



Thermodynamic Studies on Adsorption of Methanol Vapours on Metal-Exchanged Zeolite-A

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Abstract

Adsorption of methanol vapors on zeolite-4A and metals (Co, Ni, and Cu) exchanged zeolite-A has been studied as a function of temperature. Thermodynamic parameters such as ΔG° , ΔH , and ΔS° are calculated. It is observed that in most of the cases, metal exchanged zeolite samples have more adsorption affinity towards methanol as compared to parent zeolite. From adsorption data isosteric heat of adsorption were also calculated as a function of coverage and temperature, which is similar to $-\Delta H$.

Key words: Thermodynamics, Adsorption, Isotherms, Metal Exchanged Zeolite-A

Introduction

Zeolites are excellent host materials for guest molecules that undergo reactions and perform a variety of functions. Their structurally well-defined pore networks and ion-exchange properties form the basis of very significant technologies in petrochemical catalysis, water softening, and molecular separations [1]. The water molecules in the alumino-silicate framework act as guest and can be out-gassed continuously over a wide temperature range by heating in air, leaving an empty porous structure, which can be filled by other suitable molecules. The dehydrated zeolites are called as "molecular sieves" due to their property of permitting access to molecules of definite sizes and shapes depending on their channel size which are distributed uniformly throughout the crystalline alumino-silicate net-work [2-4].

A simple way of modifying the stability, adsorption behaviour, selectivity, catalytic activity and other important properties of zeolites is cation exchange. High thermal stability of the zeolite framework depends considerably on the type of

cation, their distribution among the non-framework sites, and the degree of cation exchange. Cation exchange with multivalent cations or hydrogen enhances the thermal stability [5]. Thus the porous structures of zeolites make it possible to use them for the separation of gases and vapors at suitable temperatures provided that the dimensions of the channel and cavities are suitable. Adsorption of organic vapors on carbon, silica gel, alumina, charcoal, and zeolites has been studied by Afzal *et.al.* [6-10]. The present work aims to study the thermodynamics of adsorption of methanol vapours on metal-exchanged zeolite-A which will help to create better understanding of the effect of physical parameters in the removal of toxic vapours from the air.

Experimental

Chemicals and reagents

Zeolite-4A was supplied by Merck. It was ground by agate mortar and passed through U.S. standard sieve series no. 140 having an opening of 105 micron. Metal-II-chlorides used were supplied

by Merck with the purity better than 99%. Methanol was supplied by Merck and used as such.

Procedure

Metal exchanged samples were prepared by magnetically stirring a predetermined amount of metal chloride and zeolite-4A in 100 ml distilled water at different temperatures and time intervals. Amount of metal exchange was determined by EDTA micro titration method. The metal exchanged zeolite samples are designated by the formula $M_x X$. Where M stands for Co, Ni, and Cu, x is the number of metal ions per unit cell and X is the residue. The exact number of water molecules was detected by using Shimadzu Thermal Analyser.

Adsorption data for methanol was obtained using a CAHN 1000 electro balance attached to vacuum line. A fixed amount of the adsorbent was taken in a glazed silica crucible which was placed in the weighing unit. Prior to pumping, the hang down tube was maintained at a fixed temperature using water thermostat (accurate to $\pm 0.1^\circ\text{C}$). The entire system was then evacuated at 10^{-5} mbar for two hours before taking adsorption data. Vapours of adsorptive materials were admitted and equilibrium pressure was read from mercury manometer with the aid of cathetometer. Dissolved gases were removed from the adsorptive liquid by several cycles of freeze-pump-thaw technique.

