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ASSESSMENT OF THE SURFACE TENSION OF VARIOUS DIVIDED SOLIDS

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Abstract

We have attempted to calculate the surface tension of some solids using immersion calorimetry measurements along with the interfacial model of van Oss [1, 2, 3, 4].

Keywords: divided solids, immersion enthalpy, surface tension

Introduction

The surface tension of solids is an essential factor occurring in the solid-liquid and solid-gas interfacial phenomena. Knowing this parameter is very important in the perspective of a better understanding of interfacial processes.

Unfortunately, at the moment, it is extremely difficult to measure directly the surface tension of solid phases. In order to overcome this shortcomings, "indirect" methods are often used. These ones are numerous: we can mention the inverse gas chromatography, the contact angle measurements (with 1 or 2 liquids), the solid-gas adsorption isotherm, the adsorption calorimetry and the immersion calorimetry.

Experimental

Solids

The immersion experiments have been performed on several divided solids: silica, quartz, kaolinites and illites.

The values of the specific surface areas are listed in Table 1. They have been determined by nitrogen adsorption at 77 K and application of the B.E.T. method, with an area of 16.2 Å^2 for nitrogen molecule.

– the silica is a precipitated silica SPHEROSIL X015 LS supplied by Rhône-Poulenc. M.E.B. photos carried out on a Cambridge microscope show

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that this silica is made up of spheres with a size between 100 and 200 μm, which are themselves composed of smaller spheres aggregates (about 25 μm).

– the quartz employed is a crushed quartz supplied by SIFRACO, referenced C 800. The particle size lies between 1 and 10 μm. This solid underwent the following treatments:

- separation of the granulometric brackets by sieving;
- washing with distilled water during several days and storage in water sheltered from air;
- washing with hot chlorhydric acid (2N) during a few hours, then rinsing with distiled water until complete removal of Cl^- ions in the washing water and storage sheltered from air.

– 3 kaolinites and 3 illites have been studied:

- the kaolinite from Ploemeur (kaolinite 1) is a hydrothermal, well crystallized, kaolinite (formed by the precipitation of ions in solution) and almost pure;
- the kaolinite from Charentes (kaolinite 2) is a sedimentary and inherited kaolinite (obtained by alteration and transport);
- the kaolinite from Provins (kaolinite 3) is a sedimentary and disorganized kaolinite coming from the alteration of chalk and containing 8% of quartz;
- the illite from Vosges (illite 1) is a detrimental illite (obtained by transformation and decomposition of little micas) containing quartz and feldspaths;
- the illite from Hongrie (illite 2) is a hydrothermal and interstratified illite 85% illite–15% beidellite;
- the illite from Brives-Charensac (illite 3) is generated by transformation (ions fixation) and is ferro-magnesian;

Table 1 Values of the specific surface areas of the studied solids

	Specific surface area / $m^2 \cdot g^{-1}$
silica	22
quartz	6
kaolinite 1	15
kaolinite 2	20
kaolinite 3	47
illite 1	30
illite 2	37
illite 3	127

Liquids

The liquids which have been used in the immersion experiments are water, heptane and benzene. The choice of these solvents is linked to the interfacial model employed. More explanations are given in the theretical part.

The heptane has been supplied by SDS. Its purity is 99%. The benzene has been supplied by FLUKA. Its purity is over 99.5%. Before running the experiments, these organic solvents have been dried with molecular sieve in order to eliminate remaining water which could be present.

Technique

Before running the immersion calorimetry experiment, it is necessary to make a standardisation of the solid surface. That is the reason why the solid sample, put into a 2 cm^3 glass bulb with a breakable tip at the bottom, is treated at 423K under a 10^{-2} torr vacuum during 5 hours.

The aim of this operation is to evacuate the physisorbed water and the organic or mineral impurities which are adsorbed during the preparation and preservation of the solids. If not, these substances could have a significant influence on the experimental values of the immersion enthalpy.

After this thermal treatment, the bulb holding the solid is sealed and fixed to a glass rod which will allow us to break the bulb tip from the outside of the calorimeter.

