Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 419 (2004) 291–294

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Pore size determination by thermoporometry using acetonitrile

Marie Wulff*

Amersham Biosciences, Protein Separations R&D, Björkgatan 30, SE-751 84 Uppsala, Sweden

Received 2 October 2003; received in revised form 27 February 2004; accepted 5 March 2004

Abstract

Thermoporometry by DSC is an alternative pore characterisation method to the mercury intrusion and gas sorption techniques. The method allows the study of porous materials in the liquid state. In this study, thermoporometry was performed using acetonitrile as the solvent. The technique was calibrated by using well-characterised polystyrene/DVB samples. For acetonitrile, the following relationship was found between the melting point depression (ΔT) of the solvent and the radius of the pore in which the solvent was confined:

$$R_{\rm p}\ (\text{Å}) = -\frac{309}{\Delta T} + 13.$$

Keywords: Thermoporosimetry; DSC; Acetonitrile; Porous; Synthetic polymer

1. Introduction

Thermoporometry is a technique that allows the study of pore structures of materials in the liquid state. This alternative method for determining the pore size distribution in porous materials, suggested by Kuhn et al. [1] and later derived by Brun et al. [2], uses a thermodynamical relationship known as the Gibbs–Thomson equation. The principle of the method is based on the lowering of the triple point temperature of a liquid filling a porous material. The phase transitions (crystallisation or melting) for a liquid confined within a pore are observed to shift to lower temperatures that are determined by the pore size. This difference in transition temperature, ΔT, between confined and bulk solvent can be detected calorimetrically by differential scanning calorimetry (DSC).

The thermoporometry technique has successfully been applied to a large number of different porous materials like silica gels [3], titania gel [4], hydrogels [5], elastomers [6], chemical pulps [7] and various liquid probes have been used, e.g. water, benzene, cyclohexan, nitrobenzene and carbon tetrachloride [1–9]. Due to the different physico-chemical properties of the liquids, different pore sizes can be probed, depending on the solvent used. Thermoporometry is useful in the characterisation of chromatographic media [10,11] where the pore structure is of great importance. The chromatographic performance of the material is directly related to the mesoporous structure and the specific surface area. Furthermore, as the mesoporous structure of these materials may change with swelling, thermoporometry provides a unique method compared to the traditional techniques, mercury intrusion and gas sorption, which require dry material. For hydrogels this is a great advantage since the drying procedure often destroys the original pore structure. In a recent study on polymeric chromatographic media used for oligo-nucleotide synthesis, the thermoporometry method was found very suitable. Information on the pore structure of the resin in the swollen state was gained and changes in the pore size caused by the growing oligo-nucleotide could be followed [12]. In those studies, the liquid probe of interest was acetonitrile, since it is a commonly used solvent in chromatography. The corresponding thermoporometric data for acetonitrile are however, to our knowledge, not available in the literature. In order to use acetonitrile as a condensate for thermoporometry it was necessary to obtain the numerical relationship between the triple point depression (ΔT) of the solvent and the radius of the pore. A calibration procedure was thus performed, using well-characterised

---

* Tel.: +46-18-612-12-35; fax: +46-18-612-18-44.
E-mail address: marie.wulff@amersham.com (M. Wulff).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.03.006

polystyrene/DVB materials of known pore structure, which is presented in this study.

2. Theoretical background

The triple point temperature of a solvent saturating a porous material depends on the curvature of the solid/liquid interface related to the pore size. The relationship between the depression in the triple point temperature of the confined solvent and the radius of the pore where the phase transition occurs is expressed by the Gibbs–Thomson equation:

$$\frac{\Delta T}{T_0} = \frac{2\gamma_{\mathrm{ls}}}{\Delta H_0}\frac{\nu_{\mathrm{l}}}{R_{\mathrm{p}}}, \tag{1}$$

where γ_{ls} is the liquid–solid interfacial tension, ν_{l} the liquid phase molar volume, ΔH_0 the molar heat of fusion, R_{p} the pore radius, and $\Delta T = T - T_0$ the triple point depression, with T_0 being the triple point temperature of the solvent. The equation can be generally written as

$$R_{\mathrm{p}} = -\frac{A}{\Delta T} + t, \tag{2}$$

where A is a constant depending on the solvent and t is the thickness of the layer of solvent which does not take part in the freezing or melting, but remains adsorbed on the surface of the pore.