Adsorption isosters for the systems investigated in the present work were calculated from a series of isotherms at different temperatures by reading pressure and temperature at a constant coverage. From these adsorption isosters, the values of q_{st} were calculated by the Clausius Clapeyron equation applied in the integrated form [6]

$$\ln(P)_x = -q_{st}/RT + C \quad (1)$$

Where R is gas constant in $\text{cal.mol}^{-1} \text{K}^{-1}$, P is equilibrium pressure and q_{st} is isosteric heat of adsorption at constant coverage. Isosteric thermodynamic parameters were calculated in some cases for a standard gaseous state of one

atmosphere from the equation by using the relation [6].

$$-\Delta H = q_{st} \quad (2)$$

$$\Delta G^\circ = -RT \ln(760/P) \quad (3)$$

$$\ln(760/P) = -\Delta H/RT + \Delta S^\circ/R \quad (4)$$

OR

$$\ln K = -\Delta H/RT + \Delta S^\circ/R$$

$$\Delta S^\circ = (\Delta H - \Delta G^\circ)/T \quad (5)$$

The values of q_{st} are the same as the differential enthalpy change ΔH for the adsorption process. The relation between these quantities has been given by Hill [11]. Nevertheless, the value of q_{st} and its variation with the coverage and temperature will serve as a guide to the value of ΔH and its variation with the same experimental conditions.

Results and Discussion

Adsorption isotherms were obtained by plotting weight adsorbed (X) per gram of the adsorbate against pressure. The plots of adsorption isotherms for methanol on NaA-zeolite and metal exchanged zeolite-A samples at 273K are given in Fig. 1. The kinetic and thermodynamic parameters for the system investigated in the present work were calculated from a series of isotherms at different temperatures by well known Clausius Clapeyron equation and virial isotherm expression and values are given in Tables 1-4.

Table 1. Kinetic parameters for the dehydration of metal exchanged zeolite-A

System	% weight loss	No. of water molecules	Activation Energy (kcalmol^{-1})
NaA	22.20	27.00	3.67
$\text{Co}_{3.73}\text{A}$	24.80	30.00	3.23
$\text{Co}_{5.27}\text{A}$	26.30	33.00	3.00
$\text{Ni}_{2.54}\text{A}$	25.40	31.00	3.06
$\text{Ni}_{3.61}\text{A}$	27.10	34.00	2.80
$\text{Cu}_{3.64}\text{A}$	23.40	29.00	2.97
$\text{Cu}_{5.0}\text{A}$	24.20	30.00	2.40

Table 2. Thermodynamic parameters for adsorption of methanol vapors on zeolite-A at different coverages

Coverage (mg/g)	Temperature (K)	$-\Delta G^\circ$ kcal.mol ⁻¹	$-\Delta H$ kcal.mol ⁻¹	$-\Delta S^\circ$ cal.mol ⁻¹ K ⁻¹
50	273	3.75	8.36	16.86
	283	3.50	8.36	17.15
	293	3.33	8.36	17.16
	303	3.20	8.36	17.03
	313	3.06	8.36	16.91
100	273	3.10	7.74	16.99
	283	2.88	7.74	17.16
	293	2.63	7.74	17.42
	303	2.56	7.74	17.08
	313	2.41	7.74	17.01
150	273	2.72	7.66	18.08
	283	2.39	7.66	18.61
	293	2.21	7.66	18.59
	303	2.12	7.66	18.29
	313	1.96	7.66	18.21
200	273	2.30	7.00	17.24
	283	1.95	7.00	17.86
	293	1.83	7.00	17.64
	303	1.72	7.00	17.44
	313	1.55	7.00	17.43

Table 3. Thermodynamic parameters for adsorption of methanol vapors on CO_{3.74}A at different coverage

Coverage (mg/g)	Temperature (K)	$-\Delta G^\circ$ kcal.mol ⁻¹	$-\Delta H$ kcal.mol ⁻¹	$-\Delta S^\circ$ cal.mol ⁻¹ K ⁻¹
50	273	3.68	8.30	16.93
	283	3.27	8.30	17.76
	293	3.17	8.30	17.15
	303	2.98	8.30	17.56
	313	2.81	8.30	16.53
75	273	3.17	7.85	17.12
	283	2.86	7.85	17.06
	293	2.72	7.85	17.50
	303	2.60	7.85	17.32
	313	2.45	7.85	17.24
100	273	2.83	7.34	16.53
	283	2.57	7.34	16.87
	293	2.41	7.34	16.83
	303	2.25	7.34	16.81
	313	2.17	7.34	16.54
125	273	2.62	7.78	18.88
	283	2.33	7.78	19.25
	293	2.15	7.78	19.20
	303	2.01	7.78	19.04
	313	1.84	7.78	18.96

