$):

a) self contribution ($i = j$):

$$\begin{aligned} \bar{\mu}_{11}^{\text{eff}}/\mu_0 &= \frac{1}{1 - B(Ka)} \times \\ &\times \left\{ \frac{15}{2} \frac{\sinh Ka}{Ka} \left[\frac{\sinh Ka}{Ka} - \cosh Ka \right] \frac{a^2}{r^2} \left[\left(\frac{1}{(Kr)^2} + \frac{3}{(Kr)^3} + \frac{3}{(Kr)^4} + \frac{4}{5} \frac{a^2}{r^2} \left(\frac{1}{Kr} + \frac{1}{(Kr)^2} \right) \right) (1 - P) \right. \right. \\ &- \left. \left(\frac{1}{(Kr)^2} + \frac{3}{(Kr)^3} + \frac{3}{(Kr)^4} - \frac{8}{5} \frac{a^2}{r^2} \left(\frac{1}{(Kr)^2} + \frac{3}{(Kr)^3} + \frac{3}{(Kr)^4} \right) \right) (1 + 2P) \right] e^{-Kr} \\ &+ \frac{15}{2} \frac{a^4}{r^4} \left[\frac{1}{(Kr)^2} (1 - P) - \left(\frac{1}{(Kr)^2} - \frac{8}{5} \frac{a^2}{r^2} \frac{1}{(Kr)^2} \right) (1 + 2P) \right] \\ &+ \frac{15}{8} \sinh Ka \left[-\frac{\sinh Ka}{Ka} + 3 \frac{\cosh Ka}{(Ka)^2} - 3 \frac{\sinh Ka}{(Ka)^3} \right] \frac{a^3}{r^3} \left[\left(\frac{1}{Kr} - \frac{2}{(Kr)^2} - \frac{23}{(Kr)^3} - \frac{63}{(Kr)^4} - \frac{63}{(Kr)^5} \right) \right. \\ &+ 10 \frac{a^2}{r^2} \left(\frac{1}{Kr} + \frac{6}{(Kr)^2} + \frac{21}{(Kr)^3} + \frac{45}{(Kr)^4} + \frac{45}{(Kr)^5} \right) \left. 1 - \left(\frac{1}{Kr} + \frac{30}{(Kr)^2} + \frac{177}{(Kr)^3} + \frac{441}{(Kr)^4} + \frac{441}{(Kr)^5} \right) \right. \\ &- \left. 10 \frac{a^2}{r^2} \left(\frac{-1}{Kr} + \frac{2}{(Kr)^2} + \frac{27}{(Kr)^3} + \frac{75}{(Kr)^4} + \frac{75}{(Kr)^5} \right) \right] P \left. \right] e^{-Kr} \\ &+ \frac{15}{8} \frac{a^6}{r^6} \frac{1}{(Kr)^2} \left[\left(-\frac{21}{5} + 30 \frac{a^2}{r^2} \right) 1 + \left(-\frac{147}{5} + 50 \frac{a^2}{r^2} \right) P \right] \left. \right\}. \end{aligned} \quad (2.10)$$

Where

$$B(x) = \frac{1}{3} + \frac{e^{-2x} - 1}{3x} + \frac{e^{-2x}}{3} \quad (2.11)$$

b) cross contribution ($i \neq j$):

$$\bar{\mu}_{12}^{\text{eff}}/\mu_0 = [\alpha_s(Ka) B_s(\mathbf{r}_{12}) + \alpha_d(Ka) B_d(\mathbf{r}_{12}) + B_e(\mathbf{r}_{12})] \frac{1}{1 - B(Ka)}. \quad (2.12)$$

The expressions of the different terms are :

$$B_s(\mathbf{r}) = \frac{3}{2} \frac{a}{r} \left[e^{-Kr}(1 - P) + \left(\frac{e^{-Kr}}{Kr} + \frac{e^{-Kr} - 1}{(Kr)^2} \right) (1 - 3P) \right] \quad (2.13)$$

(« screened » Oseen term)

$$B_d(\mathbf{r}) = \frac{1}{2} \frac{a^3}{r^3} (1 - 3P) \tag{2.14}$$

(dipole-dipole term)

$$B_e(\mathbf{r}) = \frac{225}{2} \frac{a^5}{r^5} \left[e^{-Kr} \frac{\sinh Ka}{Ka} \left(\frac{\sinh Ka}{Ka} - \cosh Ka \right) \left(\frac{1}{(Kr)^2} + \frac{3}{(Kr)^3} + \frac{3}{(Kr)^4} \right) + \frac{a^2}{r^2} \frac{1}{(Kr)^2} \right] P \tag{2.15}$$

(« screened » r^{-7} term)

where :

$$\alpha_s(x) = \frac{\sinh^2 x}{x^2} \tag{2.16}$$

$$\alpha_d(x) = 3 \frac{\sinh^2 x - x^2}{x^4} \tag{2.17}$$

The formulation of the cross contribution at the dipole-dipole level is the same as that found by Snook *et al.* [12] using the reflection method [the tensors B_s and B_d are identical in the two approaches, the tensor B_r of Snook *et al.* is the sum of B_s and B_d , with coefficients in (Ka)], except that the coefficients in Ka (α_s and α_d) differ. This results from the fact that the developments are not identical for the two cases. In particular, the terms neglected in our development contain both the B_s and B_d tensors with coefficients which vanish when Ka approaches zero. In the limit $Ka \ll 1$ (but not necessary $Kr \ll 1$), α_s and α_d tend to unity in the two approaches. In the absence of « screening » ($K = 0$), we again find the classical development of the mobility tensor : the self part gives the r^{-4} and r^{-6} terms with additional terms r^{-8} and r^{-10} . In the cross part, B_s reduces to the Oseen tensor, B_d is the dipole-dipole tensor, and B_e reduces to the r^{-7} term plus a

