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Water adsorption on zeolite 13X: comparison of the two methods based on mass spectrometry and thermogravimetry

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Abstract Two different experimental methods have been used for studying equilibrium adsorption of water vapour on zeolite 13X based on thermogravimetry and a novel technique using mass spectrometry. Good agreement can be found between experimental data of the adsorption isobars from these two methods. Also the isosteric heat of adsorption of this system has been determined from the equilibrium data. Water adsorption has been measured under a variety of operation conditions of the cooling systems, i.e. pressures from 12.28 to 73.84 mbar and temperatures from 50 to 230 °C.

Keywords Adsorption · Zeolite 13X · Water · Thermogravimetry · Mass spectrometry

1 Introduction

The porous solids in the cooling systems have been used from seventies ends (Tchernev 1978). This idea began with the use of the zeolite–water pair for the heat-pumping/air conditioning applications and the first prototypes of adsorption heat pumps/cooling used adsorbent beds made of zeolite loose grains (Douss et al. 1988; Restuccia et al. 1988).

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The thermo-physical properties, equilibrium adsorption data and isosteric heat of adsorption are essential data for the design of adsorption cooling systems. Thermogravimetric method "TG" and sorption isosteric method "SIM" have been widely used for obtaining the equilibrium data in application of adsorption cooling system (pressure, temperature and adsorption uptake). Several papers have studied the solid/gas thermodynamic equilibrium using TG and SIM, due to the easy sample preparation of the two methods and the simplicity in the experimental procedures. Aristov et al. (1996a, 1996b, 2002) and Gordeeva et al. (1998, 1999, 2002, 2007) have used a thermal balance CAHN C2000 for study the adsorption equilibrium of water and methanol on composites materials from 293 to 423 K at different vapour pressure in the range 8 to 133 mbar. So, Stach et al. (2005) measured gravimetrically the adsorption isotherms of water on zeolites (X, Y and modified) and composites materials at 293, 313 and 333 K with a common McBain quartz spring balance equipment with MKS Baratron pressure sensors. The authors estimated the reproducibility of the method from adsorption and desorption branches. Other authors (Yang and Rees 1997; Bülow and Shen 1998; Shen and Bülow 1998; Anashin et al. 2004; Sharonov et al. 2006) have used SIM based on the manometry to determine the solid/gas thermodynamic equilibrium and thermodynamic properties for some pairs, including water vapour. However for condensable gases, particularly water vapour, the two methods have limitations: the difficulty of maintaining the system at temperatures above the saturation temperature, condensation of water vapour in cold zones and electronic sites and uncertainties in weight measurements due to buoyancy. In addition, SIM does not guarantee a constant adsorbed amount because mass desorption at each equilibrium point increases the gaseous phase mass and, therefore, the system pressure. Of this way, it is gen-

Table 1 Surface characteristics of the zeolite 13X

Properties	Value
Surface area (m^2/g)	729
Micropore volume (cm^3/g)	0.26
Average pore diameter (nm)	0.7

erate uncertainties in the isosteric heat of adsorption around 20% (Cortés 2009). Mass desorption causes errors that are significant for high pressures and temperatures in the region of low surface coverage. Therefore, the aim of this work is to present a novel method based on the mass spectrometry (MS) for obtaining the adsorption equilibrium of water on porous solids for its application in the cooling systems, in which avoids the uncertainties in weight and equilibrium pressure due to buoyancy and to desorption, respectively.

The experimental data of zeolite 13X–water by MS were validated with the experimental data from thermogravimetry method (TG), which shows good consistency. In terms of the chiller operation condition, we investigated the water uptake on zeolite 13X, pressures from 12.28 to 73.84 mbar and temperatures from 50 to 230 °C. The isosteres and isosteric heat of adsorption were obtained from the adsorption isobars. In addition, the water adsorption on zeolite 13X was analyzed by other way, from the "Polanyi theory".

