LYOTROPIC EFFECTS AT THE SILVER IODIDE/ELECTROLYTE SOLUTION INTERFACE*

J.H.A. PIEPER, D.A. DE VOOYS and J.Th.G. OVERBEEK

Van 't Hoff Laboratory for Physical and Colloid Chemistry, University of Utrecht, Transitorium III, Padualaan 8, Utrecht - De Uithof (The Netherlands)

(Received 6th June 1975)

ABSTRACT

The lyotropic effect in the flocculation of a negatively charged AgI sol is explained on the basis of a double layer model without specific adsorption of cations. The constant potential model for the double layer interaction gives better results than the constant charge model. The theoretical results indicate furthermore that repeptization of the flocculated sol is possible.

(1) INTRODUCTION

Within the framework of the research on the stability of lyophobic colloids Klompé [1] has determined flocculation concentrations of a negatively charged AgI sol in solutions of several univalent nitrates. In the series Li—Na—K—Rb—Cs this concentration was the highest for $LiNO_3$ and decreased continuously to $CsNO_3$.

This lyotropic effect has been explained by Lyklema [2] with the aid of a double layer model which considers specific adsorption of cations. If the adsorption is described by a Langmuir isotherm the specific adsorption energy amounts to about 2 to 3 kT in going from Li to Rb.

In this paper it will be shown that the lyotropic effect can also be explained without assuming specific adsorption of cations. To this end direct measurements of the capacitance at the AgI/electrolyte solution were performed. The results were analyzed using the Gouy—Chapman—Stern picture of the double layer.

The total free energy of interaction between two particles will be calculated for spherical particles both at constant charge and at constant potential. We have used numerical data of Honig and Mul [3] who calculated the repulsion energy between two particles with the theory of Deryaguin—Landau—Verwey and Overbeek (D.L.V.O.). In the determination of the total free energy of interaction a distance of closest approach is introduced due to the finite dimensions of the ions at the interface as suggested by Frens [4] in his explanation of the repeptization of flocculated AgI sols.

---

* In honour of Academician A.N. Frumkin's 80th birthday

(2) EXPERIMENTAL PROCEDURE

The technique for the direct measurement of the capacitance at the AgI/electrolyte interface has been described earlier [5]. The method is based upon the measurement of the impedance of the cell Ag, AgI/electrolyte solution/AgI,Ag with the aid of an alternating current. Subject to certain conditions, the double layer capacitance per unit area is derived from the cell-impedance. The surface roughness was taken into account. Flat circular electrodes were used.

The measurements were carried out with solutions of Li-, Na-, K-, NH_4-, Rb- and $CsNO_3$ in water in the concentration range of 5×10^{-4} M to 1 M at $25°C$. The determination of the point of zero charge (p.z.c) is described in ref. 5 for the KNO_3 solutions. For all other solutions it was assumed that the p.z.c. lies at the same pAg as for KNO_3.

As a check on the reproducibility, KNO_3 solutions were used as a reference by performing the capacitance measurements for each concentration in the sequence K-, Li-, K-, Na-, K-, NH_4-, K-, Rb-, K-, Cs- and KNO_3.
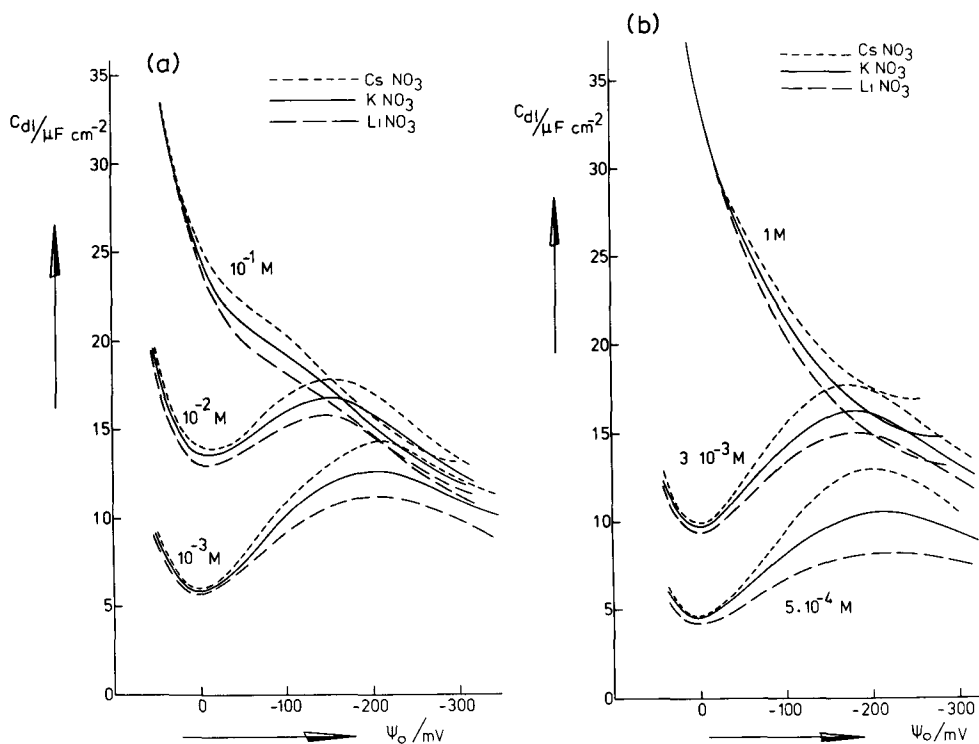

