EQUILIBRIUM AND HEAT OF ADSORPTION FOR SELECTED ADSORBENT-ADSORBATE PAIRS USED IN ADSORPTION HEAT PUMPS

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ABSTRACT

The results of theoretical studies of adsorption equilibrium for selected adsorbent-adsorbate pairs used in adsorption heat pumps were presented. The following pairs were studied: water- alumina, water- silica gel, water-zeolite 13X, ammonia-activated carbon, ammonia-charcoal, ammonia-clinoptilolite, ammonia-polymer resin. The experimental adsorption equilibrium data, taken from the literature, were described using the Dubinin-Astakhov model. Based on the Clausius-Clapeyron equation, isosteric heat of adsorption was evaluated for all studied adsorbent-adsorbate pairs.

INTRODUCTION

The adsorption method is widely used in chemical industry, environmental protection and other fields, for separation and purification of gases and liquids (Ruthven D.M, 1984, Tien C., 1994, Bathen D., Breitbach D., 2001). During the past two decades, this phenomenon has been exploited to produce cooling and heating (Cacciola G., Restuccia G., 1994, Srivastava N.C., Eames I.W., 1997, Meunier F., 1998, Demira H., Mobedi M., Ülkü S., 2008, Pilatowsky I., Romero R.J., Isaza C.A., Gamboa S.A., Sebastian P.J., Rivera W., 2011). Recently a large amount of research has been done on various types of adsorption heat pumps (San J.-Y., Hsu H.-Ch., 2009, Huang H., Oike T., Watanabe F., Osaka Y., Kobayashi N., Hasatani M., 2010), as an alternative to vapor compression systems, primarily due to environmental concerns over stratospheric ozone-depleting substances (Chahbani M.H., Labidi J., Paris J., 2004). Adsorption heat pumps have, aside from environmental benefits, several advantages compared to conventional vapor compression systems, such as: simplicity, no moving parts, low maintenance requirements, and the use of stable, non-toxic reactants, as adsorbents and adsorbates.

The operation of adsorption heat pumps is based on the ability of porous adsorbent to adsorb vapor (adsorbate) at low temperature, and to desorb it when heated.The performance of an adsorption heat pump is controlled by many parameters, such as adsorbent and adsorbate properties, system design and operating conditions.

There are several adsorbent–adsorbate working pairs for solid adsorption system (Srivastava N.C., Eames I.W., 1998, Anyanwu E.E., Ogueke N.V., 2005). The major adsorbates used are water, ammonia and methanol. Zeolite Molecular sieves, silica gel, alumina and active carbon are used as conventional adsorbents. Most new adsorbents are based on modification of existing one, to increase the adsorption capacity and to improve the heat and mass transfer.

The selection of the proper materials for heat pumping depends on the thermodynamic characteristics of the adsorbent-adsorbate pair. For this reason the optimal working pair has to be chosen individually for each configuration of heat pump.

The design of an adsorption heat pumps requires the knowledge of the adsorption equilibrium for the system of interest. For practical applications, the adsorption equilibrium must be known over a broad range of operation temperature. This information is used to calculate the heat of adsorption. Moreover, the isotherm of pure species is fundamental information for the dynamic simulation of adsorption heat pumps.

In this paper, adsorption equilibrium of selected adsorbent-adsorbate pairs used in adsorption heat pumps was studied. Based on the experimental adsorption data, the isosteric heat of adsorption was evaluated.

ADSORPTION EQUILIBRIUM

The following adsorbent-adsorbate pairs were studied:

- water-alumina,
- water-silica gel,
- water-zeolite 13X,
- ammonia-activated carbon,
- ammonia-charcoal,
- ammonia-clinoptilolite,
- ammonia-polymer resin.

The experimental adsorption equilibrium data for these pairs, determined at different temperatures and vapor pressures of adsorbates, were taken from the literature (Kim J.-H., Lee Ch.-H., Kim W.-S., Lee J.-S., Kim J.-T., Suh J.-K., Lee J.-M., 2003, Wang Y., LeVan M.D., 2009, Helminen J., . Helenius J., Paatero E., 2001). Experimental data were measured in a pressure range of 0–2.3 kPa and of 0–101 kPa for water and ammonia, respectively. The physical properties of adsorbents are given in Table 1.

