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# Enthalpy-entropy Compensation for n-hexane Adsorption on Y Zeolite Containing Transition Metal Cations

## R. Hercigonja[1*)], V. Rakić[2]

[1] Faculty of Physical Chemistry, University of Belgrade, 11158 Belgrade, Studentski trg 12, Serbia
[2] Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Belgrade-Zemun, Nemanjina 6, Serbia

*Abstract:*

*In this work, the values of entropy changes related to n-hexane adsorption onto cation exchanged Y zeolite were calculated from differential heats. Various transition metal cations ($Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Cd^{2+}$) were introduced into the lattice of the parent NaY, and the existence of enthalpy-entropy compensation effect related to n-hexane adsorption, id. est, the linearity of $-\Delta H$ vs. $-\Delta S$ plots was examined. The compensation effect was confirmed for all investigated zeolites. The compensation effect can be comprehended as governed by ion-induced dipole interaction between highly polarizing cationic centers in zeolite and nonpolar n-hexane molecules. Finally, the compensation effect and so the compensation temperature were found to depend on the type of charge-balancing cation (charge, size and electronic configuration).*

*Keywords:* Enthalpy-entropy compensation, Compensation temperatures, Zeolite, Transition metal cations.

## 1. Introduction

In the process of adsorption on zeolites, enthalpy changes ($\Delta H$) provide a measure of the energy variations occurring due to the interaction of adsorbate molecules with the zeolite adsorbent. The entropy change ($\Delta S$) may be associated with the binding or repulsive forces in the system and is associated with the spatial arrangements at the adsorbate-zeolite interface. Thus, entropy defines the degree of order or randomness existing in the adsorbate-zeolite system. Free energy change ($\Delta G$), based on its sign, is indicative of the affinity of the zeolite as adsorbent for molecules of adsorbate, and provides a criterion as to whether the adsorption is a spontaneous ($\Delta G<0$) or nonspontaneous process ($\Delta G>0$). From the Gibbs free energy expression: $\Delta G = \Delta H - T\Delta S$, if $\Delta H$ is plotted against $\Delta S$, a linear relationship is expected when $\Delta G$ is constant or zero. The linear scaling between enthalpy ($\Delta H_i$) and entropy ($\Delta S_i$) (for a set of related reactions denoted by index i), is known as the "enthalpy-entropy compensation" phenomenon. The values of $\Delta H_i$ and $\Delta S_i$ are then related by equation:

$$\Delta H_i = \alpha + \beta \Delta S_i \qquad (1)$$

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*) **Corresponding author**: radah@ffh.bg.ac.rs

In equation (1), $\alpha$ and $\beta$ are constants: $\beta$ (the slope of the plot $\Delta H_i$ versus $\Delta S_i$ is the "compensation temperature", while $\alpha$ (the y intercept of the plot) has the dimension of free energy. At the "compensation temperature" any variation in enthalpy is balanced by such variation in entropy so that the total change in free energy ($\Delta G$, the y intercept of the plot) of related event remains constant.

Extensive theoretical analyses of the compensatory enthalpy-entropy relationship were first carried out by Leffler [1]. The relationship $\Delta H_i = \alpha + \beta \Delta S_i$ has been established for the reactions in extremely wide range of areas. In many different classes of physicochemical processes researchers have observed a correlation between the enthalpic and entropic contributions to the free energy change $\Delta G$ [2 - 6]. Numerous literature sources are reported related to adsorption [7-9] and heterogeneous catalysis [10-13]. The investigation of "enthalpy-entropy compensation" effect has importance concerning fundamental studies on gas adsorption. In the case of adsorption, compensation phenomenon can be physically explained as a loss in entropy (negative value of $\Delta S_{ads}$ provoked by the reduction of freedom of motion), that is compensated by a gain in enthalpy (binding energy, negative $\Delta H_{ads}$) [14-16]. Due to the compensation effect of the entropy, the enthalpy of adsorption increases less than it would do if the compensation effect wasn't present. Generally, a stronger intermolecular interaction or binding (related to the enthalpy) will lead to a greater reduction of the configurational freedom and hence higher order of the system, related to the entropy.

