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Experimental studies on equilibrium adsorption isosteres and determination of the thermodynamic quantities of polar media on alumina Al_2O_3

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Abstract: The present work is a review of theoretical and experimental study on the adsorption performance of the adsorbent Alumina (Al_2O_3) used in the adsorption system. An experimental investigation on the equilibrium adsorption isosteres at low pressure (< 1 atm) of working pairs $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$ is carried out. The isovolume measurement method is adopted in the test setup to directly measure the saturated vapor pressures of working pairs at vapor-liquid equilibrium ($dG=0$ and $d\mu_i=0$). Quantity adsorbed is determined from pressure, volume and temperature using gas law. The isosteric heat of adsorption is calculated from the slope of the plot of $\ln P$ versus $1/T$ different amounts of adsorbate onto adsorbent as follows: 0,01 vol% $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$; 0,03 vol% $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$; 0,1 vol% $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$; 0,01 vol% $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$; 0,03 vol% $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$; 0,1 vol% $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$. This study shows that adsorption working pair $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$ has better adsorption performances than those of the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$. Surface acidity is a most important property for both adsorption and catalysis and therefore is examined structure of active sites of alumina surface. Thermodynamic parameters such as isosteric heat of adsorption, isosteric enthalpy and entropy of adsorption are critical design variables in estimating the performance and predicting the mechanism of an adsorption process and are also one of the basic requirements for the characterization and optimization of an adsorption process.

Keywords: heterogenous acid-base catalyzer, surface acidity, polar organic solvent, isosteric heat of adsorption, isosteric enthalpy and entropy of adsorption

Introduction

Studying the thermal conductivity of nanofluids, fluid suspensions of nanometer-sized particles, has grabbed the considerable attention of scientists and engineers in the last decade. The value of liquid thermal conductivity is several orders lower than most of the metals or metal oxides (Table 1).

Table 1. Thermal Conductivity Comparison [1].

Materials		Thermal Conductivity (W/m K)
Liquids	Carbon nanotube	200–6000
	Ethylene glycol	0.25
	Mineral oil	0.13
	Water	0.613
Metal oxide solids	Alumina	40
	Copper oxide	70
	Zinc oxide	60
Metallic solids	Aluminum	230
	Copper	398
	Silver	410

Only four types of generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina. Estimates of worldwide sales of these sorbents are shown in (Table 2):

Table 2. Worldwide sales of generic sorbents (Humphrey and Keller, 1997) [2].

Activated carbon	\$1 billion
Zeolites	\$100 million
Silica gel	\$27 million
Activated alumina	\$26 million

The efficiency with which electromagnetic radiation is converted into heat is dependent on the dielectric properties of a solvent, i.e., solvents with strong ability to be polarized by the electric field are particularly advantageous for rapid heating. Organic solvents with high microwave adsorbing properties are ethylene glycol, ethanol, dimethylsulfoxide, isopropanol or formic acid. Solvents without a permanent dipole moment like carbon tetrachloride, benzene or dioxane are nearly microwave transparent. Nevertheless, also these solvents can be used for microwave chemistry, as long as other reagents in the reaction mixture are polar. Furthermore, polar additives like ionic liquids can be added to otherwise low-adsorbing media to increase the absorbance. Fast and efficient heating as provided by microwave irradiation bears great potential for large-scale synthesis without suffering thermal gradient effects, and therefore this method became also interesting for the preparation of inorganic nanomaterials. The fast energy transfer directly to the reactants allows an instantaneous decomposition of nanocrystal precursors, creating highly supersaturated solutions [3].

