The water–silicas interfacial interaction energies

Ahmed K. Helmy [a,*], Silvia G. de Bussetti [a], Eladio A. Ferreiro [a,b]

[a] *Universidad Nacional del Sur, B8000 Bahía Blanca, Argentina*
[b] *Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Departamento de Agronomía, U.N.S., B8000 Bahía Blanca, Argentina*

Abstract

The water–silicas interfacial interaction energies were calculated for samples of quartz, silicas and silicas outgassed at high temperatures using own and published data of the spreading pressure of water, its surface tension, its contact angle and using formulas obtained by the combination of the Young equation with a general equation of pair interaction. The values obtained for 18 different samples were in the range 7.80–6.92 kJ mol^{-1}. Lower values of energies are for samples that contain relatively less amounts of water at $P/P_0 = 0.25$ and are characterized also by relatively low values of surface pressures.
© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Different energies may be evaluated when water and quartz coexist as a stable system. Under consideration in the present article is the energy of the solid–liquid interfacial interaction in the system described by the Young equation where three surfaces of discontinuity between three homogeneous masses (vapour, liquid and solid) meet along a line. This energy, therefore is different from those of immersion, adsorption or solution. Though these energies are different, they are quantitatively related. In contrast to the energies of immersion and of adsorption of water by silicas, the water–silicas interfacial energies have not been evaluated. Hence, in the following is reported a study aimed at the evaluation of the water–silicas interfacial interaction energies for samples of quartz, silicas and silicas outgassed at high temperatures.

2. Experimental data

2.1. Materials

Samples of quartz were from Lemit (USA) (Q1), of local natural quartz of Monte España, the province of San Luis (Argentina) (Q2), and of silica gel (SG) provided by Chemical Davison (USA). All with sizes smaller than 0.2 mm, a purity >98.9% and a density of 2.60–2.65 g cm^{-3}.

The specific surface areas determined by adsorption of water were: Q1 = 1.00 m^2 g^{-1}, Q2 = 2.01 m^2 g^{-1} and SG = 322.8 m^2 g^{-1}.

2.2. Water adsorption isotherm

Samples of 5.0 g of air dried (0.5% humidity) solids were placed in Pyrex glass weighing bottles (diameter = 50 mm, height = 30 mm) and were placed in vacuum desiccators with aqueous concentrations of H$_2$SO$_4$ of different P/P_0 values (0.058–0.37) and were maintained at 28 °C. When equilibrium adsorption was reached (constant weight) the quantities of water adsorbed per gram of sample were determined by weighing. The experiments were carried out in duplicates. The vapour adsorption isotherms are shown in Fig. 1.

2.3. The surface pressure (Π)

The difference between the surface tension (energy) of the clean surface and that of the vapour covered solid is defined as the spreading pressure of a quantity of vapour adsorbed on the solid. To fix a reference for Π, the quantity of vapour is taken as that adsorbed at $P/P_0 = 0.25$, when a monolayer of water

