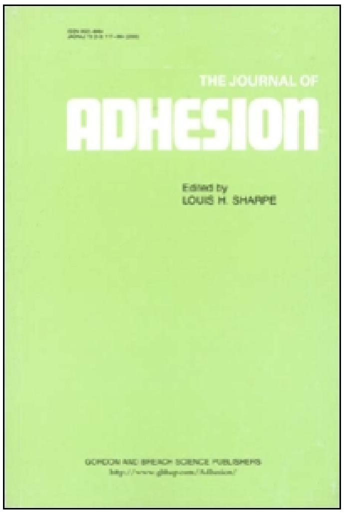
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Relationship between the Wettability and Aggregation of Ultrafine Minerals in Methanol-Water Mixtures

Jiří Škvarla[a]; Stanislav Kmeť[a]
[a] Department of Mineral Processing and Environmental Protection, Technical University, Košice, Czechoslovakia

To cite this Article Škvarla, Jiří and Kmeť, Stanislav(1992) 'The Relationship between the Wettability and Aggregation of Ultrafine Minerals in Methanol-Water Mixtures', The Journal of Adhesion, 38: 1, 19 — 30

To link to this Article: DOI: 10.1080/00218469208031265

URL: http://dx.doi.org/10.1080/00218469208031265

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1992, Vol. 38, pp. 19–30
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

The Relationship between the Wettability and Aggregation of Ultrafine Minerals in Methanol-Water Mixtures

JIŘÍ ŠKVARLA and STANISLAV KMEŤ

Department of Mineral Processing and Environmental Protection, Technical University, Park Komenského 19, 043 84 Košice, Czechoslovakia

(Received December 3, 1990; in final form February 4, 1992)

A thermodynamic expression for describing the relationship between the wettability and aggregation of fine minerals has been derived using the critical adhesion tension concept. The approach has been confirmed qualitatively by measurements of the above phenomena on magnesite and dolomite fines hydrophobized by sodium oleate in methanol-water mixtures. The role of interfacial interactions expressed through γ_{SL} has been documented.

KEY WORDS wettability; aggregation; sedimentation; colloids; interfacial tension; contact angle.

INTRODUCTION

Aggregation of colloids in non-aqueous media is rare in comparison with that in aqueous media where great progress has been made. However, the aggregation of non-aqueous disperse systems also plays an important role in various fields. The colloid stability in aqueous media has been predicted by the DLVO theory that considers at least two components of interparticle interaction, *i.e.* the van der Waals (vdW) and the electrostatic (E) contribution, respectively.[1,2] At the same time, the DLVO theory is used in the case of non-polar liquid media.[3]

On the other hand, the recent progress in sophisticated techniques of direct measurements of surface forces[4] has revealed a third type of surface interaction that operates at short distances between hydrophilic or hydrophobic surfaces.[5] These polar or structural (S) forces reflect changes in a liquid structure due to interfacial interactions.[6] Consequently, it should be useful to evaluate these forces *via* interfacial energetics as their interfacial origin is apparent. In fact, at short separations, say less than 5 to 10 nm, the total interaction energy between hydrophobic or hydrophilic objects in aqueous solutions is governed by polar surface forces.

So the surface thermodynamics conception seems to be justified, concerning the modelling of contact or close contact surface forces, mainly if surfactants, that sharply change the interfacial energetics and simultaneously complicate the DLVO approach, are present in disperse systems.

The thermodynamic approach to the problem of colloid stability based on the Young equation was published by Shchukin *et al.*[7] These authors have shown that there exists a correlation between the wettability and aggregation of methylated quartz particles in different liquids.

The aim of this paper is to verify the above correlation for systems of semisoluble minerals (magnesite and dolomite) in varying methanol-water mixtures, in the presence of a surfactant (sodium oleate), that, as known, dramatically influences the surfaces of these minerals.

