

AMMONIA SORPTION ON COMPOSITES "CaCl₂ IN INORGANIC HOST MATRIX": ISOSTERIC CHART AND FREEZLING COP

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Abstract

New composite sorbents of ammonia "CaCl₂/γ-Al₂O₃" and "CaCl₂/vermiculite" were synthesised and studied. The isosteres of ammonia sorption on these composites were measured at T = 20-90°C and P = 0.08-9 bar. It was found that the modification of host matrices by the salt dramatically increases the ammonia uptake due to the formation of CaCl₂×nNH₃ complexes. The isobaric enthalpy and entropy of ammonia sorption were calculated over the uptake range 2.5-22.5 wt. % and 21.5-68.5 wt.% for alumina and vermiculite based composite, respectively. For the confined salt both these values were significantly lower respect to those for the bulk one. The transitions between complexes CaCl₂×nNH₃ confined to alumina pores were shifted to higher ammonia pressure in comparison with those in bulk. For a single-effect non-regenerative freezing cycle, the values of COP = 0.40 – 0.48 were calculated at the evaporator temperature –18°C, condenser temperature 35 – 40°C and desorption temperature 117 – 120°C. High COP in combination with rapid sorption makes these sorbents promising for application in freezing units driven by relatively low temperature heat.

KEYWORDS

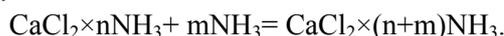
Ammonia sorption, calcium chloride, alumina, vermiculite, COP, sorption kinetics, sorption cooling

INTRODUCTION

Three main processes in sorption heat pumps can be categorised as a gas adsorption on a porous solid, a chemical reaction between a gas and a solid and a gas absorption by a liquid. Intelligent combination of these three processes in composites "salt inside porous host matrix" can give valuable opportunity to reach an augmentation and even synergism of advantages of each process [1]. It was proved by a comprehensive study of composites for advanced sorption of water vapour (so called Selective Water Sorbents) [1-4]. Contribution of each process mentioned was shown to strongly depend on the chemical nature of the salt and host matrix, pore structure of the matrix, salt content, water uptake, etc.

Similar composites for ammonia sorption have been synthesized on a basis of carbon matrices: the expanded graphite mixed with a variety of salts [5, 6], the synthetic carbon Busofit [7, 8] and the activated carbons [9] impregnated with CaCl₂. These materials have higher sorption capacity in comparison with non-impregnated carbons and better kinetics than the bulk salt. However, the salt swelling due to its reaction with ammonia could destruct the carbonaceous matrix [9], so the choice of a proper host matrix is important from practical point of view.

First attempts to combine CaCl₂ with inorganic matrices were done in [10, 11]. It was found that the modification of alumina by the salt can significantly enhance its ability to sorb ammonia. Additional amount of NH₃ was assumed to be absorbed due to the reversible chemical reaction between the salt and ammonia



No detailed study on the equilibrium of ammonia sorption by the salt confined to inorganic host matrices has been done so far. Here we present experimental isosteres of NH₃ sorption on composites "CaCl₂/γ-alumina" and "CaCl₂/expanded vermiculite" as well as make a comparison with the bulk salt.

EXPERIMENTAL

The sorbents "21.5 wt. % CaCl₂/γ-Al₂O₃" and "63.5 wt. % CaCl₂/vermiculite" were prepared by the immersion of the matrix with an aqueous 40% wt. solution of CaCl₂ followed by its drying at 200 °C. For synthesis of the sorbent "14.5 wt. % CaCl₂/γ-Al₂O₃" the matrix was impregnated with an aqueous

25% wt. solution of CaCl_2 followed by drying at 200°C . The main characteristics of used matrices are listed in Table 1. The typical grain size was 1.0-2.0 mm.

Table 1. The characteristics of matrices used for sorbent preparation

Matrix	Pore volume, cm^3/g	Surface area, m^2/g	Average pore diameter, nm
$\gamma\text{-Al}_2\text{O}_3$	0.65	190	7
Vermiculite	3.2	2	6 500

(1) 4 cm in diameter (volume 130 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 20 to 90°C . The temperature of the bath could be held constant within a variation of $\pm 0.1\text{ K}$.

The NH_3 pressure over the sorbent, which contained a certain amount of ammonia sorbed (w_1), was measured by a pressure gauge (5) with the accuracy of 1.0 rel. % (valve 1 is open, valve 2 is closed). First reading was done at room temperature. After that, the bath temperature and, hence, the sorbent temperature T was increased and new equilibrium pressure P of NH_3 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 up to $w_2 > w_1$, and new isoster was measured, and so on.