The framework structure of NaY consists of sodalite cavities linked together at tetrahedrally arranged six-rings (creating double six-ring (D6R, hexagonal prism)) and an open 3D pore system with large supercages capable of hosting hydrocarbons accessible via 12-membered ring windows. Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 S6Rs (single six-rings). The exchangeable cations that balance the negative charge of the NaY framework are located within the zeolite's windows and cavities. From the magnitude of the volume of one $\alpha$-cage of NaY zeolite (0.8 nm$^3$ [17] and the size of n-hexane molecule (kinetic diameter length, 1.03 nm [18] it follows that the $\alpha$-cages are only possible location of the n-hexane molecules.

Faujasite (FAU) type zeolites, including zeolites X and Y, are of great industrial interest in separation and catalytic processes such as alkylation, transalkylation and isomerization of xylenes and the processes which involve the transformation of organic molecules within the pores of zeolites [19, 20]. Being microporous crystalline structures, zeolites can serve as hosts for active metal ions. Their networks can be comprehended as a unique ligand system which provides multiple types of sites for coordination of cations. In this way, the active sites for the catalysis of a variety of reactions are formed. Transition metal ion-containing molecular sieves have been extensively investigated in academic and industrial laboratories because of their promising catalytic behavior in the oxidation of organic compounds and in the removal of NOx [21, 22]. The successful application of zeolites as catalysts needs the investigation of the adsorption processes which influence the behavior of guest molecules in these materials. The adsorption of hydrocarbons as probe molecules provides useful information concerning the microscopic and macroscopic aspects of hydrocarbon-zeolite interactions, which can be decisive for further catalyst development.

In this study, we investigated the thermodynamic parameters and the existence of enthalpy-entropy compensatory behavior related to n-hexane adsorption on Y zeolite exchanged with transition metal cations ($Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Cd^{2+}$). The influence of relevant parameters on compensatory behavior was discussed.

## 2. Experimental

The samples used in this work were prepared from synthetic NaY (SK-40). The transition metal ($Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Cd^{2+}$) cation-exchanged samples were obtained by

conventional ion-exchanged procedures [23]. Chemical compositions of investigated samples are presented in Tab. I.

**Tab. I** Unit cell composition of zeolites

| zeolite | unit cell composition |
|---------|----------------------|
| NaY | $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$ |
| CoY | $Na_{16}Co_{20}(AlO_2)_{56}(SiO_2)_{136}$ |
| NiY | $Na_{11}Ni_{22}(AlO_2)_{56}(SiO_2)_{136}$ |
| ZnY | $Na_{15}Zn_{20}(AlO_2)_{56}(SiO_2)_{136}$ |
| CdY | $Na_{13}Cd_{21}(AlO_2)_{56}(SiO_2)_{136}$ |

n-Hexane (Merck, reagent grade) was distilled and stored over calcined NaA zeolite. Its purity (> 99.99%) was controlled by gas chromatography (GC) and infrared spectroscopy (IR) analysis. The experimental procedure for the adsorption measurements is described in detail elsewhere [24]. The adsorption measurements were performed in an all-glass BET apparatus, using water as the thermostatic fluid. The zeolite samples were preliminarily activated at 573K and $10^{-3}$ Pa for several hours, cooled to 298K, and then the temperature was again raised to 573K and maintained at this temperature for 48 h. After degassing, the system was cooled down, immersed in the thermostatic bath and the adsorption of n-hexane was performed at 298 and 288K. The adsorption isotherms were measured up to p/p° = 0.8 (p° = 16.8 kPa at 298K).

In the process of n-hexane adsorption, the enthalpy changes, ΔH, were determined from the isotherms collected at two different temperatures (T= 288K and T= 295K), using the equation:

$$\Delta H = R \frac{T_1 T_2}{T_2 - T_1} \ln \left( \frac{p_2}{p_1} \right)_\Theta \qquad (2)$$

where $p_1$ and $p_2$ are equilibrium pressure of n-hexane at temperatures $T_1$ and $T_2$ for the specific coverage θ of the adsorber zeolite.

To calculate the changes of entropy ($\Delta S^0$) that resulted from n-hexane adsorption, the following expression was used:

$$\Delta S^0 = R \ln \frac{p^0}{p} + \frac{\Delta H^0}{T} \qquad (3)$$

where $p^o$ is the standard pressure (1 atm = 101.325 kPa), p is the equilibrium pressure at temperature T, at which the isotherm was obtained and $\Delta H^0$ is the standard enthalpy change in the process of adsorption. For isothermal conditions, neglecting the gas imperfections, $\Delta H^0$ can be taken to be equal ΔH, and calculated using the equation (2).