2 Experimental

2.1 Material

A commercial Faujasite-type zeolite (13X) in pellet was used, which exhibit a 3-dimensional framework with large supercages linked together through channels where sorbed molecules diffuse. The framework is formed by SiO_4 and AlO_4 tetrahedral whose global negative charge is balanced by exchangeable cations Na^+ sparse on many sites throughout the structure. In addition, the zeolite is commercially distributed by Sigma-Aldrich.

Textural characterization of the samples was carried out by N_2 adsorption at −196 °C in QUANTACROME AUTOSORB device. The Dubinin-Radushkevich-Stoekli (2002) equation was used for analysis of N_2 adsorption isotherms. The molecular area of N_2 at −196 °C is 0.162 nm^2. Table 1 shows the surface area, micropore volume and average pore diameter from the experimental data of nitrogen adsorption.

2.2 Equipment

2.2.1 Thermogravimetric analyzer and experiment

The thermogravimetric analyzer comprises the TA Instrument unit and an evaporator. Water vapour is generated in an oil heater bath fitted with a controller. The vapour pressure is determined by the oil bath temperature. The zeolite 13X sample was put in the furnace of the TG analyzer which has a radiant heater for maintaining constant sample temperature until equilibrium is reached. The changes of the equilibrium sample mass were measured by the microbalance for different temperatures and pressures.

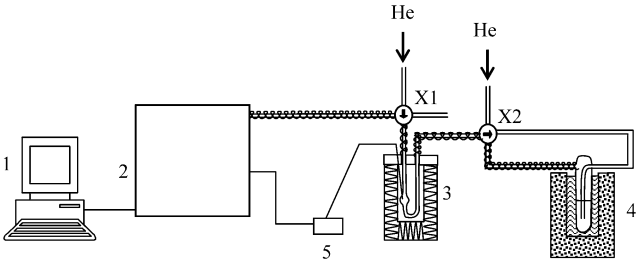

Fig. 1 Schematic representation of MS apparatus: (*1*) computer, (*2*) mass spectrometer, (*3*) reactor and furnace, (*4*) thermostatic bath and saturator, (*5*) temperature controller and transducer (*X1–X2*) valves

The sample is heated around 4 hours at 450 °C in an inert atmosphere, a helium gas flowing trough it. After adsorbent regeneration at high temperature, the system is taken to the desired temperature and the helium saturated with water (at a fixed saturation temperature) is constantly fed into the furnace until equilibrium is reached. Later the temperature is increased and the new equilibrium adsorbed mass is measured, at constant pressure. This procedure is repeated for different vapor pressure system, changing the temperature of the oil bath. To avoid condensation, the reaction cell and piping system were always kept at least (10–20) K higher than the saturation temperature of the vapour, which was achieved by wrapping heater tapes around the piping system which were also well insulated to minimize heat loss. The system was deemed to be in thermodynamic equilibrium at desired pressure and temperature when the mass of the system (adsorbed + adsorbent) remained unchanged for at least 1–2 an hour. Reproducibility of the measurements was checked by repeating the tests (at least two times).

2.2.2 Method based on the mass spectrometry and experiment

A novel experimental method was used to obtain the equilibrium data of adsorption of water on zeolite 13X and is shown in Fig. 1. The new method comprises the mass spectrometer unit (MS and computer), a reactor and an evaporator (saturator and thermostat). Water vapour is generated in an oil heater bath fitted with a controller (thermostat). The pressure of the vapour is determined by the oil bath temperature (at a fixed saturation temperature). The zeolite 13X sample (ca. 0.08 g) was placed in the reactor which has a radiant heater to keep constant sample temperature until equilibrium is reached. Afterwards, the reactor is heated to desorb the

