Colloid & Polymer Science

Colloid & Polymer Sci 263:1004-1007 (1985)

Secondary minimum analysis in the DLVO-theory

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Abstract: A simple method for determining the secondary minimum distance and energy for two parallel plane surfaces interacting with constant potential and constant surface charge density in a symmetrical electrolyte solution is presented. Both cases are treated, namely, non-retarded and retarded interaction. Two graphics which provide a quick survey for determining the secondary minimum are reported.

Key words: DLVO-theory, secondary minimum, colloid interactions.

Introduction

One of the characteristic features of the DLVO theory [1, 2] is the presence of a secondary minimum in the curves of potential energy versus the interacting surfaces' distance. If this minimum is moderately deep in relation to kT, it could give rise to a form of lax flocculation, easily reversible. Von Burzagh [3, 4], Van den Tempel [5] and Schenkel and Kitchener [6] provided experimental evidence in favour of the existence of secondary minima. Curtis [7, 8, 9] discussed the possibility of describing a certain class of cell adhesion in terms of this minima. Pethica [10] has attempted to put real values into the equations for the repulsive and attractive energies, with the result that stable contacts between cells separated by 100–200 Å as suggested by Curtis seem most unlikely energetically. Gingell and Fornés [11] studying the interaction of red blood cells with a polarized electrode also gave some experimental evidence of the existence of this minimum. For a discussion of secondary minima and their possibilities in cell contact see also Weiss [12].

2. Constant potential interaction

We consider two plane surfaces, with surface potentials Ψ_1 and Ψ_2 immersed in a solution of a symmetrical $(\nu-\nu)$ electrolyte with η ions per cm^3. Following the notation of Verwey and Overbeek [2] we have

$$y = \frac{\nu e\Psi}{kT};\ Z_i = \frac{\nu e\Psi i}{kT}\ (i = 1, 2);\ \varkappa^2 = \frac{8\pi\eta e^2\nu^2}{\varepsilon kT}$$

$$\text{and } \xi = \varkappa X$$

where e is the electron charge, Ψ the electrical potencial at any point between the surfaces, k is Boltzmann's constant, T is the absolute temperature, ε is the dielectric constant of the medium, $\varkappa$ is called the Debye-Hückel reciprocal length parameter, Z_i and y are called the reduced potentials of the surfaces and the solution respectively, X is the distance between the surfaces.

For Z_i arbitrary and large values of ξ, Verwey and Overbeek (ref. [2], eq. (10)) showed that the reduced potential in the solution as a function of the distance from one plane surface is given by

$$y = 4y_i\exp(-\xi) \text{ with } y_i = \frac{\exp(Z_i/2) - 1}{\exp(Z_i/2) + 1} \tag{1}$$

This is the starting point for the linear superposition approximation (LSA) which leads to the equations:

$$P_r = 64\eta kTy_1y_2\exp(-\xi) \tag{2}$$

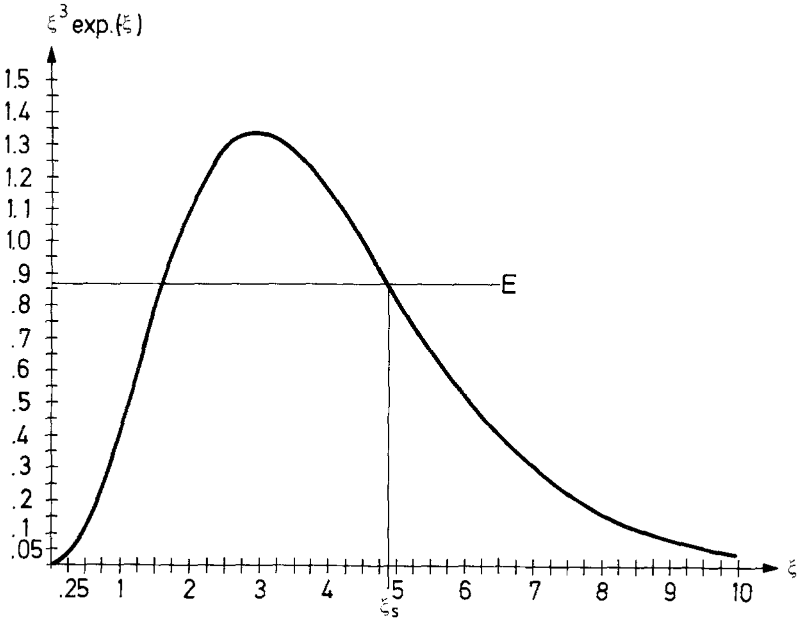

Fig. 1. Representation of equation (10)

$$V_r = \frac{64\eta kT\gamma_1\gamma_2\exp(-\xi)}{\varkappa} \tag{3}$$

where P_r, V_r are the electrostatic repulsive force and energy per unit area respectively between the two parallel plane surfaces. The main advantage of these expressions is that they coincide with exact calculations for $\xi > 3$. We have performed exact calculations for V_r in this range of ξ following Derjaguin [13] for different values of Z_i and concentrations, and the difference between the results and those obtained applying equation (3) is less than 3 %. Gregory [14] showed some curves comparing the exact results of Devereux and Bruyn [15] where we can see that values calculated using equation (3) almost coincide with exact calculations for $\xi = 3$. It is precisely this range of $\xi > 3$ where the secondary minimum appears.