To increase the NH_3 uptake it is sufficient to adsorb on the sample an additional amount of ammonia from a buffer tank (3) of 1250 cm^3 volume. The tank was preliminary pumped out of air down to the residual pressure 0.1 mbar (V2 and V4 are closed, V3 is open). Then, it was filled with ammonia from a high-pressure NH_3 container (4) up to the pressure of 5-7 bar (V2 and V3 are closed, V4 is open) and connected to the adsorber (V1 and V2 are open, V3 and 4 are closed).

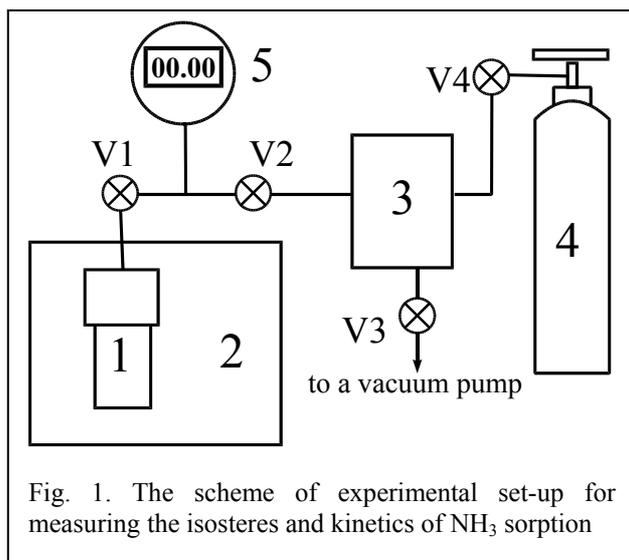


Fig. 1. The scheme of experimental set-up for measuring the isosteres and kinetics of NH_3 sorption

Isosteres and kinetics 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 130 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 20 to 90°C . The temperature of the bath could be held constant within a variation of $\pm 0.1\text{ K}$.

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The kinetic experiments were carried out as follows. The adsorber (1), maintained under vacuum, was connected through valve 3 to the buffer tank filled with ammonia (V3 and V4 are closed). The pressure decrease over the sorbent and its temperature were read each 10 seconds. The bath temperature was 31°C .

RESULTS AND DISCUSSION

1. Isosteres of ammonia sorption

1.1. Composite sorbent " $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ "

Isosters of the ammonia sorption on the composite " $14.5\text{ wt.}\% \text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ " are shown on Fig. 2. The sorption properties of the sorbent differ from those of a bulk salt:

- transitions between complexes $\text{CaCl}_2 \times n\text{NH}_3$ are shifted to higher ammonia pressure in comparison with those in bulk [12];
- both the enthalpy and entropy of reaction (1) for the confined salt are significantly reduced respect to those for the bulk one (Table 2);
- the equilibrium of reaction (1) in the confined

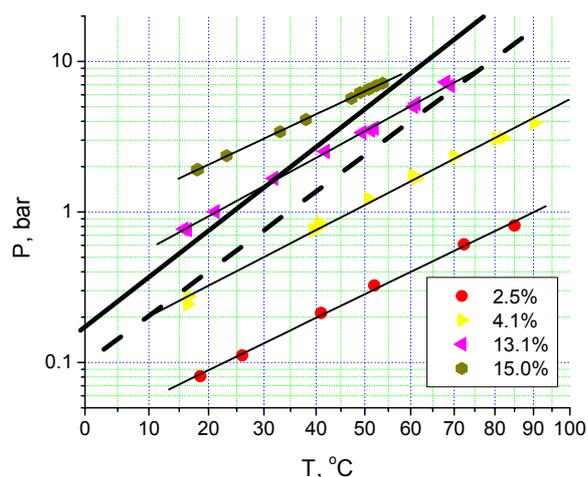


Fig. 2. The isosteres of NH_3 sorption on composite " $14.5\text{ wt.}\% \text{CaCl}_2/\text{Al}_2\text{O}_3$ ", corresponding to different uptakes (symbols) and the pressure of NH_3 over bulk $\text{CaCl}_2 \times 4\text{NH}_3$ (- -) and $\text{CaCl}_2 \times 8\text{NH}_3$ (—) [12]

- state is divariant that means the NH_3 uptake increases continuously as the ammonia pressure rises;
- d) the solid compound $\text{CaCl}_2 \cdot 8\text{NH}_3$ does not form inside alumina pores. Indeed, when the molar ratio $\text{NH}_3:\text{CaCl}_2$ increased to 6:1 – 7:1, the pressure above the sample increases drastically and the enthalpy and entropy tend to reach the corresponding values for liquid ammonia. This could be possibly caused by the formation of a CaCl_2 /ammonia solution inside the pores.