Several models are available in the literature to correlate nonisothermal adsorption equilibrium data, such as Langmuir, Toth, the Dubinin-Astakhov model, and the multitemperature viral equation of state (Do D.D., 1997). In this work the experimental isotherms were described using the Dubinin-Astakhov model. The mathematical form of the Dubinin-Astakhov (D-A) equation is as follows:

Tab. 1. Physical properties of the adsorbents

Adsorbent	Manufacturer/Supplier	Form	Mean pore diameter [nm]	BET surface area [m^2/g]	Bulk density [kg/m^3]
Activated carbon (Aldrich Darco 24,226–8)	Sigma–Aldrich Co.	Granule (0.4–0.84mm)		430	359
Alumina (Al_2O_3)	Procatalyze	Bead	51	340	810
Charcoal (Sigma C 3014)	Sigma Chemical Co.	Granule		210	239
Clinoptilolite [Mud Hills (CA), USA]		Granule (0.5–1 mm)	36		790
Polymer resin (Amberlyst 15)	Rohm & Haas Co.	Bead (0.3–0.84mm)		225	519
Silica gel	Grace Davison	Bead			
Zeolite 13X	Sigma–Aldrich Co.	Bead	23	726	689

$$V = V_o \exp\left[-\left(\frac{A}{\beta E_o}\right)^n\right] \quad (1)$$

where

$$A = RT\ln\left(\frac{p_s}{p}\right) \quad (2)$$

is an adsorption potential.

The equation (1) relates volume of adsorbed compound (V), partial pressure of adsorbate (p) and temperature (T).

The concentration of adsorbate in adsorbent (q) is given by the equation:

$$q = V\rho(T) \quad (3)$$

Saturation vapor pressure (p_s) and temperature dependent density of liquid adsorbate ($\rho(T)$) are calculated using the following equations:

$$\log_{10}(p_s) = D + E/T + F\log_{10}(T) + GT + HT^2 \quad (4)$$

$$\rho(\mathrm{T}) = BC^{-(1-T/T_c)^m} \quad (5)$$

The values of the parameters of the Equations (4) and (5) are given in Tables 2 and 3.

To find the optimal value of parameters of Equation (1), the Levenberg - Marquardt nonlinear regression method was used. The following objective function was defined:

$$L = \sum_{i=1}^{N}\left[V_i^{calc} - V_i^{\exp}\right]^2 \quad (6)$$

Values of the fitted parameters are presented in Tables 4 and 5.

Tab. 2. The value of the parameters of Equation (4) (Yaws C.L., 1999) (p_s [mmHg]; T [K])

Parameter	Ammonia	Water
D	37.1575	29.8605
E	$-2.0277\cdot10^{3}$	$-3.1522\cdot10^{3}$
F	–11.601	–7.3037
G	$7.4625\cdot10^{-3}$	$2.4247\cdot10^{-9}$
H	$-9.5811\cdot10^{-3}$	$1.8090\cdot10^{-6}$

Tab. 3. The value of the parameters of Equation (5) (Yaws C.L., 1999) ($\rho(T)$ [kg/m^3]; T [K])

Parameter	Ammonia	Water
B [kg/m^3]	236.89	347.10
C	0.25471	0.27400
m	0.28870	0.28571
T_c [K]	405.65	647.13

Tab. 4. Dubinin-Astakhov isotherm equation parameters for water on Alumina, Silica gel and Zeolite 13X

Parameters	Alumina	Silica gel	Zeolite 13X
V_o [m^3/kg]	$4.673\cdot10^{-4}$	$3.980\cdot10^{-4}$	$2.114\cdot10^{-4}$
βE_o [J/mol]	670.8	3780.8	18445.0
n	0.332	1.016	1.806