The attractive force and energy per unit area are given by

$$P_a = -\frac{A\varkappa^3}{6\pi\xi^3} \tag{4}$$

$$V_a = -\frac{A\varkappa^2}{12\pi\xi^2} \tag{5}$$

where A is the Hamaker constant [16].

The total force and energy per unit area are

$$P = 64\eta kT\gamma_1\gamma_2\exp(-\xi) - \frac{A\varkappa^3}{6\pi\xi^3} \tag{6}$$

$$V = \frac{64\eta kT\gamma_1\gamma_2\exp(-\xi)}{\varkappa} - \frac{A\varkappa^2}{12\pi\xi^2} \tag{7}$$

The condition for minimal energy is $P = 0$, which leads to

$$\xi_s^3\exp(-\xi_s) = \frac{A\varkappa^3}{384\pi\eta kT\gamma_1\gamma_2} \tag{8}$$

where ξ_s is the value of ξ at the secondary minimum.

Replacing $\eta = \mathrm{N_a}c/1000$ where c is the concentration in moles per cm^3 and $\mathrm{N_a}$ is the Avogadro number, $\varepsilon = 80$, $T = 300$ °K, we have $\varkappa = 0.32459 \times 10^8 \nu\sqrt{c}$ (cm^{-1}), and calling the right hand side of equation (8) "E", the equation becomes

$$E = \frac{1.14425 \times 10^{12} A\sqrt{c}\,\nu^3}{\gamma_1\gamma_2} \tag{9}$$

Then equation (8) is

$$\xi_s^3\exp(-\xi_s) = E \tag{10}$$

The advantage of equation (10) is that on one side we have a function only of ξ_s and on the other a function which depends on characteristics of the surfaces and medium, thus simplifying the calculations. The function $f(\xi) = \xi^3\exp(-\xi)$ has a maximum in $\xi = 3$ with $f(3) = 1.3442$. Any value of $E < f(3)$ with $\xi > 3$ implies the existence of a secondary minimum. The representation of equation (10) is shown in figure 1.

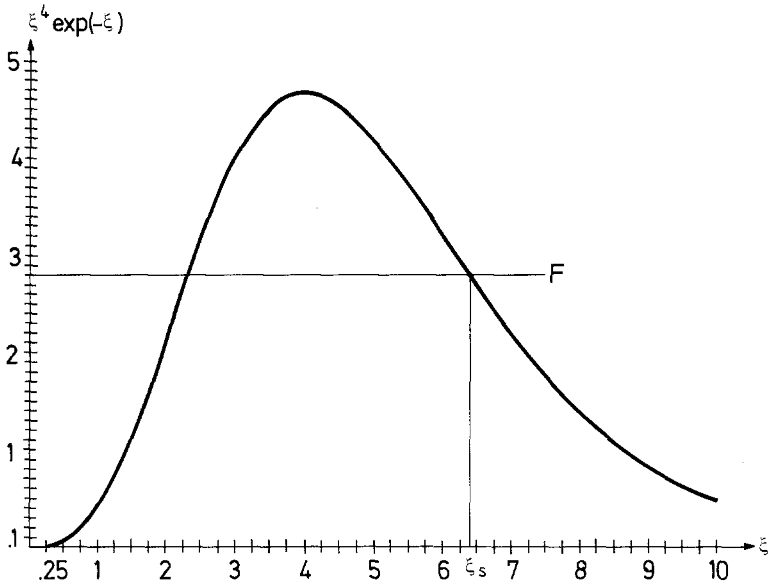

Fig. 2. Representation of equation (16)

Replacing (8) in (7) we obtain for the secondary minimum energy V_s:

$$V_s = \frac{A\varkappa^2}{6\pi}\,(\xi_s^{-3} - 0.5 \times \xi_s^{-2})$$

$$= 5.5895 \times 10^{13}\, A\nu^2 c(\xi_s^{-3} - 0.5 \times \xi_s^{-2}) \qquad (11)$$

