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# Thermodynamic Parameters of Silica Gel In View of Its Different Modifications

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**Abstract**
In the present study silica gel was selected to investigate the influence of several surface modification and coating techniques on the thermodynamic parameters of such material. These materials have relative high stability potential and can be synthesized from inexpensive starting materials. Moreover, it can be easily modified by different techniques such as calcinations, silylation, alkali metal treatment, hydrothermal treatment and special chemical treatments. Also, it can be coated and bonded using thin film of polyethylene glycol. All this modification decrease the interaction between the adsorbate and adsorbent reflecting the decrease in the activity of silica surfaces. The negative ΔH values increase in the sequence methylcyclohexane < n-heptane < toluene on all studied silica samples, the more negative the ΔH, the greater this interaction.

**Key words:-** Silica gel, Thermodynamic parameters, Modifications, silylation, alkali metal treatment, hydrothermal treatment, Polyethylene glycol

## I. Introduction

Silica gel is a common sorbent for many applications, on the surface of silica, some residual, uncondensed hydroxyl groups from the original polymeric silicic acid remain. These residual hydroxyl groups confer upon silica gel its polar properties. The chemical and adsorption properties of silica gel depend on number and reactivity of the surface silanol groups. Two forms of adsorption centers may exist over the surface of silica gel, 1) Hydroxyl group, 2) Coordinated unsaturated atoms of silicon and surfaced electronegativity atoms of oxygen nascent at dehydration of silica gel. The surface of dehydrated silica gel begins slightly to chemisorb oxygen, most likely on the centers of -Si type[1].

The main purpose of silica surface modification is shielding of the active silanol groups and attachment to the accessible adsorbent surface organic ligands which are responsible for specific surface interactions. In order to study the retention and separation mechanism of the stationary phase, the relation between retention volume and carbon number[2, 3], and the thermodynamic parameters of solution, the enthalpy of solution (ΔH), the free energy of solution (ΔG), and the entropy of solution (ΔS) were measured. Many others[4-7] studied the feasibility of GLC for the thermodynamic investigation of different stationary phases and hydrocarbon solutes.

## II. Experimental

The main methods of preparation and modification of silica gel as solid stationary phase in the present investigation are presented in Table 1. Silica was modified and coated in single and double treatment according to the methods given in Table 1. and the notation of the prepared samples was given in Table 2.

**Table 1. Preparation and modification methods of silica gel**

| No. | The experiment | The method and references |
|---|---|---|
| 1 | Preparation of silica gel | De Boer method **(172)** |
| 2 | Calcination at 500°C and at 1000°C | Puurunen et al 2002[8] |
| 3 | Hydrothermal treatment at 220°C and 15 bar for 24h | Valente et al 2003[9] |
| 4 | Silylation using dimethyldichlorosilane | Pesek and Graham 1977[10] |
| 5 | Treating with alkali metal at pH 9 | Kopecni et al 1980[11] |
| 6 | Coating with (PEG) polyethyleneglycol | Walter et al 1973[12] |
| 7 | Bonding with (PEG) polyethyleneglycol | Chein et al 1980[13] |

**Table (2): Notation of the prepared samples**

| Notation | Treatments |
|---|---|
| **Si** | Parent silica gel (60-80 mesh) |
| **$Si_{C500}$** | Silica gel calcined at 500°C |
| **$Si_C$** | Silica gel calcined at 1000°C |
| **$Si_S$** | Silylated silica gel using dimethyldichlorosilane |
| **$Si_{CS}$** | Silylated calcined Silica gel |
| **$Si_{Na}$** | Silica gel exchanged by NaCl |
| **$Si_{Na10\%}$** | Silica gel coating with NaCl and then calcined at 700°C |
| **$Si_{CNa}$** | Calcined silica gel exchanged by NaCl |
| **$Si_{HT}$** | Hydrothermally treated silica gel |
| **$Si_{CHT}$** | Hydrothermally treated pre calcined silica gel |
| **$Si_{Co25\%}$** | Silica gel coating by 25% of polyethyleneglycol |
| **$Si_{CCo10\%}$** | Calcined silica gel coating by 10% of polyethyleneglycol |
| **$Si_{Bo25\%}$** | Silica gel bonding by 25% of polyethyleneglycol |
| **$Si_{CBo10\%}$** | Calcined silica gel bonding by 10% of polyethyleneglycol |

