Adsorption Isosters Measurements on CaCl$_2$ Impregnated ACF Felt for an Application of Ammonia Scrubber

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ABSTRACT

Accidental released ammonia liquid or vapor is usually hosed down by spraying water to curtail its spread. However, ammonia absorption capacity of water is low (0.03kg-ammonia / kg-water) and hence much quantity of water is required to mitigate released ammonia.

Therefore we have developed adsorbent for an application of mobile scrubber vehicle, which allows more effective and efficient recovery of any accidental release of liquid or vapor by actively scrubbing into adsorbers. The mobile scrubber vehicle provides a versatile and mobile mitigation means to curtail the spread of toxic vapors into the environment in the event of a release by bringing the scrubber unit on site.

As for adsorbers active carbon fiber (ACF) has many advantages, which has large surface area, 1500m^2/g as well as large pore volume, 1,2 ml/g especially for micropores, 1,7 nm, which provide higher adsorption capacity and also faster adsorption as well as desorption rates than that of powder or granular activated carbon.

However the adsorption capacity of ACF is at most 0.09 kg-ammonia / kg-adsorbent under 0.1Mpa and room temperature. In order to install adsorbers within the limited space on a vehicle this amount is not sufficient. Hence we were concentrated on developing on CaCl$_2$ impregnated ACF felt which allows to increase its adsorption capacity and decreases flow resistance. In the present paper we demonstrated on its measured isosters and isotherms on ammonia adsorption.

The test sample of "31 wt% Calcium chloride impregnated carbon fibers" was synthesized using ACF felt provided by Nantong Tonghui Industrial & Trading Co.,Ltd in China and CaCl$_2$ aqueous solution. Isosters of ammonia sorption have been measured for base ACF felt and "31 wt% Calcium chloride impregnated carbon fibers" at T = 20-90°C and P = 0.1-9.0 bar. The uptake covered the range of 4.8 to 32 wt.% that corresponds to 1 - 7 mol NH$_3$ per mol of CaCl$_2$. The method used is based on the sample heating in a closed volume with registration of the NH$_3$ equilibrium pressure P as a function of temperature T. Apparent enthalpy of ammonia sorption was obtained directly from the straight isosteric lines presented as lnP vs. 1/T. Appropriate correction of this value was done to take into account the "dead" volume in the adsorber. Isotherms of ammonia sorption on the both samples were plotted using the Polanyi potential theory for temperatures 20, 30, 40, …, 90^{0}C in the pressure range 0.1-9 bar. The test results showed that adsorption capacity was larger than 0.2 wt.% that can be of practical interest for the application involved.

EXPERIMENTAL

For sample synthesis an aqueous solution of calcium chloride and ACF felt provided by Nantong Tonghui Industrial & Trading Co.,Ltd, China were used. ACF felt was

filled with a CaCl$_2$ saturated solution and dried at 200°C during 12 h. Salt content C in the synthesised sample was C=31 wt.%. The value of uptake (w) was expressed as a weight % of ammonia sorbed in respect to a dry weight of the sorbent or as a molar ratio (N) of ammonia sorbed by one mole of the CaCl$_2$ in the sample. Taking into consideration the salt content in the sample C the relationship between w (wt.%) and N (mol/mol) is as follows: w = N·C·17/111. Here 17 is a molecular weight of ammonia, 111 is a molecular weight of calcium chloride.