3. Experimental

3.1. Materials

Acetonitrile 99.99%, C_2H_3N (Merck, Germany), melting point: −45 °C. Polystyrene/DVB samples with varying pore size (R_{p} in the range 100–400 Å) prepared by suspension polymerisation with an organic porogen.

3.2. Methods

The DSC measurements were performed in an atmosphere of nitrogen using a DSC Q1000 apparatus (TA Instruments) calibrated with indium and equipped with a liquid nitrogen-cooling accessory. Samples of about 3–6 mg immersed in the solvent were put in hermetic aluminium pans. The samples were first equilibrated at −60 °C, and thereafter the melting behaviour of the solvent was analysed. A heating rate of 1 °C/min was selected to ensure maintenance of the thermodynamic equilibrium. The measurements were performed in at least triplicates.

4. Results and discussion

As stated earlier, there are no data available for acetonitrile as a condensate for thermoporometry. The aim of this study was to determine these data by using well-characterised polystyrene/DVB samples as standards for the calibration procedure. These materials were chosen because their pore structure was expected to be the same in the dry state as in the solvent acetonitrile, i.e. no swelling was presumed. This was verified by microscopic investigations and subsequent image analysis. The pore size distributions for the polystyrene/DVB samples were known by mercury porosimetry and their detailed data can be found in Table 1.

Table 1
Hg porosimetry data and thermal data for the polystyrene/DVB standards

Standard	SSA ($m^2\,g^{-1}$)	V_{p} ($cm^3\,g^{-1}$)	D_{p} (Å)	R_{p} (Å)	ΔT (°C)	Standard (°C)
I	463	0.96	270	135	−2.15	0.09 (4)
II	325	1.02	324	162	−2.05	0.03 (4)
III	459	1.18	524	262	−1.44	0.05 (3)
IV	428	1.43	808	404	−0.77	0.22 (4)

The samples were subjected to an appropriate temperature program and the thermograms for the standards are presented in Fig. 1. The peak at low temperature is due to the melting of the confined solvent while the second peak is associated with the bulk solvent. The melting point in the pores was depressed in all cases, and the magnitude of the shift increased with decreasing pore size.

From the DSC curves in Fig. 1, $\Delta T = T - T_0$ was calculated, T_0 being the melting point of pure acetonitrile $= -45 \pm 0.2\,°C$. The ΔT values with standard deviations (with number of runs in parenthesis) are presented in Table 1.

The ΔT values were correlated with the mean pore size of the calibrated polystyrene/DVB samples. In Fig. 2 the pore radii (R_{p}) is plotted as a function of the inverse of the melting point depression for the solvent.

Linear regression yields the following numerical expression for acetonitrile:

$$R_{\mathrm{p}}\ (\text{Å}) = -\frac{309}{\Delta T} + 13. \tag{3}$$

The value 13 Å represents the thickness of the solvent layer remaining adsorbed on the internal pore surface (non-freezable solvent).