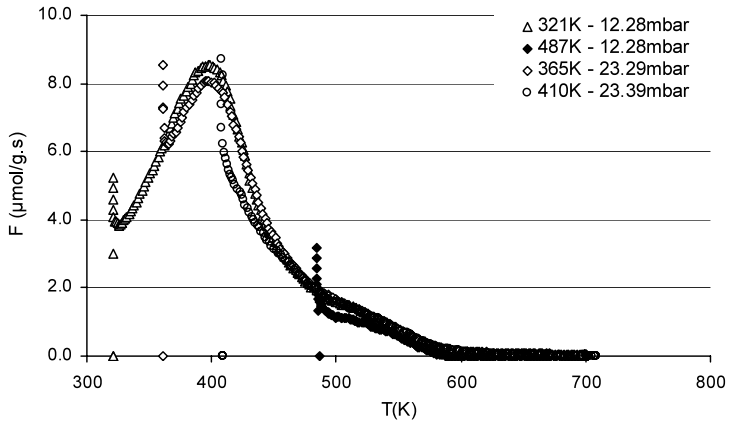

Fig. 2 Profile of water desorption at different pressure and adsorption temperature

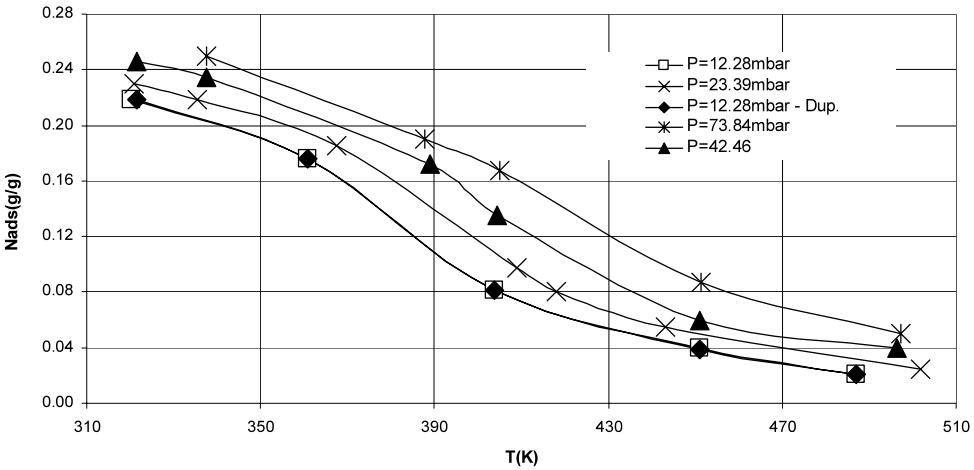

Fig. 3 Isobars of water on zeolite 13X

previously adsorbed water vapour. The desorbed uptake in zeolite 13X was measured by the MS for different temperatures and pressure.

The sample is heated around 4 hours at 450 °C in an inert atmosphere in the reactor, a helium gas is pumped trough it at 60 ml/min. After adsorbent regeneration at high temperature, the reactor is taken to the desired temperature and the helium is changed by helium saturated with water (at a fixed saturation temperature), which is constantly fed into the furnace until equilibrium is reached, around 2 hours. Again, the helium saturated with water is switched to dry helium and the sample is heated at 5 °C/min until 450 °C is reached, in order to desorb the previously adsorbed water vapour, which is measured in the MS. This procedure is repeated at different temperatures and vapor pressure system, changing the temperature of the oil bath. To avoid condensation, the reaction cell and piping system were always kept at least (10–20) K higher than the saturated temperature of the vapour, which was achieved by wrapping heater tapes around the piping system and they were also well insulated to minimize heat loss. The system was deemed to be in thermodynamic equilibrium at desired pressure and temperature when the desorbed quantity measured is equal at different time of treatment in He–H_2O atmosphere. Reproducibility of the measurements was checked by repeating the tests (at least three times).

Figure 2 shows the profiles of water desorption after its adsorption at different pressures and temperatures. These profiles were used to obtain the amount of water adsorbed on zeolite 13X at different equilibrium pressures and temperatures.