Plots of q_{st} vs temperature at different coverage for methanol-NaA system are given in Fig. 2. Plots of $\ln K$ against $1/T$ for methanol on (a) NaA-zeolite, (b) CO_{3.73}A, (c) CO_{5.27}A (Fig. 3).

Table 4. Thermodynamic parameters for adsorption of methanol vapors on Co_{5.27}A at different coverage

Coverage (mg/g)	Temperature (K)	$-\Delta G^\circ$ kcal.mol ⁻¹	$-\Delta H$ kcal.mol ⁻¹	$-\Delta S^\circ$ cal.mol ⁻¹ K ⁻¹
25	273	3.44	6.83	12.48
	283	3.16	6.83	12.97
	293	3.08	6.83	12.82
	303	3.01	6.83	12.63
	313	2.88	6.83	12.63
50	273	3.10	7.66	16.68
	283	2.83	7.66	17.06
	293	2.65	7.66	17.09
	303	2.57	7.66	16.81
	313	2.41	7.66	16.78
75	273	2.85	7.80	18.12
	283	2.55	7.80	18.52
	293	2.37	7.80	18.53
	303	2.25	7.80	18.29
	313	1.09	7.80	18.22
100	273	2.50	7.94	19.92
	283	2.24	7.94	20.14
	293	2.08	7.94	19.99
	303	1.93	7.94	19.84
	313	1.66	7.94	20.10

Interaction of zeolites with alcohols is of special interest [12]. The use of metal exchanged zeolites as catalysts and as adsorbent for organic vapors such as methanol is studied in the present work. One method of removing air pollutants from both indoor and outdoor air is to adsorb them on porous materials, such as silica gel, alumina, zeolites, and active carbon. Although zeolites and silica gel are hydrophilic, they can co adsorb various gases in the presence of water vapors [13]. Besides having offensive odours, organic solvents acts as pollutants, when present in excess in air, and may cause a number of health problems. The most common effect are headaches, narcotic action on the nervous system, and a rise in blood pressure [14,15]. The design of an adsorption process to remove these compounds from air requires pure component equilibrium data as a function of temperature and pressure. Adsorption isotherms of methanol on zeolite-4A and metal exchanged-4A are given in Fig. 1. All these isotherms followed type I, isotherm of BET classification which is typical for micro porous solids, and plateau probably represents the complete filling of very small pores by the condensed gas. As given by Berl [16] the adsorption isotherm for the zeolites usually

