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COMPARISON OF SORPTOMETRIC AND THERMOPOROMETRIC MEASUREMENTS ON POROUS GLASS AND SOME OTHERS

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Abstract

The results of surface structure investigations involving the use of thermoporometry and gas-sorptometry on porous glass, silica and a zeolite were compared. The most frequent and the mean pore width were found to be in accordance, but major differences in specific surface were observed. These two measuring methods complement each other, because with gas adsorption a dry sample is investigated, while with thermoporometry a sample immersed in a liquid is investigated. The probe molecules (nitrogen or noble gas and water or benzene, respectively) differ in size. The features of the two methods are discussed.

Keywords: adsorption, balance, gravimetry, sorption, thermoporometry

Introduction

With regard to the fractal structure [1, 2] of many dispersed and porous solids, an absolute size of the surface and its structural dimensions cannot be defined. The results of surface area and pore size determinations depend on the size of the sample used for its measurement. Therefore, it is advisable to use measuring methods which are close to the intended application and sample molecules similar in size to the molecules which in practice will come into contact with the surface. From the various analytical possibilities, in the following we compare gas-sorptometry and thermoporometry.

Both sorptometry and thermoporometry are based on the influence of the surface of the solid sample on the phase transitions of the adjoining medium. In the vicinity of a solid surface, the situation of an equilibrium state between different phases of an adjacent medium is disrupted. Since this medium is either attracted to or repelled from the sample surface, a perpendicular interface is bent and a contact angle can be observed. In small capillaries or pores, the surface of a liquid forms a meniscus, the radius of which is equal to the pore radius, corrected by the thickness of the remaining adsorbed layer. According to the Kelvin equation, the saturation equilibrium pressure above a curved liquid surface is shifted towards lower values, to an extent proportional to the mean curvature. This effect can therefore be applied to establish

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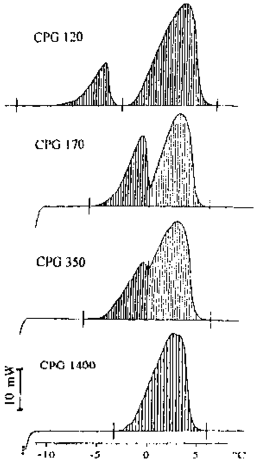
the pore size distribution. From the pore size distribution, and additionally from the measured surface coverage, the specific surface area can be derived. For this purpose, the adsorption isotherm of nitrogen or a noble gas at or near the boiling temperature is measured by means of volumetric or gravimetric techniques [3, 4].

Thermoporometry [5] makes use of the triple point depression within the porous matrix of a liquid in contact with its solid phase. This effect also depends on the curvature of the interface, and hence on the pore radius. The sample is immersed in water or benzene and the amount of liquid frozen is measured as a function of decreasing temperature at ambient pressure by means of a highly sensitive calorimeter. From this freezing curve, the pore size distribution and the specific surface area can be calculated.

Experimental

Gas adsorption investigations were performed at Mainz University, by using an automatic gravimetric apparatus [6–8] equipped with Gast vacuum balances. Samples with masses between 10 and 2000 mg were degassed in vacuum at elevated temperature. Nitrogen adsorption isotherms at 77 K and one helium isotherm at 298 K were then measured. From the isotherm, the surface area was derived according to Brunauer, Emmett and Teller (BET) [9, 10] and the pore size distribution was obtained by the method of Barrett Joyner and Halenda (BJH) [11–13]. The data were calculated and represented graphically by using a Porotec data processing program [14].