3 Result and discussion

3.1 Isobars and isosteres

Figure 3 shows adsorption isobars at pressure from ∼ 12 to 74 mbar, and temperatures from 50 to 230 °C obtained by MS. Indeed, it is possible to conclude from desorption branches at 12.28 mbar that the experimental method is reproducible. The isosteres were derived from adsorption isobars.

The isosteres show non-linearity (see Fig. 4). Since the usual phenomena is linearity on isosteres, if the assumption

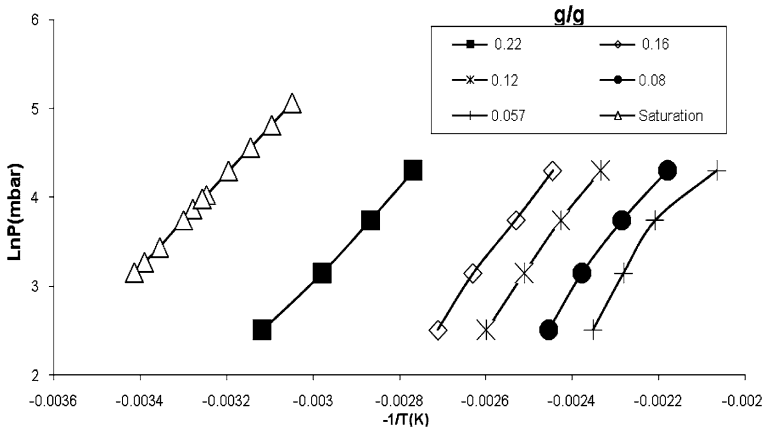

Fig. 4 Isosteres of water on zeolite 13X

of the independent of temperature in the isosteric heat is reasonable true (Yang and Rees 1997).

Although the isosteres for zeolite 13X/water does not show this behaviour, specially at low coverage, isosteres suggest that a stage occurs at pressure between ∼43 mbar and 74 mbar and there is, also, a change in slope. The deviation from linearity may be explained for the follow reasons (Bülow et al. 2002):

1) The gas phase behaviour is real gas (the use pressure instead of fugacity).
2) The molar volume of the sorption phase may be not neglecting with regard to that of the gas phase.
3) The non-negligible desorption, $N_{ads} \neq$ constant.

However, these three reasons do not explain the deviation from linearity of the isosteres because for the experimental conditions of this work: 1) the gas phase is ideal, 2) the molar volume of the sorption is neglecting with regard to that of the gas phase and 3) the isosteres present an isosteric condition.

This unusual behaviour is due to energetic heterogeneity of the adsorbent. At low-adsorbed uptake and low pressure adsorption constitutes interaction of water molecules with hydrophilic centers in the zeolite, the tetrahedrally coordinated aluminium atoms and their associated acidic protons, strongly energetic (Brönsted acidic). At high pressure (low coverage), the water bonding with other water molecules by hydrogen bonding and/or filling pore, generating lower interaction energy. This behaviour is evidence in the large difference in "free sorption energy" values between the two regions evaluated (HP and LP) at low N_{ads}, under an isosteric condition (Cortés 2009).

When uptake is close to saturation, the isosteres does not shown deviation from linearity for this range pressure, i.e. the deviation decreased with increasing uptake, because the interaction energy obeys only to mean interaction of water with water molecules by hydrogen bonding and/or filling pore (Cortés 2009).

3.2 Isosteric heat

The isosteric heat is the energy released during adsorption and can be computed as a function of pressure and temperature using the Gibbs-Helmholtz equation (GH) (Dubinin 1967). The GH equation is derived from the Dubinin Astakhov equation. This last one is commonly used for adsorption equilibrium in microporous materials such as activated carbon and zeolites. The Dubinin and Astakhov's (1971) adsorption isotherm can be represented by:

$$N_{ads} = N_{ads,\max} \exp\left[-D\left(T \ln \frac{P_s}{P}\right)^n\right] \tag{1}$$

where N_{ads} is uptake adsorbed, D the coefficient of affinity, $N_{ads,\max}$ the maximum adsorption capacity (mass of adsorbate/mass of adsorbent) and n a characteristic parameter of the adsorbent–adsorbate pair.