Sorbents with highly polar surfaces (e.g. activated alumina, silica gel, and zeolites) would be desirable for a targeted molecule that has a high dipole moment (and high polarizability). If the targeted molecule has a high quadrupole moment, sorbents with surfaces that have high electric field gradients are needed. Activated alumina is a versatile sorbent that can be tailored for many special applications. New applications continue to be developed, mainly by the aluminum companies. Little is disclosed on the details of their modifications. However, the modifications follow simple general principles of surface chemistry, such as acid-base chemistry. Two methods are used for tailoring: (1) variation of the activation process, and (2) use of dopants. The following are proven applications of various tailored aluminas [2]:

- Removal of HCl and HF from gases and liquids;
- Removal of acidic gases (COS, CO₂, H₂S, CS₂) from hydrocarbons;

- Removal of oxygenates and Lewis Bases;
- Removal of polar organic compounds;
- Removal of As^{5+} , PO_4^{3-} , Cl^- , and F^- from water;
- Scavenger for organic process liquids;
- Alkalized alumina for SO_2 removal.

In study of adsorption thermodynamics, it appears that determination of value of the thermodynamic quantities such as activation energy, activation parameters, Gibb's free energy change, enthalpy, entropy, and isosteric heat of adsorption are required [4].

Theory

As with ions in solution, the polarity and ionization of surface groups cause their solvation. The presence of a hydration layer on the surface of particles plays a major role in the behavior of colloidal dispersions. Hydrogen bonds in liquid water are responsible for a number of properties of the liquid, and that the presence of ions in the liquid does alter its local structure. The surface groups M-OH , M-OH_2^+ and M-O^- are polarized and develop very strong interactions with water. They also have a very strong structuring effect on the liquid. Measurements of immersion and adsorption heats, as well as dielectric measurements on oxide surfaces, show that the 2-3 layers of physisorbed water adjacent to the first chemisorbed water layer are immobilized by pairs of hydrogen bonds forming an order similar to that of ice. These bonds are still present at room temperature (Figure 1).

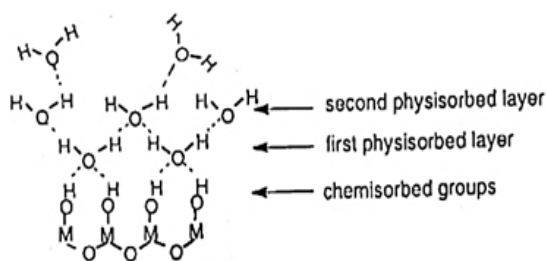


Figure 1. Adsorption of water on an oxide surface [5].

Adsorption of Organic Compounds - Hydrocarbons as well as oxygenated compounds, such as alcohols, are reactants in a large number of metal catalyzed reactions of great industrial importance. The mode and strength of adsorption of organic compounds on catalytic surfaces plays a dominant role, concerning not only the activity but, more important, the selectivity to specific products. In this respect the effect of additives, acting as poison or promoters, is crucial in determining the desired direction of a reaction where organic species participate [6].

Specific and non-specific adsorption - The effect of polarity in enhancing the energy of interaction has been discussed by Kiselev and his associates who distinguish between non-specific adsorption, where only dispersion and repulsive forces are involved and specific adsorption, where coulombic contributions are present in addition. The kinds of interactions resulting from each of the possible adsorbent-adsorbate combinations are summarized in (Table 3):

Table 3. Specific and non-specific adsorption [7].

Adsorbate group	Class of adsorbent		
	I	II	III
(a)	n	n	n
(b)	n	n + s	n + s
(c)	n	n + s	n + s
(d)	n	n + s	n + s

s = specific adsorption; n = non-specific adsorption.

(Table 4) contains both inorganic and organic compounds. Organic compounds are similar to inorganic ones when the functional groups responsible for their acid-base properties are the same. Thus, alcohols (ROH) are similar to water (HOH) in both their Brønsted acidity (ability to donate a proton from oxygen) and Brønsted basicity (ability to accept a proton on oxygen).

Table 4. Properties of some Brønsted Acids as possible adsorbates for Al_2O_3 (adsorbent class II) [8, 9, 10].