## III. Gas chromatography

All parent and modified samples were subject to an inverse gas chromatography to evaluate their efficiency when used as a solid stationary phases or solid support. The gas chromatograph used is Unicam 610 equipped with flame ionization detector (FID) and thermal conductivity detector (TCD). Nitrogen (oxygen free) and hydrogen was used as the mobile phase for FID and TCD respectively. The optimum flow rate was determined depending on the column efficiency. The optimum was found to be 30 ml min$^{-1}$. The solutes used for chromatographic characterization were selected to cover the wide range of polarity such as n-parrafin, olefins, aromatics and alcohols as well as wax, natural gases and condensate samples. The polarity indices were assessed with respect to the reference non-polar column SE-30 (20% SE-30 on chromosorb W.A.W., 60-80 mesh).

## IV. Results and Discussions

### Thermodynamic parameters

Gas chromatography affords a general technique for studying the interactions of gases with solids or liquids and determination of the thermodynamic parameters of the interaction: heat of adsorption ($\Delta H$), free energy ($\Delta G$) and entropy ($\Delta S$).
Thermodynamic parameters of normal heptane, methylcyclohexane and toluene as representative paraffin, cyclic and aromatic hydrocarbons respectively, were calculated and listed in Tables (3, 4). Figures (1, 2) show the relationships between lnVn and 1000/T for parent and modified silica stationary phases of n-heptane, methylcyclohexane and toluene. These plots give linear relationship. $\Delta H$ & $\Delta S$ could be derived from the slope and intercept of the straight line, $\Delta G$ was calculated at constant temperature (373K)[14]. The thermodynamic data of various stationary phases are summarized in Table (3, 4).

It is evident from the data that negative $\Delta H$ values increase in the sequence methylcyclohexane < n-heptane < toluene on all studied stationary phases, the more negative the $\Delta H$, the greater the interaction between the adsorbate and adsorbent. A similar study was also done by Inel et al[15], they evaluated the thermodynamic parameters ($\Delta H$, $\Delta S$ and $\Delta G$) of some probes, each representing a class of organic compounds (n-hexane, cyclohexane and benzene) on 4A and 13X Zeolites, it was found that thermodynamic parameter increase in the sequence cyclo-hexane < n-hexane < Benzene. Also, Bilgic and Askin[16], obtained the same result for activated alumina stationary phase. Although, n-heptane and methylcyclohexane interact non-specifically, but n-heptane interacts more intensively than methylcyclohexane, this result indicates a better contact of an open chain structure molecules with the surface of stationary phases[17].

The stronger adsorption of toluene on silica surface than n-heptane and methylcyclohexane most probably attributed to the contribution of the specific interaction between the $SiO_2$ surface and the $\pi$-electrons of the toluene ring. According to the Kiselev and Yashin[18], the surface modification of silica gel was studied before[19], silica has free hydroxyl groups on the surface, OH groups linked to silicon acts as a weak acid, with hydrogen partly protonized. So, silica can interact specifically with the molecules containing $\pi$-electrons. In addition to the three π-bonds of benzene ring, toluene has electon-donor character of the methyl group, which enhanced the interaction of toluene with silica surface. The influence of modification methods on the adsorption properties of parent and modified silica is given in Tables (3, 4). The parent silica sample has the highest –ΔH value indicating a strong interaction with the adsorbate. The high decrease in surface area and strongly removal of the active hydroxyl groups due to calcination lead to small ΔH value.