Tab. 5. Dubinin-Astakhov isotherm equation parameters for ammonia on Activated carbon, Charcoal, Clinoptilolite and Polymer resin

Parameters	Activated carbon	Charcoal	Clinoptilolite	Polymer resin
V_o [m^3/kg]	$3.594\cdot10^{-4}$	$7.449\cdot10^{-4}$	$1.679\cdot10^{-4}$	$3.295\cdot10^{-4}$
βE_o [J/mol]	5346.3	3803.5	25863.5	20702.7
n	1.224	1.102	2.327	2.114

Based on the Dubinin-Astakhov model, the temperature-independent characteristic curves were obtained and the values of limiting adsorption volumes (V_o) were calculated. For a given adsorbate – adsorbent system the relation between A and V (characteristic curve) is:

$$V = f(A) \tag{7}$$

For all studied adsorbent–adsorbate systems, characteristic curves, developed from the experimental data, are shown in Figures 1–7. The comparison of characteristic curves obtained for various adsorbents are shown in Figures 8 and 9 for water and ammonia, respectively. As may be seen the zeolite 13X provides the highest adsorbed volume of water at low pressures. The alumina and silica gel have highest adsorbed volume of water at the highest pressures. The clinoptilolite adsorb ammonia more effectively at low pressures.

HEAT OF ADSORPTION

The adsorption isotherms were used to determine the isosteric heat of adsorption by the Clausius-Clapeyron equation:

$$\Delta H_a = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \tag{8}$$

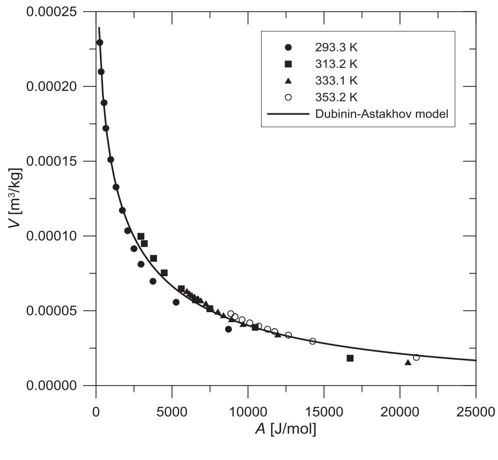

Fig. 1. Characteristic curve for water adsorbed on alumina

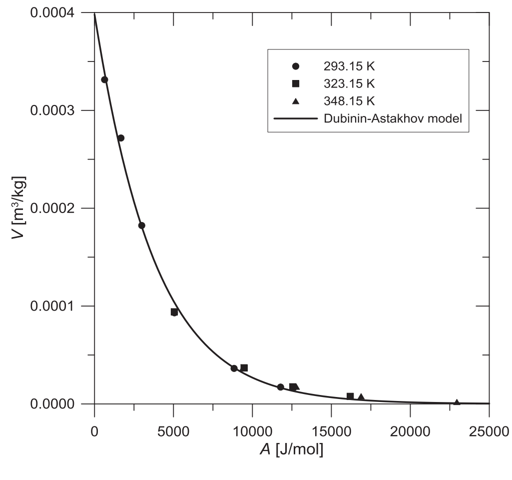

Fig. 2. Characteristic curve for water adsorbed on silica gel

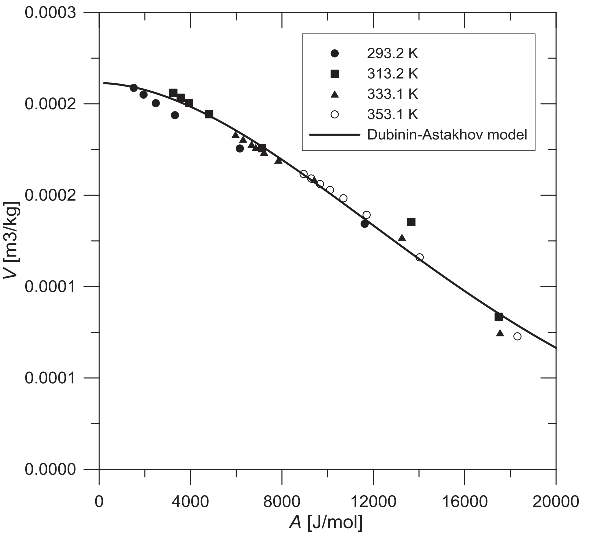

Fig. 3. Characteristic curve for water adsorbed on zeolite 13X

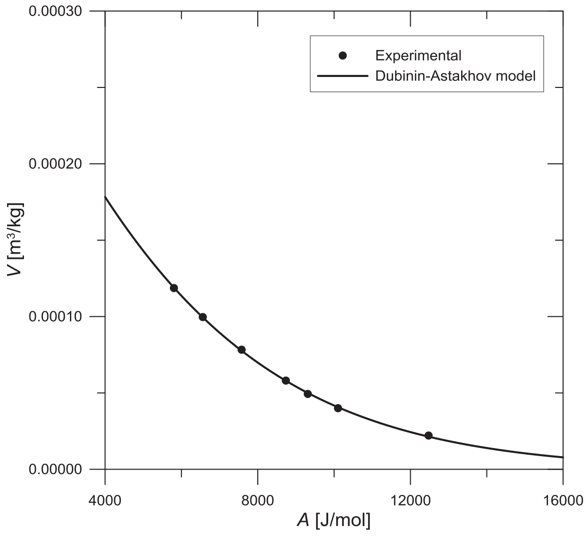

Fig. 4. Characteristic curve for ammonia adsorbed on activated carbon (T=298.15 K)

For the calculation of the pressure derivative in the above equation, the relationship between pressure and temperature was described using Dubinin-Astakhov equation (Equations. (1)–(3)). The results are shown in Figures 10 and 11.

The isosteric heat of adsorption is a measure of the interaction between adsorbate molecules and adsorbent surface atoms and may be used as a measure of the energetic heterogeneity of a solid surface. Information concerning the magnitude of the heat of adsorption and its variation with coverage can provide useful information concerning nature of the surface and the adsorbed phase. In most cases, the adsorbent has an energetic heterogeneous surface. For this reason, the isosteric heat of adsorption varies with the surface loading.

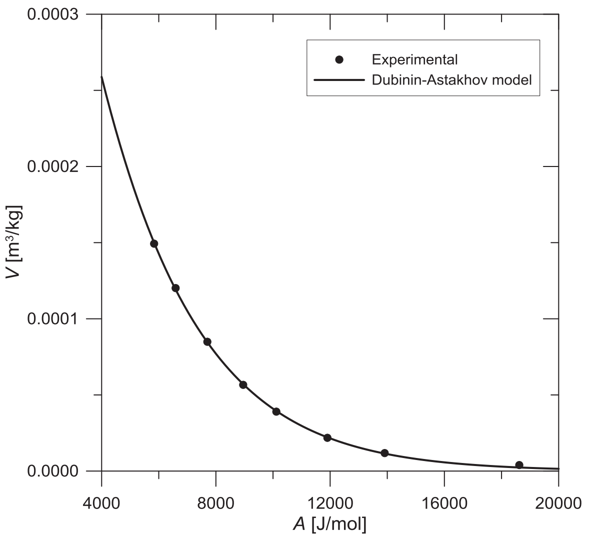

Fig. 5. Characteristic curve for ammonia adsorbed on charcoal (T=298.15 K)

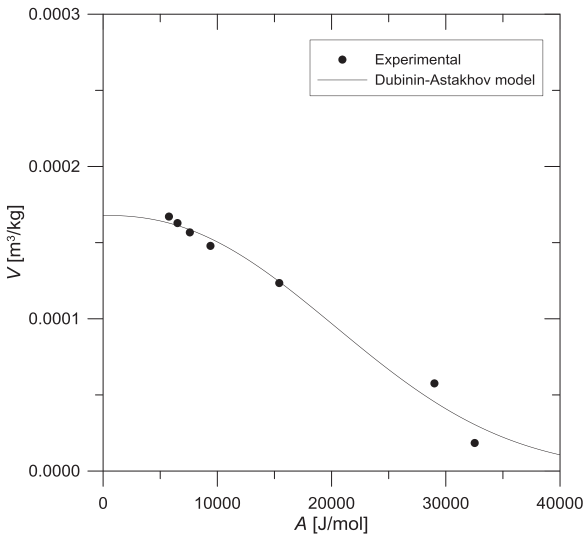

Fig. 6. Characteristic curve for ammonia adsorbed on clinoptilolite (T=298.15 K)