Fig. 1. Double layer capacity per unit of true surface area (C_{dl}) at the AgI/electrolyte solution interface as a function of the surface potential. (- - - - -) $CsNO_3$, (———) KNO_3, (— — —) $LiNO_3$. (a) 10^{-3}, 10^{-2}, 10^{-1} M; (b) 5×10^{-4}, 3×10^{-3}, 1 M.

(3) EXPERIMENTAL RESULTS

The curves of the capacitance as a function of the potential are given in Fig. 1a,b for 5×10^{-4}, 10^{-3}, 3×10^{-3}, 10^{-2}, 10^{-1} and 1 M solutions of Li-, K- and CsNO$_3$ at 25°C. The results of the Na-, NH$_4$- and RbNO$_3$ solutions are omitted for reasons of clarity. At each concentration the double layer capacitance increases in the order:

$$C_{dl}^{Li} < C_{dl}^{Na} < C_{dl}^{K} \approx C_{dl}^{NH_4} < C_{dl}^{Rb} < C_{dl}^{Cs}$$

For the KNO$_3$ solutions the reproducibility was about 1%, so that the differences between the capacitance curves in Fig. 1a,b are significant.

(4) MODEL CALCULATIONS

In the theory of the stability of lyophobic colloids, the potential in the Stern plane ψ_δ is a central parameter. In our case ψ_δ is derived from the capacitance measurements. In the following sections the results of the flocculation and capacitance measurements will be interpreted in two ways in order to explain the lyotropic effect: (a) based on the simple double layer model of Gouy—Chapman—Stern and the original D.L.V.O. theory (section 4.1); (b) based on a modification of the model and the theory (section 4.2).

(4.1) Simple approach; Gouy—Chapman—Stern and D.L.V.O. theory

In the absence of specific adsorption ψ_δ is calculated as a function of the surface potential ψ_0 or surface charge σ_0 by the following procedure, in which we limit the discussion to negative surface charges.

Integration of the experimental $C_{dl}(\psi_0)$ curves gives the relation between the surface charge and surface potential $\sigma_0(\psi_0)$. In the absence of specific adsorption σ_0 is fully compensated by the charge of the diffuse double layer σ_d:

$$\sigma_0 = -\sigma_d \tag{1}$$

The potential ψ_δ can now be calculated with the aid of the diffuse double layer theory:

$$\sigma_d = (2\ RT\ \epsilon\ c_s/\pi)^{1/2} \sinh(z\ F\ \psi_\delta/2\ RT) \tag{2}$$

for symmetrical z-z electrolytes.

The $\psi_\delta(\psi_0)$ and $\psi_\delta(\sigma_0)$ curves are given in Fig. 2; they show that for constant ψ_0 at equal electrolyte concentration $\psi_\delta^{Cs} > \psi_\delta^{Li}$, whereas for constant σ_0, $\psi_\delta^{Cs} = \psi_\delta^{Li}$.