In this study the thermoporometry technique has been used in a basic form to obtain the mean pore size of the materials of interest. It is also possible to calculate the pore-size distribution from the DSC thermal curve, indeed the pore volume in which the melting has occurred is related to the apparent enthalpy of melting of the confined solvent. Some precautions should be taken in the interpretation of the results since there are factors that can affect the reliability of the method. The Gibbs–Thomson equation is valid only for small enough ΔT and the model assumes the form of the liquid front to be spherical, which is an approximation. The method does not take into account the effect of stresses exerted on the pore wall by the solid phase when it penetrates into the pore structure during crystallisation. Nevertheless,

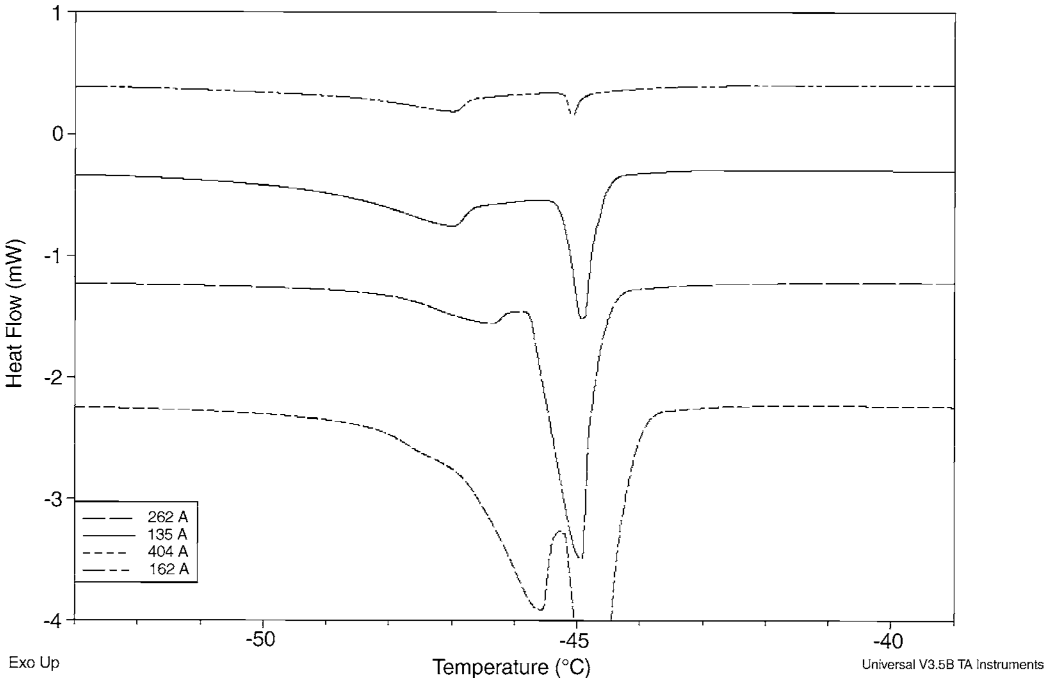

Fig. 1. DSC curves for the melting of acetonitrile in the polystyrene/DVB standards. The curves are shifted in the vertical scale for the sake of clarity.