THEORY

Representation of the Wettability Data

A quantitative measure of wettability of a solid against a liquid is the contact angle of wetting. Most of contact angle methods are based on the Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \tag{1}$$

where γ_{SV} and γ_{LV} are surface tensions of the solid and the liquid respectively in equilibrium with the saturated vapor of the liquid, γ_{SL} is the interfacial tension between the solid and the liquid, and θ is the equilibrium contact angle of the given liquid on the given surface. Eq. (1) can be rewritten in the form:

$$\gamma_S = \gamma_{SL} + \gamma_{LV} \cos\theta + \pi_e \tag{2}$$

where γ_S is the surface tension of the solid in vacuum and π_e is the so-called spreading pressure, being equal to the decrease of surface tension of the solid due to vapor adsorption, *i.e.* $\pi_e = \gamma_S - \gamma_{SV}$. It is generally accepted that if the contact angle is larger than 10° the spreading pressure can be safely neglected[8] so that $\gamma_S \approx \gamma_{SV}$ and it is possible to write the Young equation (1) or (2) in terms of the true or intrinstic solid surface tension γ_S. In other words, π_e may be neglected for solids of low surface energy when $\gamma_{SV} < \gamma_{LV}$.

The use of contact angle data in connection with the Young equation is a delicate matter. It is evident that only two of the four variables can be readily measured, that is, the liquid surface tension and the contact angle. Even with the omission of the spreading pressure term, the equation cannot be solved for the surface free energy of the solid or its interfacial free energy separately. Then, if we do not consider the Neumann's concept, as will be seen below, Eq. (1) can be solved for the difference $\gamma_{SV} - \gamma_{SL}$, called the adhesion tension.

The contact angle, θ, *versus* surface tension, γ_{LV}, data are usually represented in two different ways. One way is to plot cos θ against γ_{LV}; the so-called critical surface tension conception, CST. The critical surface tension of wetting γ_c is determined by extrapolation to $\cos\theta = 1$ of a straight line plot of the said variables. It is mathematically defined as γ_{LV} at $\theta = 0$ and its meaning can be understood by substituting the above definition in the Young equation (2):[9]

$$\gamma_c = \gamma_S - \gamma_{SL}^{o} - \pi_e^{o} \tag{3}$$

where γ_{SL}^{o} and π_e^{o} are γ_{SL} and π_e at $\cos\theta = 1$. Thus, the critical surface tension is smaller than or equal to the true solid surface tension. In physical terms, a liquid with a surface tension below this value will wet the solid whereas a liquid with a greater surface tension will not.

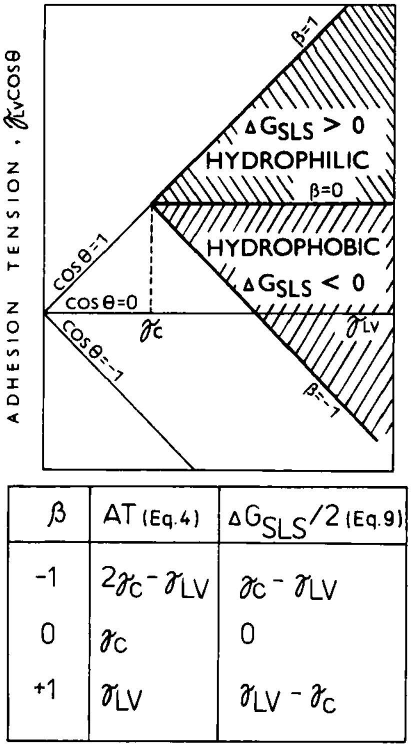
An alternative, more preferable way of representing the wettability data is through the above mentioned adhesion tension $\gamma_{SV} - \gamma_{SL} = \cos\theta\ \gamma_{LV}$ *versus* γ_{LV}; the so-called critical adhesion tension concept, CAT. In this case, the linear behaviour of the relationship can be expressed as follows:

$$\gamma_{LV}\cos\theta = \beta\,\gamma_{LV} + (1-\beta)\gamma_c \tag{4}$$

so that, as in the case of the CST concept, the wettability of a surface may be characterized by two parameters, *i.e.* γ_c and β. For the slope value, β, combining the Young's and the Gibbs' equation[10] one obtains:

$$\beta = \frac{d\gamma_{LV}\cos\theta}{d\gamma_{LV}} = \frac{\Gamma^{SV} - \Gamma^{SL}}{\Gamma^{LV}} \tag{5}$$

where Γ^{SV}, Γ^{SL} and Γ^{LV} are the relative adsorption densities of a solute from the liquid at the three interfaces. A diagram showing the adhesion tension lines for three limiting values of the surface wettability is presented in Figure 1 together with