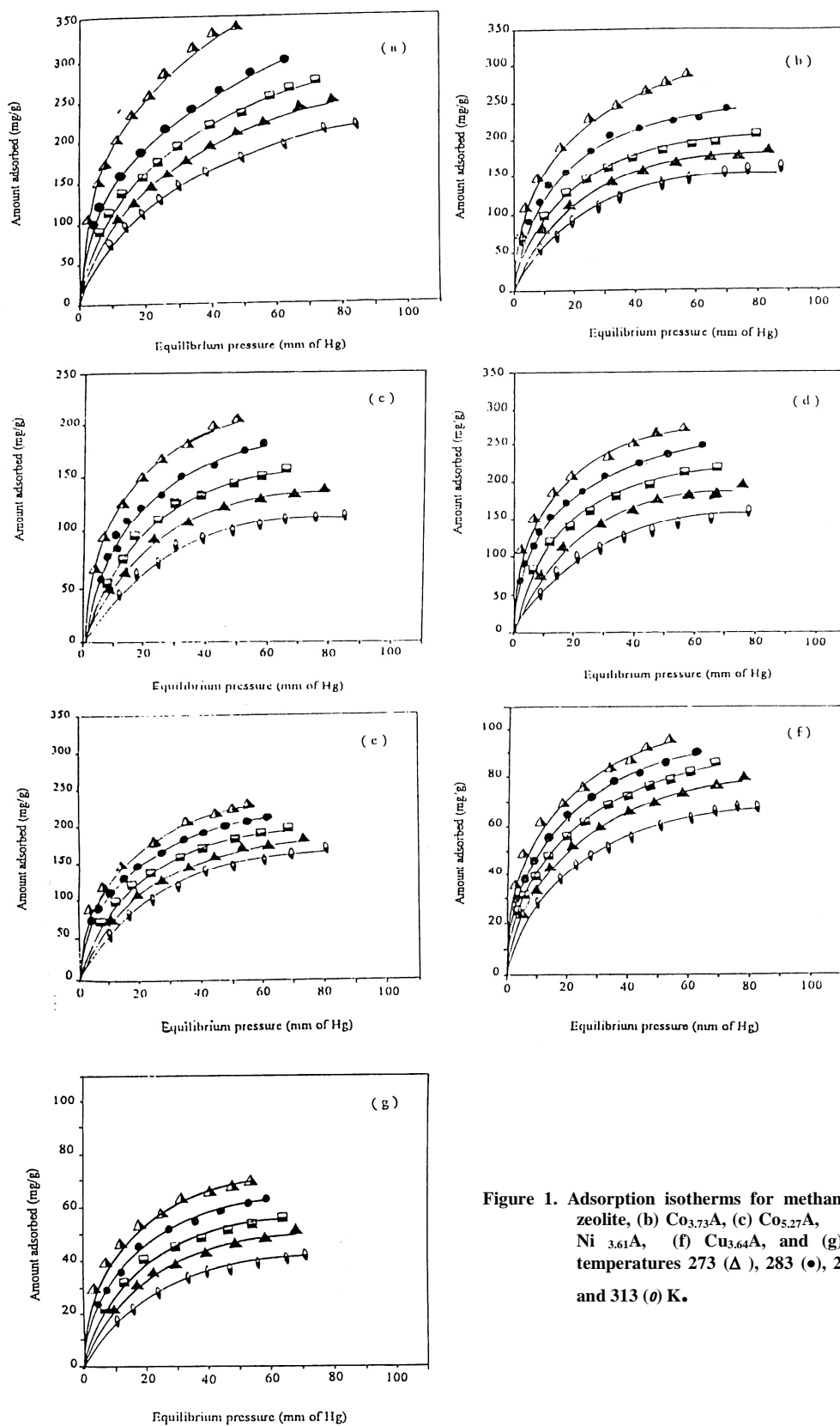


Figure 1. Adsorption isotherms for methanol on (a) NaA-zeolite, (b) $\text{Co}_{3.73}\text{A}$, (c) $\text{Co}_{5.27}\text{A}$, (d) $\text{Ni}_{2.54}\text{A}$, (e) $\text{Ni}_{3.61}\text{A}$, (f) $\text{Cu}_{3.64}\text{A}$, and (g) $\text{Cu}_{5.0}\text{A}$, at temperatures 273 (Δ), 283 (\bullet), 293 (\square), 303 (\blacktriangle) and 313 (\circ) K.