When retardation effects are necessary, equations (4), (5), (8) – (11) are transformed respectively into

$$P_a = -\frac{B\varkappa^4}{\xi^4} \qquad (12)$$

$$V_a = -\frac{B\varkappa^4}{3\xi^3} \qquad (13)$$

$$\xi_s^4\exp(-\xi_s) = \frac{B\xi^4}{64\eta kT\,\gamma_1\gamma_2} \qquad (14)$$

$$F = \frac{7.0 \times 10^{20} Bc^2\nu^4}{\gamma_1\gamma_2} \qquad (15)$$

$$\xi_s^4\exp(-\xi_s) = F \qquad (16)$$

$$V_s = B\varkappa^3\left(\xi_s^{-4} - \frac{\xi_s^3}{3}\right)$$

$$= 3.4198 \times 10^{22} B\nu^3 c^{3/2}\left(\xi_s^{-4} - \frac{\xi_s^3}{3}\right) \qquad (17)$$

where B is the retarded Hamaker constant.

The function $f(\xi) = \xi^4\exp(-\xi)$ has a maximum in $\xi = 4$ with $f(4) = 4.6888$. Any value of $F < f(4)$ with $\xi > 4$ implies the existence of a secondary minimum.

The representation of equation (16) is shown in figure 2.

Both graphics, figures 1 and 2, are quick surveys for determining the secondary minimum at constant potential.

3. Constant charge interaction

It is well known that the interaction between charged colloidal particles can be very different depending on whether the condition is of constant surface potential or constant surface charge density [17, 18]. For constant charge interaction, the surface potentials of the particles can reach very high values, even though the potentials of the isolated particles may be quite small. Consequently the linear Poisson-Boltzmann expression is not appropriate in the constant charge case. Rigorous nonlinear treatments were given by Ohshima [19, 20]. Equations (77), (78) of Ohshima (19) valid for large values of ξ state for the repulsive force and energy of the interaction per unit area

$$P_r = 64\eta kT\left\{\sqrt{1 + \left(\frac{2}{\sigma_1'}\right)^2} - \frac{2}{|\sigma_1'|}\right\}$$

$$\times \left\{\sqrt{1 + \left(\frac{2}{\sigma_1'}\right)^2} - \frac{2}{|\sigma_2'|}\right\}\exp(-\xi) \qquad (18)$$

$$V_r = \frac{P_r}{\varkappa}. \tag{19}$$

We observe that formulas (18), (19) are similar to (2), (3), just carrying out the substitution

$$y_i \rightarrow \sqrt{1 + \left(\frac{2}{\sigma_i'}\right)^2} - \frac{2}{|\sigma_i'|}. \tag{20}$$

With $\sigma_i' = \frac{ve}{kT} \frac{4\pi\sigma_i}{\varepsilon kT}$ and σ_i the surface charge density, formulas (9)-(11) and (15)-(17) continue to be valid with substitution (20), and also figures 1, 2.

References

1. Derjaguin BV, Landau LD (1941) Acta Phys Chim URSS 14:633
2. Verwey EJW, Overbeek JTG (1948) Theory of the Stability of Lyophobic Colloids Elsevier, Amsterdam
3. Burzagh A von (1929) Kolloid Z Polymere 199:13
4. Burzagh A von (1930) Kolloid Z 47:370
5. Van den Tempel MJ (1958) J Colloid Sci 13:125
6. Schenkel JH, Kitchener J (1961) Trans Faraday Soc 56:161
7. Curtis ASG (1960) Am Nat 94:37
8. Curtis ASG (1962) Biol Rev (Camb) 37:82
9. Curtis ASG (1967) The Cell Surface: Its Molecular Role in Morphogenis, Lagos Press Ltd, London
10. Pethica BA (1961) Exptl Cel Res Suppl 8:123
11. Gingell D, Fornés JA (1976) Biophys J 16:1131
12. Weiss L (1967) The Cell Periphery, Metastasis and other contact Phenomena, North-Holland Pub Co, Amsterdam
13. Derjaguin BV (1954) Disc Faraday Soc 18:85
14. Gregory J (1975) J Colloid Interface Sci 51:44
15. Devereux O-F, De Bruyn PL (1975) Interaction of Plane-Parallel Double Layers, MIT Press Cambridge MA
16. Hamaker HC (1938) Recl Trav chim 57:61
17. Frens G, Overbeck JTG (1972) J Colloid Interface Sci 38:376
18. Bell GM, Peterson GC (1972) J Colloid Interface Sci 41:542
19. Ohshima H (1974) Colloid Polym Sci 252:257
20. Ohshima H (1975) Colloid Polym Sci 253:150

Received December 1, 1983;
accepted June 20, 1985

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