Brønsted Acid (Formula)	Thermal Conductivity in W/mK (25°C)	Dielectric constant, ϵ	Dissociation constant pKa (25°C)	Conjugate base
I. Adsorbate group D: Water – high polar ($\epsilon > 40$) and Alcohols – middle polar ($\epsilon = 10\div 40$) and high polar ($\epsilon > 40$) - nonspecific and specific adsorption				
Water HOH	0,6062	80,1	14	HO^-
Ethylene glycol HO-CH₂-CH₂-OH	0,254	41,4	14,22	$(\text{CH}_2\text{O}^-)_2$
Propylene glycol HO-CH₂-CH₂-CH₂-OH	0,200	27,5	14,8	$(\text{CH}_2)_3\text{O}^-_2$
Methanol CH₃OH	0,202	33	15,54	CH_3O^-
Isopropyl alcohol (CH₃)₂CHOH	0,135	20,18	≈ 17	$(\text{CH}_3)_2\text{CHO}^-$
tert-Butyl alcohol (CH₃)₃COH	0,112	12,47	≈ 18	$(\text{CH}_3)_3\text{CO}^-$
II. Adsorbate group A: Saturated hydrocarbons – non polar ($\epsilon < 4$) – nonspecific adsorption				
n-Hexane C₆H₁₄	0,1167	1,8865	≈ 18	$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CH}_3$

Studies have shown that the more stable a carbocation is, the faster it is formed. These studies demonstrate that alkyl groups directly attached to the positively charged carbon stabilize a carbocation. Thus, the observed order of carbocation stability is:

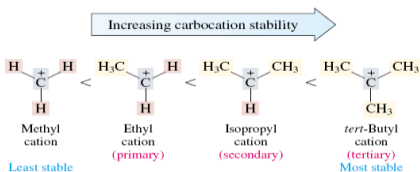


Figure 2. Increasing carbocation stability [8].

The important thermodynamic variable to describe the heat effects during the adsorption process is the isosteric heat of adsorption. The isosteric heat of adsorption Q_a is determined graphically from angular coefficient of straight line (Figure 3).

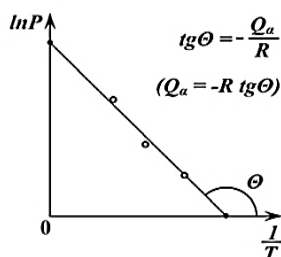


Figure 3. Isostere in $\ln P = f(1/T)$ coordinates [11].

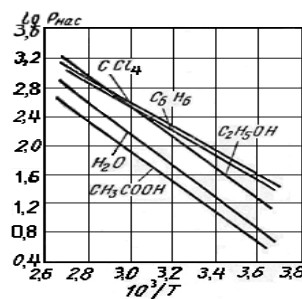


Figure 4. Isosteres of liquids [12].

If the slope of all isosteres is constant, that means, in examined interval the heat of adsorption is not depending on degree of filling of surface [13].

New adsorbents very interesting in adsorption and chromatography are porous polymers. Depending on content-rate of binding element can prepare porous polymers with specific surface area $10 \div 600 \text{ m}^2/\text{g}$. That sort of adsorbents possess specific character, activated π -bonds on their surfaces. According to Kiselev's classification, these adsorbents are class III, i.e. carry on surface negative charge. (Figure 5) shows dependence of heat of adsorption of substances on their electron polarization.

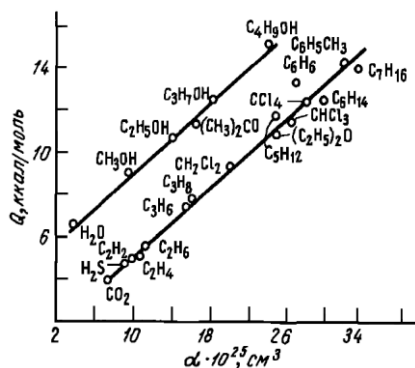


Figure 5. Dependence of heat of adsorption of substances from group A, B, D on electron polarization of their molecules on porous polymer (class III) “Xpomocopб-102” [14].

Activated alumina has higher ultimate capacities for water vapor than zeolites do. When high removals of water vapor (to very low dew points) are required, zeolites are used because their water capacities at very low concentrations are higher, as shown in (Figure 6).