β	AT (Eq.4)	$\Delta G_{SLS}/2$ (Eq.9)
-1	$2\gamma_c - \gamma_{LV}$	$\gamma_c - \gamma_{LV}$
0	γ_c	0
+1	γ_{LV}	$\gamma_{LV} - \gamma_c$

FIGURE 1 Critical adhesion tension (CAT) diagram with hypothetical adhesion tension (AT) lines for an entirely hydrophobic, indifferent, and hydrophilic ($\beta = -1$, 0, and +1, respectively) surface.

corresponding parameters from Eq. (4) and Eq. (9) (see below). By this diagram, the hydrophobic (or more strictly, lyophobic) region is limited by $\beta = -1$ and 0 while the hydrophilic domain lies between $\beta = 0$ and $+1$. So, negative slopes β are characteristic of nonpolarity while positive slopes characterize polarity of solids.

Relation of Aggregation to Wettability

According to the surface thermodynamics approach of colloidal interactions, as mentioned at the beginning, the interaction energy between surfaces immersed in a liquid is:[11]

$$\Delta G_{SLS} = -2\,\gamma_{SL}\,. \tag{6}$$

In combination with Eq. (2), Eq. (6) can be expressed as:

$$\Delta G_{SLS} = 2\,(\gamma_{LV}\cos\theta - \gamma_S + \pi_e) \tag{7}$$

In conjunction with Eq. (3), Eq. (7) can be modified as follows:

$$\Delta G_{SLS} = 2\,(\gamma_{LV}\cos\theta - \gamma_c - \gamma_{SL}^{o} + \Delta\pi) \tag{8}$$

where $\Delta\pi = \pi_e - \pi_e^o$.

As we can see, Eqs. (7) and (8) relate aggregation of colloids, ΔG_{SLS}, with their wetting in the given liquid. For low energy surfaces wetted by test liquids of low surface energy, γ_{SL}^{o} and $\Delta\pi$ are close to zero and γ_S can be replaced by γ_c. It is obvious that ΔG_{SLS} should depend on the adhesion tension (denoted AT) minus γ_c.

For entirely hydrophobic solids, as follows from Figure 1 characterized by $\beta = -1$, AT, as well as ΔG_{SLS}, is negative when $\gamma_{LV} > 2\gamma_c$ and $\gamma_{LV} > \gamma_c$, respectively. On the contrary, for hydrophilic solids with $\beta = +1$, ΔG_{SLS} and AT are positive when $\gamma_{LV} > \gamma_c$, in principle. The above considerations concerning ΔG_{SLS} become understood when combining Eq. (7) or Eq. (8) with Eq. (4):

$$\Delta G_{SLS} = 2\beta(\gamma_{LV} - \gamma_c) \tag{9}$$

Finally, when $\beta = 0$, $AT = \gamma_c$ and $\Delta G_{SLS} = 0$.

Adhesion between surfaces and thermodynamically favoured aggregation of colloids requiring $\Delta G_{SLS} < 0$ to be satisfied, is then conditioned by their partial or full hydrophobicity. In this case, decreasing the difference $\gamma_{LV} - \gamma_c$ weakens the mentioned attachments since ΔG_{SLS} becomes less negative. On the other hand, when the solids are hydrophilic, the attractive effect is not thermodynamically feasible as $\Delta G_{SLS} > 0$, in general. In all cases, when $\gamma_{LV} = \gamma_c$, $\Delta G_{SLS} = 0$. Of course, all these considerations are possible only if the spreading pressure and γ_{SL}^{o} are negligible.