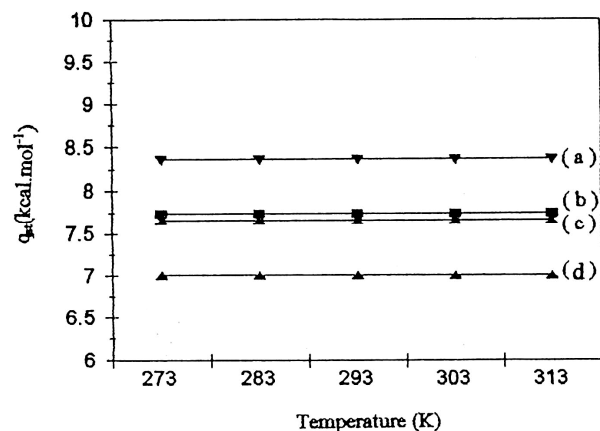


Figure 2. Plots of isosteric heat of adsorption (q_{st}) vs temperature for methanol-NaA zeolite system at different coverages (a) 50 mg/g; (b) 100 mg/g; (c) 150 mg/g; (d) 200 mg/g.

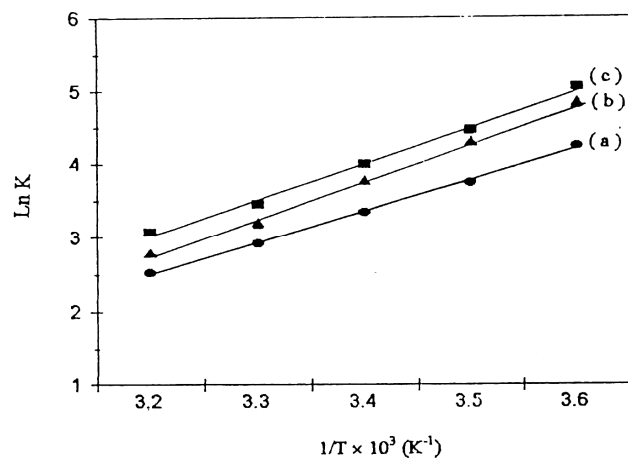


Figure 3. Plots of $\ln K$ against $1/T$ for methanol on (a) NaA-zeolite, (b) Co_{3.73}A, (c) Co_{5.27}A.

confirms to type sometimes referred as the “rectangular” isotherm, more commonly known as the Langmuir isotherm. It is evident from the data that the amount adsorbed ($\text{mg} / \text{g}^{-1}$) decreases with rise in temperature for all the systems studied, indicating that all these sorption processes are exothermic in nature as expected for gas adsorption on solid surfaces. The amount adsorbed increases as the pressure of the adsorbate increases and attained maximum values, and remained constant at high pressures. Since the zeolite samples were outgassed by heating, so more space are available inside the cavities for the incoming guest molecules. Thus the initial phase of adsorption processes is very rapid but it slows

down in the latter stages indicating the filling of pores. The area occupied by the methanol molecule is $3.46 \text{ m}^2 / \text{mg}$ at 273K.

If the size of the adsorbate molecule is greater, then less number of molecules may occupy space available inside the cavities. The adsorption processes of the methanol in zeolite systems are exothermic, more favourable at lower temperature and hence the surface area value decreases with the rise in temperature. It is clear from the data that as metal concentration increases surface area decreases but in most of the cases adsorption per unit area increases. So after the exchange of metal, efficiency of zeolite increases.

From the data, it is noted that there is some variation in the observed q_{st} values which is from 4 kcal / mol to 12 kcal / mol. It is difficult to state the exact significance of these values unless other factors such as variations with surface coverage [17] and temperature [18] are considered. It has been suggested by various authors [19, 20] that two factors mainly contribute to the experimentally observed variations in the heats of adsorption. These are (a) physical heterogeneity of the surface and (b) lateral interactions between the molecules adsorbed. According to Beebe *et al.* [17] if the adsorbent is porous, the interpretation of heat behaviour is further complicated.

If all the pores are large in diameter in comparison to adsorbate molecules, then one may expect effects which are essentially the same as in the case of non-porous powders. On the other hand, if the pore diameter is no larger than a few adsorbate molecules diameters, then it is to be expected that the adsorbate molecules will be attracted by more than one wall with a corresponding high heat of adsorption. Barrer [21] has calculated that such effects may give rise to heat values several times higher than those obtaining on plain surfaces.