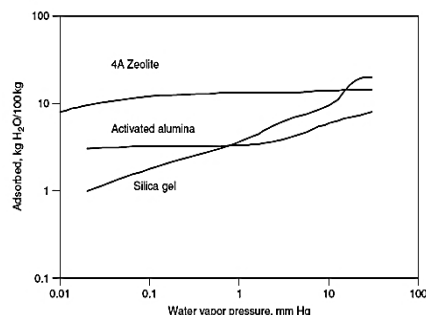


Figure 6. Comparison of water adsorption on various sorbents [2].

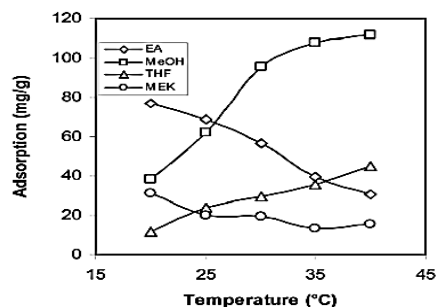


Figure 7. Adsorption isotherms of different organic solvents such as ethyl acetate (EA), methanol (MeOH), tetrahydrofuran (THF) and methylethyl ketone (MEK) on γ -alumina particles (0,1 g) at various temperatures [15].

Pore structure and surface chemistry of the activated alumina can be manipulated and controlled. The acidity of the surface can be increased by treatment with acid, such as HCl and HF (Figure 8.1). Sorption volume increases by higher electrolyte content (Figure 8.2).

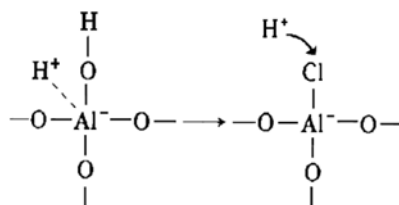


Figure 8.1. Alumina surface by the acid treatment [16]

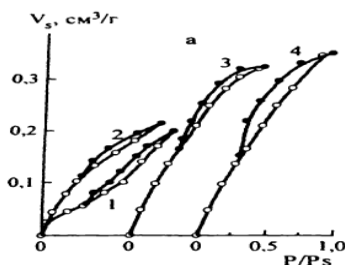


Figure 8.2. Isotherms of adsorption of water vapor on $\text{Al}(\text{OH})_3$, manipulated with supersonic (6 min) and vibration (6 min) in presence of electrolyte AlCl_3 ; 1– $\text{Al}(\text{OH})_3$, 2, 3, 4 – isotherms of adsorption on $\text{Al}(\text{OH})_3$, manipulated with supersonic and vibration in presence of 2, 4, 6 mass% electrolyte AlCl_3 respectively [17].

The investigations were carried out by constant temperatures 60 and 75 °C for pure isopropanol and nanofluids with mass concentration of nanoparticles Al_2O_3 0,05 and 0,1 mass.%. The experimental data for influence of nanoparticles on heat transfer coefficient is shown on (Figure 9). The analysis of given boiling curves show, that presence of nanoparticles in liquid can increase heat transfer coefficient at boiling with 10÷26%. This effect is observed only by small densities of heat flux and decrease with increasing of temperatures and concentrations of nanoparticles. By high densities of heat flux the presence of nanoparticles in base liquid lead to decreasing intensity of heat exchange [18].

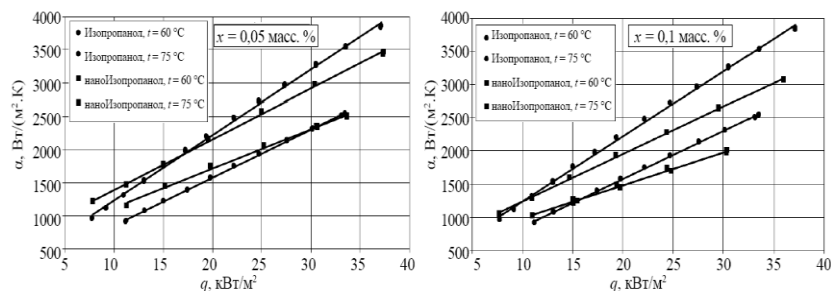


Figure 9. Dependence of heat transfer coefficient α , $\text{W}/(\text{m}^2 \cdot \text{K})$ on density of heat flux q , kW/m^2 [18].