* Corresponding author. Tel.: +54 291 459 5102; fax: +54 291 459 5127.
  E-mail address: akhelmi@criba.edu.ar (A.K. Helmy).
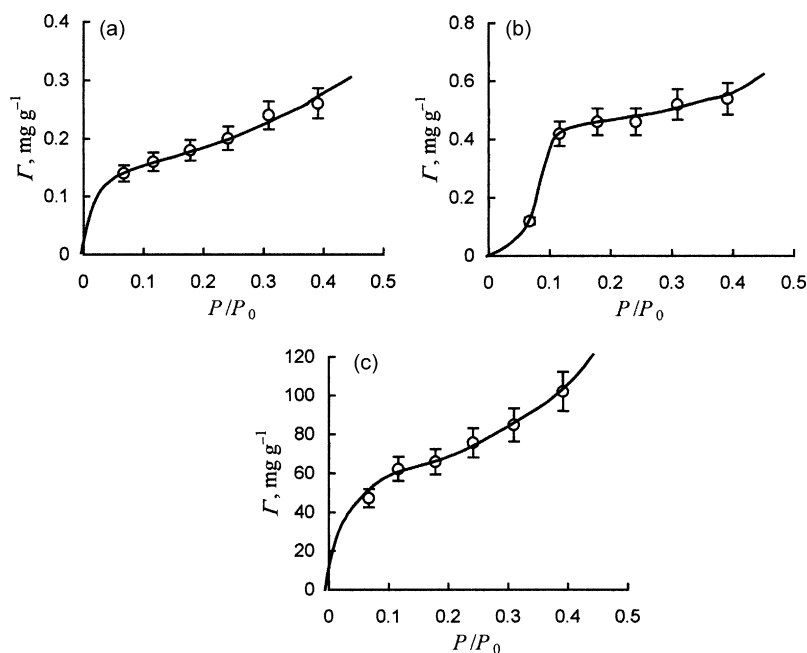
Fig. 1. Water vapor adsorption (Γ, mg g^{-1}) as a function of P/P_0 of the aqueous solutions of H_2SO_4 ($P_0 = 23.756$ Torr). The error bars are 95% confidence interval from averaging, and the line is the corresponding fit: (a) quartz 2, (b) quartz 3, and (c) silica 7. Numbers represent sample numbers in Table 1.

molecules is found on the surface (see Appendix A). Π is calculated from the Gibbs equation:

$$\Pi = \gamma_S - \gamma_{SV} = RT \int_{\ln P=0}^{\ln P_m} \Gamma \; d(\ln P), \qquad (1)$$

where P_m and P are the vapour pressure at monolayer formation and at the lowest vapour pressure and Γ is the surface density of

adsorbate. The values of Γ are determined from the water adsorption isotherm at each vapour pressure and Π is then obtained by graphical integration of the Γ versus $\ln P$ plot.

The values of Π reported in the present article include published values, values we calculated from published isotherms [1–7] as well as those determined in this laboratory for the above mentioned three samples. The Π values are given in Table 1.

Table 1
Water–silica interfacial interaction energy (γ_{SL}, ΔG), silica surface energy (γ_S) and other properties of samples of quartz, silicas and silicas outgassed at high temperatures

Sample no.	Water content (mg m^{-2})	Surface area (m^2 g^{-1})	Π (mN m^{-1})	γ_S (mN m^{-1})	γ_{SL} (mN m^{-1})	ΔG (kJ mol^{-1})	Observations
Quartz samples							
1	0.240	1.00	46.6	190.2	93.9	7.10	This work, $\theta = 47°$
2	0.240	1.00	46.6	216.0	96.6	7.27	This work
3	0.480	2.01	58.8	229.5	97.9	7.33	This work, SG
4	0.177	7.50	51.3	221.2	97.1	7.31	Whalen [18]
5	0.239	5.02	73.3	245.5	99.3	7.48	Boyd and Livingston [1]
6	0.237	5.07	110.4	285.8	102.6	7.81	Hackerman and Hall [2]
Silica samples							
7	0.239	322.8	77.9	250.4	99.8	7.52	This work
8	0.120	4.10	59.3	230.0	97.9	7.37	Muster et al. [7]
9	0.20	100	107.0	282.6	102.8	7.47	Kessaissia et al. [14]
10	0.204	104	65.0	236.3	98.5	7.42	Zettlemoyer [3]
11	0.238	164.0	29.3	196.7	94.6	7.12	Plasma processed particles [4]
12	0.185	150	86.1	259.4	100.5	7.57	PSG, Naono et al. [5]
13	0.108	358	82.4	255.4	100.2	7.54	SG, Naono et al. [5]
Silicas outgassed at high temperatures							
14	0.192	331	70.8	242.8	99.1	7.46	SG, 800 °C [5]
15	0.223	130	67.4	239.0	98.7	7.43	PSG, 800 °C [5]
16	0.036	n.d.	27.6	194.8	94.8	7.11	1000 °C, Muster et al. [7]
17	0.128	79.0	28.9	196.4	94.6	7.12	200 °C, Average of many samples [6]
18	0.075	289	8.08	172.8	91.9	6.92	1000 °C, Gel J, Baker and Sing [4]

n.d.: not determined.