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Research Article

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Determination of Adsorption Heats of Some Adsorbents on Ammonia

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ABSTRACT

Adsorption is accompanied by the evolution of heat. In this paper, adsorption isotherms were measured, at the pressure range of 6.67-53.33 kPa and at the temperature range of 303-353 K, for some adsorption working pairs: Charcoal – NH_3 , $CaCl_2 - NH_3$ and $CaCl_2$ composites – NH_3 . Isosteric heats of adsorption were determined from these isotherms. Values of isosteric heat of adsorption ranged between 13.94 and 50.71 kJ/mol for Charcoal, Charcoal + calcium chloride and calcium chloride + silica gel. 75% $CaCl_2 + 25\%$ $CaSO_4$ had the least value of isosteric heat of adsorption whilst 75% $CaCl_2 + 25\%$ charcoal had the highest value.

Key words: Adsorption, Isosteric, Heats of Adsorption

1. INTRODUCTION

The combinations of adsorbents and adsorbates that have been used in adsorption refrigeration system utilizing the solar energy include Silica gel –Water, AC-Ammonia, Zeolite-Water and Calcium-chloride-Ammonia [1,2]. The adsorption processes are exothermic. The three terms, which are often used in adsorption engineering, are:

- Integral heat of adsorption, which is the total heat, related from initial state to final state of adsorbate loading, at constant temperature.
- Differential heat of adsorption, namely the change in integral heat of adsorption with change in loading
- Isosteric heat of adsorption is defined by using adsorption isosteres and Clausisus Clapeyron relationship [3].

In [1], the differential heats of adsorption for some adsorbent/adsorbate pairs were given. In practice, the difference between the differential heat of adsorption and the isosteric heat of adsorption is so small that it can be easily be neglected. Similarly, these two can be considered identical [3]. The heat of adsorption of water vapour on silica gel is predominantly due to the heat of condensation of water [4-6].

Different kinds of adsorbent/adsorbate pairs have been investigated including activated carbon- methanol [7,8,9]; activated carbon- ethanol (Chen et al, 10); activated carbon- ammonia [11,12]; strontium chloride-ammonia [13], silica gel- water [14,15]; CaCl₂-NH₃ [16,17,18] ; compound adsorbent of activated carbon and calcium chloride- ammonia [19,20].

According to Srivastava and Eames [2] there are many commercial hydrophilic solid adsorbents. These include silica gel, activated (or porous) alumina, zeolites and calcium chloride. The commercial hydrophobic solid adsorbents include activated carbon, metal oxides, specially developed porous metal hydrides, composite adsorbents [21, 22].

In the design of adsorption refrigeration and heat pump systems, the characteristics of both adsorbent – adsorbate (refrigerant) pairs and adsorption cycles play an important role in various kinds of applications (Teng et al [23]).

Different kinds of adsorbent/adsorbate pairs have been investigated including activated carbon – methanol (Passos et. al. [24], Cacciola et. al. [25], Anyanwu et. al. [26], Wang et. al. [27] and Wang, [28]); activated carbon – ammonia (Critoph [29], Tamainot – Telto and Critoph, [30]); silica gel – water (Saha et. al. [31]). Grzech et al [32] investigated Van der Waals Interactions on heat adsorption in large pore Silicas.

Srinivasan et al [33] calculated the heat of adsorption of gases using Dubinin – Astakhov equation. Korrir et al [34] carried out a non-calorimetric determination of adsorptive heat of volatile organic compounds. Xiao et al [35] developed

a heat and mass transfer model of multicomponent adsorption system. Ng et al [36] carried out a study on a waste heat driven adsorption cooling.

2.1. The Apparatus

2. APPARATUS AND EXPERIMENT

Fig 1 shows the line diagram of the measuring apparatus for the adsorption capacity of the various samples with ammonia. The Apparatus includes an efficient pump (1) capable of achieving a high vacuum in the sample chamber (lower glass chamber) (2) a heater (3) having a temperature-regulating device so that the temperature of the gas (ammonia) could be controlled. The temperature in the sample chamber was observed by means of a mercury in glass thermometer (4).

A mercury manometer (5) was incorporated to measure the pressure of the gas. Essentially, the apparatus operated on the principle of the Mac Bain balance which a type of a dynamometer or very sensitive spring. The spiral spring (6), at whose end was hung a pan (8), was attached from the top end of the tipper glass chamber (7). A weighed amount of the sample, whose adsorption capacity with ammonia was to be determined, was placed in the pan. The cylinder (9), which contained ammonia gas, had a pressure-regulating device (10) to vary the pressure of the gas.

Barometric readings were recorded using a meteorological office kew pattern long range Barometer. The extent of adsorption was measured by sighting, with a cathetometer (11), the variation in height of a fixed point of the suspension.

2.2. Experimental Procedure

The balance was first calibrated with known weights to determine the sensitivity of the spring. Eleven powdery samples were prepared for the experiments as shown in Table 1. Before weighing, each sample was heated to 120 °C for 2 hours and cooled in a desiccator. After weighing, the samples were degassed by first heating the adsorbent chamber up to 120 °C. The chamber was then pumped for two hours while the valves (14 & 15) were opened and the valves (13 & 10) closed and kept for about 3 hours to observe the vacuum change until the vacuum was kept at nearly zero Pascal.