Differentiation of (1) with respect to temperature and rearrangement yields:

$$\left.\frac{\partial \ln Ps}{\partial T}\right|_{N_{ads}} - \left.\frac{\partial \ln P}{\partial T}\right|_{N_{ads}} = -\frac{1}{T^2}\left[\frac{1}{D}\ln\left(\frac{N_{ads,\max}}{N_{ads}}\right)\right]^{1/n} + \left(\frac{1}{TnD}\right)\left[\frac{1}{D}\ln\left(\frac{N_{ads,\max}}{N_{ads}}\right)\right]^{\frac{1}{n}-1} \frac{\partial \ln(\frac{N_{ads,\max}}{N_{ads}})}{\partial T} \tag{2}$$

Multiplying each term of the differential equation (2) by (RT^2) yields an expression for the isosteric heat:

$$Q_{isost} = Q_{vap} + RT \ln\left(\frac{P_s}{P}\right) + \left(\frac{\alpha RT}{nD}\right)\left(T \ln\left(\frac{P_s}{P}\right)\right)^{1-n} \tag{3}$$

where α is the coefficient of thermal expansion of the liquid adsorbate, which can be obtained from (Leite and Daguenet 2000):

$$\alpha = -\frac{\partial \ln(\frac{N_{ads.,\max}}{N_{ads}})}{\partial T} = \frac{1}{T^2}\frac{\partial \ln(\frac{N_{ads.,\max}}{N_{ads}})}{\partial(\frac{1}{T})} \tag{4}$$

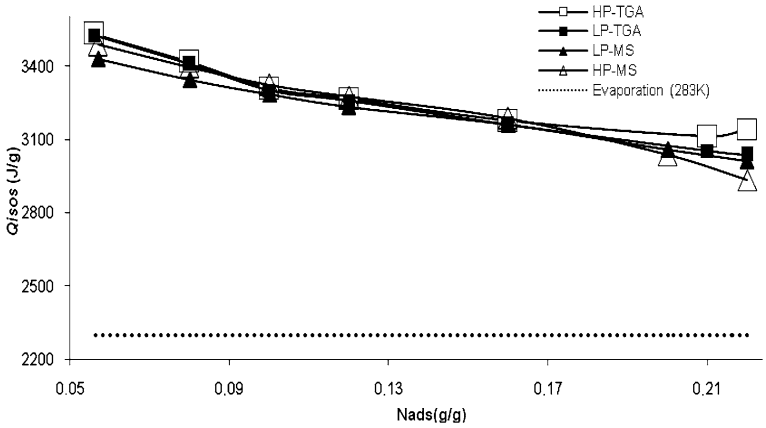

Fig. 5 Isosteric heat for the zeolite-water pair computed by GH

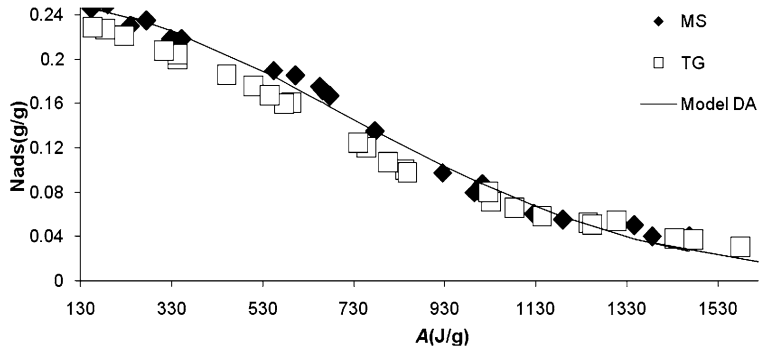

Fig. 6 Characteristic curve for water/zeolite 13X pair

To compute the isosteric heat from (3) on could use experimental data and using a single linear regression procedure to obtain the parametric values $N_{ads,\max}$, n and D in (1) and (3).

