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Compensation Theory of Adsorption: Correlation and Prediction of Henry Constants for Linear Paraffins on Zeolite Adsorbents

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Abstract. Experimental Henry's Law equilibrium data for linear paraffins show a well defined linear variation of adsorption energy with carbon number and a linear relationship between the entropy and energy of adsorption (compensation effect). Such correlations, are presented for sorption of linear paraffins on NaX, NaY, USY, silicalite and silica gel as well as for two commercial (faujasite based) catalysts and provide a concise way to predict the adsorptive behavior of the higher paraffins.

Keywords: zeolite, equilibrium, compensation effect, Henry constant, adsorption energies

Henry constants and heats of adsorption play a key role in adsorbent design as well as in the modeling of catalytic processes. For low and medium molecular weight hydrocarbons these quantities are amenable to direct experimental measurement but for carbon numbers greater than about C_{20} the Henry constant and heats of sorption become so large that direct measurement is difficult. We propose here a simple way in which, at least for the linear paraffins, the Henry constants for the higher homologs can be predicted by extrapolation from data obtained for the lighter species.

The linear paraffins provide the archetypical example of an homologous series for which the progressive change in adsorption strength with molecular weight (carbon number) can be examined. Over the last several years a substantial body of adsorption equilibrium data for linear paraffins on a range of different zeolite based adsorbents and catalysts have been accumulated and, on reviewing these data, we find that the Henry constants exhibit a very simple pattern of variation. The linear variation of heat of adsorption with carbon number was recognized many years ago by three well known pioneers of zeolite research, Barrer and Sutherland (1956), Schirmer et al. (1968), and Kiselev (1968) and, more recently, by Eder and Lercher (1997). However, without a corresponding correlation for the entropy of sorption, the linear variation of the heat of sorption does not provide a basis for the correlation and prediction of Henry constants. A review of our own files of experimental data, however, reveals that the heats (or energies) of sorption for the linear paraffins on several different zeolites show a very clear "compensation effect" i.e., there is a simple linear relationship between the entropies and enthalpies of adsorption. Taken in conjunction with the linear dependence of the heat of sorption with carbon number this provides a very simple general predictive correlation. The details of this correlation and the experimental data base on which it rests are summarized here.

Dependence of Heat of Sorption on Carbon Number

Previous experimental studies in which a linear variation of heat of sorption with carbon number have been reported are listed in Table 1. Our own data for several different zeolites, derived from Henry constant measurements over a range of temperatures, by both chromatographic and gravimetric methods, also conform to this pattern as may be seen from Fig. 1. Kiselev (1968)

Table 1. Summary of reported experimental data showing a linear variation of ΔH with carbon number.

Zeolite	Carbon number range	Reference
NaX	1–8	Barrer and Sutherland (1956)
5A	1–18	Schirmer et al. (1968) Fiedler et al. (1979)
NaX	2–10	Stach et al. (1979)
X, Y (various forms)	2–5	Alkinson and Curthoys (1981)
USY	1–10	Stach et al. (1982)
NaY, KL silicalite	1–10	Isirikian and Dubinin (1987)
NaY, HY, USY	5–12	Denayer and Baron (1996)
Silicalite, HY, NaY	3–9	Eder and Lercher (1997)

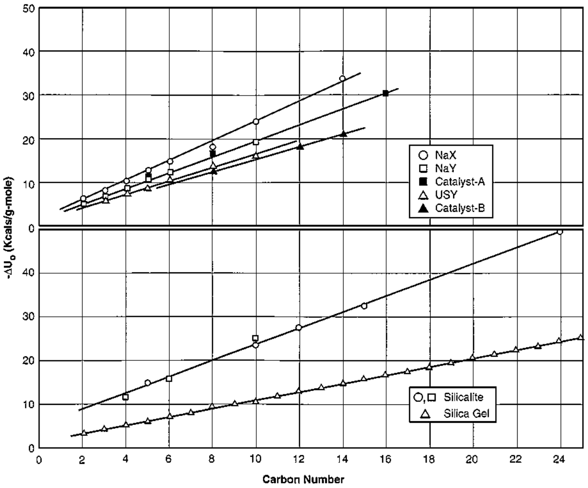

Figure 1. Linear variation of adsorption energy with carbon number for linear paraffins on various ion exchanged faujasites, silicalite and silica gel.

has pointed out that such a trend is to be expected since the polarizability increases linearly with carbon number and the strength of both the van der Waals and polarization interaction energies is directly proportional to the polarizability of the sorbate.