With the aid of the D.L.V.O. theory the repulsive energy (V_R) between two colloidal particles is determined numerically as a function of their separation [6,7]. According to these results V_R increases regularly with ψ_δ both at con-
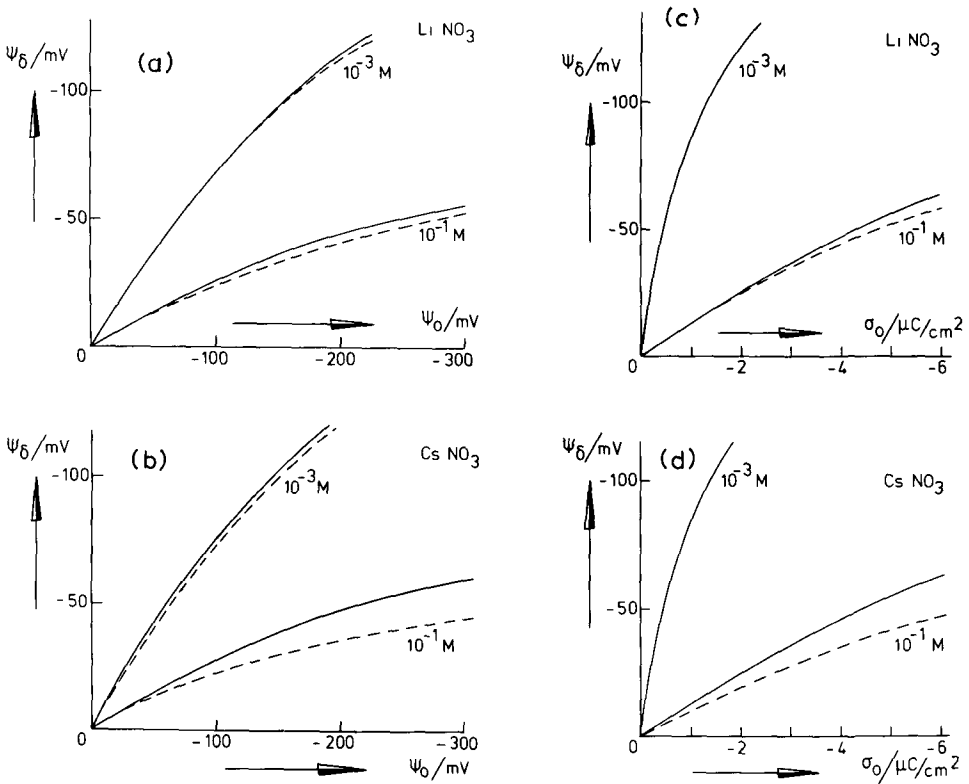
Fig. 2. Potential in the Stern plane as a function of the surface potential (a,b) and surface charge (c,d) for 10^{-3} and 10^{-1} M Li- and CsNO$_3$. (———) Based on a simple double layer model; (— — —) based on the modified double layer model.

stant potential and at constant charge. Consequently, by combination with the above-mentioned ψ_δ^{Cs} and ψ_δ^{Li} we may conclude that under these circumstances $V_R^{Cs} > V_R^{Li}$. As the van der Waals attractive energy V_A is independent of the kind of electrolyte solution between the sol particles V_A^{Cs} equals V_A^{Li} at identical separation. For the total free energy of interaction V_T, which equals the sum of V_R and V_A, we find $V_T^{Cs} > V_T^{Li}$. This means that the flocculating action of CsNO$_3$ would be smaller than that of LiNO$_3$.

The flocculation experiments of Klompé [1], however, yielded the opposite result, viz. a flocculation concentration of CsNO$_3$, c_{fl}^{Cs} equal to 0.092 M and c_{fl}^{Li} equal to 0.165 M. The flocculation concentrations of Na-, K- and RbNO$_3$ are between these values. This sequence was confirmed by Lyklema [8].

We therefore conclude that with the double layer model discussed in this section, and taking into account only differences in V_R, the experimentally observed lyotropic effect for AgI cannot be explained.

(4.2) Modifications of the simple approach

(4.2.1) Outline of the modifications

The explanation of the lyotropic effect described in this section is based on the same assumptions as mentioned in the previous one with two additional points, viz.: (a) The determination of ψ_δ is based on the modified Gouy—Chapman double layer model which was already described by Stern [9]. (b) Owing to the finite size of the ions at the interface the zero points of the distance scales of V_R and V_A are not identical [4]. These two points will first be elaborated.

(a) In the modified G.Ch.S. model of the double layer the first layer of ions at the interface is not considered to be a part of the diffuse layer, but to be adsorbed electrostatically. The "adsorption-energy" of these ions is determined completely by the Stern potential ψ_δ. If a Langmuir isotherm is used to describe the occupation of this monolayer, the surface charge can be expressed as:

$$\sigma_0 = -(\sigma_{Stern} + \sigma_{diff}) \tag{3a}$$

$$= FZ\left[\frac{1}{1 + x^{-1}\exp(-F\psi_\delta/RT)} - \frac{1}{1 + x^{-1}\exp(F\psi_\delta/RT)}\right]$$

$$+ (2\,RT\,\epsilon\,c_s/\pi)^{1/2}\,\sinh(F\psi_\delta/2\,RT) \tag{3b}$$

By using eqn. (3b), the potentials in the Stern and Gouy planes are put equal, which is allowed in cases of low surface coverage.

The maximum coverage of the monolayer, Z, is determined based on a closest array of the possibly hydrated ions of both ends of the lyotropic series, viz. Li- and $CsNO_3$. It is generally assumed that the Cs^+-ion is not hydrated [10,11], so $r_{Cs^+} = 1.67$ Å. The primary hydration number of Li^+ amounts to about 5. Recently binding energies of several Li^+-hydrate structures have been calculated [12]. It appears that the primary hydration has a tetrahedral structure in which the Li—O distance amounts to 2.03 Å. This distance is not sensitive to differences in hydration numbers. The radius of the hydrated Li^+-ion then amounts to 3.35 Å (viz. $r_{Li-O} + r_{O^{2-}} = 2.03 + 1.32$ Å). This leads to $Z_{Li} = 8.55 \times 10^{-10}$ mol cm^{-2} and $Z_{Cs} = 34.3 \times 10^{-10}$ mol cm^{-2}. The electrostatic adsorption of the nitrate ions is so small that it can be left out of consideration.

