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SURFACE TENSION OF TALC AND TALC-CHLORITE MIXTURES

J.-M. Douillard, H. Malandrini, T. Zoungrana, F. Clauss and S. Partyka*

L.A.M.M.I., U.R.A. 79, Université Montpellier II, Case 015, Place E. Bataillon, 34095 Montpellier Cedex 05, France
*Talc Luzenac France, 2, Place E. Bouillères, 31100 Toulouse-Mirail, France

Abstract

It is possible to estimate surface tension of high-energy solids combining the immersion microcalorimetry thermodynamics and Van Oss' model. In this study we have applied this method on talc and talc-chlorite samples in order to obtain thermodynamic values which permit to understand surface properties useful in the industrial applications of these solids. Some talcite samples are preferentially used in specific industrial applications because they are less hydrophobic or more lamellar. This method seems to be reliable to classify the solids and predict some properties.

Keywords: microcalorimetry, surface tension, talc and talc-chlorite mixture, thermodynamics

Introduction

The industrial applications of talc and talc-chlorite powders (paper-making industry, polymer formulation, cosmetic industry...) depend mainly on surface phenomena; consequently the behaviour of these divided solids in industry processes is related to their surface free energy.

It is difficult to obtain directly the values of the surface free energy of the mineral solids. In the case of talcites, recent results of contact angle experiments have been published [1], and they have been related to surface tension parameters. But it is well known that surface tensions linked to contact angle situations are not sufficient to describe completely the surface of a solid [2].

The immersion microcalorimetry allows to obtain the enthalpy of wetting of an outgassed solid by a pure liquid which is noted the immersion enthalpy ($\Delta_{imm}H$). It has been shown that this enthalpy is related to the surface free energy of the solid γ_s [2].

In Van Oss' model [1, 3, 4], the surface tension of solids and liquids can be separated in two additive components: a Liftshitz-Van der Waals component

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which depends on dispersion forces, orientation forces and induction forces in one hand, and a Lewis acid/base component in the other hand. We have chosen three pure liquids which all surface tension components are known [1]. The immersion of an outgassed solid in this different pure liquids, used as probes, allows to estimate the surface tension of the solid.

Experimental

Microcalorimeter [5, 6]

The experimental device was a Calvet differential calorimeter (Fig. 1). The cell is filled with the liquid studied ($=15$ cm^3). The solid sample is placed, after thermal treatment (the same as for a BET analysis), in a glass bulb under vacuum. The bulb is closed by a brittle tail.