EXPERIMENTAL

Materials

The experiments were performed with fine particles of magnesite and dolomite from Košice-Bankov, Czechoslovakia. The minerals had been finely ground to minus 40

TABLE I
Particle size distribution of mineral samples used

Size range (μm)	Magnesite (%)	Dolomite (%)
0–2	21.50	21.20
2–4	13.25	16.10
4–10	39.09	30.40
10–15	11.46	11.45
15–20	1.99	7.17
20–30	6.20	4.95
+30	6.51	8.73
mean size (μm)	7.96	8.79

μm in a porcelain mill. The size of the prepared minerals are tabulated in Table I as determined by the sedimentation analysis.

Suspending Liquid Mixtures

Aqueous methanol solutions of various surface tensions were employed as the wetting and aggregation media. Both of these liquids were chosen because of their hydrogen bonding character. Moreover, the methanol-water mixtures cover a wide range of γ_{LV}. The surface tension of the methanol solutions is shown in Figure 2 as a function of mole fraction of methanol n_{CH_3OH}. The line was drawn using the equation derived by Connors and Wright.[12]

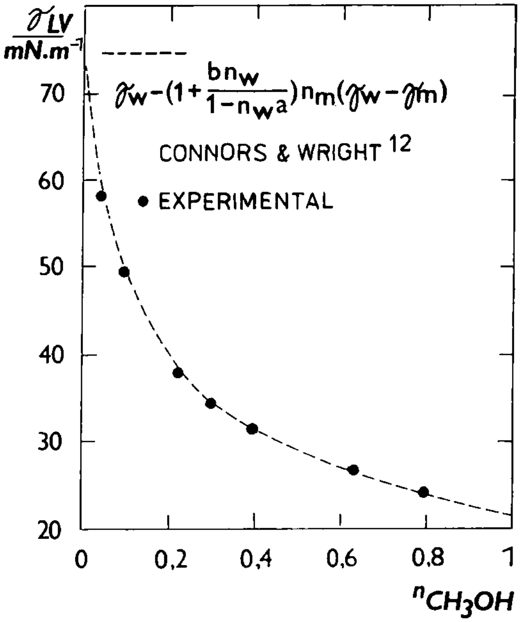


FIGURE 2 Surface tension of methanol (m)-water (w) mixtures as a function of mole fraction of methanol; $a=0.899$, $b=0.777$, $\gamma_w=72.8$ mN.m^{-1}, and $\gamma_m=21.2$ mN.m^{-1}.

Wettability (Contact Angle) Measurements

The contact angles of drops of methanol-water solution were measured on pressed discs of powdered, hydrophobized carbonates. These discs were prepared as follows: the suspensions of magnesite and dolomite were mixed in the presence of the hydrophobizing agent—sodium oleate (NaOl). After this the disperse phase was separated by filtration, dried at room temperature and homogenized. Finally, the dried powders were pressed in the form of an IR disc at a pressure of 400 MPa.

Aggregation (Sedimentation) Tests

The degree of aggregation of the fine carbonates was determined from the rate of sedimentation. The specially-adapted apparatus had enabled the recording of the time changes of optical density of the suspensions by means of a sensitive photoelectric cell. The resultant voltage changes were taken arbitrarily after a lapse of ten minutes (U_{10}). The samples for the aggregation determinations were prepared in the same way as those used in the wettability measurements, except without pressing. Typical recorder traces are depicted in Figure 3.