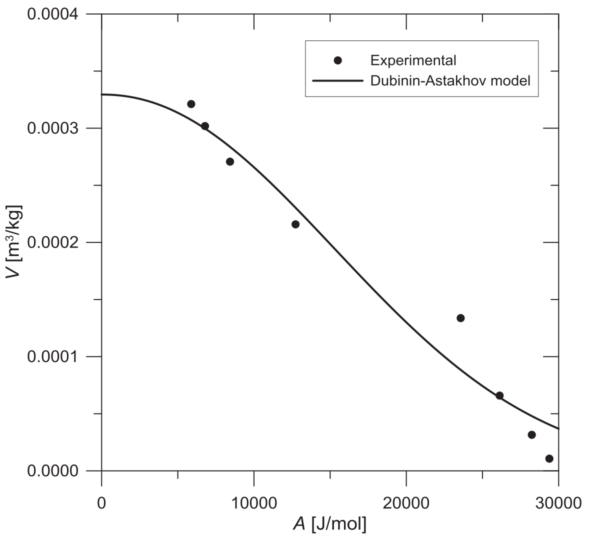

Fig. 7. Characteristic curve for ammonia adsorbed on polymer resin (*T*=298.15 K)

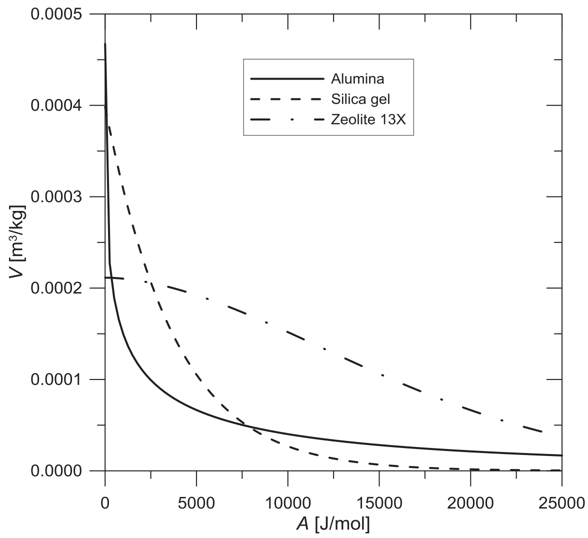

Fig. 8. Characteristic curve for water adsorbed on various adsorbents

For all adsorbent–adsorbate working pairs, the values of isosteric heat of adsorption varied with adsorbed-phase loading (Figures 10 and 11). This result indicates that all adsorbents have an energetically heterogeneous surface.