Materials and methods

Al_2O_3 is acid component and owns weak acidity. Activated alumina is crystalline and is also widely used as a desiccant. The exterior surfaces of $\gamma\text{-Al}_2\text{O}_3$ are rich in OH groups. Oxygen vacancies (defects) are easily formed on its surfaces, thus alumina has both Lewis acid sites (i.e. sites that can accept electrons, these are the Al^{3+} sites on the surfaces) and Brønsted acid sites (i.e., -OH groups that can donate protons) (Figure 10). The surface chemistry, as well as the pore structure of activated alumina, can be modified, for example, by treatment with acid (HCl or HF) or alkaline (to alter the acidity) and controlled thermal treatment (to tailor the pore structure) [2].



Figure 10. Structure of active sites of alumina surface ($\gamma\text{-Al}_2\text{O}_3$). 1-Brønsted acid sites; 2-Lewis acid site; 3- Base site [19].

As seen in (Table 5), γ -alumina has a good surface area for adsorption and a good macropore volume and mean pore size for fast transport of molecules from the surrounding to the interior.

Table 5. Typical characteristics of γ -alumina [20].

True density	2.9 - 3.3 g/cc
Particle density	0.65 - 1.0 g/cc
Total porosity	0.7 - 0.77
Macropore porosity	0.15 - 0.35
Micropore porosity	0.4 - 0.5
Macropore volume	0.4 - 0.55 cc/g
Micropore volume	0.5 - 0.6 cc/g
Specific surface area	200 - 300 m ² /g
Mean macropore radius	100 - 300 nm
Mean micropore radius	1.8 - 3 nm

Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is an organic polar solvent that can be used over a wide range of temperatures. Ethylene glycol is popular in snow-melting systems because of their moderate cost, high specific heat, and low viscosity; ease of corrosion control is another advantage. Automotive radiator antifreezes are mostly based on ethylene glycol. Owing to the strong hydrogen-bonding properties of this double alcohol, this substance is completely miscible with water and many organic liquids, and contributes only a very small vapor pressure of its own. Besides lowering the freezing point, antifreeze also raises the boiling point, increasing the operating range of the cooling system.

Heat is not a state function and the value of the heat of adsorption depends on both the experimental conditions and the employed method of measurement [21]. Method of measurement is heat of adsorption from Indirect Non-Calorimetric Method.

Results and discussion

Table 6. Observations on the equilibrium adsorption of Al_2O_3 suspensions' test samples at low pressure (< 1 atm).

Test sample №	Suspension	Surface concentration of adsorbent (Al_2O_3), m ² /mol	Q_{ads} , J/kg	ΔH_{ads} , J/kg	ΔS_{ads} , J/(kg.K)
1.1	0,1 vol % $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$	39,3743	29,56	-29,56	-4,52
1.2	0,03 vol % $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$	10,8619	30,21	-30,21	-4,54
1.3	0,01 vol % $\text{Al}_2\text{O}_3/\text{C}_2\text{H}_6\text{O}_2$	5,4309	33,46	-33,46	-4,68
2.1	0,1 vol % $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$	11,4250	35,69	-35,69	-5,73

2.2	0,03 vol % Al ₂ O ₃ / H ₂ O	3,1517	30,80	-30,80	-5,58
2.3	0,01 vol % Al ₂ O ₃ / H ₂ O	1,5759	34,14	-34,14	-5,68

The natural logarithm of p was plotted for a given surface concentration of adsorbent Al₂O₃, against the inverse of the temperature in Kelvin in (Figure 11(a)) and (Figure 11(b)). The pressure in each case was measured. This gives the isosteric plot as defined by Clausius-Clapeyron equation.

$$\ln p = \frac{\Delta H_{ads}}{R.T} - \frac{\Delta S_{ads}}{R} \quad (1)$$

From these plots is found:

- the isosteric enthalpy of adsorption ΔH_{ads} from the slope and
- the isosteric entropy of adsorption ΔS_{ads} from the intercept.