part of the r^{-9} term. For dilute hard sphere systems, the initial slope of H versus ϕ , gives a correct value of -6.39 . For $K \rightarrow \infty$, we have $\bar{\mu}_{11}^{eff} \rightarrow 0$ and $\bar{\mu}_{12}^{eff} \rightarrow 0$. In this case the hydrodynamic interaction is completely « screened ». It is interesting to note that the effective mobility tensors $\bar{\mu}_{11}^{eff}$ and $\bar{\mu}_{12}^{eff}$ do not vanish as $\exp(-Kr)$ for large values of the interparticle distance r , but as inverse powers of r , which agrees the conclusions of Mazur *et al.* [8, 9].

Mutual diffusion coefficient :

In dynamic light scattering experiments, the mutual diffusion coefficient depends on the hydrodynamic term at $q = 0$:

$$\mu_0 H(0) = C \int \hat{\mathbf{q}} \cdot (\bar{\mu}_{11}^{eff}(\mathbf{r}) + \bar{\mu}_{12}^{eff}(\mathbf{r})) \cdot \hat{\mathbf{q}} g(r) dr \tag{2.18}$$

In contrast to the unscreened case, the integral of the « screened » Oseen tensor B_s in equation (2.18) does not lead to a divergence at $q = 0$. Because this tensor is divergenceless, the function $g(r)$ can be replaced by $g(r) - 1$ in the integral of B_s without changing the value of $H(0)$, and this ensures the convergence of the integral in the limit of $K = 0$.

After angular integration and performing the integral with $g(r) = 1$ at $r \geq 2a$, we obtain the general expression of the hydrodynamic contribution at $q = 0$:

$$\begin{aligned} H(0) = & \frac{1}{1 - B(Ka)} \left\{ 4 \pi a c \frac{\sinh^2 Ka}{(Ka)^2} \int_{2a}^{\infty} e^{-Kr} r(g(r) - 1) dr - 5 \alpha_1(Ka) \phi \right. \\ & - 10 \pi a^2 c \int_{2a}^{\infty} \left[\frac{\sinh Ka}{Ka} \left(\frac{\sinh Ka}{Ka} - \cosh Ka \right) e^{-Kr} \left(\frac{3}{(Kr)^2} + \frac{9}{(Kr)^3} + \frac{9}{(Kr)^4} - \frac{8}{5} \frac{a^2}{r^2} \right. \right. \\ & \times \left. \left(\frac{1}{Kr} + \frac{6}{(Kr)^2} + \frac{15}{(Kr)^3} + \frac{15}{(Kr)^4} \right) \right] + \frac{a^2}{r^2} \left(\frac{3}{(Kr)^2} - 8 \frac{a^2}{r^2} \frac{1}{(Kr)^2} \right) \left. \right] [g(r) - 1] dr - \frac{59}{40} \alpha_2(Ka) \phi \\ & + 5 \pi a^2 c \int_{2a}^{\infty} \left[\sinh Ka \left(-\frac{\sinh Ka}{Ka} + 3 \frac{\cosh Ka}{(Ka)^2} - 3 \frac{\sinh Ka}{(Ka)^3} \right) \frac{a}{r} \left(\left(\frac{1}{Kr} - \frac{18}{(Kr)^2} - \frac{123}{(Kr)^2} - \frac{315}{(Kr)^4} - \frac{315}{(Kr)^5} \right) \right. \right. \\ & \left. \left. + 10 \frac{a^2}{r^2} \left(\frac{1}{Kr} + \frac{10}{(Kr)^2} + \frac{45}{(Kr)^3} + \frac{105}{(Kr)^4} + \frac{105}{(Kr)^5} \right) \right] e^{-Kr} \right. \\ & \left. + \frac{a^4}{r^4} \left(\frac{-21}{(Kr)^2} + \frac{a^2}{r^2} \frac{70}{(Kr)^2} \right) \right] [g(r) - 1] dr - \frac{349}{1792} \alpha_3(Ka) \phi \\ & \left. + 150 \pi a^2 c \int_{2a}^{\infty} \left[\frac{\sinh Ka}{Ka} \left(\frac{\sinh Ka}{Ka} - \cosh Ka \right) e^{-Kr} \frac{a^3}{r^3} \left(\frac{1}{(Kr)^2} + \frac{3}{(Kr)^3} + \frac{3}{(Kr)^4} \right) + \frac{a^5}{r^5} \frac{1}{(Kr)^2} \right] g(r) dr \right\} \tag{2.19} \end{aligned}$$

where :

$$\alpha_1(x) = \frac{-3}{5} \left[\frac{\sinh^2 x}{x^2} \left(\frac{2}{x} + \frac{1}{x^2} \right) e^{-2x} - \frac{1}{x^2} \right], \quad (2.20)$$

$$\alpha_2(x) = \frac{15}{118} \left[\frac{\sinh x}{x} \left(\frac{\sinh x}{x} - \cosh x \right) \left(\frac{-8}{x^2} + \frac{18}{x^3} + \frac{9}{x^4} \right) e^{-2x} + \frac{3}{x^2} \right], \quad (2.21)$$

$$\alpha_3(x) = \frac{-21}{349} \left[\sinh x \left(-\frac{\sinh x}{x} + 3 \frac{\cosh x}{x^2} - 3 \frac{\sinh x}{x^3} \right) \left(\frac{120}{x^2} - \frac{40}{x^3} - \frac{102}{x^4} - \frac{51}{x^5} \right) 5 e^{-2x} - \frac{17}{x^2} \right]. \quad (2.22)$$

The functions α_1 , α_2 , α_3 tend to unity when x vanishes.