Concerning the Na^+-, K^+- and Rb^+-ions we refer to the results mentioned in section 4.2.3.

Figure 2 shows the $\psi_\delta(\psi_0)$ and $\psi_\delta(\sigma_0)$ curves determined as mentioned above as broken lines for 10^{-3} M and 10^{-1} M Li- and $CsNO_3$. The modified double layer model yields a lower ψ_δ at the higher concentrations; only a minor difference is found at lower concentrations. Furthermore the differences between $LiNO_3$ and $CsNO_3$ become smaller and even change sign at 10^{-1} M.

Based on these ψ_δ values the fractional surface coverage θ amounts to about 0.01, so that it is allowed to use equal ψ_δ values in the Stern and Gouy plane.

(b) The determination of the total free energy of interaction V_T is based on the following points:

(1) The potential used in the expression of V_R is the Stern potential ψ_δ, so the distance-scale of V_R (symbolized by H_0) has its zero-point in the Stern plane.

(2) The van der Waals attraction acts between the sol particles, so the distance-scale of V_A starts at the solid/liquid interface.

(3) The distance of closest approach between two sol particles is governed by the dimensions of the ions at the interface, and therefore equals twice the thickness of the Stern layer: 2Δ.

These three points are summarized in the following way. In the determination of V_R the distance H_0 is used and for V_A the distance $H_0 + 2\Delta$ with $\Delta_{Li} = 3.35$ Å and $\Delta_{Cs} = 1.67$ Å.

The aim of our calculations is to find a set of $V_T(H_0)$ curves of such a nature that flocculation is obtained at 0.092 M for $CsNO_3$ and at 0.165 M for $LiNO_3$, which are the flocculation concentrations measured by Klompé [1]. At lower electrolyte concentrations the sol must be stable which means that the maximum in the $V_T(H_0)$ curve has to be high enough to prevent the sol particles combining. As an example of the latter condition we use the case of $LiNO_3$ at a concentration of 0.092 M. The above mentioned three criteria are schematically shown in Fig. 3.

(4.2.2) Calculation method of the total free energy of interaction, V_T

Using the theory of Verwey and Overbeek of the stability of lyophobic colloids [7] Honig and Mul [3] determined the repulsive energy, V_R, due to the interaction of plane parallel diffuse double layers. They converted V_R for flat planes into V_R for spherical particles by means of the Deryaguin integration method. We used the computer program of these authors to calculate V_R for spherical particles both at constant charge and at constant potential. At a certain ψ_δ^∞ (i.e. ψ_δ at infinite separation) a non-dimensional factor S (the reduced repulsive energy) is obtained as a function of the non-dimensional distance $\kappa H_0/2$. The repulsive energy V_R is derived from S by:

$$V_R = (64\,\pi\,c_s\,RT\,a/\kappa^2)\,S \tag{4}$$

Once ψ_δ^∞ is known from the capacitance measurements at a certain concentration (or κ) and pAg (or ψ_0) of the electrolyte solution, the only variable in eqn. 4 is the particle radius a. We determined S at constant charge (S^σ) and constant potential (S^ψ) under the circumstances of the flocculation experiments of Klompé, viz. pAg = 11.2, $c_{fl}^{Li} = 0.165$ M and $c_{fl}^{Cs} = 0.092$ M. At the same pAg this was done for $LiNO_3$ at a concentration of 0.092 M.

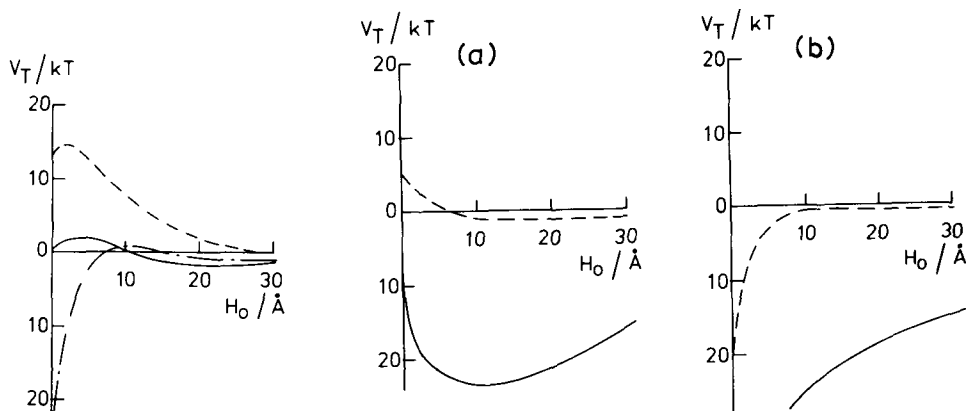The attractive energy V_A as a function of H_0 is determined with the

Fig. 3. Total free energy of interaction, V_T, as a function of the distance between the Stern planes H_0, at a constant Hamaker constant A and particle radius a. (———) $CsNO_3$ at 0.092 M; (-.-.-.) $LiNO_3$ at 0.165 M; (- - - - -) $LiNO_3$ at 0.092 M.