Isosteres of the ammonia sorption were measured using a set-up schemed on Fig.1. The core of this plant was a stainless steel cylindrical adsorber (1) 4 cm in diameter (volume 125.6 cm^3) filled with the sorbent. Two thermocouples were placed in the middle of the adsorber and near the wall to provide a direct reading of the sorbent temperature and its gradient along the bed. The adsorber was placed into a water thermostat (2) to maintain the sorbent at a constant temperature in the range of 16 to 90°C. The temperature of the bath was maintained constant within a variation of ± 0.1 K.
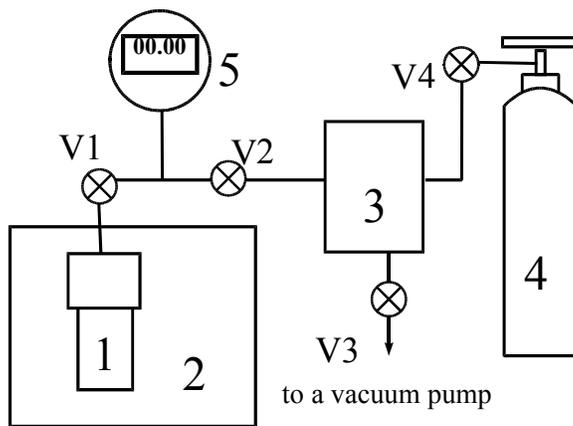

Fig. 1. The scheme of experimental set-up for measuring the isosteres of NH$_3$ sorption.

The sample was heated in an oven at 200°C for 12 h and cooled down to room temperature in dry atmosphere. After that its dry weight m$_o$ was measured. Typical dry weight was 13 g as the sample density was about 0.1 g/cm^3. After that, the sample was placed in the adsorber and evacuated at 50°C for 1 h down to the residual pressure 0.1 mbar (valves V1 – V3 are open, V4 is closed). A certain amount of ammonia was sorbed on the sample at room temperature T according to the following procedure:

a) a buffer tank (3) was connected with a high-pressure container of NH$_3$ (4) and the pressure in the tank was increased to P$_0$ (V4 was open). The pressure was measured by a pressure gauge (5) with the accuracy of 1.0 rel. %.

b) the ammonia adsorption on the sample was started (V4 was closed, V1 was open),

c) the adsorption was stopped when the pressure in the tank decreased to the value P$_1$, which was preliminary estimated to reach a given (minimal) ammonia uptake in the sample (V1 was closed),

d) the equilibrium pressure over the sample P$_{eq}$ was measured after the sorption was finished (2-20 h).

The initial uptake was calculated as

$$w_1 = [\frac{(P_0 - P_1)V}{RT} - \frac{P_{eq} V_1}{RT}]\frac{\mu}{m_0} \quad , \tag{1}$$

where T is the room temperature (K), V is the tank volume (V = $1.25 \cdot 10^{-3}$ m^3), V_1 is the volume of the gas phase restricted by valve V2, R is a universal gas constant (R = 8.31 J/(mol·K)), μ is the molecular weight of ammonia. The "dead" volume V_1 includes the volume of the pressure gauge, the volume of connecting lines and the volume of the gas phase in the adsorber. The latter volume is the volume of adsorber minus the volume occupied by a solid phase of adsorbent skeleton. The "dead" volume was estimated to be V_1 = (1.10 ± 0.05)·10^{-3} m^3. It is worthy to mention that the second term in equation (1) is much smaller than the first one as $V_1 < V$ and $P_{eq} << (P_0 - P_1)$.

The NH$_3$ pressure over the sorbent with the initial uptake w_1 was measured as a function of temperature at constant volume V_1 (valve V1 was open, valve V2 was closed). After the first reading at minimal temperature the bath temperature and, hence, the sorbent temperature was increased and new equilibrium pressure P(T) of ammonia was recorded. Plotting ln(P) vs. 1/T, we obtained the isoster of ammonia sorption, which corresponds to the uptake w_1. Then, the uptake was increased to $w_2 > w_1$, and the new isoster was measured, and so on. To increase the NH$_3$ uptake an additional amount of ammonia was sorbed on the sample from the buffer tank. The procedure was as follows:
   a) the sample was cooled down to the room temperature,
   b) the pressure in the tank was decreased to preliminary estimated value $P_2 < P_1$,
   c) the equilibrium pressure over the sample P_{eq} was measured after the sorption was finished (2-20 h).
The equilibrium uptake w_2 can be calculated according to methodology similar to that described above. Conditions of the measurements done are summarized in Table 1.