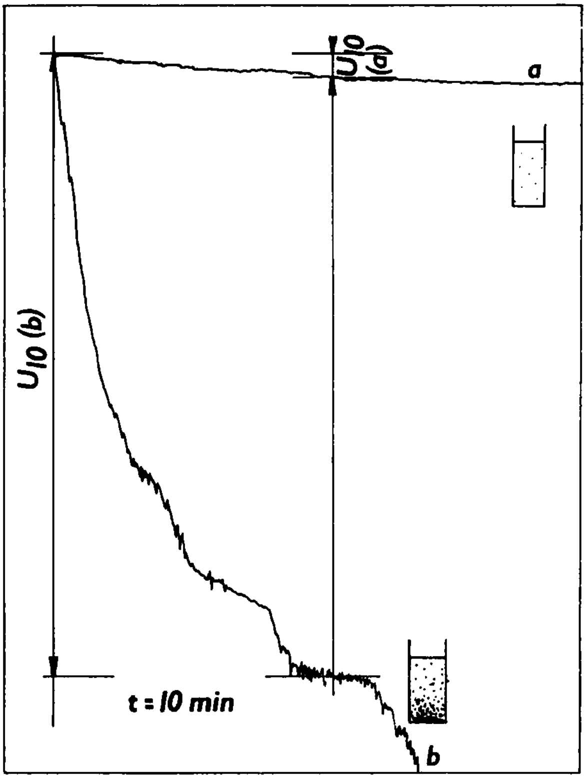


FIGURE 3 Typical sedimentation records for a stable (a) and an aggregated (b) suspension. U_{10} is a related voltage change taken after ten minutes.

RESULTS AND DISCUSSION

Adhesion Tension Measurements

The adhesion tension diagrams for magnesite and dolomite hydrophobized to various degrees of hydrophobicity, established by methanol solutions, are shown in Figure 4 and Figure 5, respectively. From these figures it can be seen that the hydrophobicity of the carbonates was markedly affected by an increase in the additive concentration of NaOl. The conversion from a hydrophilic to a hydrophobic character ($\beta = 0$) of the carbonates was observed at 10^{-4} M NaOl. The linear behaviour of the AT lines, as indicated by Eq. (4), can be observed for strongly hydrophobic surfaces treated with 2.5×10^{-4} M NaOl. It may be noted that the slope values, β, are close to -1, with the water contact angle roughly 105°, as those for fully hydrophobic polymers such as paraffin and Teflon. The simplest explanation for the linear AT lines is an equal adsorption of the solute at the S/L and L/V interfaces ($\Gamma^{SL} = \Gamma^{LV}$ and $\Gamma^{SV} = 0$; see Eq. (5)) in the course of measuring with varying methanol-water mixtures, which fact would justify us in proposing and using the CAT conception, at least in this case. The diagrams show that the γ_c value is about 27–28 mN/m for both the carbonates hydrophobized at 2.5×10^{-4} M NaOl. For comparison, the published β and γ_c values of various mineral specimens are summarized in Table II.

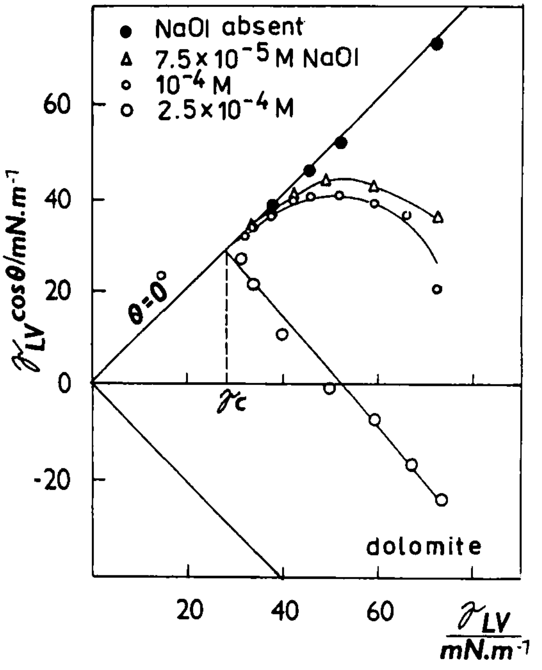


FIGURE 4 Adhesion tension diagrams for hydrophobized dolomite.

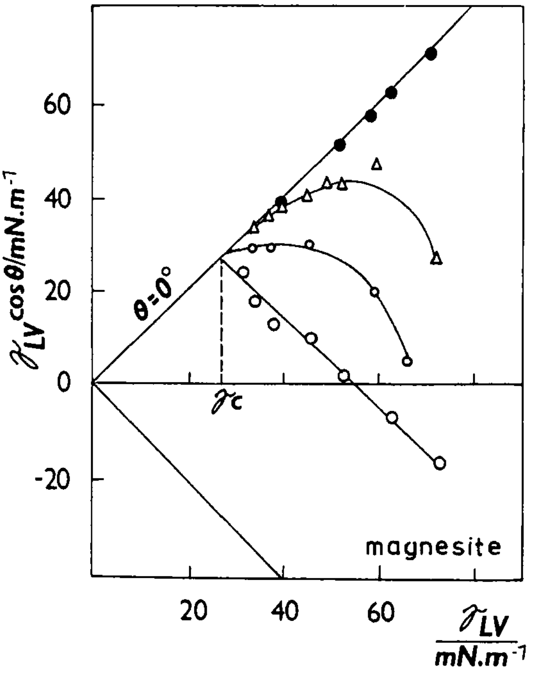


FIGURE 5 Adhesion tension diagrams for hydrophobized magnesite.