Fig. 4. Total free energy of interaction, V_T, as a function of the distance H_0. Constant charge model, $A = 10^{-19}$ J. (- - - - -) $a = 100$ Å; (———) $a = 500$ Å. (a) $LiNO_3$ at 0.165 M; (b) $CsNO_3$ at 0.092 M.

Hamaker expression for non-retarded van der Waals attraction [13]:

$$V_A = -\frac{A}{6}\left[\frac{2}{u^2 + 4u} + \frac{2}{(u + 2)^2} + \ln\frac{u^2 + 4u}{(u + 2)^2}\right] \tag{5}$$

where $u = (H_0 + 2\Delta)/a$. The variables in eqn. 5 are the Hamaker constant A and the particle radius a.

Combination of eqns. 4 and 5 gives the total interaction energy V_T as a function of H_0. We have determined V_T for values of a between 50 Å and 500 Å and values of A between 10^{-19} J (metals) and 10^{-20} J (non-conducting materials).

(4.2.3) Results
(a) Total free energy of interaction, V_T, at constant charge (Figs. 4 and 5).
For a given value of A, V_T decreases with increasing particle radius a, which means that attraction will be stronger. At higher values of a, a secondary minimum in the V_T (H_0) curves occurs.

Flocculation is found for $CsNO_3$ at 0.092 M and several values of A and a. A different picture is shown by the V_T (H_0) curves of both $LiNO_3$ concentrations, viz. great secondary minima arise both at the flocculation concentration of 0.165 M and at 0.092 M where the sol would be stable. Moreover V_T becomes highly positive at short distances and values of $A \leqslant 6 \times 10^{-20}$ J. It appears therefore impossible to indicate combinations of values of A and a
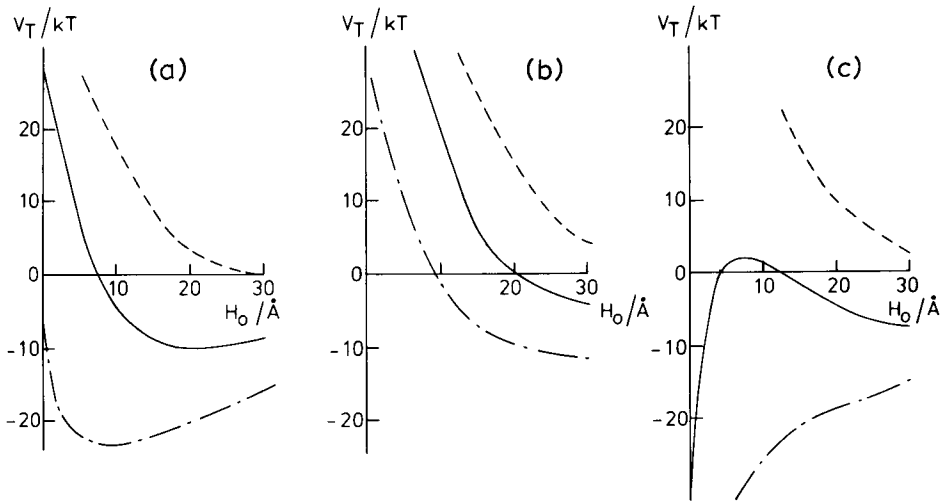
Fig. 5. Total free energy of interaction, V_T, as a function of the distance H_0. Constant charge model, $a = 500$ Å. $A = 10^{-20}$ J (- - - - - -), 6×10^{-20} J (————), 10^{-19} J (-·-·-·-). (a) LiNO$_3$ at 0.165 M; (b) LiNO$_3$ at 0.092 M; (c) CsNO$_3$ at 0.092 M.

at which flocculation with LiNO$_3$ at 0.165 M and CsNO$_3$ at 0.092 M but stability with LiNO$_3$ e.g. at 0.092 M can occur.