Table 1. Description of the experiments performed with the sample "Calcium chloride impregnated carbon fibers"

N, mol/mol	w, wt.%	Δw, wt.%	T_{min}, °C	T_{max}, °C	P_{min}, bar	P_{max}, bar
1.0	4.8	±0.05	20.6	84.2	0.07	0.28
2.0	9.6	±0.3	38.2	88.0	0.30	1.31
3.0	14.3	±0.5	20.2	81.4	0.61	3.64
4.0	19.1	±0.9	15.8	89.2	0.68	7.61
5.0	24.0	±1	21.4	79.0	1.18	8.74
6.1	29.0	±1	20.4	78.6	1.61	7.67
7.0	33.0	±1	15.2	58.8	1.94	8.01

RESULTS AND DISCUSSION

The isosters plotting as lnP vs. 1/T can be approximated by a straight line lnP = A + B/T, where A = -ΔS/R, B = ΔH/R (ΔH and ΔS are enthalpy and entropy of ammonia sorption, R is a universal gas constant).

Experimentally measured isosters are presented on Fig. 2. It is necessary to take into consideration that during measuring a single isoster the uptake is not strictly constant because some amount of ammonia can be desorbed from the sample as the temperature increases. THis effect is caused by the existence of "the dead volume" in the adsorber. This effect can be significant for samples with a low apparent density like the studied carbons. Appropriate correction of the uptake was done for each experimental isoster. Table 1 demonstrates that the actual uptake can differ from the average one within 1-5 rel.

%. The difference is higher for larger uptakes because larger amount of ammonia is desorbed from the sample as the temperature is increased. The effect of "the dead volume" results in the underestimation of the equilibrium pressure over the sample and, as a consequence, leads to lower value of the isosteric heat of ammonia sorption. The real values of the sorption heat can be obtained by using the Polaniy potential theory [1] (see below).
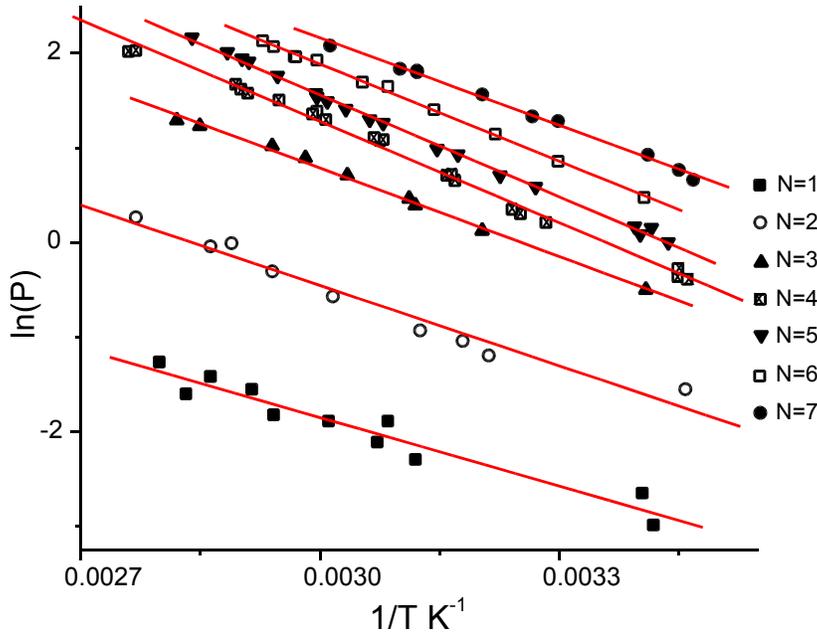

Fig. 2. Experimental isosters of ammonia sorption.

<u>**Sorption equilibrium and isotherms of ammonia sorption**</u>

The Polyanyi potential theory declares a one-to-one correspondence between the uptake and so called adsorption potential $\Delta F = - R \cdot T \cdot \ln(P/P_{sat})$, where R is the universal gas constant, P is the actual pressure, Ps is the saturated pressure at fixed temperature T [1]. Indeed, if plot the uptake *w* vs. ΔF, it gives the temperature-invariant curve of ammonia sorption (Fig. 3).

