

## INFLUENCE OF POLAR SURFACE FORCES ON MAGNETIC FLOCCULATION OF FINE PARAMAGNETIC MINERALS.

### I. THEORY

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**Abstract** A new surface-thermodynamic conception of apolar and polar interfacial interactions, operating between hydrophilic and/or hydrophobic mineral surfaces, was proposed for the van der Waals and polar (structural) surface force components. Using this model, the interaction energy functions calculated for two interacting paramagnetic model spheres showed that the polar forces play a dominant role in magnetic flocculation.

### INTRODUCTION

The process of magnetic flocculation of fine paramagnetic minerals has stimulated considerable theoretical [1 - 6] and experimental [7 - 10] effort. Substantial progress in the understanding of surface forces acting between colloidal objects has been made since the introduction of the DLVO theory [11-13], which attributes the inter-particle interactions to the van der Waals (vdW) and electrostatic (EL) contributions.

The effect of a uniform magnetic field in the process of magnetic flocculation has been included in the DVLO theory through the magnetic dipolar force component [1 - 10, 40 - 43].

It is, however, widely recognized that the interactions between hydrophobic [14 - 22], as well as hydrophilic [22 - 33] entities cannot be adequately described by the classical DLVO theory and that additional forces should be taken into account.

The origin of these so-called polar (non-DLVO) forces remains controversial; a putative decrease in the orientation of water molecules in the vicinity of

hydrophobic surfaces has been invoked as an explanation of the attractive effect of the polar forces.

On the other hand, the repulsive interaction between hydrophilic surfaces is the outcome of the interaction between opposing layers of oriented water molecules of hydration [34].

Taking into account that most minerals are naturally hydrophilic, hydrophobic or are hydrophobised by surfactants, there is a need to include polar forces in the theory of magnetic flocculation.

Although the roles of hydrophobicity and of the corresponding attractive polar (hydrophobic) forces operating between fine hydrophobised paramagnetic siderite and rodochrosite in the magnetic field have been demonstrated by Lu Shouci et al. [35], their effects have not been quantified.

Van Oss et al. [36] have shown that although the problem is extremely difficult, polar forces can be quantitatively accounted for by the acid-base (AB) polar interfacial interactions. This concept was successfully used to determine coagulation behaviour of naturally hydrophobic hectorite [37], as well as hydrophobised magnesite and dolomite fines [38].

The aim of this study is to establish the effect of polar forces on the flocculation behaviour of fine paramagnetic minerals under the influence of a uniform magnetic field.

## THEORETICAL

### Surface forces

Let us consider a system of two identical spheres of radii  $a$  and surface-to-surface separation  $h$ , in an external magnetic field. In order to interpret the effect of polar forces on magnetic flocculation, it is necessary to consider the total interaction energy function  $V$ , which includes the van der Waals ( $V^{vdW}$ ), electrostatic ( $V^{EL}$ ), Born short-range ( $V^B$ ) and magnetic ( $V^M$ ) contributions, together with the polar contribution ( $V^S$ ):

$$V = V^{vdW} + V^{EL} + V^B + V^M + V^S \quad (1)$$

In calculating the van der Waals energy, semi-empirical expression derived by Gregory [39] was employed:

$$V^{vdW} = - (A_0 a / 12h) [1 - (k^* h / \lambda^*) \ln(1 + \lambda^* / k^* h)] \quad (2)$$

where  $A_0$  is the overall Hamaker constant of the system, and  $\lambda^* = 10^{-7}$  m, and  $k^* = 5.32$  are the empirical constants.

The first term of the expression represents the Hamaker (dispersion) interaction energy for two spheres in the non-retarded correction for larger separation.

The electrostatic interaction was calculated using the linear approximation of Poisson-Boltzmann equation in the form [11, 13]:

$$V^{EL} = 2\pi a \epsilon \psi_s^2 \ln [1 + \exp(-\kappa h)] \quad (3)$$

in which  $V^{EL}$  is related to the Stern layer (or zeta potential)  $\psi_s$ , and the reciprocal Debye length  $\kappa$ , and  $\epsilon$  is the dielectric constant of water. This expression is valid for low surface potentials (< 50 mV) and for relatively high ionic strengths and/or large particles ( $\kappa a > 10$ ).