However, there have been suggestions, notably by Burgess et al. (1964) and Pal et al. (1983), that the linear dependence breaks down at higher carbon numbers (above C_{10}). Because of the decreasing volatility and increasing strength of sorption it becomes increasingly difficult to make accurate measurements of the Henry constants at higher carbon numbers and the high heats of sorption limit the temperature range over which such measurements can be made, thus reducing the accuracy with which the isosteric heats can be determined. In our own experimental measurements we saw no evidence of any deviation from the linear correlation at higher carbon numbers, although the accuracy with which the heat of sorption could be measured certainly decreases and, for carbon numbers greater than 24, it proved impossible to obtain reliable values. Therefore, it seems likely that the deviations from linearity reported by Burgess et al. (1964) and Pal et al. (1983) probably reflect the difficulty of obtaining reliable data at higher carbon numbers rather than any real deviation from the linear relationship.

Compensation Effect

Many years ago it was found that the rate constants for catalytic reactions commonly show a linear "Compensation Effect" meaning that, if the rate data are correlated in terms of the usual Arrhenius relation:

$$k = k_{\infty} e^{-E/RT} \tag{1}$$

then, when rate constants for a particular reaction over a series of different but related catalysts or for the reaction of a series of different but related compounds over the same catalyst, are examined, a linear relationship between E and $\ln K_{\infty}$ is observed (Constable, 1925). It should be noted that a spurious relationship of this kind can arise simply from random errors in the experimental data, particularly if factorial experiments are used (Ruthven, 1968). However, when the variations in E and $\ln k_T$ significantly exceed the margin of error of the experimental data, such an explanation can be ruled out. Cremer (1955) lists several possible explanations for this effect and his first explanation, that there may be a simple linear relationship between the entropy and energy of activation seems plausible and would account for the widespread occurrence of this type of correlation in many different systems. Regardless of the origin of the effect it can provide a useful basis for correlation of experimental kinetic data, as has been shown by Ranganathan et al. (1977).

Compensation effects have also been observed in adsorption systems, particularly for light paraffins on several different adsorbents (Eder and Lercher, 1997; Atkinson and Curthoys, 1981; Barrer and Rees, 1961; Katsanos et al., 1978; Eder et al., 1996). The temperature dependence of the Henry constant is given by

$$K_p = K_\infty e^{-\Delta H/RT} \quad \text{or} \quad K = K_\infty e^{-\Delta U/RT} \tag{2}$$

Since

$$\Delta G^o = -RT \ln K = \Delta H - T\Delta S \tag{3}$$

$$\ln K_\infty \propto \Delta S/R \tag{4}$$

and a linear relationship between $-\Delta H$ (or $-\Delta U$) and ln K_∞ therefore implies a linear relationship between the enthalpy and entropy changes on adsorption. A detailed justification of such a relationship for vapor-liquid equilibrium has been given by Bakaev (1982) and, by extension of these arguments, it seems reasonable to expect similar behavior in physical adsorption.

Our experimental data for a series of linear paraffins on several different zeolites, (summarized in Figs. 1 and 2) confirm that a linear compensation effect is indeed observed spanning several orders of magnitude in the Henry Constants. Somewhat remarkably our data for the linear paraffins on several different forms of faujasite conform to the same compensation plot. Although, for different cationic forms, the relationship between ΔH and n is different, the relationship between ΔH (or ΔU) and ln K_∞ remains invariant.