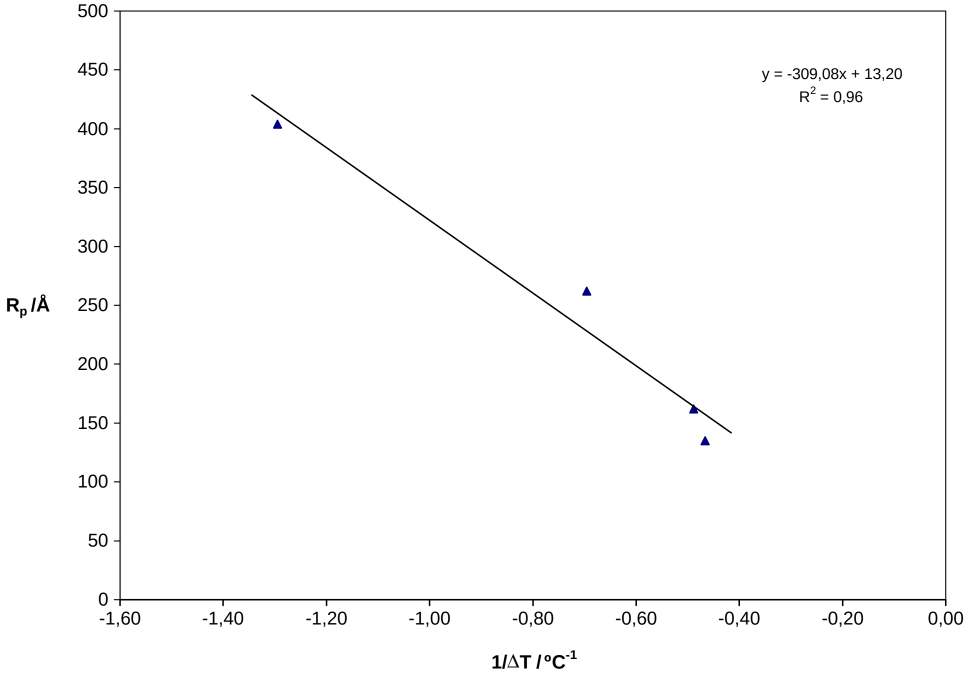

Fig. 2. Pore radii (R_p) of the polystyrene/DVB standards as a function of the inverse of the melting point depression ($1/\Delta T$) for acetonitrile.

thermoporometry is a very useful method for studying mesoporous materials in the liquid state.

5. Conclusions

Thermoporometry by DSC is a new, alternative pore characterisation method to the traditional techniques, mercury porosimetry and gas sorption, which require dry material. Since the method allows the study of mesoporous materials in the liquid state, it is very suitable for the characterisation of various chromatographic media. Furthermore, the thermoporometry technique requires little material and is certainly a less time-consuming method. It is also advantageous for materials with pore structures that change in the liquid state, for example, by swelling. In a recent chromatographic study [12], the use of acetonitrile as the solvent for the thermoporometric measurements was desirable. For this purpose, a calibration against well-characterised polystyrene/DVB samples was performed for the solvent. The melting point of the solvent in the pores was depressed and the magnitude of the shift increased with decreasing pore size. A numerical relationship between pore radii and the melting point depression was obtained and is reported in this study.

Acknowledgements

Tobias Söderman is gratefully acknowledged for synthesising and providing the polystyrene/DVB samples. The author would also like to thank Dr. Anders Larsson, Dr. Bo Medhage, and Dr. Ronnie Palmgren for valuable discussions on this manuscript.

References

[1] W. Kuhn, E. Peterli, H. Majer, J. Polym. Sci. 16 (1955) 539–548.
[2] M. Brun, A. Lallemand, J.-F. Quinson, C. Eyraud, Thermochim. Acta 21 (1977) 59–88.
[3] K. Ishikiriyama, M. Todoki, K. Motomura, J. Coll. Interface Sci. 171 (1995) 92–102.
[4] J.-F. Quinson, N. Tchipkam, J. Dumas, C. Bovier, J. Serughetti, C. Guizard, A. Larbot, L. Cot, J. Non-Cryst. Sol. 99 (1988) 151–159.
[5] M. Iza, S. Woerly, C. Danumah, S. Kaliaguine, M. Bousmina, Polymer 41 (2000) 5885–5893.
[6] M. Baba, J.-M. Nedelec, J. Lacoste, J.-L. Gardette, M. Morel, Polym. Degrad. Stab. 80 (2003) 305–313.
[7] X. Wang, T. Maloney, H. Paulapuro, Appita (2002) 469–473.
[8] C. Jackson, G. McKenna, J. Chem. Phys. 93 (1990) 9002–9011.
[9] M. Sliwinska-Bartkowiak, J. Gras, R. Sikorski, Langmuir 15 (1999) 6060–6069.
[10] M. Brun, J.-F. Quinson, R. Spitz, M. Bartholin, Makromol. Chem. 183 (1982) 1523–1531.
[11] J.-F. Quinson, M. Brun, R. Spitz, M. Bartholin, Makromol. Chem. 185 (1984) 1105–1116.
[12] U. Tedebark, F. Elwinger, M. Wulff, in preparation.