SIMULTANEOUS DETERMINATION OF HEATS, EQUILIBRIUM AND KINETICS OF ADSORPTION
1- Ethoxy-2-propanol vapours

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Abstract

The heat, equilibrium, and kinetics of adsorption of 1-ethoxy-2-propanol vapours on granulated activated carbon were determined simultaneously by a reaction calorimeter SETARAM C80 D at T=298.15 K at various relative vapour pressures ($0.1< p/p_s <0.8$). The adsorption isotherm was correlated by the Freundlich equation. It was observed that the enthalpies of adsorption decrease slightly with increasing of the relative vapour pressure of the adsorptive. The rate of adsorption were calculated from analysis of the heat flux signals and it was found that the mass-transfer coefficient for 1-ethoxy-2-propanol vapours in granulated activated carbon increased with increasing relative vapour pressure of the adsorptive.

Keywords: adsorption, enthalpy, equilibrium, 1-ethoxy-2-propanol, granulated activated carbon, kinetics, reaction calorimetry

Introduction

Control of air emissions of organic vapours is one of the major aims of the industry. 1-ethoxy-2-propanol is recently widely used as a component of thinner and cleaner for the new high solid protective coatings. If there are significant actual emissions in their application, the local removal of their vapours by adsorption might be worth. The knowledge of the enthalpies, equilibrium conditions and kinetics of adsorption of the vapours is useful for the design of an adsorber. Because activated carbon is one of the most effective adsorbent, its adsorption characteristics for the common hazardous air pollutant solvents (hydrocarbons, aromatics) are well studied and known. However, no equilibrium, enthalpic and kinetic data are found in the literature for the adsorption of the 1-ethoxy-2-propanol on activated carbon.

Most of the calorimeters used to study adsorption operate under static conditions at constant temperature. They were applied for parallel determination of adsorption enthalpies and isotherms [1–3]. It was found that the values of adsorption enthalpies were relatively constant for low coverage region and decrease sharply to reach the enthalpy of condensation at high coverages of organic vapours [4–6].

The linear driving force (LDF) model for gas adsorption kinetics is frequently and successfully used for analysis of adsorption dynamic data and for adsorption pro-

cess design. The mass transfer of adsorption of organic vapours was found to be macropore-controlled in activated carbon and it was observed that the values of mass-transfer coefficient gradually increase with increasing concentration of the substrate in the gas phase [7–9].

The loadings, enthalpies and mass-transfer coefficients of adsorption of 1-ethoxy-2-propanol (CAS RN: [1569-02-4], common name: propylene glycol monoethyl ether) on granulated activated carbon at T=298.15 K at various relative vapour pressures ($0.1 < p/p_s < 0.8$) are given in this paper.

Experimental

The adsorbent, AP4-60 extruded activated carbon composed of cylindrical grains with 4 mm in diameter (Chemviron Carbon) is characterized by 470–550 kg m^{-3} apparent density, max. 12% ash content and a hardness number of min. 90 (ASTM D3802). Its BET specific surface area obtained from 77 K nitrogen adsorption isotherms (Micrometrics ASAP 2000) reaches 1130 m^2 g^{-1}, the single point total pore volume of pores less than 356 nm diameter is 0.54 cm^3 g^{-1}, the average pore diameter 1.9 nm. Analytical grade 1-ethoxy-2-propanol {>99.4 % (m/m)} was supplied by Thommen & Co. The nitrogen gas (Messer Griesheim) had a purity of 99.999% (v/v).

The calorimetric measurements were carried out in SETARAM C80 D calorimeter using standard vacuum/high pressure vessels made from Hastelloy C. The calorimeter was calibrated electrically using the Joule-effect by means of a special cell with calibrated heaters as recommended by IUPAC [10]. The vessels were connected to a vacuum line constructed from stainless steel tubes. The pressure in the vacuum line was tested by a Pyrani vacuum meter. The solvents were degassed by periodical evacuation during freezing/thaw cycles using liquid nitrogen as freezer material. The degassed adsorptive was stored in liquid state in a thermostated and evacuated Pyrex vessel, which was jointed to the vacuum line. The equilibrium pressure of the adsorptive was adjusted by the temperature of the liquid, which was controlled by a thermostate (±0.05 K).

Prior to preparation the adsorbent sample, the carbon pellets were dried in pure nitrogen gas stream at 150°C during 16 h and after cooling they were stored under N$_2$. Before each measurement, the carbon grains were putted into the measuring cell of the calorimeter filled with nitrogen. The measuring and reference cells were placed inside a metallic block of the calorimeter and the carbon was evacuated *in situ* during 4 h. The working temperature of the experimental cells (298.15±0.05 K) was measured by means of a 100 Ω platinum resistance thermometer located between the two vessels. When thermal equilibrium was reached, the vacuum line was closed and solvent vapours were introduced into both vessels. The pressure in the vessels was measured by a pressure transducer with temperature compensation connected to a digital manometer. The differential heat-flux was then recorded, and integrated as a function of time to give the heat changes during adsorption. The quantity of vapours adsorbed were determined by gravimetry.