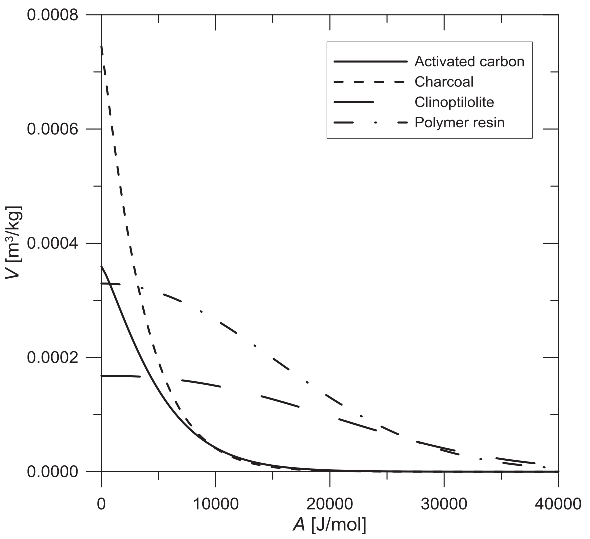

Fig. 9. Characteristic curve for ammonia adsorbed on various adsorbents

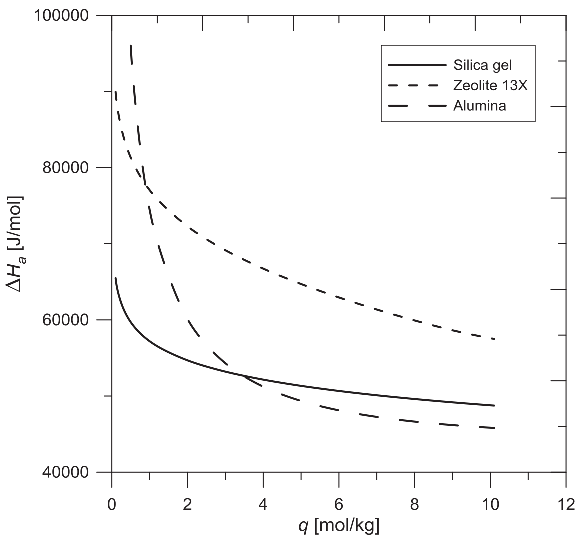

Fig. 10. Isosteric heat of adsorption of water on various adsorbents (*T*=298.15 K)

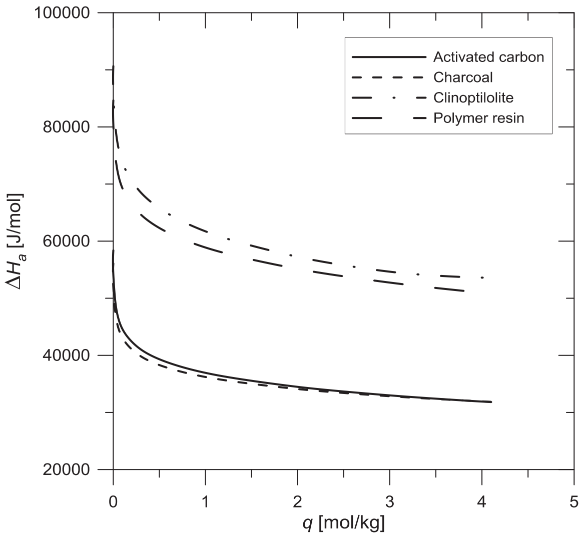

Fig. 11. Isosteric heat of adsorption of water on various adsorbents (*T*=298.15 K)

CONCLUSIONS

Adsorption equilibrium of water and ammonia on various adsorbents were studied. The adsorbents tested were activated carbon, alumina, charcoal, clinoptilolite, polymer resin, silica gel and zeolite 13X. Experimental data were correlated using the Dubinin-Astakhov model. Based on this model, the characteristic curves were obtained for all studied adsorbent-adsorbate systems. The isosteric heat of adsorption was derived using the Clausius-Clapeyron equation. For all adsorbent–adsorbate working pairs, the value of isosteric heat of adsorption varied with adsorbent-phase loading.

NOMENCLATURE

A	adsorption potential, J/mol
E_o	characteristic energy of the adsorbent, J/mol
ΔH_a	isosteric heat of adsorption, J/mol
N	number of data points
n	constant in the Dubinin-Astakhov equation
p	vapor pressure of adsorbate, Pa
p_s	saturation vapor pressure of adsorbate, Pa
q	amount adsorbed, mol/kg
q_s	saturation loading limit, mol/kg
R	gas constant, J/(molK)
T	temperature, K
V	volume adsorbed, m^3/kg
V_0	limiting adsorption volume, m^3/kg
β	affinity coefficient,
δ	mean absolute percent deviation
$\rho(T)$	temperature dependent density of liquid adsorbate, mol/m^3

Subscripts

calc	calculated
exp	experimental

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