Thermochimica Acta, 49 (1981) 49—52
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

DETERMINATION OF PORE SIZE DISTRIBUTION by SETARAM DSC 101(THERMOPOROMETRY)

by M. BRUN - Institut National des Sciences Appliquées - LYON (France)
J.F. QUINSON - Université LYON I - LYON (France)
L. BENOIST - SETARAM - LYON (France)

The use of porous materials needs the knowledge of their structure and their pore size distribution.

The used technics (mercury porosimetry B.J.H.) allow to determine this distribution but apply neither to compressible materials nor to materials swelling in their medium of use.

The calorimetric method, called THERMOPOROMETRY, uses the melting or solidification thermogram of a pure liquid contained inside the porous substance (1 - 2 - 3).

PRINCIPLE

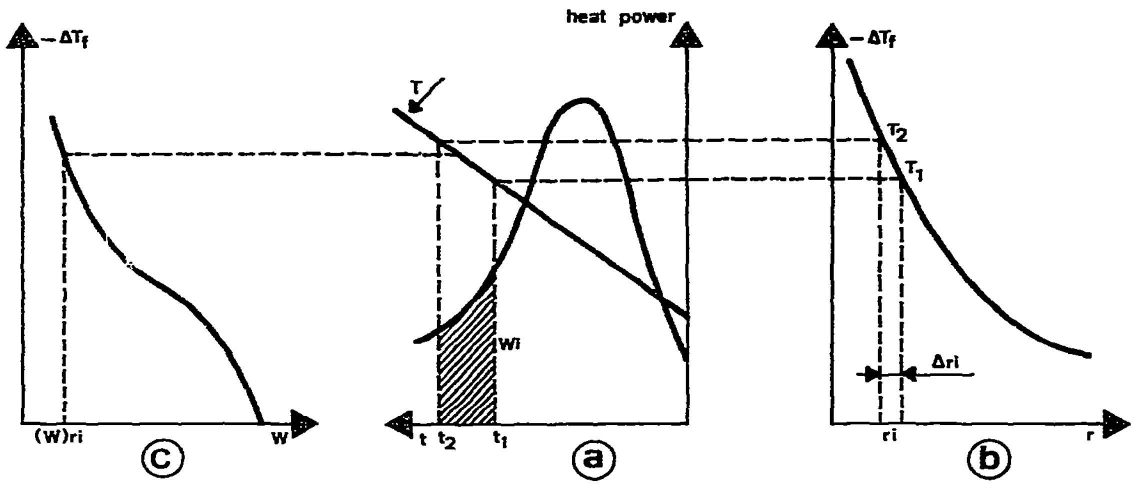
The porous sample to analyze is saturated with liquid and the solidification thermogram is observed.

Before the record of the thermogram, the sample is first cooled down to about 250 K in order to produce cristallisation germs, then heated up just below the normal freezing point. In that way the excess benzene stays frozen.

The curve recorded the cooling (curve 2) at 30 $K.h^{-1}$ shows only cne exotherm due to solidification of benzene in the alumina pores.

The same test has also been carried out with water condensed in a duolite anionic resin (curve 4).

The pore size distributions are shown on the curves 3 and 5.

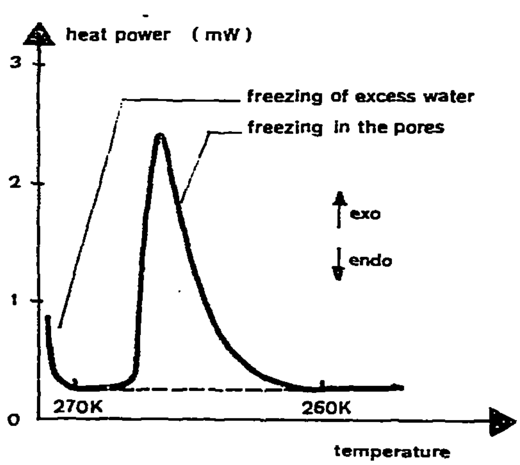


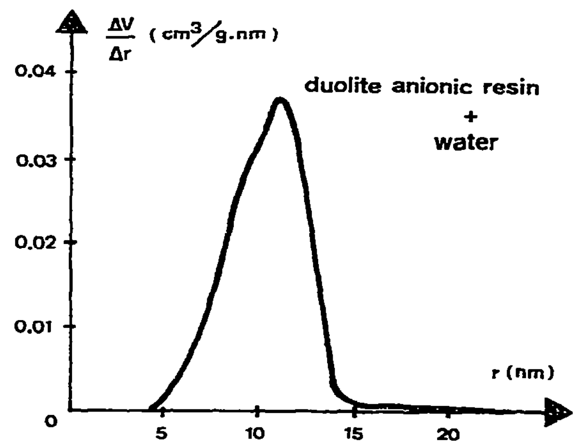
transformation energy per volume unit of liquid = f (solidification temperature)