TABLE II
Comparison of the wetting parameters for inherently hydrophobic (a) and hydrophobized (b) mineral surfaces obtained using aqueous solutions of methanol (data from Kelebek[10])

Sample	β	$\gamma_c/mN.m^{-1}$
(a)		
sulphur III	−0.77	31.5
sulphur I (crystal face)	−0.48	26.9
graphite II	−0.47	33.4
molybdenite I (crystal face)	−0.43	29.2
talc II	−0.20	29.0
sulphur II (disc)	0.05	33.0
coal	0.31	35.5
stibnite II	0.33	32.5
molybdenite II (disc)	0.34	41.7
talc III (disc)	0.50	35.5
stibnite III	0.71	39.5
(b)		
alkyl group of chemisorbed xanthate on galena		
methyl	0.3	36.5
ethyl	0.1	32.8
propyl	−0.1	32.6
butyl	−0.3	31.4
pentyl	−0.5	30.8
hexyl	−0.6	27.0
decyl	−0.8	26.1
magnesite and dolomite with 2.5×10^{-4} M sodium oleate (this study)	−1.0	27–28

At moderate concentrations of NaOl, *i.e.* below 10^{-4} M NaOl, the predicted linear AT lines have not been confirmed. This must be connected with an irregular variation of γ_{SL}, for example, due to a dissolution of the hydrophobic coating by concentrated methanol solutions. There might be other reasons associated with the measurement of contact angles on compacted powders. Capillary penetration could, for example, be a factor.

Aggregation Tests

The aggregation behaviour of magnesite and dolomite fines evaluated by U_{10} is shown as a function of surface tension of the methanol-water mixtures in Figure 6 for entirely hydrophobic, and in Figure 7 for moderately hydrophobic, particles. For more detailed information the corresponding contact angles are shown as well.

Over a certain surface tension range the aggregation drastically decreases for the entirely hydrophobic carbonates. The aggregation/nonaggregation transitions are directly related to the nonwettable/wettable transitions. Both these transitions may be characterized by γ_c of the carbonates determined from AT lines (Fig. 4 and Fig. 5).

ΔG_{SLS} Implications

When a hydrophobicity appears, AT<γ_c and ΔG_{SLS} becomes negative and aggregation is possible. As our intention is to show the correlation between aggregation

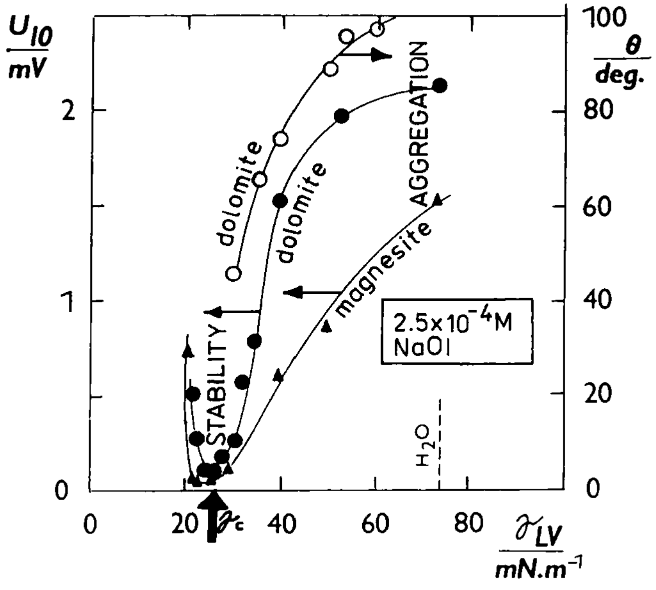


FIGURE 6 Sedimentation (U_{10}) of maximally hydrophobized carbonates as a function of surface tension of the aqueous methanol solutions.