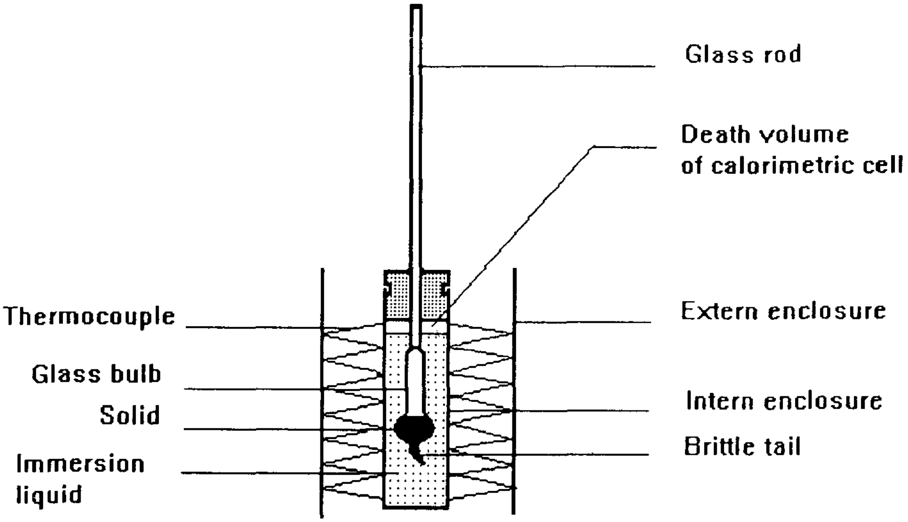

Fig. 1 Tian-Calvet microcalorimeter

The glass bulb is then placed in the calorimetric cell, and the insulation of the cell is maintained by a ring seal. When the thermic equilibrium is obtained, the brittle tail is broken, and the liquid comes into the bulb. The heat furnished by the tail break is statistically calculated, after some blank experiments, and subtracted from the real experiment. The other terms measured during an immersion experiment are: the enthalpy of liquefaction of the vapour previously filling the bulk, and the enthalpy of vaporisation of the saturated vapour which has to fill the volume liberated by the lowering of the liquid level. These terms have been measured performing the experiment with an empty bulb, and have been shown to be in agreement with standard literature values. The different sources of error in the experiments of immersion calorimetry have been detailed elsewhere [5, 6]. All the experiments have been confirmed three times. The values reported below are mean values. The accuracy of calorimetry is better than 3%. All the experiments were performed at 293 K.

Samples

Solids

In this study we have tried to estimate the surface tension of six talc and talc-chlorite mixtures. The specificities of the samples are noted in Table 1.

Table 1 Specific areas (*S.S.*) are estimated by the volumetric technique of adsorption of nitrogen (16.2 Å^2) at 77 K and application of BET theory [7]

Samples	% talc	% chlorite	*S.S.* / m^2·g^{-1}
1	97.0	1.0	6.5
2	97.5	0.0	18.5
3	93.5	5.0	1.9
4	40.0	58.0	2.5
5	94.5	2.5	3.0
6	89.5	7.5	11.0

Table 2 Characteristics of immersion liquids

Liquid	Density	Purity / %	γ_l^{LW} / mJ·m^{-2}	γ_l^+ / mJ·m^{-2}	γ_l^- / mJ·m^{-2}
Heptane	0.6838	99.0	20.4	0	0
Benzene	0.874	99.5	26.5	0.22	1.94
Water	1		21.5	25.5	25.5

The samples number 2 and 6 are obtained by crushing of the samples 1 and 5.

The samples number 1 and 2 are formed by a disorganized entanglement of small lamellae and the other samples are formed by regular stack of large lamellae.

The samples used have been furnished by Talc Luzenac France.

Liquids

The two organic liquids used have been furnished by SDS and Aldrich, and dried on molecular sieves. The water was desionized.

Theoretical background

Van Oss' model [1, 3, 4]

The Fowkes' model, describes the surface tension as a sum of two independent contributions: a polar and an apolar one [8, 9]. Van Oss' proposes to separate the surface tension in an apolar Liftshitz-Van der Waals component (γ^{LW}) which includes dispersions forces, orientation forces and induction forces and a polar Lewis acid/base component (γ^{AB}) [1, 3, 4]. This last component is the geometric average of an acid and a base component (noted γ^{+} and γ^{-}). All these terms are linked by the following relation:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\left((\gamma_s^{LW}\gamma_l^{LW})^{1/2} + (\gamma_s^{+}\gamma_l^{-})^{1/2} + (\gamma_s^{-}\gamma_l^{+})^{1/2}\right) \tag{1}$$

Application of Van Oss' model to immersion microcalorimetry

The immersion free enthalpy is described by the following equation [2]:

$$\Delta_{imm}G = \gamma_{sl} - \gamma_s \tag{2}$$

We can introduce immersion free enthalpy in Van Oss' Eq. (1):

$$-\Delta_{imm}G = -\gamma_l + 2\left((\gamma_s^{LW}\gamma_l^{LW})^{1/2} + (\gamma_s^{+}\gamma_l^{-})^{1/2} + (\gamma_s^{-}\gamma_l^{+})^{1/2}\right) \tag{3}$$

Immersion microcalorimetry allows to estimate immersion enthalpy. To link up this value to the Eq. (1) we have to fix a hypothesis, often applicable at room temperature in the case of liquids at first level of approximation [10]:

$$\Delta_{imm}G = \Delta_{imm}H/2 \tag{4}$$

We obtain an equation which links experimental results of immersion enthalpy to the components of surface tension of the solids and the liquids:

$$-\Delta_{imm}H/2 = -\gamma_l + 2\left((\gamma_s^{LW}\gamma_l^{LW})^{1/2} + (\gamma_s^{+}\gamma_l^{-})^{1/2} + (\gamma_s^{-}\gamma_l^{+})^{1/2}\right) \tag{5}$$

We have used three immersion liquids: heptane (apolar), benzene and water (polar).