The closest possible approach of one atom to another is determined by an overlap of their electron orbitals. The resulting short-range Born repulsion,  $V^B$ , is dominant at very short distances between interacting surfaces and the critical separation,  $h_{cr} = 0.2$  nm, was chosen as the distance of the closest (equilibrium) approach in the following thermodynamic considerations.

The magnetic dipolar energy between the spheres was given as:

$$V^M = -8\pi a^6 \chi^2 B^2 [9\mu_0 (2a + h)^3]^{-1} \quad (4)$$

where  $\chi$  is the volume magnetic susceptibility of the particles (paramagnetic or diamagnetic),  $B$  is the magnetic induction of the external magnetic field and  $\mu_0$  is the magnetic permeability of vacuum.

The interaction energy between two plates due to polar forces is often estimated by the empirical formula:

$$E^S = E^{So} \exp(-h/\lambda) \quad (5)$$

in which  $E^{so}$  and  $\lambda$  are empirical constants. This relation was obtained from the direct measurements of surface force. The larger the value of positive  $E^{so}$  for hydrophilic surfaces, the more repulsive are the polar forces. For hydrophobic surfaces, the more negative  $E^{so}$  is, the more attractive are the polar forces.

However, reconsidering the published direct measurements of surface force and the corresponding values of  $E^{so}$  and  $\lambda$  in equation (5), it can be noticed that an apparent increase in  $\lambda$  with  $h$  exists, and the log-log method of plotting the energy of polar interaction  $E^s$  versus  $h$  produces a straight line [44].

Thus, in both repulsive and attractive regimes, the polar forces seem to decay by a power law function with the distance dependence of  $h^{-1.7}$  to  $h^{-2.3}$  (plate/plate formulation), rather than by a single exponential function [38].

Taking these facts into account, the polar interaction energy between spheres can be restated ( $V = \pi a_h f^\infty E$ ) as:

$$V^S = \pi a E_{cr}^S h_{cr}^x h^{1-x} (x - 1)^{-1} \quad x = 1.7 \text{ to } 2.3 \quad (6)$$

In this relation,  $E_{cr}^S$  is the value of  $E^s$  at a critical (contact) separation  $h_{cr}$ . In calculating  $V^S$ ,  $x$  was taken to be equal to 2, so that

$$V^S = \pi a E_{cr}^S h_{cr}^2 h^{-1} \quad (7)$$

### Interfacial interactions

The Fowkes approach to interfacial interactions is based on the assumption that the surface or interfacial free energy of a solid and of a liquid can be divided into many parts: a part due to dispersion interaction ( $d$ ), dipole-dipole interaction ( $p_1$ ), dipole induced-dipole interaction ( $i$ ), hydrogen bonding ( $h$ ),  $\pi$ -bonding ( $\pi$ ), electrostatic interaction ( $e$ ) and acceptor-donor interaction ( $ad$ ):

$$\gamma = \gamma^d + \gamma^{p1} + \gamma^i + \gamma^h + \gamma^\pi + \gamma^e + \gamma^{ad} \quad (8)$$

According to van Oss et al. [36], all three electrodynamic van der Waals interactions ( $d$ ,  $p_1$  and  $i$ ) should be incorporated into a single apolar-Lifshitz-van

der Waals (LW) term,  $\gamma^{\text{LW}}$ , and the remaining interactions (h,  $\pi$  and ad) into a single polar-acid base (AB) term  $\gamma^{\text{AB}}$ , so that:

$$\gamma = \gamma^{\text{LW}} + \gamma^{\text{AB}} \quad (9)$$

For the apolar component of interfacial tension between the solid (S) and liquid (L), the Good-Girifalco-Fowkes combining rule is applicable [36]:

$$\gamma_{\text{SL}}^{\text{LW}} = [(\gamma_S^{\text{LW}})^{1/2} - (\gamma_L^{\text{LW}})^{1/2}]^2 \quad (10)$$