**Table (3): Thermodynamic parameters of some selected solutes on parent and modified silica stationary phases**

| Columns | Solutes | ˜ □ G KJmol$^{1}$ | ˜ □ H KJmol$^{1}$ | ˜ □ S Jmol$^{1}$degree$^{-1}$ |
|---|---|---|---|---|
| **Si** | n-Heptane | 12.38 | 37.66 | 67.79 |
| | Methylcyclohexane | 12.19 | 35.12 | 61.47 |
| | Toluene | 18.35 | 45.79 | 73.54 |
| **Si$_{Co25\%}$** | n-Heptane | 6.37 | 21.06 | 39.39 |
| | Methyl Cyclohexane. | 6.82 | 20.95 | 37.88 |
| | Toluene | 9.25 | 25.37 | 43.21 |
| **Si$_{Bo25\%}$** | n-Heptane | 13.13 | 27.93 | 39.68 |
| | Methyl cyclohexane | 12.95 | 26.98 | 37.61 |
| | Toluene | 14.91 | 32.27 | 46.54 |
| **Si$_{S}$** | n-Heptane | 9.01 | 28.45 | 52.12 |
| | Methyl cyclohexane | 9.29 | 27.58 | 49.03 |
| | Toluene | 10.20 | 31.32 | 56.62 |
| **Si$_{Na}$** | n-Heptane | 8.89 | 36.58 | 74.25 |
| | Methylcyclohexane | 9.45 | 32.76 | 62.49 |
| | Toluene | 12.77 | 41.19 | 76.22 |
| **Si$_{Na10\%}$** | n-Heptane | 12.2 | 24.84 | 33.9 |
| | Methylcyclohexane | 12.07 | 23.86 | 31.62 |
| | Toluene | 15.30 | 28.27 | 34.78 |
| **Si$_{HT}$** | n-Heptane | 7.99 | 35.61 | 74.04 |
| | Methylcyclohexane | 6.87 | 29.19 | 59.85 |
| | Toluene | 11.95 | 37.65 | 68.90 |
| **Si$_{C500}$** | n-Heptane | 9.38 | 34.89 | 68.38 |
| | Methylcyclohexane | 9.10 | 31.27 | 59.44 |
| | Toluene | 14.01 | 40.84 | 71.93 |
| **Si$_{C}$** | n-Heptane | 4.55 | 26.68 | 59.33 |
| | Methylcyclohexane | 4.37 | 25.21 | 55.88 |
| | Toluene | 9.39 | 29.81 | 54.73 |
| **Si$_{CCo10\%}$** | n-Heptane | 4.29 | 14.99 | 28.18 |
| | Methyl cyclohexane | 5.32 | 11.58 | 16.77 |
| | Toluene | 10.12 | 29.96 | 53.19 |
| **Si$_{CBo10\%}$** | n-Heptane | 4.11 | 9.15 | 13.51 |
| | Methyl cyclohexane | 4.50 | 8.29 | 10.17 |
| | Toluene | 8.78 | 29.22 | 54.82 |
| **Si$_{CS}$** | n-heptane | 4.78 | 23.54 | 50.3 |
| | methyl cyclo hexane | 5.36 | 23.27 | 48.03 |
| | Toluene | 6.37 | 24.82 | 49.48 |
| **Si$_{CNa}$** | n-Heptane | 8.48 | 21.37 | 34.56 |
| | Methylcyclohexane | 8.64 | 19.86 | 30.10 |
| | Toluene | 10.75 | 23.63 | 34.53 |
| **Si$_{CHT}$** | n-Heptane | 7.60 | 35.05 | 73.59 |
| | Methylcyclohexane | 6.60 | 33.05 | 70.92 |
| | Toluene | 11.52 | 39.56 | 75.20 |