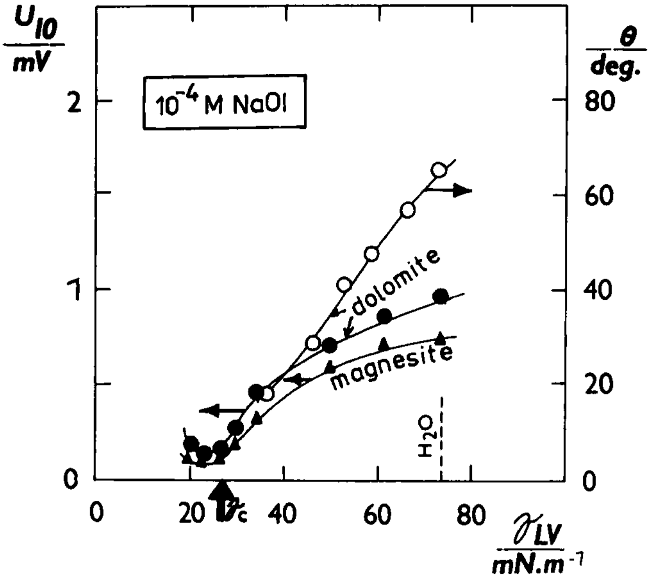


FIGURE 7 Sedimentation (U_{10}) of moderately hydrophobized carbonates as a function of surface tension of the aqueous methanol solutions.

and wettability of the carbonates, Figure 8 demonstrates the relationship. Within the framework of the theory (see Eq. (7)), we have plotted U_{10} against $\Delta G_{SLS} = 2(\gamma_{LV} \cos\theta - \gamma_c)$. Since this relation has been constructed for the maximally hydrophobized carbonates with $\beta = -1$, Eq. (9) yields $\Delta G_{SLS} = 2(\gamma_c - \gamma_{LV})$. From the figure we can see the aggregation of these suspensions really corresponds to its thermodynamically favourable condition, *i.e.* $\Delta G_{SLS} < 0$ for higher surface tensions of the methanol-water mixtures. The calculated $\Delta G_{SLS} = 0$, predicting no degree of aggregation, has also been confirmed experimentally when $U_{10} \sim 0$ for $\gamma_{LV} = \gamma_c$.

Of course, this dependence is not linear as expected because the U_{10} parameter is not a direct measure of ΔG_{SLS}. Since the surfaces carrying the adsorbed oleate molecules that are responsible for their moderate hydrophobicity do not obey Eq. (4), due to some irregularities as mentioned above, the correlation between U_{10} and ΔG_{SLS} was not satisfactory.

Related Approaches

In order to explain the effect of aggregation of fine polymer and coal particles in various binary liquid mixtures Vargha-Butler *et al.*[13-15] evolved a conception of suspension stability based on Eq. (6). They suggest, in accord with our concept, that aggregation between particles of the same kind embedded in a liquid is governed by the free energy of cohesion ΔG_{SLS}. Nevertheless, they have also combined Eq. (6) with the explicit Neumann's relationship for γ_{SL}:

$$\gamma_{SL} = \frac{((\gamma_{SV})^{1/2} - (\gamma_{LV})^{1/2})^2}{1 - 0.015\,(\gamma_{SV}\gamma_{LV})^{1/2}} \qquad (10)$$

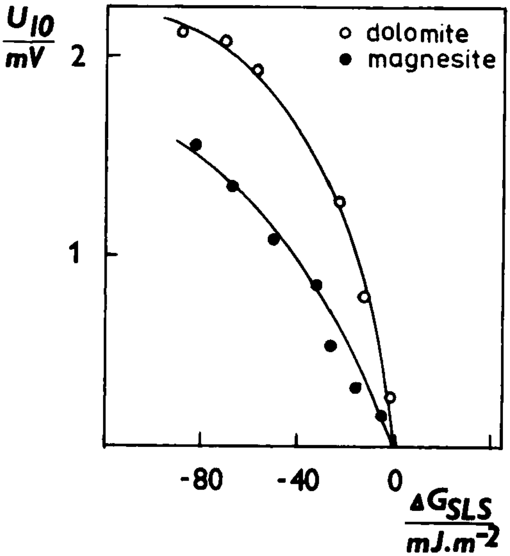


FIGURE 8 Correlation between sedimentation (U_{10}) and calculated ΔG_{SLS} (Eq. (7)) parameters for the maximally hydrophobized carbonates.