For the polar component of the interfacial tension:

$$\gamma_{\text{SL}}^{\text{AB}} = 2 [(\gamma_S^+ \gamma_S^-)^{1/2} + (\gamma_L^+ \gamma_L^-)^{1/2} - (\gamma_S^+ \gamma_L^-)^{1/2} - (\gamma_S^- \gamma_L^+)^{1/2}] \quad (11)$$

In equations (10) and (11),  $\gamma^{\text{LW}}$ ,  $\gamma^+$  and  $\gamma^-$  are the Lifshitz-van der Waals, acceptor and electron donor parameters of the solid and liquid, respectively.

When equation (11) is compared with equation (10), it becomes clear that while  $\gamma_{\text{SL}}^{\text{LW}}$  cannot be less than zero,  $\gamma_{\text{SL}}^{\text{AB}}$  is negative, when:

$$\gamma_S^+ > \gamma_L^+ \quad \text{and} \quad \gamma_S^- < \gamma_L^- \quad \text{or} \quad (11a)$$

$$\gamma_S^+ < \gamma_L^+ \quad \text{and} \quad \gamma_S^- > \gamma_L^- \quad (11b)$$

The interaction energy between the solid surfaces immersed in the liquid is:

$$\Delta G_{\text{SLS}} = -2\gamma_{\text{SL}} \quad (12)$$

and more strictly,

$$\Delta G_{\text{SLS}}^{\text{LW}} = -2\gamma_{\text{SL}}^{\text{LW}} \quad (13)$$

and

$$\Delta G_{SLS}^{AB} = -2\gamma_{SL}^{AB} \quad (14)$$

Identifying the LW interactions with the van der Waals (dispersion) surface forces, i.e. combining equations (2), (10) and (13), and the AB interactions with the polar surface forces (equations (7), (11) and (14),  $E_{cr}^s = \Delta G_{SLS}^{AB}$  ), one can postulate:

$$V^{vdW} = -2\pi a [(\gamma_S^{LW})^{1/2} - (\gamma_L^{LW})^{1/2}]^2 K h_{cr}^2 h^{-1} \quad (15)$$

where  $K = [1 - (k^* h / \lambda^*) \ln(1 + \lambda^* / k^* h)]$

$$V^S = -4\pi a [(\gamma_S^+ \gamma_S^-)^{1/2} + (\gamma_L^+ \gamma_L^-)^{1/2} - (\gamma_S^+ \gamma_L^-)^{1/2} - (\gamma_S^- \gamma_L^+)^{1/2}] h_{cr}^2 h^{-1} \quad (16)$$

#### A MODEL OF MAGNETIC FLOCCULATION

Equations (15) and (16), replacing equations (2) and (7), respectively, allow us to estimate the apolar and polar surface forces using LW and AB components of interfacial tension, respectively, between the surfaces of the mineral and the liquid.

It is well known that the value to be taken for the Hamaker constant  $A_0$  in equation (2) is generally very uncertain [1], and that any discrepancy between the calculated and measured quantities for interacting entities are compensated for by adjusting the constant.

Comparing equations (15) and (2) one obtains:

$$A_0 = 24\pi h_{cr}^2 \gamma_{SL}^{LW} \quad (17)$$

It is noteworthy that for a system of identical bodies interacting through a liquid

$$A_0 = (A_S^{1/2} - A_L^{1/2})^2 \quad (18)$$

When comparing equation (18) with equation (10), it is clear that a direct correlation between A and  $\gamma_{SL}^{LW}$  exists in principle, and for  $h_{cr} = 0.2 \text{ nm}$ :

$$A = 3 \times 10^{-18} \gamma_{SL}^{LW} \quad (19)$$

As follows from Figure 1, in which known values of  $\gamma_{SL}^{LW}$  and  $\gamma_{SL}^{AB}$  for various minerals in contact with water are shown, assuming that the minerals are monopolar (i.e.  $\gamma^+ > > \gamma^+$ ), there is a correlation between the apolar and polar surface forces.