In addition to the factors mentioned above the heats of adsorption are also complicated by other factors such as cross sectional area of the adsorbate molecule, polarity of the adsorbate molecules, symmetry of the molecules, orientation of the molecules, vertical interactions (adsorbate-

adsorbent molecules) and horizontal interactions (adsorbate-adsorbate molecules) and many more [19] In the same way, heats of adsorption are influenced by nature of the adsorbent, impurities incorporated in the surfaces, porous nature of the adsorbents, pore size distribution of the adsorbents, geometric arrangement of the molecules of the solids and so on. According to Clark [22] metals generally show a pronounced decrease in heat of adsorption with coverage. The decrease has been attributed to various factors including (i) adsorbate-adsorbate interactions, (ii) change in work function of the metal by chemisorption (iii) alteration of bonding with coverage, and (iv) inherent non-uniformity of the metals surface. Adsorbate-adsorbate interaction may be the result of mutual repulsion of parallel oriented dipoles of adsorbate, of short range repulsive forces or of attraction forces, or of attraction between adsorbate atoms caused by Vander Waals forces. However, these interactions can account for only a small part of the total decrease. It may be tentatively concluded that heats of adsorption correspond to physical adsorption.

The difficulty in interpreting the smaller heats of adsorption in terms of physical or chemisorption may be made clear by pointing out that the thermodynamic quantity which determines the adsorption equilibrium is not the heat of adsorption but the free energy of adsorption,

$$\Delta G_{ad} = \Delta H_{ad} - T\Delta S_{ad} \quad (6)$$

Where symbols have their usual meaning. For physical adsorption to occur spontaneously ΔG must be negative. ΔS will be negative since if only physical adsorption is assumed there will be no change in chemical bonding of adsorbate or adsorbent, but merely a change in the number of degrees of freedom of the adsorbate. This implies that ΔH for the process must be negative, i.e., heat will be given out in the adsorption process.

If chemisorption occurs the bonding of the adsorbate and the adsorbent may change and ΔS for the process could be positive or negative. As a result the ΔH values obtained for such a process could be negative and small or positive and still

corresponds to a negative ΔG values for process. We must conclude that small values of heats of adsorption are ambiguous and could correspond to a weak physical adsorption or to chemisorption. Only a discussion of how the heat adsorption in a particular system varies with coverage and temperature can lead to a clarification of this point. At higher temperature when an appreciable fraction of the adsorbate molecules have energies comparable with activation energy the chemisorption will occur to an appreciable extent. At low temperature the Vander Waals type adsorption will predominate, while at temperature such that kinetic energy is comparable to heat of adsorption in the Vander Waals layer the physical adsorption will occur to a small extent.

The surface of zeolite will in their normal state be covered with an adsorbed film which may contain oxygen, water and other impurities both chemically and physically adsorbed. By heating to about 500°C all the physically adsorbed impurities will be removed leaving on the surface sites some chemisorbed species. We may therefore assume, as the characterization of zeolite samples already revealed, that the surface used in this work are heterogeneous containing sets of different activities. Adsorption under such conditions may be physical or chemisorption, will occur first on the most active sites and then, as the pressure of adsorbate is increased, on sites of decreasing activity [23] To a first approximation therefore we might expect the heat of adsorption to decrease steadily with coverage if no new processes are brought into play at particular coverage [24]. An examination of results in tables 2-4 show that in some cases such as methanol- $\text{Co}_{3.74}\text{A}$ system the isosteric heats of adsorption increases with the increase of coverage. It may be due to strong adsorbate-adsorbate interactions as given by others [25]. It means in this case some new sites are formed. While in most of cases isosteric heat of adsorption first increases and then decreases with increase of coverage and in some cases first decrease and then increase is also observed. This is observed after metal exchange, so it may be concluded that after exchange surface become more heterogeneous as compared to parent zeolite. It can be assumed that initial adsorption whether physical or chemical could occur first on the most active sites and then, as the pressure of the

adsorbate is increased, on sites of decreasing activity. It can be seen from the data that in most of cases isosteric heat of adsorption increases for metal exchange zeolites than parent zeolite at the same coverage. It means after exchange, there may be coordination of alcohol molecules with metal vacancies dispersed in the internal surface of zeolite.