Results and discussion

The loadings of 1-ethoxy-2-propanol on activated carbon extruded grains is shown in Fig. 1. The equilibrium data resembled physicosorption isotherm of Type III of the IUPAC recommendations [11], which represents multilayer adsorption and indicates that the adsorption takes place also in the pores of the adsorbent.
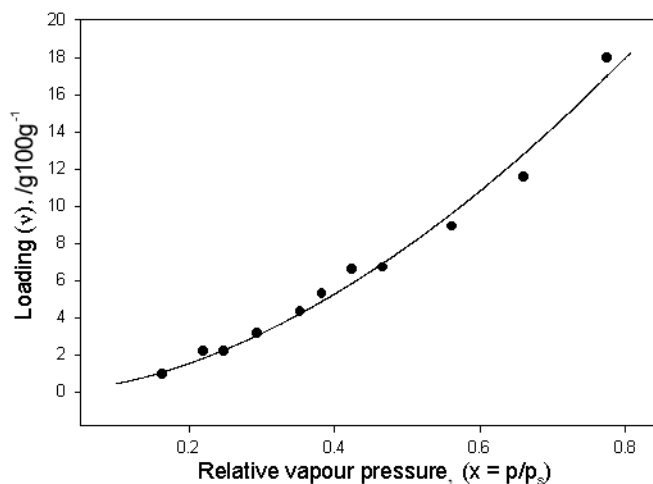

Fig. 1 Adsorption isotherm of 1-ethoxy-2-propanol on activated carbon extruded grains at 298.15 K. ● experimental data point, — least-squares fit using Eq. (1)

The experimental data were fitted to the Freundlich-type equation:

$$v = v_m x^n \tag{1}$$

where v is the loading (g adsorbate / 100 g adsorbent) at equilibrium, $x=p/p_s$ is the relative vapour pressure of the adsorptive, p_s is the saturated pressure of vapour at 298.15 K, v_m and n are adjustable coefficients. An unweighted least-squares procedure used resulted in the following parameters: v_m=26.67 g/100 g, n=1.766, with the correlation coefficient r=0.992, Student's F=566 and standard deviation $S.D.$=0.66g/100 g.

The exothermic enthalpy changes during the adsorption are given in Fig. 2, where $\Delta_{ads}H_m$ values expressed as of kJ mol^{-1} adsorbate is plotted against the relative vapour pressure of the 1-ethoxy-2-propanol. Figure 2 reveals that the values of heats of adsorption obtained are 2.5 times higher than the heat of condensation of the vapours at low relative vapour pressures indicating strong adsorbate-adsorbent interactions. The value of heat of condensation of the vapours, symbolised as dotted line in Fig. 2, was calculated from the vapour pressure – temperature data of 1-ethoxy-2-propanol using the Clausius–Clapeyron equation. The molar enthalpies of adsorption of 1-ethoxy-2-propanol ($\Delta_{ads}H_m$) decrease slightly with increasing of the relative vapour pressures of the adsorbate up to p/p_s=0.8 and can be described by the empirical correlation equation:

$$\Delta_{ads}H_m / \text{kJ mol}^{-1} = a + b\ln(c+dx) \tag{2}$$

with the parameters a=75.687, b=8.1675, c=28.2005 and d=–28.1824. The correlation coefficient is r=0.992, the Student's F=162 and the standard deviation of the fit is $S.D.$= 2.4 kJ mol^{-1}. The adsorbate-adsorbent interactions may be characterised energetically by the molar enthalpy of adsorption at zero filling. Its value obtained by extrapolating Eq. (2) as $x \to 0$ is $\Delta_{ads}H_m^o$=103 kJ mol^{-1}.