Then, the bulb is introduced in the calorimetric cell containing the immersion liquid (5 cm^3). The whole thing is set inside the calorimeter. In this way, we make a closed system whose airtightness is assured by two seals.

When the thermal equilibrium is obtained in the calorimeter, the fragile tip is mechanically broken by pushing down the glass rod.

As the solid inside the bulb is under vacuum, the liquid gets into the bulb and brings about the immersion of the solid.

The signal obtained is recorded on a computer and, via the integration of the peak and the calibration of the calorimeter, we get the experimental value for the immersion of the solid in the liquid.

For our works, we have used a conduction calorimeter (TIAN-CALVET type) which characteristics have been described before [5].

Theoretical description

Model

As stressed before, if we want to calculate the surface tension of a solid via immersion experiments, it is necessary to describe the interactions occuring at the solid-liquid interface. Among the different proposed models, we have used the van Oss one; this description is based on a clear-cut distinction between apolar Lifshitz–van der Waals interactions, comprising the dispersion, orientation and induction interactions on the one hand and polar interactions on the other hand, designated in the largest sense as Lewis acid/base or electron donor/electron acceptor interactions.

This theory allows to put the solid-liquid interfacial tension under the following form:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2} - 2(\gamma_S^{+}\gamma_L^{-})^{1/2} - 2(\gamma_S^{-}\gamma_L^{+})^{1/2} \tag{1}$$

where:

γ_i^{LW} is the "Lifshitz–van der Waals" component of the surface tension of the phase i.

γ_i^{+} is the "acid" component (electron acceptor effect) of the surface tension of the phase i.

γ_i^{-} is the "basic" component (electron donor effect) of the surface tension of the phase i.

Application to the immersion calorimetry

From a thermodynamic point of view, the change in the free enthalpy during the immersion process can be written as:

$$\Delta_{imm} G = \gamma_{SL} - \gamma_S \tag{2}$$

If we apply the van Oss equation concerning the solid-liquid interfacial tension, we obtain:

$$-\Delta_{imm} G = -\gamma_L + 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^{+}\gamma_L^{-})^{1/2} + (\gamma_S^{-}\gamma_L^{+})^{1/2}] \tag{3}$$

Furthermore, the thermodynamic value measured by the immersion experiments is the enthalphy of immersion $\Delta_{imm} H$. The relation between $\Delta_{imm} H$ and $\Delta_{imm} G$ is:

$$\Delta_{imm} H = \Delta_{imm} G - T\frac{\partial(\Delta_{imm} G)}{\partial T} \tag{4}$$

We see that if an assumption is made on the entropic contribution of the immersion, $\Delta_{imm} G$ can be known via $\Delta_{imm} H$. Immersion experiments carried out in appropriate solvents permit to calculate the surface tension components of the solid and then the total surface tension of the solid.

The following method is used:

1 – Immersion in an alcane (e.g. heptane)

$$\gamma_L^+ = \gamma_L^- = 0;\ \ \gamma_L = \gamma_L^{LW}$$

hence:

$$-\Delta_{imm} G = -\gamma_L + 2(\gamma_S^{LW}\gamma_L^{LW})^{1/2}$$

and:

$$\gamma_S^{LW} = \left[\frac{-\Delta_{imm} G + \gamma_L}{2(\gamma_L^{LW})^{1/2}}\right]^2 \tag{5}$$

2 – Immersion in two solvents with non-zero values of surface tension components (e.g. water, benzene)

$$\gamma_L^{LW} \neq 0;\ \gamma_L^+ \neq 0\ ;\gamma_L^- \neq 0;$$

thus:

$$-\Delta_{imm} G = -\gamma_L + 2[(\gamma_S^{LW}\gamma_L^{LW})^{1/2} + (\gamma_S^+\gamma_L^-)^{1/2} + (\gamma_S^-\gamma_L^+)^{1/2}]$$

We obtain two equations with two unknowns and the resolution of this system allows us to know γ_S^+ and γ_S^-.

The total surface tension of the solid is: $\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$ where γ_S^{AB} represents the acid/base component of the solid surface tension. This parameter is expressed as the geometric mean of γ_S^+ and γ_S^-.