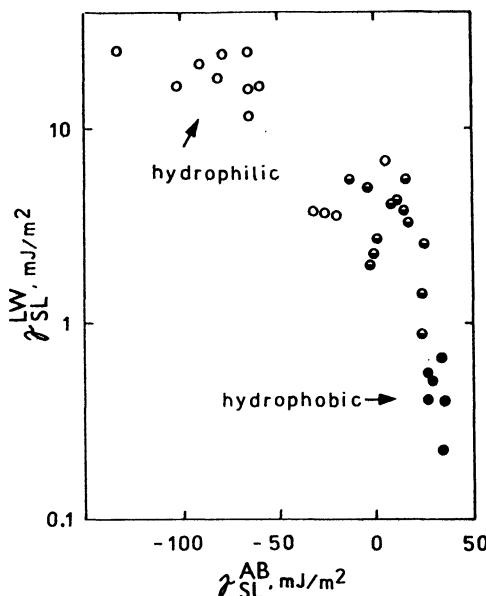


FIGURE 1 Connection between the apolar and polar components of interfacial tension between minerals and water. The water contact angle for the hydrophilic minerals is less than 30 °. for the hydrophobic minerals the angle is greater than 70 °.

Hydrophilic minerals such as silicates are characterized by highly negative values of  $\gamma_{SL}^{AB}$  and by higher positive values of  $\gamma_{SL}^{LW}$  (up to  $30 \text{ mJ.m}^{-2}$ ). Thus, although the van der Waals attraction is relatively strong, these minerals will be stable in their suspensions due to the repulsive polar forces ( $V^s > 0$ ), reflecting a strong adhesion of water on the minerals.

On the other hand, the values of  $\gamma_{SL}^{LW}$ , characteristic for hydrophobic or hydrophobised minerals are small and  $\gamma_{SL}^{AB}$  values are again considerable (but in

the positive regime). Hence, only the attractive polar forces ( $V^s < 0$ ) can lead to a strong attraction between hydrophobic minerals and can result in their aggregation.

Note that for all minerals,  $\gamma_{SL}^{LV}$  is always positive while  $\gamma_{SL}^{AB}$  can vary from negative to positive values. This means that  $V^{vdw}$  is always attractive and  $V^s$  is attractive or repulsive. Moreover,  $V^s >> V^{vdw}$  for most minerals. This is why the parameter  $K$  in equation (15) can be neglected in our calculations.

## RESULTS

In order to explain the influence of polar forces of paramagnetic minerals on their magnetic flocculation, for a wide range of hydrophobicity, total interaction energies have been calculated combining equations (15) and (16) with equations (2) and (3). The total interaction energies were calculated for identical spheres of radii 1  $\mu\text{m}$  as a function of their separation for  $B = 0$  and 1 Tesla.

From these results, three types of interaction have been identified:

- 1 - the interaction leading to separation of the particles: stable suspension
- 2 - the interaction leading to an attachment of the particles in the secondary minimum (secondary aggregation)
- 3 - the interaction leading to an attachment of the particles in the primary minimum (primary aggregation).

The criteria used to distinguish the above criteria from one another have been taken assuming that the kinetic energy of the particles is  $10 kT$ . In all cases, the value of  $A$  was chosen to be  $10^{-20} \text{ J}$ , corresponding to  $\gamma_{SL}^{LV} = 3.3 \text{ mJ.m}^{-2}$  (see Figure 1). The value of  $\chi$  was held constant at  $5 \times 10^{-3}$  (SI).

In Figure 2, zones of the three given types of interaction, without taking  $V^s$  into account ( $\gamma_{SL}^{AB} = 0$ ) are shown as a function of zeta potential and of the magnetic induction, assuming  $\kappa = 10^8 \text{ m}^{-1}$ .

It is seen in Figure 2 that the magnetic field of  $B > 0.1 \text{ T}$  induces secondary aggregation of a given paramagnetic mineral, for zeta potential above 15 mV. For lower values of zeta potential, the primary aggregation is expected, and the region representing the stability exists only for zeta potential above 7 mV and  $B < 0.1 \text{ T}$ .