solidification thermogram

solidification temperature depression = f (pore radius)

cu-ve 1





curve 4 : thermogram of duolite resin (21,5 mg) + water (30,4 mg); aluminium cell; cooling rate = 15 $K.h^{-1}$

curve 5 : $\frac{\Delta V}{\Delta r} = f(r)$

The curve (a) represents the thermogram. Between the instants t_1 and t_2 (the temperature varies from T_1 to T_2), a fraction of liquid has solidified evolving the energy W_i represented by the "dashed" area.

The calibration curve (b) giving the solidification temperature depression versus the pore radius allows to determine the correspondant pore size.

The calibration curve (c) gives the transformation energy per volume unit of fluide w versus the solidification temperature.

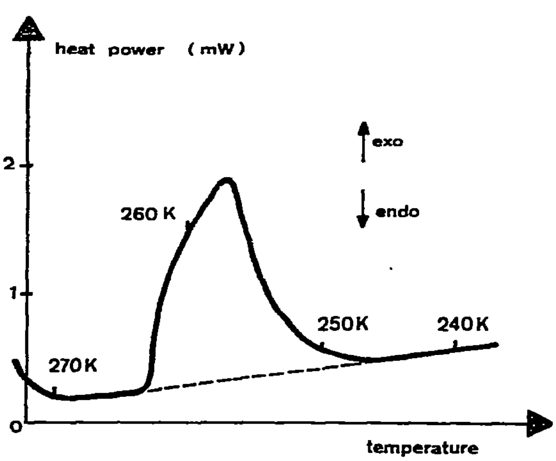
You can get the total volume ΔV_i of pores in the considered Δr_i radii range thanks to the values of W_i and correspondant w.

For various condensates, calibration curves can be established by means of the thermodynamic relation ships which link triple joint depression and transformation energy to the curvature of condensate particle.

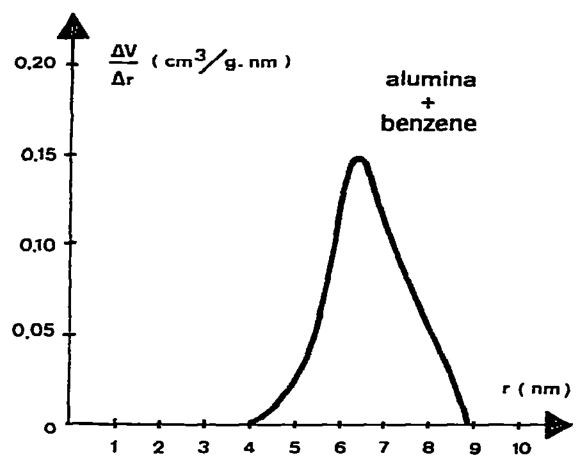
EXPERIMENTS

The used calorimeter is the SETARAM DSC 101 with its subambient cooling system.

The samples are analyzed in aluminium cell. The studied material is alumina saturated with benzene.



curve 2 : Thermogram of Alumina (57,5 mg) + Benzene (50 mg) ; aluminium cell; cooling rate = 30 $K.h^{-1}$



curve 3 : $\frac{\Delta V}{\Delta r} = f(r)$

CONCLUSION

The use of the SETARAM DSC 101 allows the study of pore-size distribution by the thermoporometry method. This method has an application range of 20 to 2000 Å. It measures the actual size of the pore cavity and not the pore opening as the traditional methods. Besides, the degree of hysteresis between the solidification and fusion thermograms give informations on the pore shape.

REFERENCES

1 - M. BRUN, A. LALLEMAND, J.F. QUINSON and C. EYRAUD
Thermochimica Acta, 21 (1977) 59-88

2 - M. BRUN and all.
J. Chim. Phys. 6 (1973) 973

3 - M. BRUN J.F. QUINSON, P. LE PARLOUËR, R. SPITZ and M. BARTHOLIN
Actes des Journées de Calorimétrie et d'Analyse Thermique, Barcelone (Juin 1980).