The self part of the hydrodynamic interaction used for the calculation of the self diffusion coefficient corresponds to the 3d, 4th, 5th, 6th terms in equation (2.19).

Now, the ϕ dependence of the screening parameter K ($Ka = K_0 f(\phi)$) must be chosen. The first assumption is $f(\phi) = \sqrt{\phi}$ which can be derived in the case of the porous medium. In this case the screening force in the effective Navier-Stokes equation is proportional to ϕ . The short coming of this choice is that the development of D_m versus ϕ will have terms in 1 , ϕ , $\phi^{3/2}$, ϕ^2 , $\phi^{5/2}$, ... Whereas the real development is in 1 , ϕ , ϕ^2 , ϕ^3 , ϕ^4 , ... corresponding to 1, 2, 3, 4 particles interactions. Fortunately, Mou and Adelman [11] found a linear ϕ dependence for the screened constant ($Ka \approx \phi$) in the case of Brownian particles, which gives a correct development for D_m as a function of ϕ . In order to test the sensitivity of the theoretical results to the choice for $f(\phi)$, we shall investigate the two forms $f(\phi) = \sqrt{\phi}$ and $f(\phi) = \phi$. In both cases, the constant K_0 is adjusted to give the best agreement with experimental data. The distinction between the different expressions for K is illustrated in figure 1 using physical parameters which correspond to a micellar solution with 10^{-2} M added salt (see 3). All the theoretical curves have the same behaviour at $\phi \rightarrow 0$, showing that the « screening » effect starts at the second order in ϕ . It becomes clear that the unscreened pair mobility tensor fails for concentrated solutions ($\phi > 0.1$) and gives negative values of D_m for large concentrated systems. The hydrodynamic screening (K in $\sqrt{\phi}$ and in ϕ) reduces the decrease of D_m with ϕ and gives correct values at large ϕ . Note that the curves corresponding to $f(\phi) = \sqrt{\phi}$ and $f(\phi) = \phi$ are not very different for $\phi < 0.2$. In this region of intermediate concentration, the agreement of the theoretical curves with experimental measurements is thus not very sensitive to the choice of $f(\phi)$.

3. Experimental methods.

3.1 MATERIALS. — Tetradecyltrimethyl ammonium bromide (TTAB) was prepared by the reaction between tetradecylamine and methyl bromide in absolute ethanolic medium at 60 °C (under reflux for

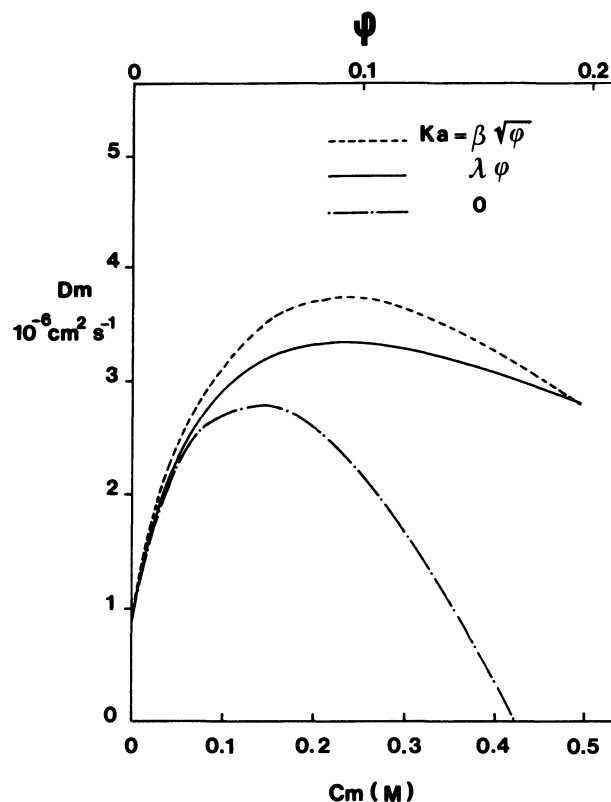


Fig. 1. — Theoretical mutual diffusion coefficient D_m versus the micellized monomer concentration C_m . The physical parameters, which correspond to micellar solutions of TTAB with 10^{-2} M of salt (KBr), are listed in table I. The three curves correspond to different expressions for the hydrodynamic screening, $\beta = 0.45$ and $\lambda = 0.98$.

2-3 days) and purified by three recrystallizations in acetone and ethylacetate. TTAB forms aqueous cationic micelles above a critical micellar concentration (CMC) of 3.4×10^{-3} M in pure water. Salt modifies the values of the CMC and induces size variations of aggregate formation. The micelles are characterized by the following parameters : an aggregation number N which varies with the surfactant and salt concentrations, and an effective charge Z_{eff} or ionization degree $\alpha = \frac{Z_{\text{eff}}}{N}$. The average size of the micelle was derived from the diffusion coefficient at the CMC.