The isosteric heat was computed at 12.28 and 73.84 mbar, which is entitled low and "high" pressure. Figure 5 shows the isosteric heat at low and "high" pressure calculated from the (1) at uptake adsorbed. For each uptake adsorbed there is an equilibrium temperature value, which is used to compute the isosteric heat. At low pressure (LP) by MS, the isosteric heat decreases with coverage, from ca. 3430 J/g to ca. 3010 J/g when uptake increases from ca. 0.06 g/g to ca. 0.22 g/g, which corroborate the heterogeneity energetic of the adsorbent. When the adsorbent is close to its maximum uptake, the thermodynamics properties of adsorption are close to properties of pure water. i.e., the isosteric heat of adsorption is close to the pure water latent heat. In addition, the isosteric heat is higher than pure water latent heat (see Fig. 5).

At "high" pressure (HP) by MS, the isosteric heat is similar to the low pressure. The isosteric heat decreases with increases the uptake, from ca. 3490 J/g to ca. 2930 J/g when uptake increases from ca. 0.06 g/g to ca. 0.22 g/g. The isosteric heat of adsorption obtained by MS and TG methods yielded similar results as shown in Fig. 5.

3.3 Characteristic curve of the system

For understanding the adsorption phenomena of the water/zeolite 13X from other way, the theory of volume filling pore (TVFM) was used. This theory is based on Dubinin-Astakhov equation, which is commonly used for adsorption equilibrium in microporous materials, especially in activated carbon and zeolites. The Dubinin and Astakhov's (1971) "D-A" adsorption isotherm can be represented by (1).

The theory postulates the temperature invariance of the relative adsorption plotted as a function of the adsorption potential, as a direct consequence of the Polanyi Theory of adsorption (taken from Dubinin 1967). The experimental data obtained from TG and MS are depicted in Fig. 6 and show a similar pattern.

Parameters of (2) obtained were $N_{ads,\max} = 0.24$ g/g, $n = 1.6$ with a coefficient correlation $R^2 = 0.997$. The D-A model was applied within a wide range of adsorption potential "A" (ca. $130 < A < 1650$). However, with this model is not possible observe the striking and unusual behaviour as is showed in the Clapeyron Diagram (see Fig. 4) at low uptake ($N_{ads} < 0.16$ g/g) because postulate temperature invariance is not valid for this pair.

4 Conclusion

Adsorption equilibrium studies of water vapour on zeolite 13X have been investigated independently by TG and novel MS methods. In this work was found that the method is reproducibility and experimental data could be reproduced by the other independent method "TG". This supports the reliability of our present study. In addition, the Dubinin Astakhov was used to describe the behaviour of this pair. This provides a good correlation for the experimental data, although this model does not show the deviation of the isosteres from linearity at low uptake. The experimental data of adsorption from MS are similar to those from TG, which shows good consistency in terms of the reproducibility and validity of the new proposed method.

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References

Anashin, V.V., et al.: The vacuum studies for LHC beam screen with carbon fiber cryosorber. In: Proceedings of APAC, Gyeongju, Korea (2004)

Aristov, Yu.I., Tokarev, M.M., Restuccia, G.: Selective water sorbents for multiple applications, 1. CaCl2 confined in mesopores of silica gel: Sorption properties React. Kinet. Catal. Lett. **59**, 325–333 (1996a)

Aristov, Yu.I., Tokarev, M.M., Restuccia, G., Cacciola, G.: Selective water sorbents for multiple applications. 2. CaCl2 confined in micropores of silica gel: sorption properties. React. Kinet. Catal. Lett. **59**, 335 (1996b)

