Report on research activity

of Dr. L. Gordeeva

during her visit to CNR-ITAE in June 3th – June 18th 2015.

Introduction

Owing to encouraging energy saving potential and the use environmentally benign working fluids, adsorption heat transformers (AHT) are considered as promising alternative to compression systems. However the enhancement of their efficiency and specific power is required for their broader dissemination. In our opinion the great advance in the AHT can be related to the development of new efficient adsorbents. It has recently been shown that the composite adsorbent LiBr/silica gel KSK possesses an advanced sorption capacity towards ethanol vapor that makes it promising for AHTs [L. Gordeeva, A. Frazzica, A. Sapienza, Yu. Aristov, A. Freni, Energy 75 (2014) 390-399].

However, it is known that the sorption properties, means both the equilibrium and dynamics, are affected strongly by the salt content of the composite. The main purposes of the activity, carried out in frame of the visit, was the study the effect of LiBr content on the equilibrium and dynamics of ethanol adsorption on the composite sorbent LiBr/silica gel KSK. On the base of the obtained results the recommendations on the optimization of the adsorbent composition are formulated.

Experimental

The silica gel KSK (Russia) (pore volume $V_t = 0.9$ cm^3/g, surface area $S_{sp} = 360$ m$_2$/g, average pore size $d_{av} = 15$ nm, grain size $D_{gr} = 0.4 - 0.6$ mm) was used as the matrix. The composites were synthesized by an insipient wetness impregnation of the silica gel, previously dried at 160 °C, with an aqueous LiBr solutions followed by thermal drying at 160 °C. The salt content in the composites was determined by weighting dry samples before and after impregnation.

Two composites LiBr(14.6)/silica and LiBr(23.8)/silica were prepared with the salt content of 14.6 and 23.8 wt.%, respectively.

Ethanol adsorption isobars were measured by thermogravimetric method using a CAHN C2000 thermal balance in the temperature range T = 30–100 °C and for ethanol pressure P = 31.1mbar. The sample of the adsorbents (c.a. 20 mg) was heated up to 100 °C under continuous evacuation (the residual pressure ≈ 0.01 mbar) until reaching the dry weight m_0. Then, the sample was exposed to ethanol vapour with a fixed pressure and cooled to a fixed temperature to start the equilibrium tests.

The amount of ethanol sorbed at equilibrium $m(P,T)$ was measured as the final increase in the sample weight at fixed T and P. The methanol sorption was characterized by the methanol content $w = m(P,T)/m_0 \cdot 100\%$.

The isothermal ethanol adsorption dynamics was studied by the differential step isothermal method [Crank, J., 1956. Mathematics of Diffusion. Oxford University Press, London.]. The adsorbent sample (c.a. 20 mg) was placed in the the Chan balance measuring cell and heated up to 100 °C under continuous evacuation. Then the sample was cooled down to a fixed temperature and then connected to the evaporator thus, the pressure over the sample was jumped up sharply that initiated adsorption. After the equilibration, the sample was disconnected from the evaporator, and the temperature of the latter was increased and the next pressure jump was applied. The data on the temperature, pressure, and the sample weight were recorded by a data acquisition system. The dimensionless uptake q(t) was calculated as

$$q(t) = \frac{m(t) - m(t=0)}{m(t \to \infty) - m(t=0)}. \tag{1}$$

The data on the adsorption dynamics were evaluated in accordance of the the differential step isothermal method, described in details in [Ruthven, D.M., 1984. Principles of adsorption and Adsorption Processes. Wiley, New York.]. According to this method a simplified expression for the initial region of the uptake curve may be obtained as

$$\frac{m(t)}{m_\infty} = \frac{2S}{V}\sqrt{\frac{D_{ap}t}{\pi}} = A\sqrt{t} \tag{2}$$

Where S/V is the ratio of external area – to – particle volume ($S/V = 3/R_p$ for a spherical particle), D_{ap} is an apparent diffusivity. This diffusivity depends on the pore diffusivity De, the grain porosity ε and the shape of the water sorption isotherm (the local slope of the isotherm K=(dw/dc)):

$$D_{ap} = D_e/(\varepsilon+(1-\varepsilon)K). \tag{3}$$

Results

Ethanol sorption isobars for the composites LiBr(14.6)/silica and LiBr(23.8)/silica are presented in Figure 1. The sorption at $T > 70$ °C is minor and relates to the ethanol adsorption on the active surface centres on the silica gel surface. At decreasing temperature the salt starts to react with ethanol according to reaction LiBr + EtOH = LiBr·EtOH that is indicated by the sharp increase in sorption w from 2 to 17 % on the isobar for LiBr(23.8)/silica composite. The step for the LiBr(14.6)/silica is less pronounced, probably due to interaction of the salt with the silica gel surface. The sorption on the composite LiBr(23.8)/silica with the larger salt content is somewhat higher for all the temperatures, which is due to the fact that namely the salt is a primary sorbing component of the composites. The uptake w_{max}, corresponding to the typical adsorption chilling cycle (T=30 °C, P= 31.1 mbar), reaches 48 and 32 % for LiBr(23.8)/silica and LiBr(14.6)/silica, respectively. It is worth noting that the volume of ethanol adsorbed on LiBr(23.8)/silica is $v = w_{max}/\rho = 0.6$ cm^3/g that is very close to the total pore volume of the composite $V_t = 0.68$ cm^3/g. Thus, the further increase in the salt content may results in the "LiBr – ethanol" solution formed inside the composite pores pours out into the space between the sorbent particle. That can promote the decrease in the sorption capacity and the corrosion of the metal part of the adsorber. Thus, further increase in the salt content is not recommended.