Physical adsorption is always accompanied by exothermic heats of adsorption which are in many cases 1-2 times the normal latent heat of condensation of the adsorbate. With molecular sieve, however, since the adsorptive forces are much stronger than with the usual adsorbents, the heats of adsorption are appreciably higher. They are twice as high as the latent heat of condensation of the adsorbate taken at the temperature of the adsorption [16]. The high heat at low coverage are explained as due to heterogeneities in the surface which became smeared out at higher coverage. In general it would be expected that heats would drop to the value of the heat of liquefaction at the monolayer volume, although in most cases it appears that there is some effect of the forces of the solid beyond the first layer [26, 27].

Isosteric thermodynamic parameters such as standard free energy ΔG° , ΔS° , and ΔH of sorption system were calculated for a standard gaseous state of one atmosphere and are given in tables 2-4. The negative values of ΔG° for all these system indicate that all these sorption processes are spontaneous in nature. It is evident from the data that $-\Delta G^\circ$ values decreases with increase in temperature and surface coverage. It further confirm our previous reasoning that the decrease in the values of $-\Delta G^\circ$ with increase in temperature indicate that all these sorption processes are exothermic and amount sorbed decreases with increase in temperature. The decrease in the values of $-\Delta G^\circ$ with increase in surface coverage may be explained on the basis that initially more empty space are available inside the zeolite cavities and the tendency to enter in the cavities of these adsorbate molecules are high at the initial stages and then it decreases because the active sites of increasing activity are occupied. Another point of interest is that the $-\Delta G^\circ$ values are high for the

adsorptive molecules having smaller size which can easily enter into the zeolite cavities and lower for greater size molecules which face difficulty of passing through the narrow pores of zeolites.

The values of differential heat of adsorption ($-\Delta H = q_{st}$) are the same as for isosteric heat of adsorption. It is evident that the value of $-\Delta H$ in methanol system for NaA-zeolite is 8.357 kcal.mol⁻¹, for Co_{3,74}A 8.302 kcal.mol⁻¹ and for Co_{5,27}A 7.662 kcal.mol⁻¹ at the same coverage (i.e. 50 mg/g). As we go to higher coverage such as 100mg/g, the value of $-\Delta H$ first decreases for Co_{3,74}A then increases for Co_{5,27}A as compared to parent zeolite. In case of Ni_{2,54}A the value increases then decreases for high metal value Ni_{3,63}A system.

From all above discussion it is concluded that in most cases the values of ΔH are more negative for metal exchanged zeolite as compare to parent zeolite. This reflects the increase in the interaction forces between the adsorbate molecules and metals of the adsorbents. These interactions may be between polar adsorbate molecules and metal sites present on the surface of the adsorbent as reported earlier [6,7, 28]. They studied the adsorption of methanol on metal doped carbon and reported that methanol is adsorbed strongly on the metal sites present on the surface causing an increase in the isosteric heat of adsorption.

The advantages of applying the virial isotherm equation is that it does not include the monolayer capacity or the micropore volume and provide the thermodynamic data irrespective of the mechanism of adsorption or the adsorbate-adsorbate interactions. The approach of virial analysis is analogous to the statistical thermodynamic treatment of imperfect gases and solutions and its strength lie in the fact that no model has to be assumed before analysis of the adsorption data. An empirical equation of the form

$$P = n \exp(c_1 + c_2n + c_3n^2 + \dots) \quad (7)$$

has been applied by Kiselev and Co-workers. This equation can be applied to low coverage region at which it is reduced to Henry's law [29].