(b) Total free energy of interaction, V_T, at constant potential (Figs. 6,7,8). The general characteristics of the $V_T (H_0)$ curves in this case are similar to those of the constant charge case, viz. attraction is higher and the secondary
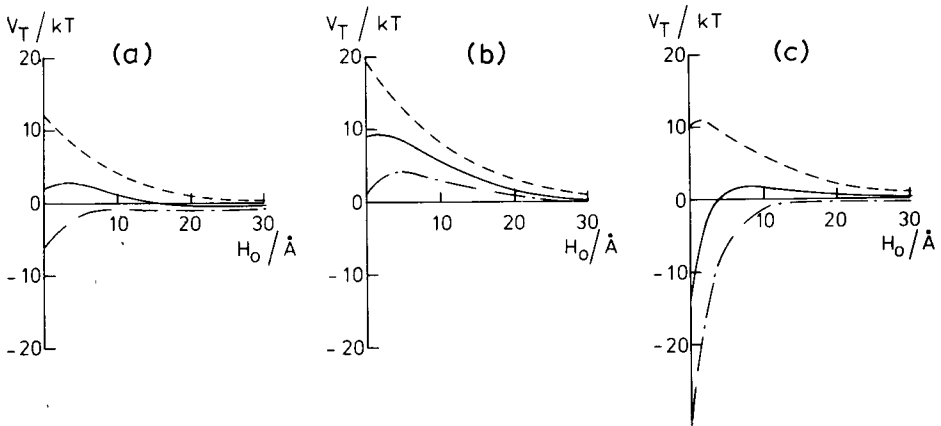

Fig. 6. Total free energy of interaction, V_T, as a function of the distance H_0. Constant potential model, $a = 100$ Å. $A = 10^{-20}$ J (- - - - -), 6×10^{-20} J (————), 10^{-19} J (-·-·-). (a) LiNO$_3$ at 0.165 M; (b) LiNO$_3$ at 0.092 M; (c) CsNO$_3$ at 0.092 M.
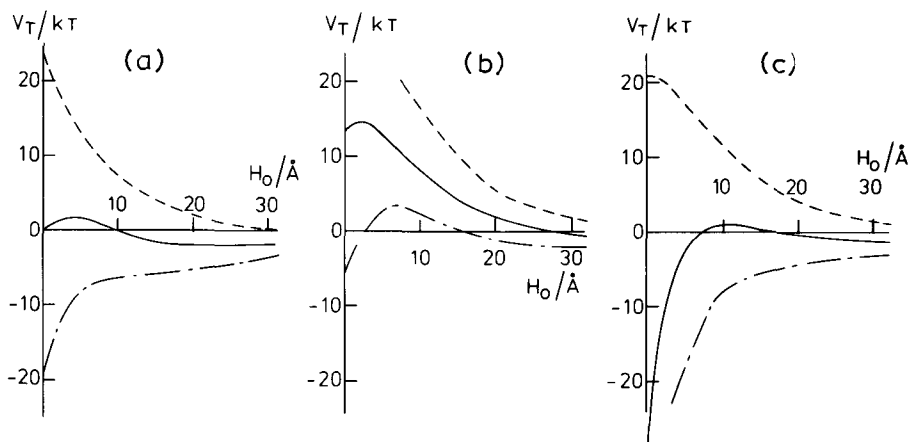
Fig. 7. The same as in Fig. 6, except $a = 200$ A.

minima are more pronounced with increasing particle radius. The difference lies in the shape of the curves for both $LiNO_3$ concentrations.

In this constant potential case it is possible to indicate combinations of values of A and a where flocculation or stability occurs at the desired concentrations. Good agreement is found if A amounts to about 6×10^{-20} J and for a range of particle radii between 100 Å and 500 Å. For the smallest particles a somewhat greater A is necessary to find the same agreement, and similarly for larger particles a smaller A is required. This trend is seen in Figs. 6—8.

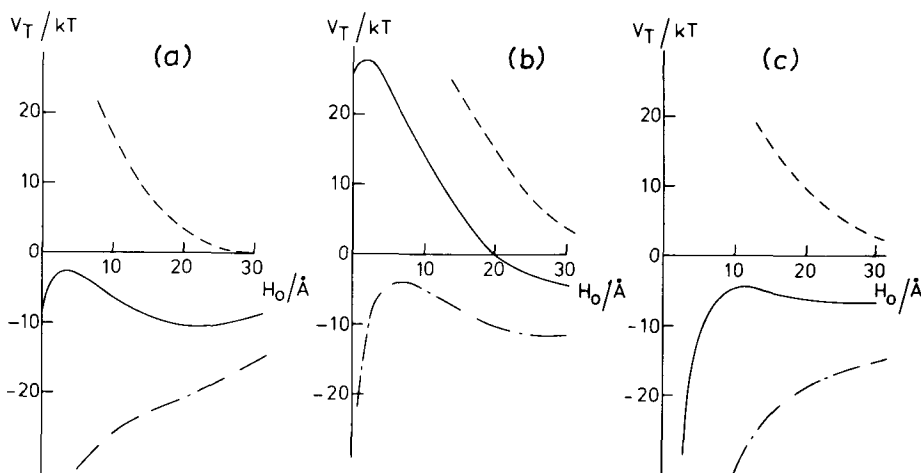The shape of the $V_T(H_0)$ curves with $A = 6 \times 10^{-20}$ J of Figs. 6—8 shows

Fig. 8. The same as in Fig. 6, except $a = 500$ A.

that repeptization of the flocculated AgI sol is possible. The flocculated sol is in the situation represented by Figs. 6a—8a; on diluting the situation is changed to that of Figs. 6b—8b. In the latter figures the difference between $V_T(H_0 = 0)$ (the flocculated situation) and V_T in the maximum is sufficiently small to allow the particles to separate. The $V_T(H_0)$ curves with $A < 6 \times 10^{-20}$ J do not show a maximum, so the repeptization would occur spontaneously after diluting the flocculated sol.

