JOURNAL OF MATERIALS SCIENCE **22** (1987) 4011–4014

Studies of the surface free energy of sulphur

P. STASZCZUK
Department of Physical Chemistry, Institute of Chemistry, M. Curie-Sklodowska University, M. Curie-Sklodowska Sq. 3, 20-031 Lublin, Poland

From adsorption isotherms the water film pressure values on a sulphur surface were determined. An interpretation of the changes with film thickness and the value of the work of wetting processes is proposed. It is concluded that the characteristic film pressure values determined correspond to the work of immersional, adhesional and immersional–cohesional wetting. On the basis of water film pressure values, values of the dispersion component of sulphur surface free energy were determined.

1. Introduction

A very important problem, which has caused more interest recently, is knowledge of the process of wettability of minerals. Mineral–water interaction is the decisive factor for various processes, for example the infiltration of rain water through soil, destruction of roads and buildings, exploitation of crude oil from bore holes, etc. Water is of essential importance for the rheological properties of mineral–water suspensions. The effective viscosity, plasticity, thixotropy, load-bearing capacity and other mechanical properties of suspensions and sediments depend on the water content [1].

The phenomenon of surface wetting can be described thermodynamically when the surface free energy is known. In a previous paper [2] the properties of water films on hydrophobic sulphur surface were reported. On the basis of water vapour adsorption isotherms at 20 and 30° C, thermodynamic functions such as the isosteric heat of adsorption, adsorption free enthalpy, entropy and activation energy were calculated. On the basis of these values it has been found that water film properties change when the amount of water adsorbed on a sulphur surface changes. This results from the interaction between sulphur and water molecules situated in the neighbourhood of this surface (dispersion interactions). In order to obtain a more complete picture of hydrophobic mineral–water interactions in thermodynamic terms, the water film pressure and surface free energy of the solid must be known [3].

The surface free energy of sulphur, on the basis of contact angle and zeta potential measurements, has been determined [4, 5]. In the present paper a method of calculating water film pressure and surface free energy of sulphur from water vapour adsorption data [6–8] is presented.

2. Theory

2.1. Surface film pressure and surface free energies

Thermodynamically, the surface film pressure and surface free energies are defined and related as [3, 8]

$$-\Pi = \left(\frac{\mathrm{d}G}{\mathrm{d}A}\right)_{p,T,n} = \gamma_s^g - \gamma_{SF} \qquad (1)$$

where G is the Gibbs free energy of the adsorbed film, A is the specific surface area of the mineral per gram, p is the equilibrium pressure of the adsorbate, n is the quantity of moles of a gas or vapour adsorbed on to the solid at a temperature T, γ_s^g is the surface free energy of the solid and γ_{SF} is the surface free energy of solid covered with a film of the liquid.

The surface film pressure, Π, may also be obtained from the Gibbs adsorption isotherm equation where it has been shown that

$$\mathrm{d}\Pi = RT\frac{a}{A}\,\mathrm{d}(\ln p) \qquad (2)$$

where a is the amount of adsorbed of gas or vapour.

The film pressure at a given temperature can be evaluated from Equation 2 by integration [6–9]:

$$\Pi = \frac{RT}{A}\int_0^p a\,\mathrm{d}(\ln p) \qquad (3)$$

In calculating the surface film pressure in $\ln p$ is plotted against the amount of liquid absorbed on the surface at a constant temperature T. According to Equation 3, the area under the curve gives the surface film pressure.

2.2. Surface tension or interfacial tension

The mechanical properties of an interfacial layer between two fluid phases can be expressed in terms of those of a geometrical surface of uniform tension called the surface of tension, whose location is dependent on the distribution of the stress tensor within the interfacial layer [10]. The tension acting in the surface of tension is called the surface tension or interfacial tension and is expressed in terms of force per unit length. The surface tension between two bulk phases 1 and 2 is written γ_{12} or σ_{12}, and that between Phase 1 and its equilibrium vapour or a dilute gas phase γ_1 or σ_1.