One can see that at $\Delta F > 11$ kJ/mol sorption equilibrium in the system is monovariant. It means that in a wide range of the Polyanyi potential the uptake is constant and equals to w=4.7 wt.% that corresponds to 1 mol of NH_3 per 1 mol of $CaCl_2$. This is caused by the formation of a stable $CaCl_2 \cdot NH_3$ complex and results in an uncertainty for the plotting of the isosteric line at uptake N=1 mol NH_3 per 1 mol of $CaCl_2$. At lower values of ΔF (2.8 kJ/mol < ΔF < 11.0 kJ/mol) the sorption equilibrium in the system is divariant.

For approximating the dependence $w(\Delta F)$ in the region that corresponds to a divariant type of equilibrium we used the polynomial expression [3, 4]

$$\text{Ln}(w) = a + b \cdot \Delta F + c \cdot \Delta F^2, \tag{2}$$

where *a*, *b* and *c* are fitting coefficients.

The results of the approximation are displayed on Figs. 3, 4 and fitting coefficient are presented in Table 3. It is seen that all the data obtained experimentally can be well

described in the range of 2.8 kJ/mol < ΔF < 11 kJ/mol by the approximation suggested. Thus, it can be used for calculating isotherms of ammonia sorption.
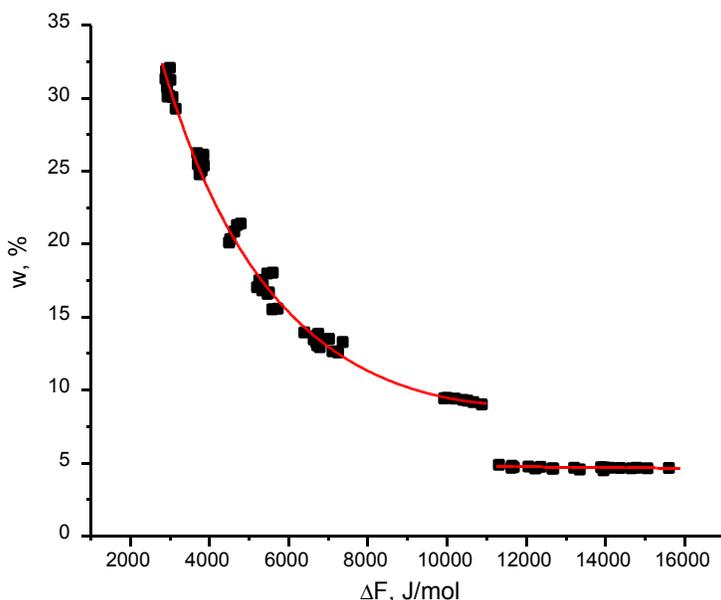

Fig. 3. Dependence of the uptake vs. the free energy of adsorption for "Calcium chloride impregnated carbon fibers". Symbols – experimental data, line-approximation.

Table 3. Fitting coefficients of equation (2).