Table 2. The enthalpy and entropy of NH_3 sorption on composite “14.5 wt.% $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ ”

Ammonia uptake		ΔH , kJ/mol	ΔS , J/(mol K)
wt. %	mol/mol CaCl_2		
2.6	1.15	-30.5	-84.0
4.1	1.82	-34.5	-110.7
4.6	2.07	-33.0	-103.0
4.7	2.10	-35.7	-107.7
5.2	2.34	-33.5	-108.0
7.9	3.56	-31.7	-105.0
8.1	3.65	-35.8	-117.8
10.4	4.68	-37.0	-127.4
13.1	5.90	-34.1	-116.13
14	6.30	-29.7	-105.7
15	6.75	-29.0	-106.4

The increase of CaCl_2 content in the composite leads to the rise in the equilibrium ammonia uptake (see isotherms on Fig. 3). Besides, the transitions between various ammonia-salt complexes became sharper (Fig.3). As, in principle, it is profitable to increase the amount of salt inside pores, materials with large pore volume could be attractive as hosts for new composite sorbents of NH_3 .

The difference in the thermodynamic properties of the confined and bulk CaCl_2 could be caused either by the contribution of the surface energy of salt nanocrystallites confined to the pores of alumina or by the interaction between the salt and the host matrix.

1.2. Composite sorbent “ CaCl_2 /vermiculite”

One of such promising host matrix could be an expanded vermiculite, which pore volume reaches $3.0 \text{ cm}^3/\text{g}$ [13]. It allows the inserting inside the pores a large amount of salt, for instance, 63.5 wt % of CaCl_2 in our case. The sorption capacity of “63.5 wt % CaCl_2 /vermiculite” is about 5 times higher than that for “21.5 wt.% $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ ” (Fig.3). The enthalpy and entropy of sorption are close to the literature values for the bulk salt (Table 4). This is probably due to the big enough crystallites of the salts confined in the relatively large pores of vermiculite (Table 1).

One more very important advantage of vermiculite, which results from its large pore volume, is that it can accommodate the salt swelling due to its reaction with ammonia.

Table 3. The enthalpy and entropy of ammonia sorption on composite “21.5 wt.% $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ ”

Ammonia uptake		ΔH , kJ/mol	ΔS , J/(mol K)
wt. %	mol/mol CaCl_2		
7.7	2.3	-33.7	-108.2
8.6	2.6	-33.1	-106.5
10.7	3.2	-31.7	-106.8
12.0	3.7	-32.1	-106.5
14.8	4.5	-35.7	-120.0
17.8	5.4	-35.2	-118.7
20.1	6.1	-33.6	-114.4
22.5	6.8	-25.7	-97.7

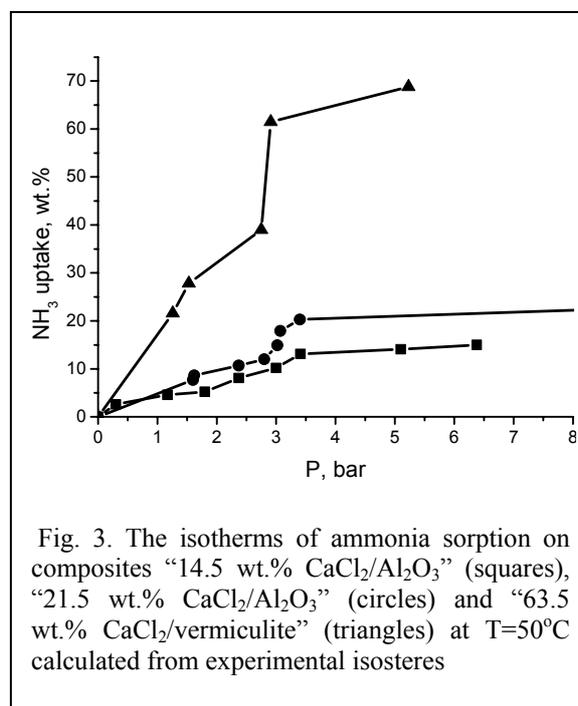


Fig. 3. The isotherms of ammonia sorption on composites “14.5 wt.% $\text{CaCl}_2/\text{Al}_2\text{O}_3$ ” (squares), “21.5 wt.% $\text{CaCl}_2/\text{Al}_2\text{O}_3$ ” (circles) and “63.5 wt.% CaCl_2 /vermiculite” (triangles) at $T=50^\circ\text{C}$ calculated from experimental isotherms