Surface tension may be written as a sum of polar and dispersion components of surface free energy [11]:

$$\gamma = \gamma^p + \gamma^d \tag{4}$$

The solid–liquid interfacial tension is defined as [11–13]

$$\gamma_{SL} = \gamma_S^g + \gamma_L^g - 2(\gamma_S^d\gamma_L^d)^{1/2} - 2(\gamma_S^p\gamma_L^p)^{1/2} \tag{5}$$

where γ_S^g is the surface tension of the solid, γ_L^g is the surface tension of the liquid, γ_S^d, γ_L^d are the dispersion components of solid and liquid surface free energy, and γ_S^p, γ_L^p are the polar components of solid and liquid surface free energy, respectively.

2.3. Wetting

The wetting process may be characterized by spreading wetting, immersional wetting and adhesional wetting [10].

2.3.1. Spreading wetting

This is a process in which a drop of liquid spreads over a solid. A liquid L when placed on the surface of solid S, both previously in contact with a fluid phase g, will tend to spread on the surface if the spreading tension σ_{spr} defined by

$$\sigma_{spr} = \gamma_S^g - \gamma_L^g - \gamma_{SL} = W_{spr} \tag{6}$$

is positive. σ_{spr} is also equal to the work of spreading per unit area (W_{spr}).

Substituting an appropriate value for γ_{SL} (Equation 5) in Equation 4, the spreading wetting work can be expressed in the form [6–8, 14]

$$W_S = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} - 2\gamma_L^g \tag{7}$$

2.3.2. Immersional wetting

This is a process in which a solid S is covered with a liquid L, both of which were initially in contact with a gas g, without changing the area of the L–g interface. The work of immersional wetting per unit area, or wetting tension W_I, is the work done on the system when the process of immersional wetting involving unit area of phase S is carried out reversibly:

$$W_I = \gamma_L^g - \gamma_{SL} \tag{8}$$

and substituting Equation 5 for γ_{SL} we obtain

$$W_I = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} - \gamma_L^g \tag{9}$$

2.3.3. Adhesional wetting

This is a process in which an adhesional joint is formed between two phases. The work of adhesion per unit area W_A is the work done on forming an interface of unit area which is separated reversibly to form unit areas of each of the L–g and S–g interfaces. The work of adhesion is defined by

$$W_A = \gamma_L^g + \gamma_S^g - \gamma_{SL} \tag{10}$$

and substituting Equation 5 for γ_{SL} we obtain [11]

$$W_A = 2(\gamma_S^d\gamma_L^d)^{1/2} + w(\gamma_S^p\gamma_L^p)^{1/2} \tag{11}$$

2.3.4. Work of cohesion

The work of cohesion per unit area W_C of a single pure liquid L is the work done on the system when a column of L of unit area is split reversibly, normal to the axis of area in contact with the equilibrium gas phase:

$$W_C = 2\gamma_L^g \tag{12}$$

2.3.5. Immersional–cohesional wetting

This is defined by the expression [15]

$$W_{IC} = W_A + \gamma_L^g = W_I + 2\gamma_L^g = W_I + W_C \tag{13}$$

or

$$W_{IC} = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} + \gamma_L^g \tag{14}$$

Investigations concerning the silica gell–water system [15] suggest that the immersional–cohesional wetting process is related to energy changes in the water molecules, which in turn are influenced by the solid surface properties.

2.3.6. maximal surface film pressure

The maximal Π value (Π_{max}) corresponds to the work of formation on the solid surface of liquid layers possessing the properties of the bulk phase (adsorption equilibrium, maximum value of the adsorbed liquid) [6, 15]:

$$W_{max} = \Pi_{max} = W_A + 2\gamma_L^g = W_A + W_C = W_I + 3\gamma_L^g \tag{15}$$

or

$$W_{max} = 2(\gamma_S^d\gamma_L^d)^{1/2} + 2(\gamma_S^p\gamma_L^p)^{1/2} + 2\gamma_L^g \tag{16}$$

Investigations concerning water film pressure on marble [6], silica gel [15], quartz [7, 8] and n-heptane film pressure on a sulphur surface [5] suggest that suitable wetting work for the adsorption of vapours is related to characteristic inflection points on the curve representing the relationship between Π and film thickness. It has been concluded that the characteristic film pressure values determined correspond to the work of spreading, immersional, adhesional, immersional–cohesional and total wetting.