Assuming that the paramagnetic mineral is fully hydrophobic ( $\gamma_{SL}^{AB} = 50 \text{ mJ.m}^{-2}$ ) and incorporating the attractive polar forces into the calculations, the domain of the primary aggregation widens and simultaneously, the domain of secondary aggregation narrows down to zeta potential of approximately 30 mV (Figure 3).

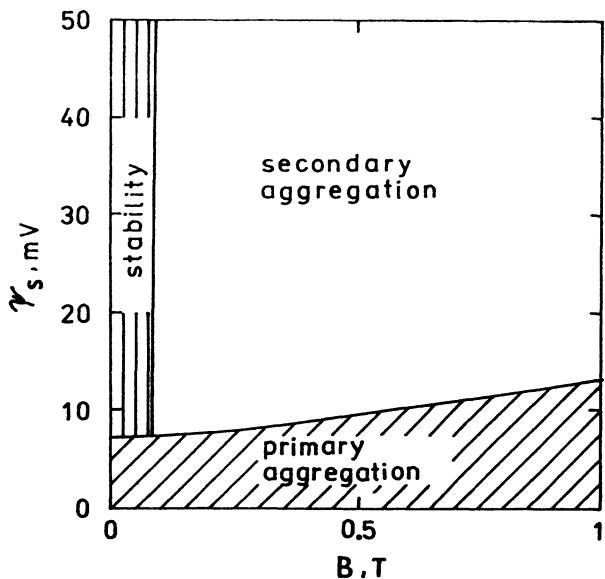


FIGURE 2 Interaction zones for the model of paramagnetic colloid (polar forces are absent).  $\kappa = 10^8 \text{ m}^{-1}$ .

If a higher concentration of 1-1 electrolyte is considered ( $\kappa = 3.3 \times 10^8 \text{ m}^{-1}$ ) under otherwise constant conditions (Figure 4), the boundary between the regions further shifts towards higher values of zeta potential (46 mV).

It is clear from Figures 2 and 3 that  $V^M$  does not change the zones appreciably. In other words,  $B$ , that is required to cause the primary or secondary aggregation, is constant for a given zeta potential and hydrophobicity ( $\gamma_{SL}^{AB}$ ) of the mineral.  $V^M$  does not influence the interaction and  $V^S$  and  $V^{EL}$  are the dominant terms for the primary aggregation of hydrophobic minerals.

An opposite situation occurs when the paramagnetic mineral is assumed to be hydrophilic, i.e.  $V^S > 0$ . Such a pattern,  $\gamma_{SL}^{AB} = -20 \text{ mJ.m}^{-2}$ , is shown in Figure 5.

In this case, only the stability region can be identified, and the region of the primary aggregation vanishes due to strong repulsive polar forces.

The secondary aggregation develops only under the influence of magnetic field greater than approximately 0.11 T. It is interesting to note that neither  $\kappa$  nor  $\psi_s$ , i.e.  $V^{EL}$  changes the observed picture. This means that only  $V^S$  and  $V^M$  are responsible for the interaction between hydrophilic paramagnetic mineral fines.

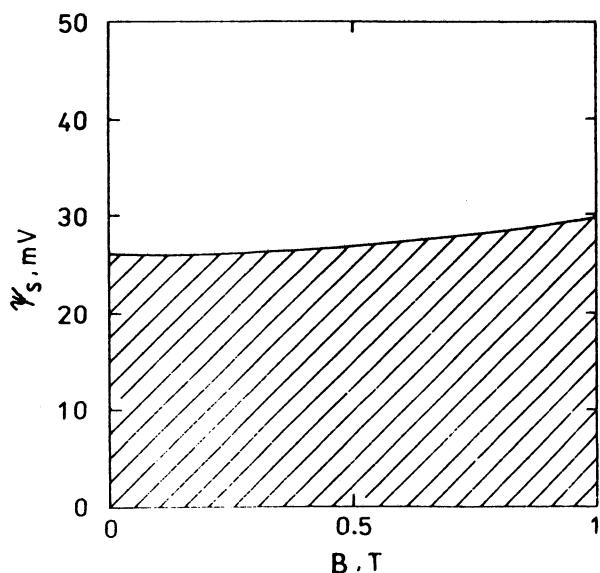


FIGURE 3 Interaction zones for the model hydrophobic colloid ( $\gamma_{\text{SL}}^{\text{AB}} = 40 \text{ mJ.m}^{-2}$ ),  $\kappa = 10^8 \text{ m}^{-1}$ .