Table 4. The enthalpy and entropy of ammonia sorption on composite “63.5 wt.% CaCl_2 /vermiculite”

Ammonia uptake		ΔH , kJ/mol	ΔS , J/(mol K)
wt. %	mol/mol CaCl_2		
21.5	2.2	-40.5	-128.0
27.5	2.8	-39.7	-126.8
38.8	4.0	-41.6	-137.2
61.0	6.3	-38.1	-127.4
68.5	7.1	-23.9	-87.7

2. Estimation of the freezing COP

The coefficient of performance (COP) is accepted as the most important thermodynamic parameter of sorption heating/cooling device. The experimentally obtained isosteres were used for plotting and analyzing a single-effect non-regenerative freezing cycle based on the working pair “NH₃ – “CaCl₂/matrix (γ-Al₂O₃, vermiculite)”.

The input parameters of the cycle (T_{ev}, T_c, T_g) are presented in Table 5 and Fig. 4. We calculated the COP as

$$COP = \frac{Q_{ev} \cdot (w_2 - w_1)}{Q_{des} \cdot (w_2 - w_1) + (C_{pCaCl_2} \cdot \omega_{CaCl_2} + C_{pMatrix} \cdot (1 - \omega_{CaCl_2}) + C_{pNH_3} \cdot w_2)(T_g - T_c)}$$

where Q_{ev} is the heat of NH₃ evaporation, Q_{des} is the isosteric heat of NH₃ desorption, w₁ and w₂ are the NH₃ uptakes on weak and rich isosteres, C_{pCaCl₂}, C_{pMatrix} and C_{pNH₃} is the specific heat of CaCl₂, matrix and ammonia sorbed, ω_{CaCl₂} is the salt content. For our estimations we took Q_{ev} = 1370 J/g, C_{pCaCl₂} = 0.7 J/(g K), C_{pMatrix} = 0.9 J/(g K) and C_{pNH₃} = 3.2 J/(g K). We took the isosteric heat average between weak and rich isosteres as Q_{des}, namely, 2.1 kJ/g for “CaCl₂/alumina” and 2.3 kJ/g for “CaCl₂/vermiculite”.

The Carnot COP was calculated according

$$COP_{Carnot} = \frac{1 - \frac{T_c}{T_g}}{\frac{T_c}{T_g} - 1}$$

are listed in Table 5.

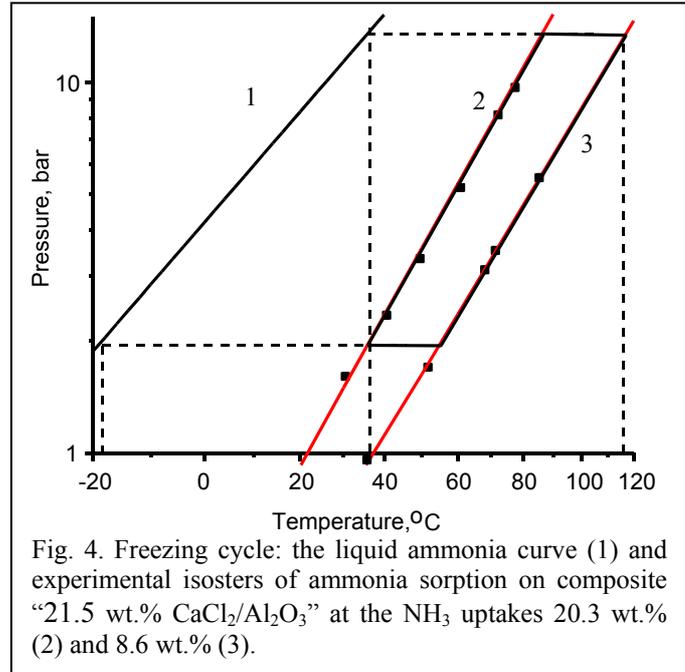


Fig. 4. Freezing cycle: the liquid ammonia curve (1) and experimental isosteres of ammonia sorption on composite “21.5 wt.% CaCl₂/Al₂O₃” at the NH₃ uptakes 20.3 wt.% (2) and 8.6 wt.% (3).