The hydrodynamic radius R_H is given by the Stokes-Einstein relation : $D_0 = \frac{k_B T}{6 \pi \eta R_H}$ where $k_B T$ is the Boltzmann factor, η is the viscosity of the solvent, and D_0 is the extrapolated mutual diffusion coefficient at the CMC. From the aggregation number and the partial specific volume of the TTAB micelle, it is possible to deduce the dry radius R_1 of the micelle. The difference between R_1 and R_H corresponds to the hydration layer.

Two other systems were investigated : dodecyltrimethylammonium bromide and decyltrimethylammonium bromide in water which have smaller charge and size.

The sample solutions were filtered through a $0.22 \mu\text{m}$ millipore membrane into the light scattering cell which had been thoroughly rinsed with purified alcohol and dried with dust-free air.

All manipulations were made in an air-cleaned hood and the samples were centrifuged at 5 000 rpm for one hour before measurement.

The apparatus, cell filling method, homodyne detection, and cumulant data analysis of the autocorrelation function are identical with those used for the study of polyelectrolytes [22, 23] and micellar solutions [24].

3.2 QUASI-ELASTIC LIGHT SCATTERING (QLS). — QLS was used to derive the effective mutual diffusion coefficient D_m from the correlation time $\tau_c = (D_m q^2)^{-1}$. The concentration dependence of D_m was determined at 25°C in aqueous solutions of TTAB at different ionic strengths obtained by addition of KBr of concentrations from 0 M to 0.16 M. Figure 2 shows the plots of D_m as a function of the concentration of TTAB in water for the different concentrations (C_s) of KBr. At low TTAB concentrations (near the CMC), D_m varies linearly with the surfactant concentration C for one salt concentration and we have $D_m \simeq D_0(1 + k_D C)$. From the slope k_D we can derive the effective charge of micellar aggregate [25]. In a preceding publication [24], we have reported an investigation on these solutions and deduced the values of R_H and Z_{eff} as a function of the KBr concentration (C_s). The molecular weight of the TTAB micelles, as determined from the intensities, was found to increase from 26 900 at $C_s = 0$ to 53 800 at $C_s = 0.16$ M. The values of R_H , N , and Z_{eff} are reported in table I. Note that the aggregation number strongly varies with the TTAB concentration [26]. A linear dependence of the aggregation number N with the micellar concentration is assumed and the radius taken to increase as $N^{1/3}$. The radius a was taken to be the hydrodynamic size previously determined. However the results reported here are not sensitive to its exact value.

In pure water, the strong electrostatic interaction between micelles induced a very large positive slope in the plot of D_m versus the surfactant concentration. A neat maximum of D_m is reported at 0.1 M (the maxi-

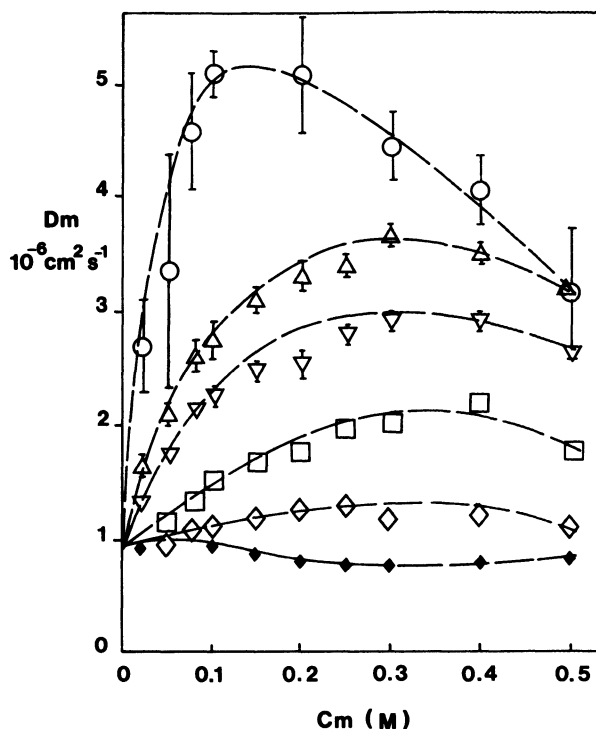


Fig. 2. — Experimental curves for the mutual diffusion coefficients of TTAB versus the micellized monomer concentrations (C_m) at different salt (KBr) concentrations (C_s): \circ : 0M, Δ : 0.01 M, ∇ : 0.02 M, \square : 0.05 M, \diamond : 0.10 M and \blacklozenge : 0.16 M.

Table I. — Physical parameters for the tetradecyltrimethylammonium bromide solutions at different KBr concentrations C_s : hydrodynamic radius $R_H = a$ at the CMC, aggregation number N from the CMC to 0.5 M [28] of micellized monomer concentrations, effective charge Z and ideal coefficient diffusion D_0 .

C_s (KBr) (M)	CMC (M)	R_H (Å)	N (CMC $C_m = 0.5$)	Z	D_0 (10^{-6} $\text{cm}^2 \text{s}^{-1}$)
—	—	—	—	—	—
0.00	0.0034	24	80 → 160	16	0.93
0.01	0.0017	24.5	85 → 170	17	0.93
0.02	0.0011	25	90 → 180	18	0.93
0.05	0.0006	25.5	120 → 240	20	0.93
0.10	0.0004	26	140 → 280	22	0.93
0.16	—	—	—	—	—

imum value of D_m is about $5 \times 10^{-6} \text{cm}^2/\text{s}$) and from 0.1 M to 0.5 M in micellized monomer concentration one observes a decrease of D_m . The addition of KBr reduces the slope of D_m versus C and the curvature is shifted to large volume fraction. For large KBr concentrations (0.10 M and 0.16 M), there is a slight slope in the plots of D_m versus surfactant concentration. Under these conditions, an attractive potential affects the behaviour of D_m [25] and the value of the effective charge deduced from the slope, assuming only a

screened Coulombic hard sphere potential, is not correct. In this work, we have only investigated the curves of D_m as a function of surfactant concentrations for sufficiently low salt concentrations ($C_s < 0.1$ M) where this attractive effect can be neglected. Let us note that all the linear plots of D_m versus TTAB concentration converge to an approximate common intercept D_0 in the limit of zero micellar volume fraction ($D_0 \approx 0.93 \times 10^{-6}$ cm²/s and $R_H \approx 25 \pm 2$ Å).