Heat of adsorption and enthalpy of adsorption [22]:

$$Q_{ads} = -\Delta H_{ads} \quad (2)$$

The adsorption of gases and vapors on solids is always an exothermic process.

$$Q_{ads} > 0, (\Delta H < 0) \quad (3)$$

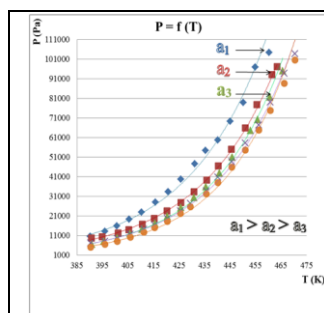


Figure 11. (a)

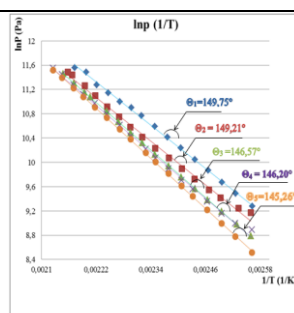


Figure 12. (a)

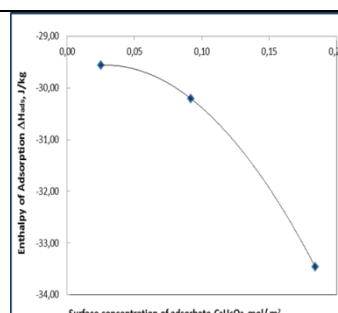


Figure 13. (a)

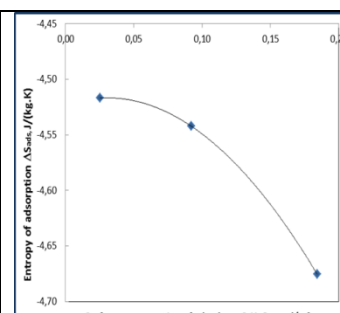


Figure 14. (a)

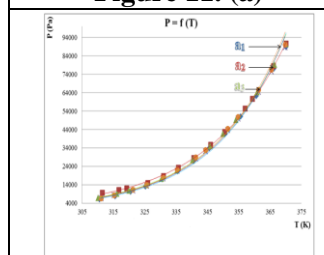


Figure 11. (b)

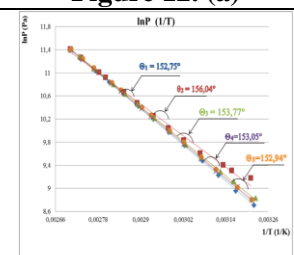


Figure 12. (b)

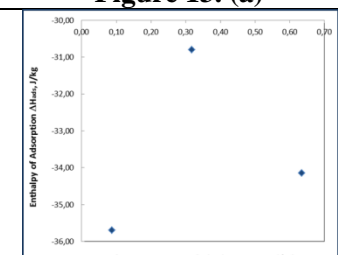


Figure 13. (b)

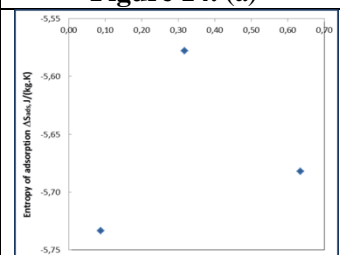


Figure 14. (b)

Figure 11. Equilibrium adsorption isotherms $p = f(T)$ by $a = \text{const}$ of the composite adsorbent: (a) Al₂O₃ / C₂H₆O₂ and (b) Al₂O₃ / H₂O.

Figure 12. Equilibrium adsorption isotherms $\ln p = f(1/T)$ by $a = \text{const}$ of the composite adsorbent: (a) Al₂O₃ / C₂H₆O₂ and (b) Al₂O₃ / H₂O.

Figure 13. Isosteric enthalpy of adsorption as a function of surface concentration of adsorbate: (a) C₂H₆O₂ on adsorbent Al₂O₃ and (b) H₂O on adsorbent Al₂O₃.