## 3. Results and discussion

The heat evolved due to the adsorption of n-hexane on the investigated zeolites is the result of the interactions of adsorbed molecules with the zeolite lattice (i.e. the pore walls), the highly polarizing cationic centers in zeolite and other adsorbed molecules. Generally, the values of entropy changes include changes in the entropy of the adsorbent but, because of zeolite' rigid crystalline structure and the fact that cation mobility is reduced in dehydrated samples, this factor may be regarded as negligible. Hence, the values of entropy changes achieved during the adsorption of n-hexane include only the changes in the entropy of the

adsorbate. Here, lateral interactions between adsorbate molecules can be also excluded, because the low-coverages of adsorbate molecules that were achieved.

The plots of adsorption enthalpies versus the assigned entropies for the adsorption of n-hexane on parent NaY and $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ cation-modified zeolites are presented in Fig. 1.
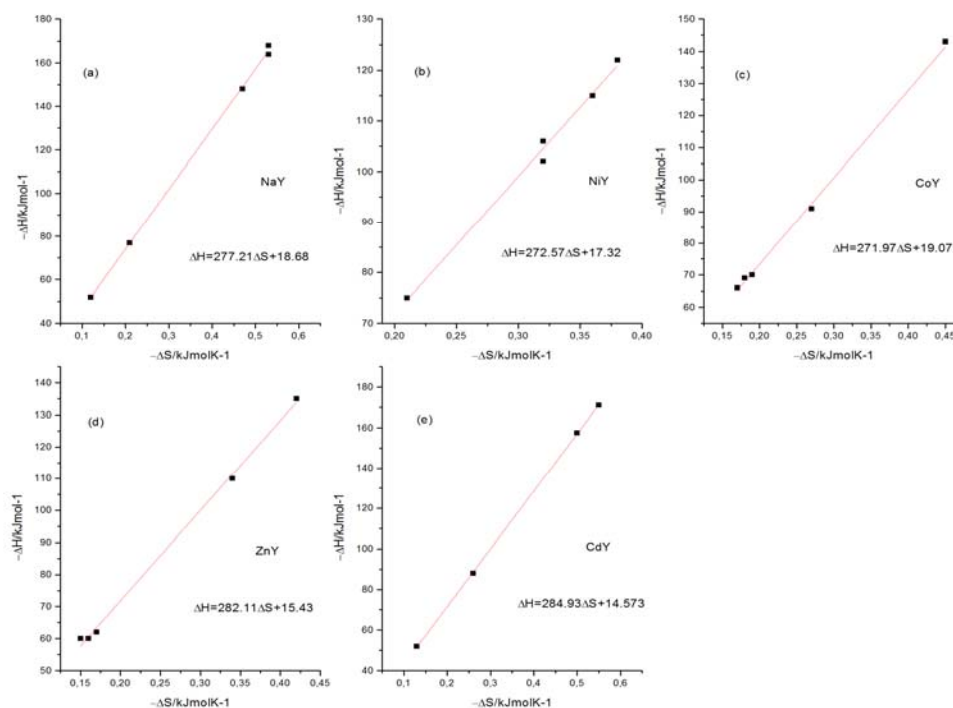


**Fig. 1**. Enthalpy-entropy compensation plots for n hexane adsorption on (a) NaY; (b) NiY; (c) CoY; (d) ZnY and (e) CdY.

As it can be seen, the graphs of enthalpy vs. entropy changes (Fig. 1) for the adsorption of n-hexane on NaY and $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ cation-modified samples express highly linear trends, with the correlation coefficients $R^2$ higher than 0.99. As the values of correlation coefficient are normally used as a criterion to judge if compensation effect exists, it means that the enthalpy-entropy compensation effect was found during the process of adsorption of n-hexane on NaYand its $Ni^{2+}$, $Co^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ cation-modified forms. The values of correlation coefficients $R^2$ and the compensation temperatures β are summarized in Tab. II.