The aim of this study is to explain the behaviour of D_m at large volume fractions and mainly the large curvatures observed at very low salt concentrations. This effect could result from a variety of causes : a modification of the micellar size, shape and polydispersity, a strong attractive potential at large volume fractions and also a large effect of hydrodynamic interaction.

We know the variation of the sizes as a function of C_m , this effect is too small to produce a strong concentration dependence of the diffusion constant. An attractive potential at low salt concentrations and large volume fractions is not reasonable. Polydispersity is generally more important at large micellar concentration, according to neutron scattering measurements [27]. It induces a non-exponential behaviour for the auto-correlation function, specially at low salt concentrations, but it cannot explain the decrease of the diffusion coefficient at large volume fraction. The last effect to consider is the hydrodynamic interaction which could be amplified by the charge effect. It is the purpose of this study.

4. Results and discussion.

4.1 TETRADECYLTRIMETHYLAMMONIUM BROMIDE MICELLES. — The experimental curves of the mutual diffusion coefficient D_m as a function of the TTAB concentration at different concentrations of salt (KBr) have been fitted using the effective pair mobility tensor. The ideal mutual diffusion coefficient D_0 obtained at the critical micellar concentration (CMC) is nearly unchanged by the presence of salt. Thus, for simplicity, we have used the same value of D_0 for the different salt concentrations : ($D_0 = 0.93 \times 10^{-6}$ cm²/s). The last two curves, which correspond to large salt concentrations (0.1 and 0.16 M), show, by their linear behaviour at the origin, that they are sensitive to attractive effects. Since these effects are not taken into account in the present work, the screening parameter K is adjusted by fitting the lowest three salt concentration curves. For this calculation, we have accounted for the salt and monomer concentration dependence of the aggregation number N , in the same way as for the modification of the radius a , and the effective charge Z . The dependence of the CMC with salinity [24] has been introduced (see Table I). Fortunately, the theoretical curves are not very sensitive to these variations and a correct behaviour of D_m versus ϕ can be illustrated by some fits with average parameters \bar{N} , \bar{a} and \bar{Z} , independent of C_s and C_m .

We have fitted the experimental curves with the two approaches proposed in section 2.

The first one corresponds to $Ka = K_0 \sqrt{\phi}$ and the best fit value found for K_0 is 0.45 ± 0.05 . The resulting fits are shown in figure 3 and the agreement with the experimental data is good, except, of course, at large salinity. The second approach corresponds to $Ka = K_0 \phi$. We recall that, in this case, and contrary to the preceding one, the hydrodynamic term H can be developed in entire powers of the concentration. The best fit gives $K_0 = 1.05 \pm 0.1$, and is shown in figure 4. The precise value $K_0 = 0.98$ used in this figure is justified *a posteriori* (see 4.3). The agreement between theoretical curves and experimental data is still good. The choice of the relationship of K with ϕ is not crucial.

The fit of different curves with only one parameter, independent of C_s , can appear surprising. It results from the fact that, at large volume fractions, all solutions behave (from the hydrodynamic point of view) nearly as uncharged hard sphere solutions, the excluded volume interactions being much more important than the others. All experimental curves in figure 2 present very different behaviours at low micellar concentrations but seem to converge to the same limit at large concentrations. The differences between the various curves at $C_m = 0.5$ M are essentially due to the structure factor term $S(0)$. This effect is illustrated in figure 5 where the theoretical hydrodynamic term $1 + H(0)$ is plotted as a function of C_m for different

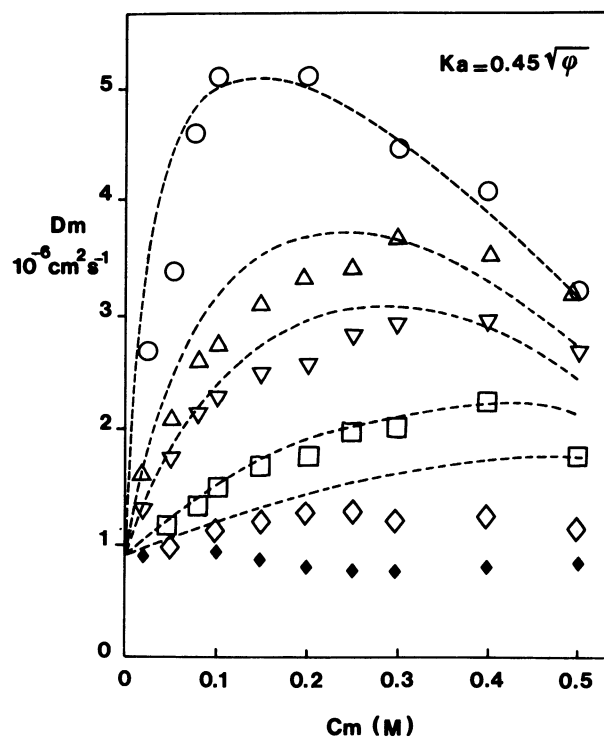


Fig. 3. — Experimental data and theoretical curves of the mutual diffusion coefficients. Same legend as for figure 2. Ka is given by $Ka = 0.45 \sqrt{\phi}$.