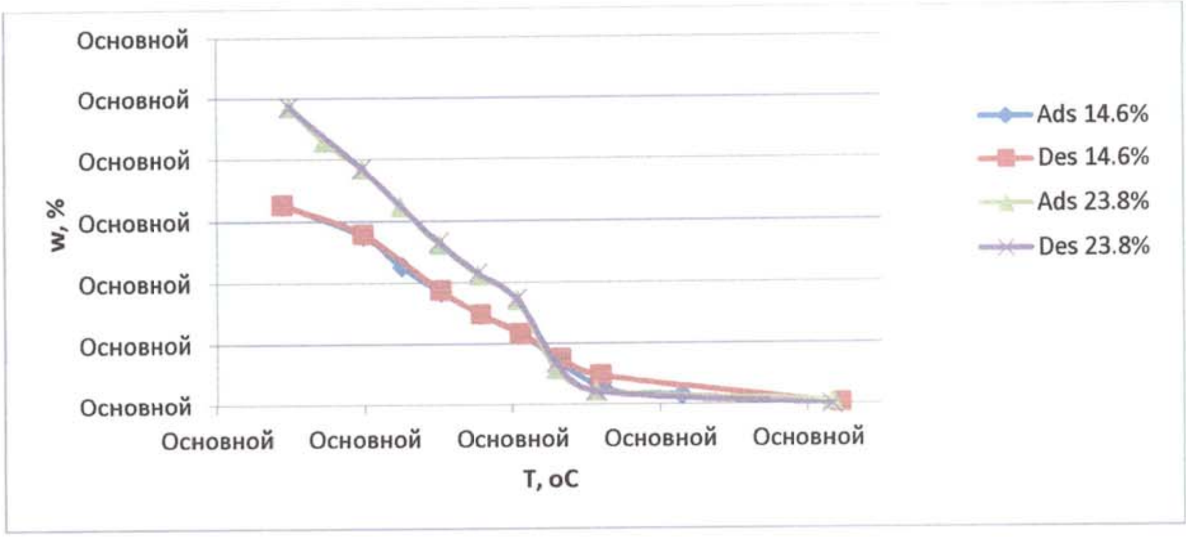
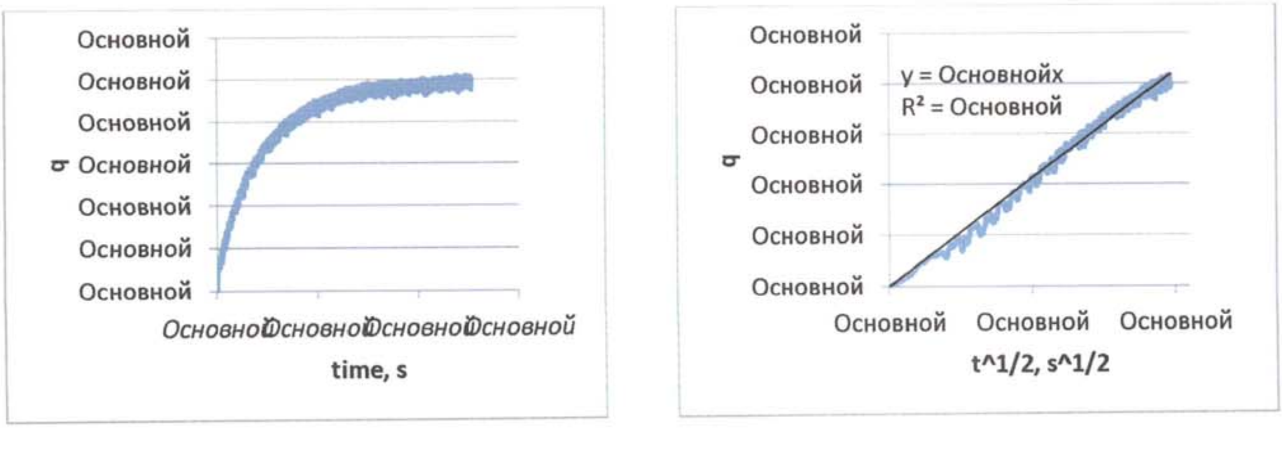


Figure 1. Ethanol sorption equilibrium for LiBr(14.6)/silica and LiBr(23.8)/silica, $P = 31.1$ mbar.