(c) Compared with Li- and $CsNO_3$ at their flocculation concentrations, curves of the same nature for the total free energy of interaction are obtained for the flocculation concentrations of Na-, K- and $RbNO_3$ if the radii of the latter cations are taken as 3.0, 2.7 and 2.3 Å, respectively. This requires configurations in the Stern layer, in which, on the average, the lines through the centers of the cations and the hydration molecules in contact with the surface are not perpendicular to the surface but inclined to it.

(5) DISCUSSION

(5.1) Lyklema's explanation

The explanation of the lyotropic effect (section 4.2) is presented as an alternative to that by Lyklema [2], who applied a double layer model which includes specific adsorption of cations. As a background to our criticism we will summarize Lyklema's method for determining the amount of specifically adsorbed cations.

From potentiometric titrations of AgI suspensions in inert electrolyte solutions with potential determining ions (Ag^+ or I^-) a relation is obtained between the surface charge σ_0 and the surface potential ψ_0. At 85°C there appeared to be no difference between the $\sigma_0(\psi_0)$ curves in Li-, K- and $RbNO_3$ solutions, while the flocculating concentrations were also nearly identical. According to Lyklema these results indicate that the cations are desorbed from the Stern layer, so that the diffuse double layer theory of Gouy—Chapman may be applied. In this way the Stern potential ψ_δ is calculated from the $\sigma_0(\psi_0)$ curves at 85°C (see eqns. 1 and 2, section 4.1). With the aid of an approximate equation of the D.L.V.O. theory for the relation between the flocculation concentration and the Stern potential, the Hamaker constant, the only unknown, is determined at 85°C.

The same Hamaker constant is used at 25°C, where specific adsorption would occur, together with the flocculation concentrations at 25°C to determine the Stern potential at this temperature. Now the charge of the diffuse double layer (σ_d) at 25°C can be calculated (eqn. 2, section 4.1). Combination of this charge and the experimentally determined surface charge σ_0 (at 25°C) yields the adsorbed charge σ_a, because $\sigma_0 = -(\sigma_a + \sigma_d)$. The description of this adsorption with a Langmuir isotherm gives an adsorption energy of 2.1 kT for Li^+, 2.5 kT for K^+ and 2.9 kT for Rb^+.

Lyklema's explanation is open to the following criticisms:

(1) The relation between the flocculation concentration and the Stern potential is derived from the D.L.V.O. theory for flat double layers; furthermore an approximation is used. The size of the particles is not taken into account.

(2) The interpretation is based upon the assumption that the maximum in the total interaction free energy curve equals zero for the flocculation concentration, which means that we deal with the transition from slow to rapid flocculation. The experiments, however, refer to slow flocculation, which means that the interaction energy has a positive value.

(3) The assumption that the Hamaker constant does not depend on the temperature is an approximation. Recently it was demonstrated that a temperature dependence may have to be taken into account [16,17].

(5.2) Constant charge or constant potential

The calculations of section 4 suggest that the lyotropic sequence in the flocculation of AgI may be explained better with the constant potential model than with the constant charge mcdel. This conclusion is, however, in contradiction with that of Frens [4]. If the sol particles should meet each other in a Brownian collision, then in the case of constant potential the charge of the particles must be adjusted in about 10^{-7} s by desorption of I^- ions or adsorption of Ag^+ ions. This process would require a very high exchange current density of about 10 A cm^{-2}, so that the constant charge model is more probable. The slowness of the charge adjustment has been experimentally demonstrated by Frens, Engel and Overbeek [14].

In a justification of the constant potential model it is necessary to examine the above mentioned ideas somewhat further:

(1) As a consequence of the remaining electrostatic repulsion and the hydrodynamic interaction the mobility decreases strongly with decreasing separation of the particles [13], which in turn prolongs the collision time.

(2) Most of the flocculation experiments of Klompé were performed with a sol of pAg = 11.2. The experiments of Frens et al. [14] on the slow charge adjustment were performed in the pAg range between about 4.5 and 10. At a pAg > 10 and < 4 these experiments are not practicable anymore with the used measuring technique because there the charge adjustment is very rapid.

(3) Klompé's experiments used a fairly slow flocculation as the criterion for the flocculation concentration. The flocculation time of several hours may be more relevant for the rate of the charge adjustment than the duration of a single collision.