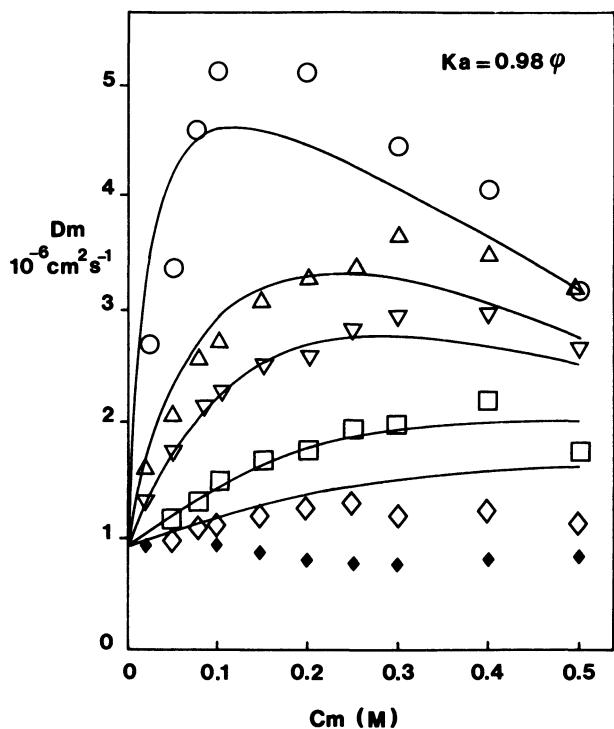


Fig. 4. — Same legend as for figure 3 except that $Ka = 0.98 \phi$.

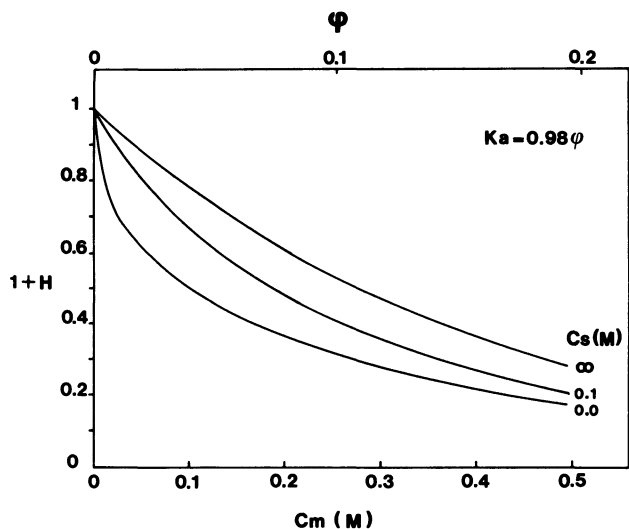


Fig. 5. — Theoretical hydrodynamic term $1 + H$ versus C_m at three KBr concentrations : 0 M, 0.1 M and ∞ M which corresponds to an uncharged hard sphere system. The physical parameters are : $a = 25 \text{ \AA}$, $Z = 20$ and $N = 100$.

ionic strengths. For simplicity, the physical parameters such as N , a and Z , are kept constant.

This figure shows that the difference between the salt-free solution ($C_s = 0$) and the excess salt solution ($C_s = \infty$, uncharged hard sphere system) is small for the largest volume fraction (20%). It would certainly be much smaller for more concentrated solutions. It results from this observation that one can hope to account for the hydrodynamic behaviour at large

concentrations of many other systems (like other charged micellar solutions or hard sphere systems), with the identical « screened » pair mobility tensor used with the same K_0 value.

4.2 DECYL AND DODECYL TRIMETHYL AMMONIUM BROMIDE MICELLES. — The experimental data of the mutual diffusion coefficient of decyl and dodecyl-trimethylammoniumbromide micellar solutions as a function of the surfactant concentration are plotted in figure 6. These salt-free solutions present the same behaviour as the TTAB solutions : first, we obtained a large increase of D_m with increasing monomer concentration and then, over a certain volume fraction, a decrease with increasing monomer concentration. The sizes, charges and aggregation numbers of these micelles are smaller than those of TTAB micelles. The values of the main physical parameters are listed in table II. From these quantities, the theoretical values of D_m are calculated with the identical effective pair mobility tensor and with the same value of K_0 . The curves are plotted in figure 6, using both $Ka = 0.45\sqrt{\phi}$ and $Ka = 0.98\phi$. The agreement is still correct and this illustrates the remark of the preceding paragraph : the hydrodynamic behaviour at large concentrations essentially depends on the volume

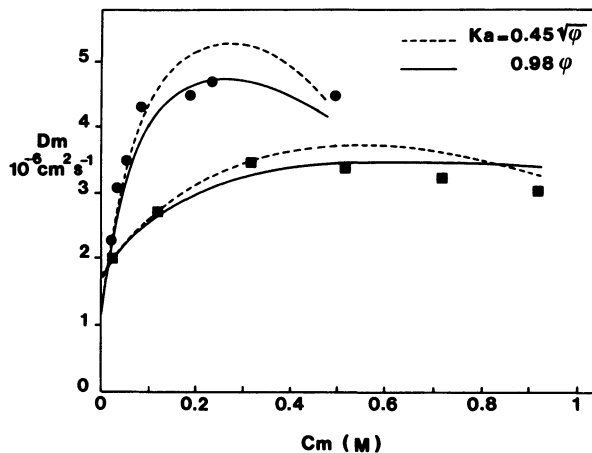


Fig. 6. — Experimental data and theoretical curves of the mutual diffusion coefficient versus the micellized monomer concentration for the decyl (■) and dodecyl (●) trimethylammoniumbromide solutions without added salt.