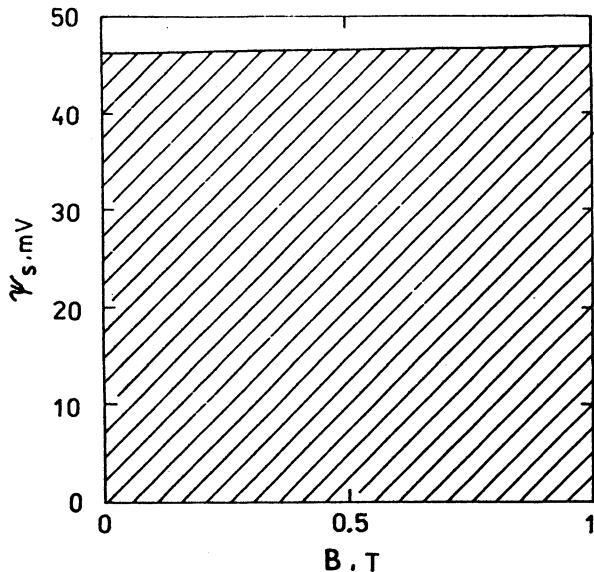


FIGURE 4 Interaction zones for the model hydrophobic colloid ( $\gamma_{\text{SL}}^{\text{AB}} = 50 \text{ mJ.m}^{-2}$ ),  $\kappa = 3.3 \times 10^8 \text{ m}^{-1}$ .

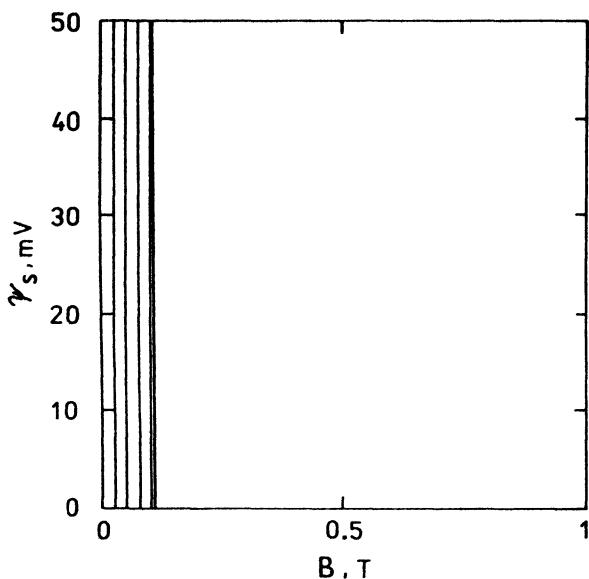


FIGURE 5 Interaction zones for the model hydrophilic colloid ( $\gamma_{SL}^{AB} = -20 \text{ mJ.m}^{-2}$ ).

### CONCLUSION

It has been shown that the external magnetic field can induce aggregation of hydrophilic paramagnetic minerals in the so-called secondary minimum and that the primary aggregation is prevented by repulsive polar forces, irrespective of repulsive electrostatic forces. On the other hand, hydrophobic paramagnetic minerals can be aggregated in the primary minimum, due to attractive polar forces. The aggregation is not sensitive to magnetic attraction, but is strongly influenced by the electrostatic forces in this case.

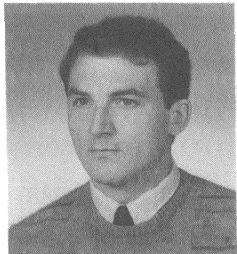
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**Keywords:** magnetic flocculation, DLVO theory, polar forces, interaction energy, paramagnetic minerals, hydrophobic colloids.