(4) In a collision between two spherical particles only a small fraction of the total charge has to be desorbed. Most of the charge adjustment may take place by migration of the charge along the surface away from the region of contact. Therefore the exchange current density needed is a good deal lower than 10 A cm^{-2}.

(5) Measurements of the impedance of the cell AgI/electrolyte solution/AgI at different frequencies showed that the exchange current density amounts to about 25 mA cm^{-2} at a pAg of 11 [15].

Summarizing these points we conclude that the exchange current density is too low to adjust the charge if the sol particles meet in a simple Brownian collision. The constant potential model is exact only if the repulsion can sufficiently slow down this movement.

It is probably approximately correct if the migration of charge along the surface and the long flocculation times are taken into account.

(6) CONCLUSION

Calculations of the total free energy of interaction of spherical colloidal particles with the aid of a model which only takes into account the finite ion size and does not suppose ion-specific interactions yield a good explanation of the experimentally determined lyotropic differences in flocculating concentrations.

LIST OF SYMBOLS

A	Hamaker constant
a	particle radius
C_{dl}	double layer capacitance
c_s	concentration of indifferent electrolyte (mol l^{-1})
c_{fl}	flocculation concentration
F	Faraday's constant
H_0	distance between Stern planes of two colloidal particles
k	Boltzmann's constant
R	gas constant
S	reduced repulsive energy of two spherical particles
T	absolute temperature
u	$(H_0 + 2\Delta)/a$
V_A	van der Waals energy of attraction
V_R	electrostatic free energy of repulsion
V_T	total free energy of interaction
x	mole fraction of indifferent electrolyte in the solution
Z	maximum occupation of the Stern layer (mol/unit area)
z	valency of ions
ϵ	permittivity of the solution
θ	fractional occupation of the Stern layer
κ	Debye-Hückel reciprocal length
Δ	thickness of the Stern layer
σ_a, σ_0	adsorbed and surface charge respectively
σ_d	charge of the diffuse double layer
ψ_δ	potential in the Stern plane
ψ_0	surface potential

REFERENCES

1 M.A.M. Klompé, Thesis, Utrecht, 1941; M.A.M. Klompé and H.R. Kruyt, Kolloid Beih., 54 (1942) 484.
2 J. Lyklema, Croat. Chim. Acta, 42 (1970) 151.
3 E.P. Honig and P.M. Mul, J. Colloid Interface Sci., 36 (1971) 258.
4 G. Frens, Thesis, Utrecht, 1968; J. Colloid Interface Sci., 36 (1971) 286.
5 J.H.A. Pieper and D.A. De Vooys, J. Electroanal. Chem., 53 (1974) 243.
6 H.R. Kruyt (Ed.), Colloid Science, I, Elsevier, Amsterdam, 1952, ch. VI.
7 E.J.W. Verwey and J.Th.G. Overbeek, Theory of the Stability of Lyophobic Colloids, Elsevier, Amsterdam, 1948, ch II, III.
8 J. Lyklema, Discuss. Faraday Soc., 42 (1966) 81.
9 O. Stern, Z. Elektrochem., 30 (1924) 508.
10 J.O'M. Bockris, Quart. Rev. Chem. Soc., 3 (1949) 173.
11 J.O'M. Bockris, M.A.V. Devanathan and K. Müller, Proc. Roy. Soc., 274A (1963) 55.
12 P.A. Kollman and I.D. Kuntz, J. Amer. Chem. Soc., 96 (1974) 4766.
13 E.P. Honig, G.J. Roebersen and P.H. Wiersema, J. Colloid Interface Sci., 36 (1971) 97.
14 G. Frens, D.C.J. Engel and J.Th.G. Overbeek, Trans. Faraday Soc., 63 (1967) 418.
15 D.A. De Vooys and J.H.A. Pieper, to be published.
16 V.A. Parsegian and B.W. Ninham, Biophys. J., 10 (1970) 664.
17 E.R. Smith, D.J. Mitchell and B.W. Ninham, J. Colloid Interface Sci., 45 (1973) 55.

Note added in proof

Recently the manuscript of a paper by Lyklema and de Wit, to be published in the present issue of this journal [1], came to our attention.

In this paper the model of the interaction between colloidal particles was improved, so that a part of our criticism towards a former model applied by Lyklema, is removed. However, the reason why specific adsorption does occur is in the present form not convincing. In our paper we have chosen for a double layer and interaction model with the least number of parameters. Possibly supplementary experimental data [2,3] will lead to the fact that a more elaborated model has to be used.

References

1 J. Lyklema and J.N. de Wit, J. Electroanal. Chem., 65 (1975) 443
2 J N. de Wit, Meded. Landbouwhogeschool, (1975) in press.
3 J N. de Wit and J. Lyklema, to be published.