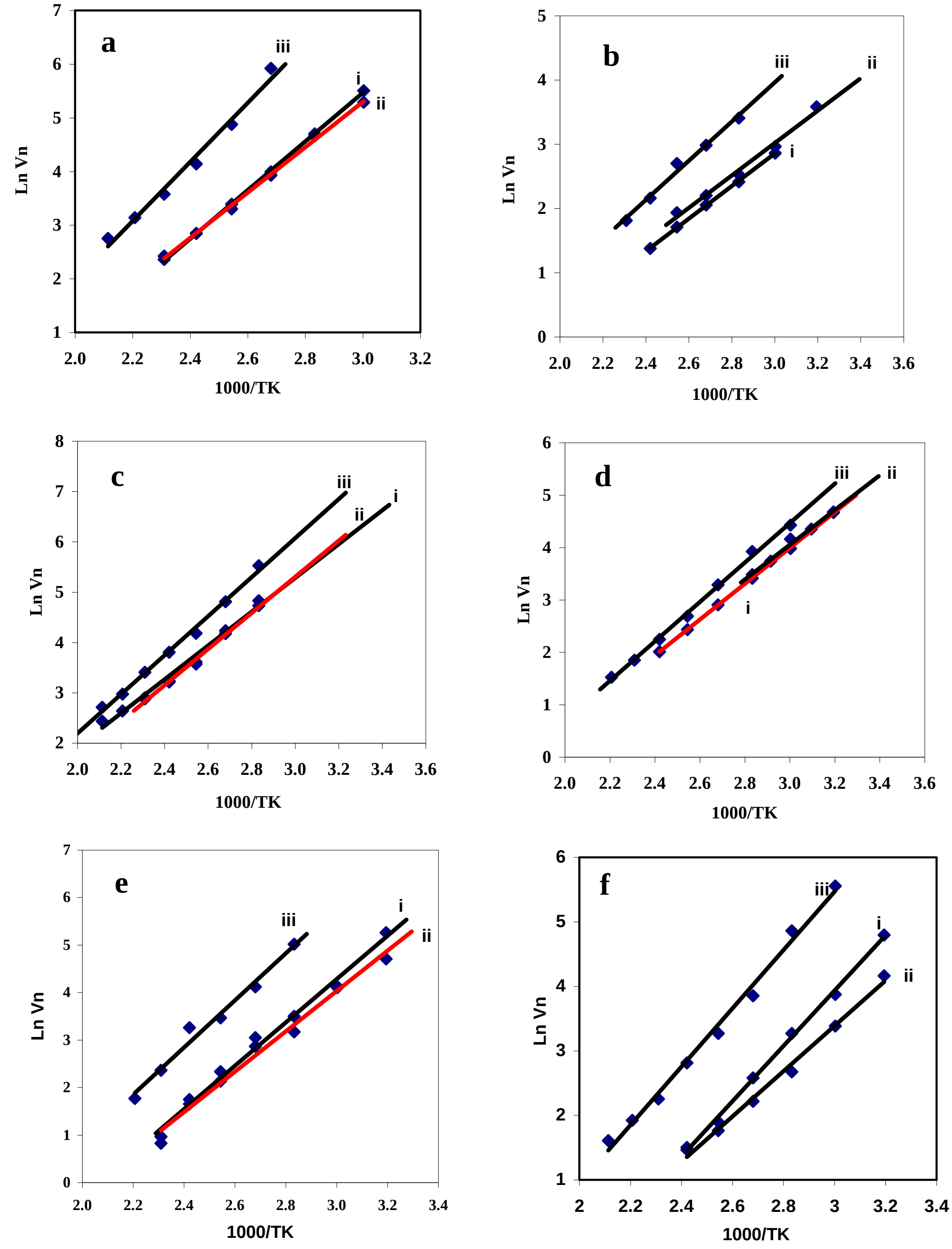

***Figure (1): Plots of lnV$_n$ versus 1000/T of n-heptane (i) Methyl cyclo hexane (ii) Toluene (iii) for silica and modified silica stationary phases:***
***a- Si b-Si$_{Co25\%}$ c-Si$_{BO25\%}$ d-Si$_S$ e-Si$_{Na}$ f-Si$_{HT}$***