In the case of the sulphur–water system $\gamma_S^p = 0$. Thus Equations 7, 9, 11, 14 and 16 may be written in the form

$$W_S = \Pi_S = 2(\gamma_S^d\gamma_W^d)^{1/2} - 2\gamma_W^g \tag{17}$$

$$W_I = \Pi_I = 2(\gamma_S^d\gamma_W^d)^{1/2} - \gamma_W^g \tag{18}$$

$$W_A = \Pi_A = 2(\gamma_S^d\gamma_W^d)^{1/2} \tag{19}$$

$$W_{IC} = \Pi_{IC} = 2(\gamma_S^d\gamma_W^d)^{1/2} + \gamma_W^g \tag{20}$$

$$W_{max} = \Pi_{max} = 2(\gamma_S^d\gamma_W^d)^{1/2} + 2\gamma_W^g \tag{21}$$

where $\gamma_W^d = 21.8\,\mathrm{mJ\,m^{-2}}$ is the dispersion component of water surface free energy, γ_S^d is the dispersion component of sulphur surface free energy and $\gamma_W^g = 72.8\,\mathrm{mJ\,m^{-2}}$ is the surface tension of water.

The calculations proposed in this paper has been supported thermodynamically in the paper dealing with the marble–water system [6] and arises from separate and independent thermal analysis and chromatographic experiments with silica gel and quartz systems [7, 8, 15].

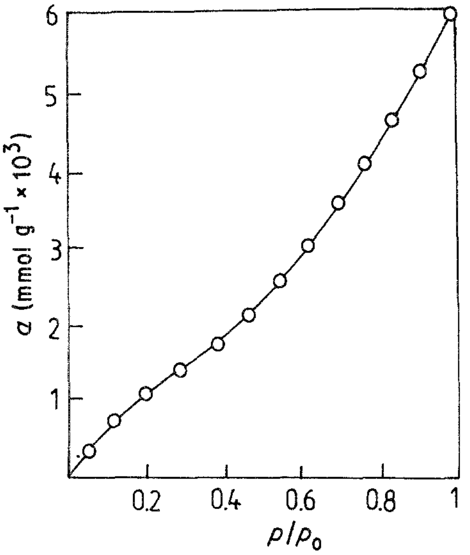

Figure 1 Isotherm of adsorption of water vapour on sulphur at 20° C.

3. Experimental techniques

Measurements of water vapour adsorption at 20° C were carried out by the method described in detail elsewhere [7, 16]. The reproducibility of the data in this method is ca. 5%. For these studies, crystalline sulphur of analytical grade (99.98%) and a grain size of 0.25 to 0.3 mm was used. The sulphur was dried in a nitrogen atmosphere at 60° C for 12 h and stored in a dessicator filled with a 0.5 nm molecular sieve.

The specific (BET) surface area of sulphur samples was $0.057\,\mathrm{m^2\,g^{-1}}$, determined by the gas chromatography method [2].