A theoretical treatment of Henry's law behaviour was given by Baker and Everett [30] who put forward a high temperature adsorption method for surface area determination. This method depends on the application of Boltzmann distribution law to energetically uniform surface to allow the calculations of thermodynamic constant and virial coefficients from the adsorbate-adsorbate interaction energy. Everett concluded that serious difficulties are involved if the surface is heterogeneous, with microporous solid. Anderson [31] formulated the virial expression by considering the osmotic equation of state and successfully applied it to the microporous solids.

The values of thermodynamic parameters (ΔG° , ΔH° , ΔS°) calculated from thermodynamic constant as shown by Fig. 4 reveals that the values of free energy of adsorption are negative for all the systems as expected for spontaneous adsorption process. These values decrease with increasing temperature indicating that zeolite samples have a higher adsorption affinity for organic vapors at low temperature. The results also indicate that the values of free energy of adsorption are more negative for parent than metal exchanged zeolite. It means that adsorption of organic vapors is more favourable for parent zeolite. It is observed that as molecular size increases adsorption affinity decreases. The more the negative values of free energy, the more is the adsorption on zeolite samples. The negative values of ΔH° show that adsorption of methanol vapors is exothermic in nature. The high negative values of enthalpy of adsorption for zeolite samples are due to strong adsorbate-adsorbent interactions. From the data, it is evident that in case of methanol-vapor system the value of ΔH° is more negative for metal exchange zeolite and as go to higher metal concentration, the value become less negative except Cu-exchange zeolite. It means that in case of low metal concentration the adsorbate-metal interactions are strong. As comparison of low and high metal concentration, the $-\Delta H^\circ$ value first increase then decrease as metal concentration increases. From the Fig. 5, it can be seen that ΔS° remains nearly constant with temperature, but vary from sample to sample.

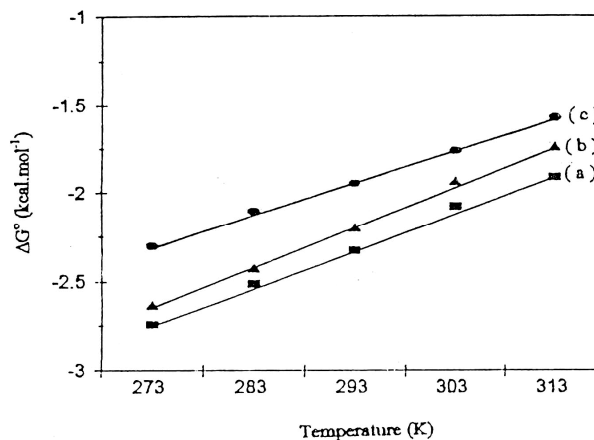


Figure 4. Plots of ΔG° vs temperature for methanol on (a) NaA-zeolite, (b) $\text{Co}_{3.73}\text{A}$, (c) $\text{Co}_{5.27}\text{A}$.

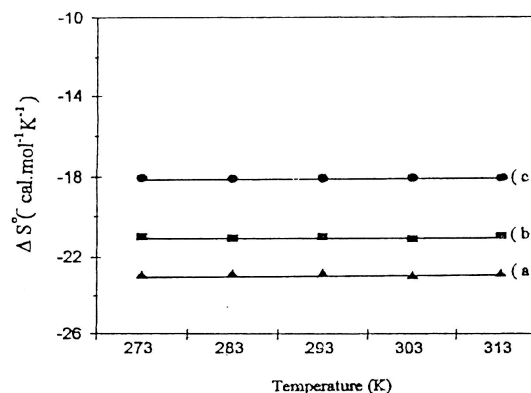


Figure 5. Plots of ΔS° vs temperature for methanol on (a) NaA-zeolite, (b) $\text{Co}_{3.73}\text{A}$, (c) $\text{Co}_{5.27}\text{A}$.

Exchange of Na metal ion of zeolite-A with transition metal ions create new surfaces which have different thermodynamic and kinetic properties as compared to the parent zeolite.

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