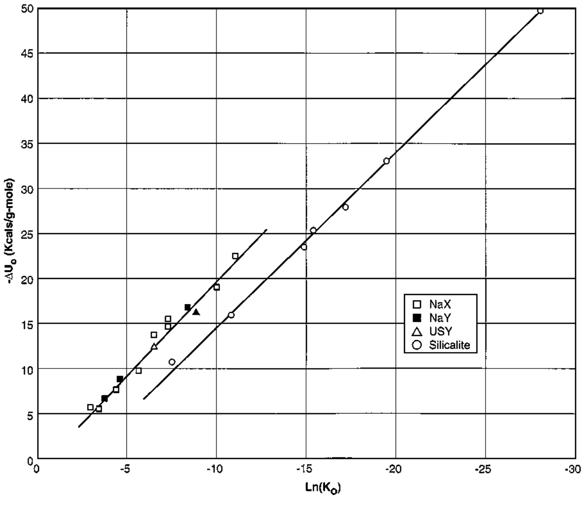

Figure 2. Compensation plot showing linear relationship between ln K_∞ and $-\Delta U$ for linear paraffins in various forms of faujasite and in silicalite. Note that the different forms of faujasite all conform to the same line.

For a system that shows a linear compensation effect (ln $K_\infty \propto \Delta H$) we may write:

$$\ln K_\infty = \ln K_\infty^1 + \frac{(-\Delta U_o)}{R\theta} \tag{5}$$

and hence, for the temperature dependence of K:

$$\ln K = \ln K_\infty^1 + \frac{\Delta U_o}{R}\left[\frac{1}{\theta} - \frac{1}{T}\right] \tag{6}$$

It is thus evident that there will be a temperature (θ) at which all the vant Hoff plots intersect (the compensation temperature). If the compensation effect is fortuitous and arises merely from error propagation, the compensation temperature will lie in the middle of the experimental range. For the present systems the compensation temperatures are about 1035 K for faujasite and 970 K for silicalite; well outside the experimental range.

A Simple Predictive Correlation of Henry Constants

The linear dependence of $-\Delta H$ (or $-\Delta U$) on carbon number, coupled with the linear compensation plot (Eq. (5)) provides, in effect, a simple general predictive correlation for the Henry constant (Eq. (6)) which can be used to extrapolate to higher carbon numbers. The parameters for this equation are summarized in Table 2. In view of the difficulty of making accurate Henry Constant measurements for the higher homologs, for carbon numbers greater than about 20, such predictions are probably more reliable than experimental values.

Nomenclature

E	Activation energy
ΔH	Enthalpy change on adsorption
k	Rate constant
K_p	Henry's law constant based on partial pressure
K	Dimensionless Henry constant
n	Carbon number
R	Gas constant
ΔS	Entropy change on adsorption
T	Absolute temperature
ΔU	Internal energy change on adsorption
θ	Compensation temperature
	Subscript ∞ denotes pre-exponential factor

Table 2. Summary of experimental data from present study.

			Parameters for compensation correlation (Eq. (6))	
Zeolite	n (range)	$-\Delta U_o = a + bn$ (k · cal)	ln K_∞^1	$\theta(K)$
NaX	2–10	$2.0 + 2.25\ n$	0.485	1035
NaY	2–10	$2.0 + 1.77\ n$		
REY*	2–16	$2.0 + 1.77\ n$		
USY	2–10	$1.5 + 1.53\ n$		
HY*	2–14	$1.7 + 1.37\ n$		
Silicalite	2–14	$5.5 + 1.85\ n$	2.43	972
Silica gel	2–25	$2.0 + 0.96\ n$		

$-\Delta U_o + RT = -\Delta H_o$.

*Data obtained for commercial catalysts with these components as the active ingredients. K is dimensionless Henry constant.

The temperature range of the measurements is constrained by the following considerations:

1. For the lighter species at high temperatures the amount adsorbed becomes too small to measure with accuracy.
2. For the heavier species at lower temperature adsorption is so strong that, within the Henry region, the pressures are too small for accurate measurement.
   At high temperatures measurements are restricted by cracking and coke formation.

The temperature ranges used in most of the measurements are as follows:

n	$T_{\min}$ (K)	$T_{\max}$ (K)
2	200	325
4	300	450
6	475	625
8	525	650
12	575	675
16	600	675

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