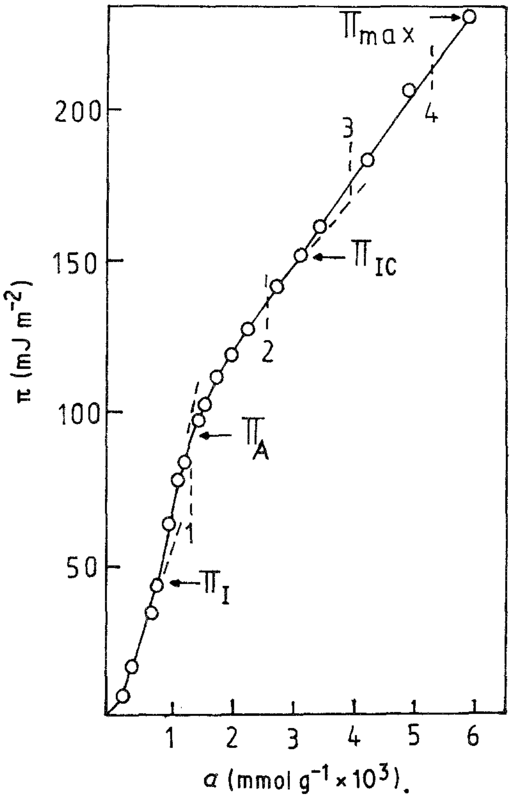

Figure 2 Changes of water film pressure on sulphur in relation to the amount of adsorbed water.

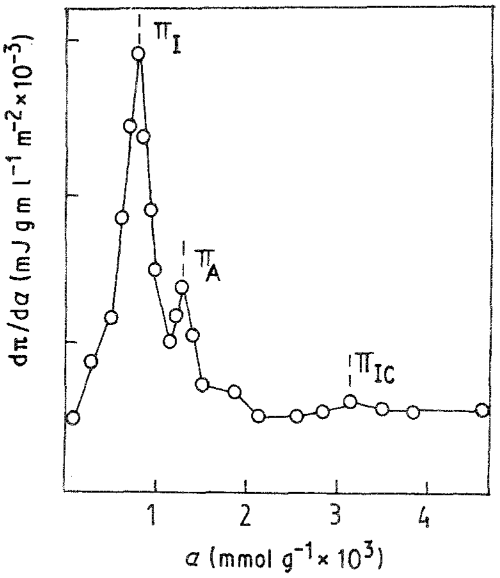

Figure 3 Graphical differention of the curve from Fig. 2. Changes $\mathrm{d}\Pi/\mathrm{d}a$ as a function of the amount of adsorbed water.

4. Results and discussion

Fig. 1 shows an adsorption isotherm obtained for water vapour at 20° C on the surface of sulphur. From this figure it appears that the maximal adsorption of water is $6 \times 10^{-3}\,\mathrm{mmol\,g^{-1}}$, i.e. 4.5 statistical water monolayers (assuming a surface area of $0.0706\,\mathrm{nm^2}$ for a water molecule). The isotherm obtained was used to determine the water film pressure Π as a function of water adsorption by graphical integration of the isotherm. This pressure can be calculated from the equation of Bangham and Rozouk, based on Gibb's equation [9], using Equation 3.

The Π changes obtained are presented in Fig. 2 as a function of the amount of adsorbed water. The calculated monolayers of water adsorbed are denoted on the curve. Fig. 2 shows that the changes of Π values with a values are characterized by three inflection points. A graphical differention of the curve in Fig. 2, to precisely define the inflection points, has been made. The obtained $\mathrm{d}\Pi/\mathrm{d}a$ changes are presented in Fig. 3 as a function of the amount of adsorbed water.

From Fig. 3 it is seen that the inflection points correspond to water adsorption values of 0.875×10^{-3}, 1.35×10^{-3} and $3.15 \times 10^{-3}\,\mathrm{mmol\,g^{-1}}$ and to film pressures of 45, 93 and $151\,\mathrm{mJ\,m^{-2}}$, respectively. According to earlier papers [5–8, 15] the above water film pressures correspond to immersional, adhesional and immersional–cohesional wetting, respectively.