Table II. — Same legend as for table I but for the salt-free decyl and dodecyl trimethylammonium bromide solutions.

Micelle	CMC (M)	R_H (Å)	N (CMC)	Z	D_0 ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)
—	—	—	—	—	—
Decyl . . .	0.07	13.2	22 →	6	1.77
Dodecyl .	0.016	21	60 →	18	1.15

fraction and seems to be fairly insensitive to the charge of the particles. Only the amplitude of the maximum of D_m is strongly influenced by the charges of macroions.

4.3 UNCHARGED HARD SPHERE SYSTEM. — The study of the hydrodynamic interactions in hard sphere systems is interesting in this work for many reasons :

First, it allows us to test our model on a classical system. Second, the advantage of uncharged hard sphere systems is that the interactions are very well defined and that everything depends on a onedimensional parameter, the volume fraction ϕ . Third, some experimental data obtained in light scattering at larger ϕ up to 50 % can be fitted with the model. Lastly, all the preceding theories published in the literature (Mazur *et al.* [8, 9], Snook *et al.* [12]) are applied to uncharged hard sphere systems and are tested with the same experimental data. The data are reported in figure 7 where the mutual and self diffusion coefficients are plotted as a function of the volume fraction. It is worth noting that the concentration dependence of D_m is very weak contrary to the preceding cases and that the relative uncertainties of the experimental values are not negligible.

The theoretical curves of the present work are plotted in the same figure, with both $Ka = 0.45\sqrt{\phi}$ and $Ka = 0.98\phi$. For large volume fractions, we use the Verlet-Weiss [28] correction for the pair distribution function and the Carnahan-Starling [29] expression for the structure factor $S(0)$.

First, for $\phi > 0.2$ we observe a large disagreement between the experimental data of D_m and the theoretical curve corresponding to $Ka = 0.45\sqrt{\phi}$. It is not possible to find an agreement using a small increment of K_0 , hence the hydrodynamic interactions are not screened enough. With larger values of K_0 (near 0.65) the agreement is not as bad but the fit is lost for the micellar solutions.

Second, for $Ka = (0.98 \pm 0.01)\phi$, we find a good fit for the mutual diffusion coefficient, even for volume fractions near 50 %. The fit of the micellar solutions is preserved with this value. These remarks are in agreement with the conclusion of Mou and Adelman [11] who derived the form $f(\phi) = \phi$ for the screening parameter in colloidal solutions. The behaviour of the theoretical curve $D_m(\phi)$ with ϕ larger than 30 % is strongly sensitive to the value of K_0 (see Ref. [12], Fig. 3, for the same effect).

For volume fractions larger than 20 %, we must consider that the curves are also very sensitive to the truncation in the development of the effective pair mobility tensor. For example, we have performed the calculation of $D_m(\phi)$ without the last term of the development, namely without the r^{-7} term. In this case, the agreement is poor with $K_0 = 0.98\phi$; the value of K_0 which gives the best fit is 1.15, but the fit is not good for volume fractions larger than 30 %. The r^{-7} contribution, which is very small for the slope of D_m versus ϕ at low concentrations, seems to be important at large

concentrations. This observation can be explained by the following argument : for large volume fractions the values of both $1 + H$ and S are very low. A small relative uncertainty on the hydrodynamic interactions H leads to a large relative uncertainty on the mutual diffusion coefficient D_m . Thus, the fit at large concentrations would certainly be different if the first neglected terms in the development of the mobility tensor were introduced (namely r^{-8}).

The theoretical curves for the self-diffusion coefficient show a disagreement with the experimental data at large ϕ , for both definitions of K . The adjustment cannot be obtained with a small change in the K_0 value, but it is easily obtained using a low value of K_0 . In fact, the D_s experimental results are fairly well reproduced even with the unscreened pair mobility tensor (see Fig. 2 of Ref. [12]). In the same way, some very simple expressions such as $D_s/D_0 = 1 - 1.73\phi$ given by Felderhof [2] or $D_s/D_0 = 1 - 1.73\phi + 0.88\phi^2$ given by Beenakker and Mazur [8] lead to a correct fit. These results show that it is easy to reproduce the concentration dependence of the self diffusion coefficient D_s without reproducing the corresponding concentration dependence of D_m . In particular, the best fit with our « screened » pair mobility tensor is obtained for the following values of the parameter Ka : $0.20\sqrt{\phi}$ and 0.17ϕ . The latter is in good agreement with that found by Snook *et al.* from their empirical tensor with two screening constants ($Ka = 0.125\phi$, see Fig. 5 of Ref. [12]). We take this opportunity to mention that we do not agree with figure 3 of reference [12] : the variation of the self-diffusion coefficient does not present the correct behaviour at small concentrations as is observed in figure 2 of reference [12]. Moreover at large volume fractions, the position of the calculated curve $D_s(\phi)$ is too low and corresponds, in fact, to a lower value of the screening parameter. A justification of this comment can be made by a close examination of figure 2 ($K_0 = 0$),