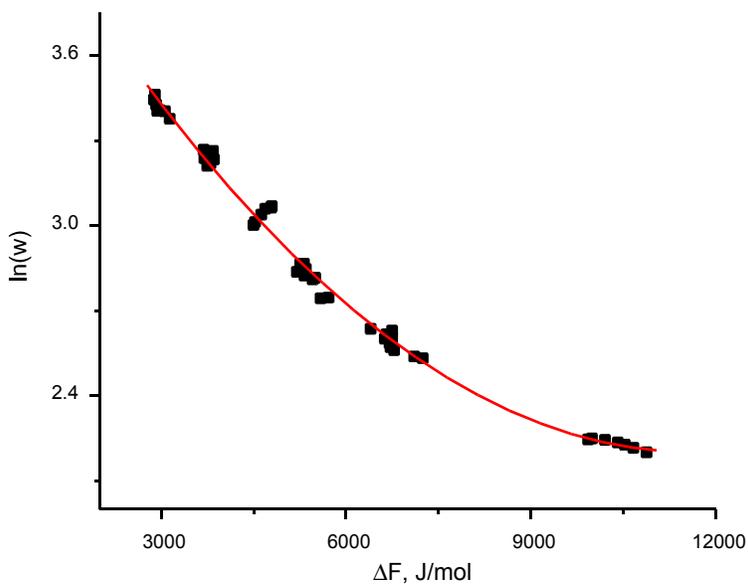| Uptake is expressed as	a	b	c
W, wt.%	4.3974	$-3.7225 \cdot 10^{-4}$	$1.5742 \cdot 10^{-8}$
N, mol NH_3/mol $CaCl_2$	2.8414	$-3.7225 \cdot 10^{-4}$	$1.5742 \cdot 10^{-8}$

Fig. 4. Approximation of the experimental data by polynomial equation (2) for "Calcium chloride impregnated carbon fibers" (symbols – experiment, line – calculation).

Using equation (2) with the coefficients presented in Table 3 it is easy to calculate isotherms of ammonia sorption in the pressure range 0.1 - 9 bar and temperatures 20, 30, ..., 90 $^{\circ}$C (Fig. 5).
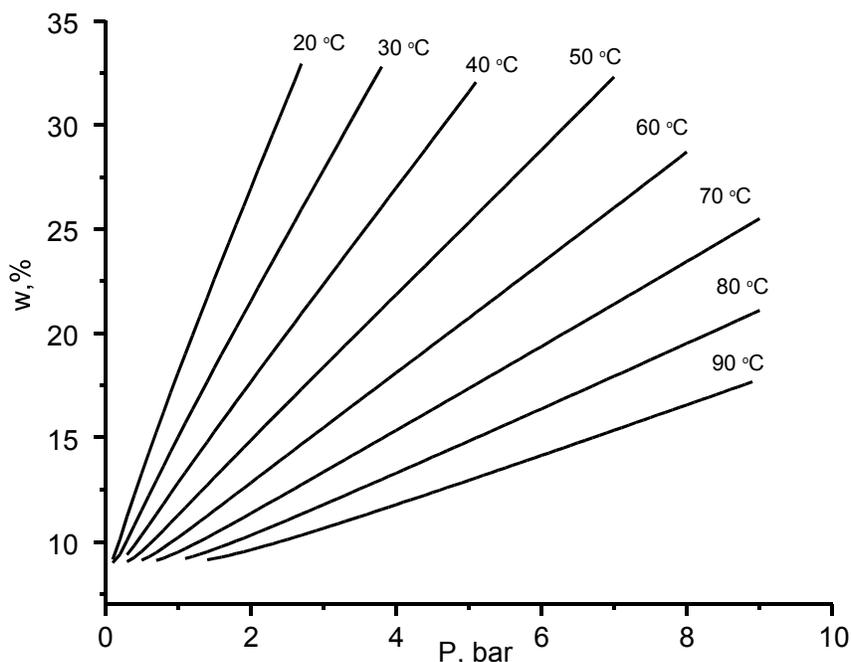

Fig. 5. Isotherms of ammonia sorption on "Calcium chloride impregnated carbon fibers" re-plotted from the experimental data using equation (2).

Isosteric heat of ammonia sorption

Values of isosteric heat of ammonia adsorption calculated directly from experimental data are presented in Table 4. One can see that the values of ΔH obtained from the experimental isosters at uptakes w=4.8 wt.% and w=9.6 wt.% are lower than the heat of ammonia evaporation. This is a result of the effects of "the dead volume" and the formation of $CaCl_2 \cdot NH_3$ complex. The formation of this stable complex leads to a monovariant sorption equilibrium in the system that results in the strong underestimation of measured pressure over the sample. The lower is a slope of isotherm (isobar, temperature-independent curve), the larger is the effect of "the dead volume" and the higher is the underestimation of isosteric heat.