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

Results and discussion

- The immersion experiments have been run at 301 K
- We assume that $\Delta_{imm} G$ represents half of $\Delta_{imm} H$ at this temperature
- The values of the γ^+, γ^- and γ^{LW} components of the liquids are reported in Table 2
- The various results are presented in Table 3 and 4

At first, it is very important to note that the values of the surface tension components and subsequently the total surface tensions obtained are only estimations because they depend on the assumption that we put forward about the entropic contribution during the immersion process. In the present state of our work, we chose a simplifying hypothesis, for lack of enough precise experimental data. Moreover, another limit to the reliability of these "absolute" values is due to the van Oss model itself because the values of γ_L^+ and γ_L^- for water are assumed by van Oss to be equal, and the calculations of γ_L^+ and γ_L^- for other solvents are made from this assumption. But there is no experimental or theoretical evidence showing that this hypothesis is true. Thus, we do not consider our re-

Table 2 Values of the surface tension components of the solvents

Compounds	γ_L^{LW}/mJ·m^{-2}	γ_L^- / mJ·m^{-2}	γ_L^+ / mJ·m^{-2}	γ_L / mJ·m^{-2}
heptane	19.6	0	0	19.6
benzene	26.5	1.94	0.22	27.8
water	21.5	25	25	71.5

Table 3 Values of the enthalpy of immersion of the solids in the different solvents

$-\Delta_{imm}H$/mJ·m^{-2}	heptane	benzene	water
silica	78	122	365
quartz	90	136	332
kaolinite 1	98	160	426
kaolinite 2	104	176	422
kaolinite 3	86	150	410
illite 1	90	166	443
illite 2	103	192	520
illite 3	83	123	330

Table 4 Solids surface tension components and total solids surface tension

Compounds	γ_S^{LW}/mJ·m^{-2}	γ_S^+ / mJ·m^{-2}	γ_S^- / mJ·m^{-2}	γ_S / mJ·m^{-2}
silica	44	1.9	319	93
quartz	53	6.9	206	128
kaolinite 1	60	19	286	207
kaolinite 2	65	52	184	260
kaolinite 3	50	31	242	222
illite 1	53	63	213	285
illite 2	64	87	268	370
illite 3	48	0.9	265	79

sults as the real values of the solids surface tensions, but they allow us to make a comparative study of the solids.

In this way, we can observe that all the studied solids have a fundamentally donor behaviour: whatever is the solid, the γ_S^- component is always considerably greater than the other components. If we go deeper, it seems that the kaolinites belong to a quite homogeneous family while the illites can give some distinct results according to their origins. For example, we can see that the γ_S^- components for this family are in the same range but on the other side, it is evident that the γ_S^+ components are so different that the illite 3 appears to be closer to the silica than to the other illites, from the surface tension point of view.

Those first results show that these calculations about the solids surface tension are efficient in the characterisation and the classification of the solids. The immersion calorimetry is a simple experimental way for getting "relative" values of these tensions; moreover, it is certainly the most approprite and the most reliable technique for the study of high-energy divided solids. The coupling with a method permitting the estimation of $\Delta_{imm} G$ and suppressing the error linked to the hypothesis that we had to use will allow to reach real values for the solids surface tension. This is in that way we are going to work soon.

References

1 C. J. van Oss, L. Ju, M. K. Chaudhury and R.J. Good, J. Colloid Interface Sci., 128 (1989) 313.
2 C.J. van Oss, R. J. Good and M. K. Chaudhury, Langmuir, 4 (1988) 884.
3 C.J. van Oss, R.F. Giese Jr and R. J. Good, Langmuir, 6 (1990) 1711.
4 R. F. Giese, P. M. Costanzo and C. J. van Oss, Phys. Chem. Minerals, 17 (1991) 611.
5 S. Partyka, F. Rouquerol and J. Rouquerol, J. Colloid Interface Sci., 68 (1979) 21.

Zusammenfassung — Unter Berücksichtigung des van Oss'schen Grenzflächenmodelles [1, 2, 3, 4] wurde mittels Immersionskalorimetriemessungen ein Versuch zur Berechnung der Oberflächenspannung von Feststoffen unternommen.