Table 5. The input parameters, estimated and Carnot COP of freezing cycle involved

Sorbent	w ₁ , wt.%	w ₂ , wt.%	T _{ev} , °C	T _c , °C	T _g , °C	COP, est.	COP, Carnot
14.5 wt.% CaCl ₂ /γ-Al ₂ O ₃	4.7	13.1	-18	37	120	0.40	0.98
21.5 wt.% CaCl ₂ /γ-Al ₂ O ₃	8.6	20.1	-18	37	118	0.43	0.96
63.5 wt.% CaCl ₂ /vermiculite	21.5	61.0	-18	42	117	0.48	0.82

On the one hand, the estimated values of COP for the tested sorbents are rather large (0.40-0.48) for such high T_c and relatively low T_g. On the other hand, they are 1.6-2.5 times smaller than the Carnot COP that means there is a room for improving the cycle operation.

CONCLUSIONS

Composite ammonia sorbents “14.5 wt. % CaCl₂/γ-Al₂O₃”, “21.5 wt. % CaCl₂ /γ-Al₂O₃” and “63.5 wt. % CaCl₂/ vermiculite” were synthesized and studied. The isosteric heat of ammonia sorption was measured. It was found that the thermodynamic properties of confined CaCl₂ differ from the properties of the bulk one. For the confined salt both enthalpy and entropy of ammonia sorption were significantly lower respect to those for the bulk one. The transitions between complexes CaCl₂×nNH₃ confined to alumina pores were shifted to higher ammonia pressure in comparison with those in bulk. The COP of the single-effect non-regenerative freezing cycle was estimated to be 0.40 – 0.48, what could be of interest for practice. High COP in combination with fast sorption (see Appendix 2) makes these sorbents attractive for application in freezing units driven by relatively low temperature heat.

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Appendix 1

Verification of the method of isoster measurement

To verify the experimental procedure applied in this work we measured the isoster of ammonia sorption by a bulk CaCl_2 which corresponds to the transformation $\text{CaCl}_2 \times 2\text{NH}_3 + 2\text{NH}_3 = \text{CaCl}_2 \times 4\text{NH}_3$. A mixture of 15.4 g CaCl_2 (crystal size less than 0.25 mm) and 250 g of cast-iron fillings was placed in the adsorber to decrease its “dead” volume and to improve the heat transfer. The initial uptake was 2.7 mol of ammonia per 1 mol of CaCl_2 . The isosteric enthalpy and entropy of ammonia sorption were measured to be -42.6 kJ/mol and -132.3 J/(mol K), respectively. Good agreement with literature data [15] ($\Delta H = -42.1$ kJ/mol, $\Delta S = -134.1$ J/(mol K)) gives the evidence of applicability of this method for measuring isosteres of the ammonia sorption.

Appendix 2

Kinetics of ammonia sorption on “ $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ ” and “ $\text{CaCl}_2/\text{vermiculite}$ ”: preliminary results

For estimation of the cooling power we performed measurements on the kinetics of ammonia sorption on composites “ $\text{CaCl}_2/\gamma\text{-Al}_2\text{O}_3$ ” and “ $\text{CaCl}_2/\text{vermiculite}$ ”. The procedure is described above. To improve the heat transfer, the sorbent was mixed with the cast-iron filling. The variation of the ratio “sorbent:filling” from 1:5 to 1:30 almost does not affect the sorption rate. It indicates that the heat resistance in the sorbent layer is less important than between the sorbent and the adsorber wall, which defines the global heat transfer coefficient. For this reason the sorption rate does not depend on the grain size (0.5 – 2.2 mm), matrix nature and salt content.

First 10-20 seconds it exceeds 50 mmol/s of NH_3 per 1 mol of CaCl_2 (Fig. 5a) that corresponds to the cooling power of 7 W/g, then it sharply decreases. The cooling power for “ $\text{CaCl}_2/\text{vermiculite}$ ” achieves 1 W/g for first 500 seconds that could allow the realization in practice rather compact freezing sorption unit.

For the bulk CaCl_2 the sorption rate was 4-6 times lower than for the composite sorbents, although the heat sink was better because of closer contact between the salt and filling. As a consequence, the increase of the layer temperature was also lower (Fig. 5b).