Thermoporometric measurements were carried out in the Mettler-Toledo laboratory at Giessen, with a TA 3000 heat-flux differential scanning calorimeter with a DSC 30 low-temperature measuring cell. The measuring procedure and the calcula-



Figs 1–4 Fusion curves of a series of controlled pore glasses (CPGs) with increasing pore width. Sample mass 20 mg, rate of temperature increase 0.5 K min^{-1}

Table I Results of determination of the specific surface area and the pore size distribution by means of sorptometry (S) and thermoporometry (T). o=not measurable

Sample	Measuring method	Sorptive or fluid	Specific surface area/$m^2\ g^{-1}$	Specific mesopore volume/$mm^3\ g^{-1}$	Specific micropore volume/$mm^3\ g^{-1}$	Most frequent pore radius/nm	Mean pore radius/nm
Vycor 7930	S	N_2	201.2	232		2.17	
	S	N_2	201.6	228			
	T	H_2O	123.7	146	128	2.98	2.93
CPG 75 B (NPL)	T	H_2O	180.2	532	85	4.13	4.51
CPG 75-120 (Sigma)	S	N_2	140.2			6.31	6.20
	S	N_2	141.5			6.21	6.18
	T	H_2O	183.9	533	85	6.04	6.23
CFG 120 (NPL)	S	N_2	119.7	590		7.72	7.61
	S	N_2	121.2	580		7.70	7.59
	T	H_2O	165.3	595	80	7.72	7.60
	T	H_2O	173.7	612	76	7.64	7.42

Table 1 Continued

Sample	Measuring method	Sorptive or fluid	Specific surface area/$m^2\ g^{-1}$	Specific mesopore volume/$mm^3\ g^{-1}$	Specific micropore volume/$mm^3\ g^{-1}$	Most frequent pore radius/nm	Mean pore radius/nm
CPG 170 (NPL)	T	H_2O	121	820	63	8.21	8.53
CPG 350 (NPL)	T	H_2O	83	900	70	16.1	16.3
CPG 1400 B (NPL)	T	H_2O	63	1100	70	70	70
	S	N_2	24				
SiO_2 2.1 μm spheres	S	N_2	2.2				
	S	He	110				
	T	H_2O	96.7	56	97	1.88	1.94
Zeolith ZSM-5 H-shaped	S	N_2	o	o	145		
	T	H_2O	o	o	34		
Sponge	S	N_2	o	o	o		
	T	H_2O	o	o	o		

tions corresponded to the instructions of Quinson *et al.* [15]. The sample was immersed in water. Then, in a first run which included cooling down to about 258 K and heating up to 273 K, seeds were prepared for a fast crystallization in the subsequent measuring run. To establish the pore size distribution, the cooling curve was evaluated, whereas for calculation of the total pore volume, the heating curve was utilized.

Results and discussion

The results are summarized in Table 1. Figures 1 to 4 present fusion curves of a series of porous glasses (CPGs) with increasing pore width. The right-hand peak is due to melting at 273 K of ice from the free bulk water in which the sample was immersed. The left-hand peak at lower temperature is due to the melting of ice within the porous structure. For samples with a coarser pore structure, this peak is shifted towards higher temperatures, and finally the peak merges into the free ice peak. This effect causes a practical detection limit towards larger pores. The resolution near that limit can be improved and the measuring range extended by reducing the quantity of water for sample immersion as far as possible.

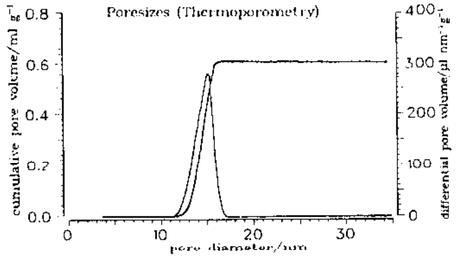


Fig. 5 Pore size distribution of CPG 120, derived from the solidification curve

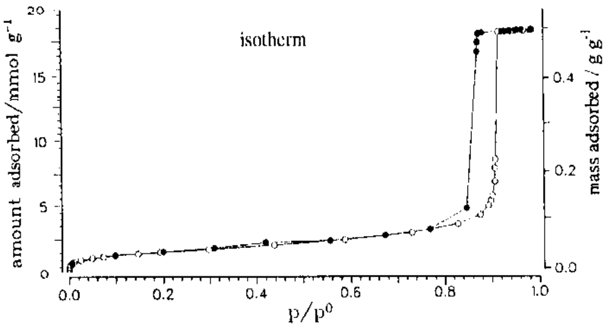


Fig. 6 Nitrogen adsorption isotherm at 77 K on CPG 120, obtained from gravimetric measurement