For a linear alkane like heptane, Liftshitz-Van der Waals component is equal to surface tension of the liquid. The other components are equal to zero. The components of water are estimated by Van Oss [1] and we have calculated the benzene components starting from the water/benzene interfacial tension, at room temperature.

Discussion

Firstly we have realised the calorimetric experiment in an apolar liquid, defined only by the Liftshitz-Van der Waals component. Hence using Eq. (5), we obtain the Liftshitz-Van der Waals component of the solid. With the two other polar liquids, we obtain two equations with two unknown values (γ_s^+, γ_s^-). It is hence possible to obtain all the components of the surface tension of the solid. They are reported in Table 3.

Table 3 The immersion enthalpy, the surface tension components of the solids and surface tension of the solids are in mJ/m^2

Solid	$\Delta_{imm}H$			γ_s^{LW}	γ_s^+	γ_s^-	γ_s
	heptane	benzene	water				
1	193.0	240.5	473.0	167.5	2.3	408.7	228.8
2	155.5	170.8	233.9	118.1	14.2	157.5	212.7
3	301.9	385.0	321.1	359.8	114.3	25.4	467.6
4	348.4	541.9	735.2	464.1	880.3	34.4	812.1
5	194.0	334.0	311.2	168.9	767.8	291.1	1114.4
6	110.4	159.2	230.4	70.0	35.83	20.4	124.1

The surface tension is a combination of these components [1, 3, 4]:

$$\gamma_s = \gamma_s^{LW} + 2(\gamma_s^+ \gamma_s^-)^{1/2} \tag{6}$$

Generally we obtain large values for solids which are expected to be hydrophobic. In fact these values are similar to those obtained in the case of clays [11] or oxides [10]. These results are very different from Van Oss' results concerning talc, but it must be remembered that values obtained by contact angle techniques are solid-vapour surface tension. Hence there is a difference between immersion and contact angle results, related to vapour adsorption [2].

The sample 4 (58% of chlorite) has a great value of surface tension, expected to be explained by the presence of more polar groups (hydroxyl) on the basal surface.

When the sample is crushed, the surface tension decreases. It is impossible to explain this phenomena because we do not know the alteration induced by the crushing on the basal/lateral surface ratio of talc.

The sample 1 formed by a disorganized entanglement of small lamellae has a surface tension lower than the samples 3 and 5, formed by a regular stack of large lamellae.

Van Oss argued that the hydrophobicity of the talc under atmospheric pressure is induced by a weak value of Lewis base component [7], generally expected for all the talcites; we can confirm this point on the samples 3, 4, 5 and 6. But the results of the samples 1 and 2 are not in agreement with Van Oss' arguments. It must be noted that these samples are formed by disorganized entanglements of small lamellae and are less hydrophobic.

Conclusions

The surface tension component values allow to understand some properties of talc and talc-chlorite mixtures. The immersion microcalorimetry thermodynamics associated with the Van Oss' model seems to be a reliable method to estimate the surface tension of high energy solids.

The approximation concerning $\Delta_{\mathrm{imm}}G$ can be removed, by temperature studies or by adsorption isotherms measurements. It is hence possible to obtain, with this method, values of surface tension of mineral solids.

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Zusammenfassung — Durch Kombination der Thermodynamik der Eintauchmikrokalorimetrie mit dem Van Oss'schen Modell ist eine Schätzung der Oberflächenspannung von Hochenergie-Feststoffen möglich. Vorliegend wurde diese Methode an Talk- und Talkchloritproben zur Gewinnung von thermodynamischen Werten angewendet, die uns das Verständnis von Oberflächeneigenschaften erlauben, was bei der industriellen Anwendung dieser Feststoffe nutzbringend ist. Einige Talkproben werden vorzugsweise zu speziellen industriellen Anwendungen benutzt, da sie weniger Hydrophob oder mehr lamellar sind. Diese Methode erscheint als zuverlässig zur Klassifizierung von Feststoffen und zur Vorhersage einiger Eigenschaften.