From the equation it is apparent that ΔG_{SLS}, in contrast to our own approach, is always negative implying that there will always be an attraction between like particles suspended in a liquid. This conclusion results from the fact that the numerator in Eq. (10) is positive in principle, regardless of whether $\gamma_{SV} > \gamma_{LV}$ or $\gamma_{SV} < \gamma_{LV}$. In other words, such a concept does not allow one to consider negative interfacial tensions γ_{SL} as predicted by Eq. (6) for a repulsive interaction between hydrophilic surfaces. However, in the limiting case $\Delta G_{SLS} = 0$ when $\gamma_{SV} = \gamma_{LV}$, which assumption is congruent with that pointed out earlier. As a result, in a sedimentation volume experiment these authors observed an extremum in the sedimentation volume at $\gamma_{LV} = \gamma_{SV}$, varying γ_{LV}.

CONCLUSION

This study shows that:

1. The expression for describing the relationship between the wettability and aggregation of fine minerals was confirmed partially. This expression assumes the interfacial tension γ_{SL}, reflecting interfacial interactions, to be the major driving force for both these phenomena.
2. In order to confirm the presented approach there is a need to perform experiments on more definable systems. Especially, precise contact angle measurements are needed.

References

1. B. V. Derjaguin, N. V. Churaev and V. M. Muller, *Surface Forces* (Nauka, Moscow, 1985), 398 pp. (in Russian).
2. B. V. Derjaguin, N. V. Churaev, *Zhurnal Vsesojuznogo Chimicheskogo Obshchestva* im. D. I. Mendeleeva, **34,** 7–14, (1989) (in Russian).
3. B. Vincent, Z. Király, S. Emmett and A. Beaver, *Colloid Surfaces,* **49,** 121–132 (1990).
4. J. Israelachvili, *Accounts of Chemical Research,* **20,** 415–421 (1987).
5. H. K. Christenson, P. M. Claesson and R. M. Pashley, *Proc. Indian Acad. Sci., Chem. Sci.,* **98,** 379–389 (1987).
6. C. J. van Oss, M. K. Chaudhury and R. J. Good, *Chemical Reviews,* **88,** 927–941 (1988).
7. E. D. Shchukin, in *Colloid Chemistry,* A. Seludko, Ed. (Mir, Moscow, 1984), pp. 302–314 (in Russian).
8. M. Morra, E. Occhiello and F. Garbassi, *Advances in Colloid Interface Sci.,* **32,** 79 (1990).
9. T. Hata, Y. Kitazaki and T. Saito, *J. Adhesion,* **21,** 177 (1987).
10. S. Kelebek, *J. Colloid Interface Sci.,* **124,** 504–514 (1988).
11. C. J. van Oss, R. F. Giese and P. M. Costanzo, *Clays Clay Miner.,* **38,** 151–160 (1990).
12. K. A. Connors and J. L. Wright, *Anal. Chem.,* **61,** 194 (1989).
13. E. I. Vargha-Butler, D. R. Absolom, A. W. Neumann and H. A. Hamza, in *Interfacial Phenomena in Coal Technology,* G. D. Botsaris and Y. M. Glazman, Eds. (M. Dekker, New York, 1989), pp. 33–84.
14. E. I. Vargha-Butler, E. Moy and A. W. Neumann, *Colloid Surfaces,* **24,** 315–324 (1987).
15. E. I. Vargha-Butler, T. K. Zubovits, D. R. Absolom and A. W. Neumann, *Chem. Eng. Commun.,* **33,** 255–276 (1985).