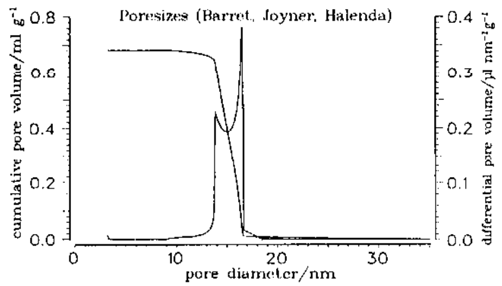


Fig. 7 Pore size distribution of CPG 120, calculated from the nitrogen isotherm by using the BJH method for the adsorption branch

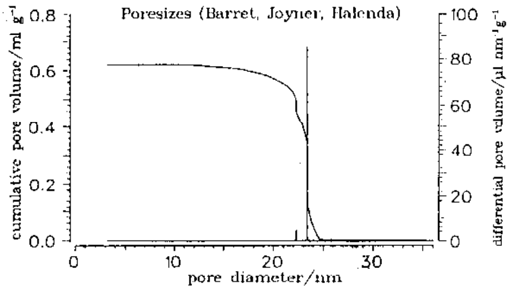


Fig. 8 Pore size distribution of CPG 120, calculated from the nitrogen isotherm by using the desorption branch

Figure 5 depicts the pore size distribution for CPG 120. Figure 6 shows the nitrogen adsorption isotherm at 77 K on CPG 120. From this, the pore size distribution is calculated by using the BJH method for both the adsorption and the desorption branch (Figs 7 and 8). For all samples, the most frequent pore width obtained from the desorption branch gives a better fit to the result of thermoporometry. This is rather surprising, because the solidification process is related to the inner pore size, as is the gas adsorption process, whereas gas desorption is dominated by the smaller pore entrance. The mean pore widths are in good agreement. Large and unsystematic deviations are observed in the specific surface area. For the SiO_2 sample, the nitrogen molecule obviously could not enter the void sphere, which was accessible for the small helium and water molecules. Only the micropore volume could be determined for the sample of large ZMS5 crystals. Whereas the value obtained from gas adsorption is found to be in agreement with theoretical predictions, thermoporometry gives a far too slow result. In the dry state, a sponge exhibits only a small surface and no mesopores could be detected by means of nitrogen adsorption measurements. On swelling in water, neither a surface area nor mesopores could be measured by thermoporometry.

Table 2 Comparison of the features of gas-sorption and thermoporometry

	Gas-sorptometry	Thermoporometry
Sample preparation	Drying in vacuum at elevated temperature	–
Sample surface	No restrictions	Liquophile
Measuring range	Mesopores – micropores	Mesopore, micropore volume
Pore shape determination		Possible
Layer thickness of sorbate or liquid	Pressure-dependent	Constant
Measuring methods	Gravimetric, volumetric, calorimetric	Calorimetric

Conclusions

Sorptometry and thermoporometry yield different information on the surface structure, though methods are based on the influence of the surface of the solid sample on the phase transitions in the adjoining medium. In sorptometry, the gas-liquid phase transition for the dry sample is applied. The measuring range, from about 0.6 to 300 nm pore width, covers micropores and mesopores. In thermoporometry, the liquid–solid transition is used to characterize humid surfaces and swollen pore structures. Though determinations of pore distributions up to 300 nm pore width have been reported [16], in practice the measuring range is restricted in general to about 1.5 and 60 nm. Under favourable conditions, thermoporometry allows a distinction between cylindrical and slit pores. The sample preparation and measuring procedure in thermoporometry are much simpler and faster, and a fully automated apparatus including a sample changer for rapid product control seems possible. However, thermoporometry is not yet a standardized method as is gas-sorptometry. Table 2 compares the features of the two methods. Taking into account the different sizes of the probe molecules (nitrogen or noble gas and water or benzene, respectively) and the different sample states (dry and humid), the two methods complement each other.

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