Substituting appropriate values in Equations 18, 19, 20 and 21, i.e. $\Pi_\mathrm{I} = 45\,\mathrm{mJ\,m^{-2}}$, $\Pi_\mathrm{A} = 93\,\mathrm{mJ\,m^{-2}}$, $\Pi_\mathrm{IC} = 151\,\mathrm{mJ\,m^2}$ and $\Pi_\mathrm{max} = 231\,\mathrm{mJ\,m^{-2}}$, the values of the dispersion components of sulphur surface free energy, $\gamma_\mathrm{S}^\mathrm{d}$, have been calculated which are 159.1, 99.2, 70.1 and $83.6\,\mathrm{mJ\,m^{-2}}$, respectively. The average $\gamma_\mathrm{S}^\mathrm{d}$ value calculated from Equations 18 to 21 is $103.0\,\mathrm{mJ\,m^{-2}}$. This is between the values presented in the literature: $97.6\,\mathrm{mJ\,m^{-2}}$ [5] and $124.15\,\mathrm{mJ\,m^{-2}}$ [4].

From the calculations cited above and from Equation 21 it appears that water adsorption on a sulphur surface continues as long as a water adsorption layer possessing the properties of bulk water (vapour condensation) is formed in the last adsorbed layers. This amount of water is adsorbed by dispersion forces at lattice defects, where induced dipoles exist [2]. The mode of adsorption is clusters of water molecules around these areas [17].

The inflection related to spreading wetting observed in the cases of marble–water [6], silica gel–water [15] and quartz [7, 8] systems is absent in this case (Fig. 2). This results from the hydrophobic properties of the sulphur surface. Spreading wetting on a sulphur surface does not exist. This results from the negative spreading coefficient, the value of which for the sulphur–water system is calculated from the Harkins equation [9]:

$$S_{\mathrm{W/S}} = \gamma_{\mathrm{S}} - \gamma_{\mathrm{SW}} - \gamma_{\mathrm{W}} \qquad (22)$$

The appropriate spreading value W_{S} becomes negative ($-50.8\,\mathrm{mJ\,m^{-2}}$). This value was calculated by geometric means of dispersion interactions, using Equation 17 with $\gamma_{\mathrm{S}}^{\mathrm{d}} = 103\,\mathrm{mJ\,m^{-2}}$.

References

1. F. R. EIRICH, "Rheology, Theory and Applications" (Academic, New York, 1960) p. 249.
2. P. STASZCZUK, *Powder Technol.* **32** (1982) 211.
3. M. AFZAL and J. AHMED, *Coll. Polym.* **253** (1975) 635.
4. B. JAŃCZUK, Habilitation thesis, UMCS, Lublin (1984).
5. E. CHIBOWSKI and A. WAKSMUNDZKI, *J. Coll. Interface Sci.* **66** (1978) 213.
6. B. JAŃCZUK, E. CHIBOWSKI and P. STASZCZUK, *ibid.* **96** (1983) 1.
7. P. STASZCZUK, B. JAŃCZUK and E. CHIBOWSKI, *Mater. Chemi. Phys.* **12** (1985) 469.
8. P. STASZCZUK, *Chromatographia* **20** (1985) 724.
9. A. C. ZETTLEMOYER, in "Hydrophobic Surfaces", edited by F. M. Fowkes (Academic, New York, 1969) p. 1.
10. "Manual of Symbols and Terminology for Physicochemical Quantities and Units", Appendix II, Part I. 31–4 (International Union of Pure and Applied Chemistry, Butterworths, London, 1972) p. 579.
11. F. M. FOWKES, in "Hydrophobic Surfaces", edited by F. M. Fowkes (Academic, New York, 1969) p. 151.
12. *Idem, J. Phys. Chem.* **67** (1963) 2538.
13. *Idem, J. Adhesion* **4** (1972) 155.
14. B. JAŃCZUK, T. BIAŁOPIOTROWICZ, *J. Mater. Sci.* **21** (1986) 1151.
15. P. STASZCZUK, *J. Thermal Anal.* **29** (1984) 217.
16. A. WAKSMUNDZKI and P. STASZCZUK, *Zesz. Probl. Post. Nauk Roln.* **220** (1983) 459 (in English).
17. M. J. SPARNAAY, "The Electrical Double Layer" (Pergamon, Oxford, 1972) p. 1.

Received 23 December 1986
and accepted 18 February 1987