Aristov, Yu.I., Restuccia, G., Cacciola, G., Parmon, V.N.: A family of new working materials for solid sorption air conditioning systems. Appl. Therm. Eng. **22**, 191–204 (2002)

Bülow, M., Shen, D.: In: Meunier, F. (ed.) Fundamentals of Adsorption-6, p. 87. Elsevier, Paris (1998)

Bülow, M., et al.: Measurement of sorption equilibria under isosteric conditions The principles, advantages and limitations. Appl. Surf. Sci. **196**, 157–172 (2002)

Cortés, F.B.: Adsorción de Agua en Materiales compuestos y en Zeolita. Doctoral Thesis. Universidad Nacional de Colombia, Sede Medellín, Colombia (2009)

Douss, N., Meunier, F., Sun, L.M.: Predictive model and experimental results for a two-adsorber solid adsorption heat pump. Ind. Eng. Chem. Res. **27**, 310–316 (1988)

Dubinin, M.M.: Adsorption in Micropores. J. Colloid Interface Sci. **23**, 487–499 (1967)

Dubinin, M.M., Astakhov, V.A.: Development of the concepts of volume filling of micropores in the adsorption of gases and vapors by microporous adsorbents. Russ. Chem. Bull. **1**, 5–11 (1971)

Gordeeva, L.G., Cacciola, G., Restuccia, G., Aristov, Yu.I.: Selective water sorbents for multiple applications: 5. LiBr confined in mesopores of silica gel: sorption properties. React. Kinet. Catal. Lett. **63**, 81–88 (1998)

Gordeeva, L.G., Mrowiec-Bialon, J., Jarzebski, A.B., Lachowski, A.I., Malinowski, J.J., Aristov, Yu.I.: Selective water sorbents for multiple applications, 8. sorption properties of CaCl2−SiO2 sol-gel composites. React. Kinet. Catal. Lett. **66**, 113–120 (1999)

Gordeeva, L.G., Restuccia, G., Freni, A., Aristov, Yu.I.: Water sorption on composites "LiBr in a porous carbon". Fuel Process. Technol. **79**, 225–231 (2002)

Gordeeva, L.G., Freni, A., Restuccia, G., Aristov, Y.I.: Influence of characteristics of methanol sorbents "salts in mesoporous silica" on the performance of adsorptive air conditioning cycle. Ind. Eng. Chem. Res. **46**, 2747–2752 (2007)

Leite, A.P.F., Daguenet, M.: Performance of a new solid adsorption ice maker with solar energy regeneration. Energy Convers. Manag. **41**, 1625–1647 (2000)

Restuccia, G., Recupero, V., Cacciola, G., Rothmeyer, M.: Zeolite heat pump for domestic heating. Energy. **13**, 333–342 (1988)

Sharonov, V.E., et al.: Ammonia sorption on composites 'CaCl2 in inorganic host matrix': isosteric chart and its performance. Int. J. Low Carbon Technol. **1**, 191–200 (2006)

Shen, D., Bülow, M.: Isosteric Study of Sorption Thermodynamics of single gases and multi-component mixtures on microporous materials. Microporous Mesoporous Mat. **22**, 237–249 (1998)

Stach, H., et al.: Influence of cycle temperatures on the thermochemical heat storage densities in the systems water/microporous and water/mesoporous adsorbents. Adsorption **11**, 393–404 (2005)

Stoeckli, F., Guillot, A., Slasli, A.M., Hugi-Cleary, D.: The comparison of experimental and calculated pore size distributions of activated carbons. Carbon **40**, 383–388 (2002)

Tchernev, D.I.: In: Sand, L.B., Mumpt, F.A. (eds.) Natural Zeolites: Occurrence, Properties and Use, pp. 479. Pergamon, London (1978)

Yang, Y., Rees, L.V.C.: Adsorption of normal hexane in silicalite- 1: an isosteric approach. Microporous Mater. **12**, 117–122 (1997)