Samples	% Composition			
	Charcoal	CaCl ₂	Silica gel	CaSO ₄
1	100	-	-	-
2	25	75	-	-
3	50	50	-	-
4	75	25	-	-
5	-	75	25	-
6	-	50	50	-
7	-	25	75	-
8	-	100	-	
9	-	75	-	25
10	-	50	-	50
11		25		75

 Table -1 Percentage Composition of the Samples

Valves (10, 13 & 14) were opened to get the connection between the adsorption chamber and the ammonia cylinder while valve (15) was closed. The measurement was started. Pressures were measured on a mercury Manometer. The barometric readings were recorded and corrected for temperature, latitude gravity and altitude-gravity.

A complete isotherm was measured by starting around 6.67 kPa and compressing the gas in pressure increments of about 6.67 kPa to cover the range 6.67-53.33 kPa. Isotherms were measured at 10 K interval in the range 303 - 353 K. Lines of constant volume were drawn on the plotted adsorption isotherms thus providing data on the variation of pressure with temperature at constant volume for the adsorbent/adsorbate pairs.

The adsorbent was heated by means of a heater band (12) placed around the glass chamber whose temperature was regulated and controlled by a thermostat enclosed within a heater panel. The actual temperature within the adsorbent chamber was measured by means of a mercury in glass thermometer. The temperature, upon stabilization for 10 minutes was recorded.

The extent of adsorption was measured by means of the cathetometer, which was used to sight the variation in the height of a fixed point on the suspension from the spiral spring.

3. RESULTS AND DISCUSSION

Plots of ln P Vs I/T for adsorption capacity of $30 \text{cm}^3/\text{g}$ for all the samples are shown in Fig 2. Empirical relations governing these plots with the values of R² are showing in Tables 2. Equation (1) has been used to compute the values of isosteric heat of adsorption, q_{st} which are shown in Table 2 for the various adsorbent / adsorbate pairs.

$$q_{st = -R \left| \frac{\partial lnp}{\partial (1/T)} \right|_{v}}$$

(1)



(1) Vacuum Pump; (2) Lower Glass Chamber; (3) Heater Panel; (4) Mercury in Glass Thermometer; (5) Manometer;
(6) Spring; (7) Upper Glass Chamber; (8) Pan; (9) Ammonia Gas Cylinder; (10) Regulating Valve; (11) Cathetometer;
(12) Heater band; (13, 14, 15) Valves; (16) Vacuum Gauge.







Sample	Empirical Relation	К
1	$\ln p = -4.01(1/T \times 10^3) + 22.43$	0.9998
2	$\ln p = -6.10(1/Tx10^3) + 28.82$	0.9999
3	$\ln p = -5.79(1/\mathrm{Tx}\ 10^3) + 28.20$	0.9999
4	$\ln p = -4.26(1/Tx10^3) + 22.92$	0.9999
5	$\ln p = -3.22(1/Tx10^3) + 20.12$	0.9998
6	$\ln p = -3.66(1/Tx10^3) + 21.02$	0.9185
7	$\ln p = -2.49(1/Tx10^3) + 17.30$	0.9998
8	$\ln p = -2.80(1/Tx10^3) + 17.91$	0.9934
9	$\ln p = -1.67(1/Tx10^3) + 14.34$	0.9991
10	$\ln p = -3.91(1/Tx10^3) + 21.23$	0.9998
11	$\ln p = -3.02(1/Tx10^3) + 18.94$	0.9997

Table -2 Plot of ln p against 1/T x 10³ for the various powdery samples at adsorption capacity of 30 cm³/g

Table -3 Computed values of heat of adsorption at capacity of 30 cm³ of adsortbate/g of adsorbent

Sample	Heat of Adsorption (kJ/kg)	
1	1961	
2	2983	
3	2832	
4	2083	
5	1575	
6	1790	
7	1218	
8	1369	
9	820	
10	1912	
11	1477	

4. DISCUSSION

The size of difference between the temperature T_i and T_j at which the isotherms were measured, influenced the accuracy of the heats of adsorption, q_{st} in a two fold manner. First the relative error due to the factor $(I/T_i - I/T_j)$ decreased with increasing $(T_i - T_j)$: second, the relative error of $\ln(P_i - P_j)$, also decreased with increasing $(T_i - T_j)$. Table 3 shows the values of isosteric heat of adsorption, q_{st} for all the samples for the volume of adsorbate (ammonia) adsorbed at 30 cm³/g. These values ranged between 13.94 and 50.71 kJ/mol.

The principal test for distinguishing *chemisorption* from *physisorption* was based on the size of the enthalpy of adsorption. Values less than 25 kJ/mol were taken to signify *physisorption* and values more than 40 kJ/mol were taken to signify *chemisorption*. However, this criterion was by no means foolproof [37].

It was therefore conjectural to state that *chemisorption* took place in samples 2 and 3 (75% $CaCl_2 + 25\%$ Charcoal; 50% $CaCl_2 + 50\%$ Charcoal) upon adsorption of ammonia whilst *physisorption* took place in samples 8 and 9 ($CaCl_2$; 75% $CaCl_2 + 25\%$ CaSO₄). Spectroscopic techniques that identify the adsorbed species are needed to give clear evidence of either *chemisorption or physisorption*.

5. CONCLUSION

Although there is available a large amount of heat of adsorption data in the literature on systems of various types, no data on the heat of adsorption of the admixture of calcium chloride with substances such as calcium sulphate, silica gel and charcoal on ammonia have been previously reported. The result of this work therefore appears to be the first contribution to the knowledge of the heat of adsorption of ammonia (an adsorbate) on the admixtures of the adsorbents.

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