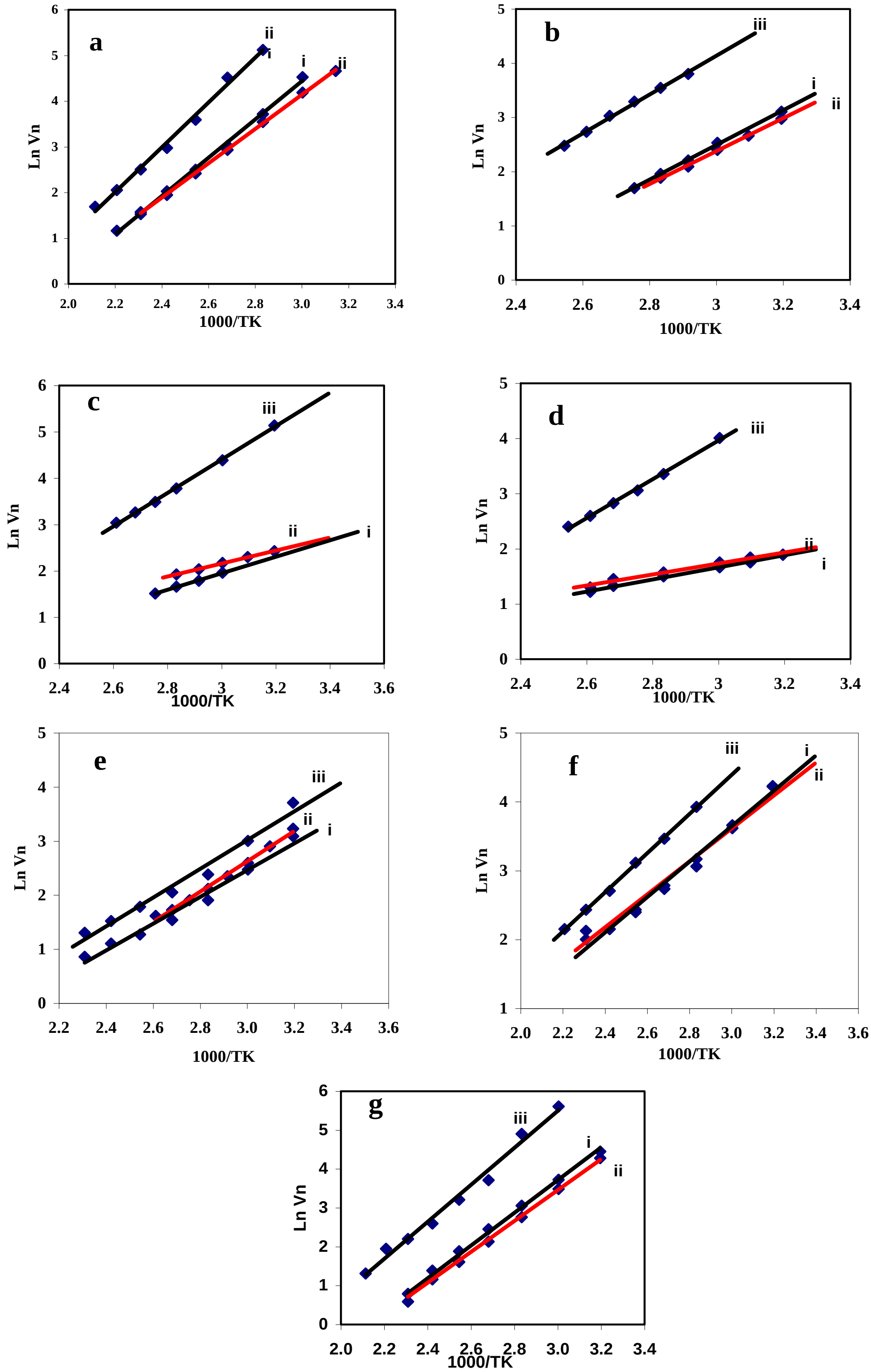

*Figure (2): Plots of* $\ln V_n$ *versus 1/T of n-heptane (i) Methyl cyclo hexane (ii) Toluene (iii) for silica and modified silica stationary phases:*
*a-* $Si_{C500}$ *b-* $Si_C$ *c-*$Si_{CCo10\%}$ *d-*$Si_{CBo10\%}$ *e-* $Si_{CS}$ *f-* $Si_{CNa}$ *g-*$Si_{CHT}$

Chemical modification of silica sample with PEG and DMDCS also deactivates the silica surface decreasing, thus the thermodynamic parameters. In alkali metal modification the methodology of preparation cause a great effect on thermodynamic parameters, -ΔH value of $Si_{Na}$ was found to be higher than that for $Si_{Na10\%}$. This may be attributed to the drastic decrease of OH group of $Si_{Na10\%}$, as a result of its calcination at 700°C. Furthermore, the lower negativity of the entropy of $Si_{Na10\%}$ may reflect the inertness of surface associated with lower degree of freedom.

## V. Conclusion

Thermodynamic parameters assisted to study interaction between the adsorpents and probs of different polarities and elucidate the type of application. All these modifications decrease this interaction reflecting the decrease in the activity of silica surfaces. The negative ΔH values increase in the sequence methylcyclohexane < n-heptane < toluene on all studied silica samples, the more negative the ΔH, the greater the interaction between the adsorbate and adsorbent. The stronger adsorption of toluene on silica surface than n-heptane and methylcyclohexane was attributed to the contribution of the specific interaction between the $SiO_2$ surface and the π-electrons of the toluene ring.

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