**Tab. II** Characteristic parameters for enthalpy-entropy relationship

| Zeolite | $R^2$ | α / kJmol$^{-1}$ | β /K |
|---------|-------|------------------|------|
| NaY | 0.9989 | 18.68 | 277.21 |
| NiY | 0.9985 | 17.32 | 272.57 |
| CoY | 0.9895 | 19.07 | 271.97 |
| ZnY | 0.9972 | 15.43 | 282.11 |
| CdY | 0.9985 | 14.57 | 284.93 |

From the data presented in Tab. II, it is evident that the introducing the transition metal cations in zeolite lattice alter the compensation temperature (β, Tab. II). The higher slope of the -ΔH vs. -ΔS plot, i.e. the higher values of the compensation temperature means that the same change in ΔH is accompanied by the larger change in ΔS. The presence of transition metal cations alters the compensation temperature: $Ni^{2+}$ and $Co^{2+}$ cause decrease,

while the $Zn^{2+}$ and $Cd^2$ cause increase of the compensation temperature, in comparison to the parent NaY (Tab. I). The only kind of interactions between the adsorbed n-hexane molecules and $Na^+$, $Zn^{2+}$ and $Cd^{2+}$ cations are the ion-induced dipole and dispersion interactions. As the charge of $Zn^{2+}$ and $Cd^{2+}$ is the twice the charge of $Na^+$, ion-induced dipole interactions in ZnX and CdX are stronger than in NaY. Because of that, the loss of entropy for the same value of the enthalpy is higher in the case of ZnY and CdY than in the case of NaY, so the compensation temperatures of ZnX and CdX are higher than that one of NaY. The $Ni^{2+}$ and $Co^{2+}$ cations have the same charge, but smaller ionic radii than $Zn^{2+}$ and $Cd^{2+}$, so electrostatic interactions between n-hexane and $Ni^{2+}$ and $Co^{2+}$ should be stronger than that of $Zn^{2+}$ and $Cd^{2+}$. In spite of that, the lower values of the compensation temperatures of NiY and CoY than of ZnY and CdY were obtained.

Obviously, the strength of the electrostatic field (trough the size and charge of the charge balance cations) is not the only factor which determines the compensation temperature. Transition metal cations used in this work differ in electron configurations. The cobalt and nickel cations are spin unpaired, while the zinc and cadmium cations are spin paired. The d electrons (of incomplete d orbitals) in $Co^{2+}$ and $Ni^{2+}$ can form bonds with oxygen atoms from the lattice, as well as with adsorbed molecules (specific cation-n-hexane interactions). If these d electrons allow the interaction with the oxygen of the lattice, the interaction of n-hexane with oxygen atoms is reduced, while the cations partly lose the possibility of interaction with n-hexane. Both effects cause the smaller entropy change for the appropriate values of the enthalpy change and consequently, the compensation temperature decreases.

In conclusion, it can be inferred that the compensation effect is not only governed by fundamental physical properties such are the intensity of the electric field of zeolite' surface, the charge and radius of charge-balancing cation, but also by the specific interactions between cation and n-hexane molecule which depend on its electronic configuration.

## 4. Conclusion

The results presented in this paper confirmed the existence of the enthalpy-entropy compensation effects during the process of adsorption of n-hexane on faujasite-type NaY zeolite and its transition metal modified forms: CoY, NiY, ZnY and CdX. It was shown that the main characteristic parameter of the compensation effect, the compensation temperature, depends on the nature of the type of the extra-framework cation (charge, size and electronic configuration). Charge balancing cations $Co^{2+}$ and $Ni^{2+}$, being spin unpaired, decrease the compensation temperature while the spin paired cations $Zn^{2+}$ and $Cd^{2+}$ increase the compensation temperature comparing to that of the parent NaY. The confirmed existence of compensation effect is important since it allows prediction of adsorption behavior and the catalytic ability of considered solids.

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**Садржај:** *У овом раду су промене ентропије адсорпције н-хексана на катјонски измењеном Y зеолиту одређене на основу диференцијалних топлота адсорпције. Различити катјони прелазних метала (Co²⁺, Ni²⁺, Zn²⁺ and Cd²⁺) су убачени у кристалну решетку полазног NaY и постојање енталпијско-ентропијског компензационог ефекта у току адсорпције н-хексана, односно линеарна зависност између –ΔH и –ΔS је била испитивана. Компензациони ефекат је потврђен за све испитиване зеолите. Може се сматрати да је компензациони ефекат контролисан јон-индукованом дипол интеракцијом између високо поларизованих катјонских центара у зеолиту и неполарних молекула н-хексана. Такође је утврђено да компензациони ефекат , као и компензациона температура, зависе од врсте катјона који компензује негативно наелектрисање решетке зеолита (наелектрисања, величине и електронске конфигурације).*

**Кључне речи:** *енталпијско-ентропијска компензација, компензациона температура, зеолит*