The Polaniy potential theory can be used for calculation of the true isosteric heat of ammonia sorption using the equation:

$$\Delta H_{cal} = \Delta H_0 + \Delta F(T,P),$$

which is valid if sorption data are described by equation (2) [4]. Here ΔH_0 is the heat of ammonia evaporation, $\Delta F(T,P)$ is the Dubinin adsorption potential. Note, that at $\Delta F > 11$ kJ/mol we can not use the approximation by equation (2), however Fig. 3 demonstrate that beginning of $CaCl_2 \cdot NH_3$ complex formation takes place at $\Delta F=11.3$ kJ/mol. This makes it possible the estimation of the minimal value of isosteric heat of the ammonia sorption despite of the uncertainty caused by monovariant type of equilibrium in the system. This value was found to be 34.8 kJ/mol (Table 4), that is much larger than the condensation heat. This increase is due to the chemical bonding between ammonia and the salt. The value of **ΔH** decreases with the raise in the uptake.

Table 4. Experimental and calculated isosteric heats of ammonia sorption

N, mol/mol	w, wt.%	ΔH_{exp}, kJ/mol	ΔF, kJ/mol	ΔH_{calc}, kJ/mol
1.0	4.8	20 ±2	11.3 ±0.1	34.8*
2.0	9.6	24 ±2	9.7 ±0.1	33.0
3.0	14.3	25.9 ±0.6	6.4 ±0.1	29.7
4.0	19.1	29.6 ±0.6	4.9 ±0.1	28.2
5.0	24.0	29.8 ±0.3	4.0 ±0.1	27.3
6.1	29.0	28.3 ±0.4	3.2 ±0.1	26.5
7.0	33.0	25.6 ±0.6	2.8 ±0.1	26.1

* Estimation of the minimal value.

PRACTICAL Application of AMMONIA SCRUBBER ON VEHICLE

A well-designed, constructed, operated and maintained storage tanks has a very low probability of discharge accidents. Most of the accidental discharge occurs during transport or transfer.

Table 4 shows the design conditions of ammonia scrubber on vehicle against a 4MT storage tank. Its allowable store amount is taken 2000 kg as 85% of its capacity.

Table 4 Design conditions

	Liquid line released accident	Gas line released accident
Diameter of released line	25.4 mm ϕ	25.4 mm ϕ
Released rate	56.7 litter/min	10 m^3/min
Flash rate to adsorber	10 m^3/min as gas 20% vaporization of discharge liquid: due to expansion to atmosphere	20% of stored amount due to self cooling by expansion to 1atm with decrease of inner pressure
Recovery	To adsorber as gas 240kg/h & to container as liquid 1760kg/h	To adsorber as gas 240kg/h

Table 5 shows the specification of adsorber and Figure 6 shows a photo of ammonia scrubber vehicle., respectively. It is comprised of 2 parallel channels; each channel has 5 adsorber cells in parallel and each cell has 5 adsorber modules with 4 cooling disks.

Table 3 Specification of scrubber vehicle

Adsorbent	CaCl$_2$impregnated ACF-1300
Weight ratio CaCl$_2$/ACF	40 w%
One module Outer / inner diameter Height weight	Cylindrical shape 700/100 mm ϕ 295 mm 16 kg
One cell	80kg-5 modules
Total weight of adsorbent	800kg-10 cells

Flow velocity	0.15m/sec
Contact time	>2 sec
Cooling capacity	134kW
Flow rate	$20m^3/h$
Blower Volume flow rate Power Fan static pressure	$5000m^3/hr$ 23.8 kW 50 in wg

Fig. 7 Illustration of Field testing of ammonia scrubber vehicle

CONCLUSIONS

1. The newly developed $CaCl_2$ impregnated ACF felt and its characteristics of adsorption on ammonia were clarified.
2. Mobile ammonia scrubber vehicle was constructed based on experimental data and its field-testing was successfully done.

LITERATURE

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