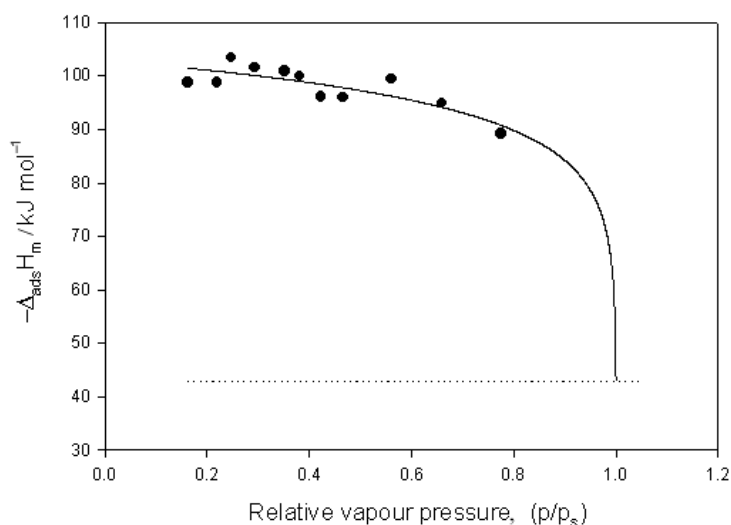**Fig. 2** Molar enthalpies of adsorption ($\Delta_{ads}H_m$) of 1-ethoxy-2-propanol on activated carbon extruded grains at 298.15 K ● experimental data point, ··· heat of condensation of 1-ethoxy-2-propanol , — least-squares fit using Eq. (1)

The uptake rate of 1-ethoxy-2-propanol on activated carbon grains are investigated by the linear driving force (LDF) mass transfer model, which describes the rate of isothermal adsorption by

$$m_t / m_\infty \cong v_t / v = 1 - \exp(-kt) \tag{3}$$

where m_t and m_∞ are the adsorbed amount at time t and at equilibrium ($t \to \infty$), respectively, and k is the overall mass-transfer coefficient.

The mass-transfer coefficient may be estimated from gravimetric measurements, or in indirect way, using calorimetric data, because the enthalpy of adsorption depends on the amount adsorbed. The relationship between specific enthalpy of adsorption and adsorbate uptake is linear for 1-ethoxy-2-propanol/activated carbon system in the 0–18 g/100 g uptake range investigated and can be given by

$$Q_{ads} / v = 983 - 6.43v \tag{4}$$

where Q_{ads} is the total heat of adsorption at equilibrium. The negative slope of Eq. (4) indicates that the heat of adsorption of the first layer is greater than the heat evalua-
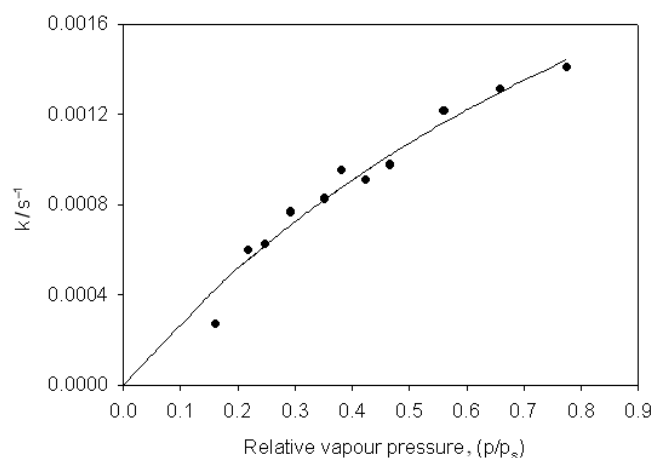
Fig. 3 Mass transfer coefficients (k) of 1-ethoxy-2-propanol on activated carbon extruded grains at 298.15 K. ● experimental data point, — least-squares fit using Eq. (6)

tion during the uptake of the molecules of vapours on the top of already adsorbed molecules. Because Eq. (5) describes the integral heat/loading ratio over a wide range of adsorbed amounts, the relative uptake might be estimated as

$$\frac{v_t}{v} \cong \frac{Q_t}{Q_{ads}} \frac{983 - 6.43v}{983 - 6.43(Q_t/Q_{ads})v} = 1 - \exp(-kt) \tag{5}$$

where $Q_t = \int_0^t \dot{Q} \mathrm{d}t$ is the integral heat of adsorption evolved at time t, and $\dot{Q}$ is the differential heat-flux recorded during the experiment. The k values, predicted by regression of Eq. (5) between the initial time (t=0) and a final time corresponding to 50% of the equilibrium loading for each experiment, are plotted in Fig. 3 *vs.* relative vapour pressures. It is apparent that the values of mass transfer coefficients increase to the vapour pressure however, not proportional. The mass transfer coefficient data were fitted to an empirical correlation functions:

$$k/s^{-1} = 0.00297x/(1+0.773x) \tag{6}$$

with the correlation coefficient r=0.979, standard error $S.D.$=0.0001 and F=210.

Conclusions

The heat, equilibrium, and kinetics of adsorption of 1-ethoxy-2-propanol vapours on activated carbon can be studied simultaneously by reaction calorimeter. The adsorption isotherm could be correlated by the Freundlich-type equation. The values of heats of adsorption obtained are higher than the heats of condensation of the 1-ethoxy-2-propanol vapours and the enthalpies of adsorption decrease with increas-

ing of the relative vapour pressures of the adsorptive. The mass transfer coefficients determined from enthalpic data were found to increase to the vapour pressure.

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