A typical dynamic curve of ethanol adsorption is presented in Fig. 2 (a) as the function of the dimensionless uptake q vs. time. The total time of the complete adsorption depends on the variation in uptake and did not exceed 5-15 minutes. The initial parts (up to q = 0.7-0.8) of the dynamic curves appeared to be linear function of $\sqrt{t}$ (Fig. 2b) that allows us to estimate the coefficient A (eq. 2) and the apparent diffusivity D_{ap}

$$D_{ap} = {\pi A^2}/{36R^2} \tag{4}$$



a) b)

Fig 2. The dynamic curves of ethanol adsorption on the LiBr(23.8)/silica composite. $T = 42$ °C, $P_{in} = 25.9$ mbar, $P_{fin} = 31.9$ mbar.

The results on the evaluation of the apparent diffusivity as function of the ethanol relative pressure P/P_0 are presented in Table 1.

Table 1. The apparent diffusivity D_{ap} of ethanol vapour in pores of LiBr/silica composites.

LiBr(14.6)/silica					
$T_{ads} = 58$ °C			$T_{ads} = 42$ °C		
P/P_0	dw, g/g	D_{ap}, $*10^{10}$, m^2/s	P/P_0	dw, g/g	D_{ap}, $*10^{10}$, m^2/s
0.05	0.003	4.93	0.11	0.011	9.51
0.07	0.011	7.03	0.13	0.022	10.75
0.08	0.061	0.95	0.16	0.026	9.65
0.09	0.010	16.80	0.19	0.027	11.66
0.11	0.020	15.90	0.23	0.030	9.22
0.12	0.013	15.66	0.26	0.019	12.81
0.14	0.016	14.25	0.29	0.019	12.27
0.15	0.016	14.20	0.33	0.021	10.48
			0.34	0.010	12.31
LiBr(23.8)/silica					
$T_{ads} = 58$ °C			$T_{ads} = 42$ °C		
P/P_0	dw, g/g	D_{ap}, $*10^{10}$, m^2/s	P/P_0	dw, g/g	D_{ap}, $*10^{10}$, m^2/s
0.05	0.014	3.64	0.11	0.024519	6.63
0.07	0.109	0.88	0.13	0.037085	6.36
0.08	0.028	12.69	0.16	0.038862	6.33
0.09	0.014	14.38	0.19	0.034624	8.07
0.11	0.025	11.94	0.23	0.037273	10.82
0.12	0.017	11.90	0.26	0.027682	8.45
0.14	0.019	11.14	0.29	0.027202	8.27
0.16	0.020	10.90	0.32	0.029398	9.33
			0.36	0.028812	7.84

The apparent diffusivities D_{ap} at $T = 42$ °C is somewhat lower than those at $T = 58$ °C for both the composites. The diffusivities $D_{ap} = (0.95 - 4.93)\cdot 10^{-10}$ at low $P/P_0 < 0.08$, is much lower than those at higher P/P_0. That is probably caused by the fact that at this P/P_0 the main adsorption mechanism is the reaction of the solid LiBr with ethanol vapour. Actually, according to the equilibrium data the formation of the complex LiBr·EtOH occurs at P=31.1 mbar and $T = 60$ °C, that corresponds to

P/P_0= 0.07. Thus, at $P/P_0 < 0.07$ the adsorption dynamics is controlled by the reaction rate rather than by the diffusion.

The apparent diffusivities D_{ap} for LiBr(23.8)/silica is always lower than those for LiBr(14.6)/silica composite. The probable reason of this difference could be as follows. The apparent diffusivities D_{ap} depends on local slope of the isotherm K=(dw/dc) (see eq. 3). The amount of the ethanol adsorbed dw on the LiBr(23.8)/silica for all the pressure jumps is higher for this composite as compared to the composite with lower salt content LiBr(14.6)/silica, which means higher K-value. Consequently, at the same efficient ethanol diffusivity D_{ef}, the apparent diffusivity D_{ap} is lower for the composite with larger salt content. However, it should be taken into account, that the absolute rate of adsorption $dw(t)/dt = 0.5w_\infty At^{-0.5}$ (eq. 2) is proportional to the product w_∞A. The average value $w_\infty A$ = 1.0-1.3 and 1.3-1.5 g/(gs) for LiBr(14.6)/silica and LiBr(23.8)/silica, respectively. Thus, the increase in salt content of the composite LiBr/silica results in both the rise of its sorption capacity and the adsorption rate. This promotes the augmentation of both the Coefficent of Perfomance (COP) and Specific Cooling Power (SCP) of AHT, utilizing "LiBr/silica – ethanol" working pair. Thus, the optimum salt content, which is recommended for the enhancement of COP and SCP of the AHT, can be estimated as ca 24 wt%.

Resume

The ethanol adsorption isobars on two composite sorbents LiBr(14.6)/silica and LiBr(23.8)/silica were measured. The isothermal dynamics of ethanol adsorption on LiBr(14.6)/silica and LiBr(23.8)/silica composite was studied. The increase in the salt content is shown to result in the enhancement of both the sorption capacity and sorption rate. The optimum salt content, which is recommended for the enhancement of COP and SCP of the AHT, can be estimated as ca 24 wt%.

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17 June 2015
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