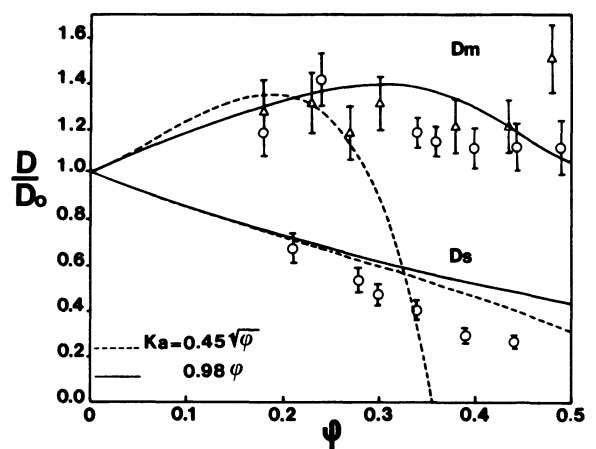


Fig. 7. — Normalized mutual and self diffusion coefficients for hard sphere solutions. Experimental data for D_s are taken from reference [16] (lower dots); the data for D_m are taken from reference [17] (triangles) and 18 (upper dots).

figure 3 ($K_0 = 1.1$) and figure 5 ($K_0 = 0.125$) of reference [12].

The main problem which still needs to be solved is now to improve the theoretical representation of the hydrodynamic interactions in order to fit the concentration dependence of both the mutual and self diffusion coefficients at large volume fractions.

A first way would be to use two different screening parameters for the self and the cross part of the mobility tensor, as was done by Snook *et al.* [12]. This ensures a good fit but is not theoretically justified and introduces an additional parameter.

The formalism described by Mazur and Beenaker [8, 9], which is theoretically more justified (it does not have adjustable parameters), gives a correct agreement for the self-diffusion coefficient but must be confirmed for the mutual diffusion coefficient at large volume fractions ($\phi > 30\%$).

As foresaid, the inclusion of higher order terms in the development of the mobility tensor could improve the theoretical results. If the first of them (r^{-8} contribution for $K = 0$) is introduced, the fit of the self diffusion coefficient curves will be different, because this term is a self part of the mobility tensor, and because the value of the screening constant K_0 will change to preserve the same behaviour for the mutual diffusion coefficient. But these considerations are somewhat speculative.

Lastly, in order to examine the validity of the « screening » mobility tensor for the self-diffusivity of charged systems, we report in figure 8 the expected concentration dependence of D_s for an idealized micellar solution ($N = 100$, $R = 25 \text{ \AA}$, $Z = 20$) between the two extremes in salinity. The theoretical lines calculated with the « screening » constant ($Ka = 0.98\phi$) present a small slope and, contrary to the mutual diffusivity, it is approximately independent of the salt added.

5. Conclusion.

The main goal of this investigation was to study the decrease of the effective diffusion coefficient in charged micellar systems at large volume fractions. The many-body hydrodynamic interactions can explain this behaviour. In order to resolve this complex problem we have introduced an effective pair mobility tensor calculated up to the seventh order in the inverse particle distance. An « empirical » constant has been derived by fitting the experimental mutual diffusion coefficients measured in light scattering over a large concentration range for micellar solutions. It has been shown that the same value of the single parameter leads to a good agreement with data obtained for some solutions of cationic micelles with or without added salt and for a classical hard-sphere system. Our approach is different from that proposed by

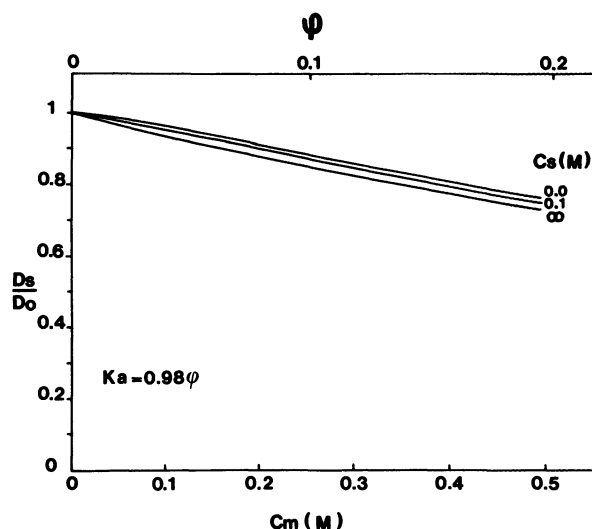


Fig. 8. — Theoretical concentration dependence of self diffusion coefficient in micellar solutions. Same legend as figure 5.

Snook *et al.* [12] who suggested an apparent pair mobility tensor with three adjustable parameters.

All the systems which have been investigated show the same hydrodynamic behaviour for large volume fractions ($\phi > 0.3$). Thus, the influence of the electrostatic interaction or attractive contribution is only predominant at low volume fractions.

This approach is, of course, empirical for the determination of the constant K_0 , but it can give a correct fit for many concentrated systems such as micellar solutions or microemulsions, without the difficulties encountered in the full calculation of three, four, ... body hydrodynamic interactions.

To improve our investigation, it would be interesting to introduce higher order terms in the development of the mobility tensor and to test both the self and mutual diffusion coefficients of charged and uncharged systems. A greater effort should be devoted to new experimental measurements : for example the determination of self diffusion coefficients of charged micellar systems or colloidal solutions at large volume fraction. Finally, some preliminary investigations have been carried out to interpret the dynamics of microemulsions in organic phases for large volume fractions. In this case, we have an attractive interaction between droplets and the pair distribution function can be calculated from HNC methods [30]. The analysis of experimental data derived from light scattering [31] will be the subject of a future paper [32].

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