Figure 14. Isosteric entropy of adsorption as a function of surface concentration of adsorbate: (a) C₂H₆O₂ on adsorbent Al₂O₃ and (b) H₂O on adsorbent Al₂O₃.

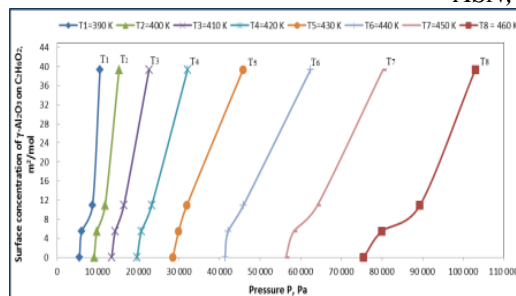


Figure 15. Saturation of phase boundary of test sample №1.1, №1.2 and №1.3 (according Table 6).

Equilibrium adsorption isosteres $p=f(T)$ correspond to increasing quantity of adsorption $a_1 > a_2 > a_3$ (Figure 11). The straight lines mean that the enthalpy of adsorption can be regarded as a negligible function of temperature. The results for the isosteric enthalpy and entropy of adsorption are plotted in (Figure 13(a), Figure 13(b), Figure 14(a) and Figure 14(b)). The values in both plots are changing with surface concentration of adsorbate (a) $C_2H_6O_2$ (b) Distilled water H_2O . In (Figure 13(a) and Figure 14(a)) both decrease with increasing surface concentration of adsorbate $C_2H_6O_2$. The isosteric enthalpy varies between -29,56 and -33,46 J/ kg. The isosteric entropy varies between -4,52 and -4,68 J/ (kg.K). The effect of the concentration is much more noticeable on the value of the enthalpy ΔH_{ads} , 390% of change, than on the entropy ΔS_{ads} , 16% of change, indicating large enthalpic effects on the surface. The conclusion is that the system has characteristic properties for physisorption.

Conclusions

A set of specific adsorption in the system solid-solvent organic and nonorganic molecules is explained in the work as a result of theoretical and experimental material. Key conclusions can be summarized as follows:

- The higher adsorption of $C_2H_6O_2$ on the alumina surface is accompanied by the formation of hydrogen bond as both alumina surface and $(HO-CH_2-CH_2-OH)$ contain hydroxyl groups and $C_2H_6O_2$ has weaker acid properties in comparison with H_2O .
- The higher adsorption of $C_2H_6O_2$ is due to higher surface concentration of $Al_2O_3/ C_2H_6O_2$ in comparison with Al_2O_3/ H_2O (Table 6).
- From Figures 11(b), 12(b), 13(b) and 14(b) can see negligible change of isosteric heat of adsorption, enthalpy and entropy for suspension of polar adsorbate H_2O on Al_2O_3 , i.e. negligible adsorption and in this instance alumina surface can treat with acid, such as $AlCl_3$ (Figure 8) or can replace with other adsorbent like zeolite (Figure 6) .
- The enthalpy values of $\Delta H_{ads} < 50 \text{ kJ.mol}^{-1}$ for $Al_2O_3/ C_2H_6O_2$ and Al_2O_3/ H_2O confirm that physisorption was involved in the adsorption process.
- Negative ΔH_{ads} and ΔS_{ads} suggest that the adsorption of gases and vapors H_2O and $C_2H_6O_2$ onto solid Al_2O_3 was exothermic ($Q_{ads}>0$) and nonspontaneous ($\Delta S<0$).
- Type IV isotherm, multilayer adsorption for suspensions high porosity Al_2O_3/ H_2O and $Al_2O_3/ C_2H_6O_2$.

- The heat of adsorption increase with increasing of alkyl groups in primary, secondary and tertiary alcohols (Figure 5) from studied literature.
- Adsorption and heat transfer coefficient at boiling decrease with increasing of temperatures, densities of heat flux and concentrations of nanoparticles (Figure 9) from studied article.

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