

SUPPLEMENTARY MATERIAL TO
An inverse gas chromatography study of the adsorption of organics on zeolite and zeolite/iron oxyhydroxide composite at the infinite and finite surface coverage

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THEORETICAL BACKGROUND – INVERSE GAS CHROMATOGRAPHY

Zero surface coverage

The primary experimental parameter measured in IGC, the net retention volume, V_N , in cm^3 , can be calculated from the maxima of the chromatographic peaks and the dead time using the expression:¹

$$V_N = jF_f \frac{(p_0 - p_w)}{p_0} \frac{T}{T_f} (t_R - t_0) \quad (\text{S-1})$$

where t_R is the retention time (min), t_0 the dead time (min), T is column temperature (K), T_f is ambient temperature (K), p_0 is the outlet column pressure, p_w is the vapour pressure of water at T_f (Pa), F_f is the carrier gas flow rate ($\text{cm}^3 \text{min}^{-1}$) and j is the James–Martin compressibility factor.

The free energy change of adsorption, ΔG_a is related to V_N as follows:

$$\Delta G_a = -RT \ln \left(\frac{V_N \cdot p_{s,g}}{m \cdot S_a \cdot \Pi_S} \right) \quad (\text{S-2})$$

where R is the gas constant, $p_{s,g}$ is the adsorbate vapour pressure in the gaseous standard state, equal to 101 kN m^{-2} (101 kPa), S_a is specific surface area of the adsorbent ($\text{m}^2 \text{g}^{-1}$), m is the mass of adsorbent in the column (g) and Π_S is the reference two-dimensional surface pressure, equal to 0.338 mN m^{-1} .²

The differential heat of adsorption of adsorbates at zero coverage, ΔH_a , was obtained from the temperature dependence of V_N according to Eq. (S-3):

$$\Delta H_a = -R \frac{d \ln V_N}{d(1/T)} \quad (\text{S-3})$$

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The entropy of adsorption of adsorbates, ΔS_a , is given by:

$$\Delta S_a = \frac{\Delta H_a^0 - \Delta G_a^0}{T} \quad (\text{S-4})$$

The surface free energy of an adsorbent, γ_s (J/m^2), is expressed as the sum of the dispersive component, γ_s^d , and the specific component, γ_s^s , corresponding to the dispersive and specific interactions, respectively.³ The dispersive properties of the solid surface are characterized by γ_s^d , while the specific properties can be described by the IGC-derived K_A and K_D parameters, characterising the ability of surface to acidic (acceptor of electrons) and basic (donor of electrons) interactions.

The dispersive component of the surface energy can be determined using the retention times of *n*-alkanes, because there are no acid–base interactions between alkanes and the stationary phase:

$$\gamma_s^d = \frac{\Delta G_{\text{CH}_2}^2}{4\gamma_{\text{CH}_2} \cdot N^2 \cdot a_{\text{CH}_2}^2} \quad (\text{S-5})$$

where N is Avogadro's number, a_{CH_2} is the cross-section of a $-\text{CH}_2$ group (0.06 nm^2), and γ_{CH_2} (mJ m^{-2}) is the surface tension of a surface consisting of $-\text{CH}_2$ groups, given as a function of temperature ($\gamma_{\text{CH}_2} = 35.6 + 0.058 (293 - T)$), while ΔG_{CH_2} represents the free energy of adsorption of a methylene group, defined as the energy difference between the adsorptions of two successive alkanes; ΔG_{CH_2} can be determined from the dependence of ΔG_a^S for alkanes on the carbon number, *i.e.*, as the slope of the straight line referred to as the “alkane line”:

$$\Delta G_{\text{CH}_2} = -RT \ln \left(\frac{V_{N,n}}{V_{N,n+1}} \right) \quad (\text{S-6})$$

where $V_{N,n}$ and $V_{N,n+1}$ are the specific retention volumes of two consecutive *n*-alkanes having *n* and *n*+1 carbon atoms, respectively.

The specific interaction can be estimated from the retention data of polar probes. The probes used for to study the specific forces were chosen based on their acidic or basic character, as determined by Gutmann.⁴ The polar probes interact more strongly with the solid than *n*-alkanes, as dispersive and specific forces are involved, and the values of ΔG_a for polar probes are situated above the “alkane line”. The difference between the values of ΔG_a for polar probes and the values of ΔG_a for a real or hypothetical *n*-alkane with the same boiling point, T_b ,⁵ is equal to ΔG_a^S :

$$\Delta G_a^S = RT \ln \left(\frac{V_N}{V_{N,\text{ref}}} \right) \quad (\text{S-7})$$

where V_N is the net retention volume for the polar probe and $V_{N,\text{ref}}$ is the net retention volume for the *n*-alkane with the same boiling point, T_b .

The specific enthalpy of adsorption, ΔH_a^S , and the specific entropy of adsorption, ΔS_a^S , can be determined as the slope and the intercept, respectively, of the straight line obtained by plotting $\Delta G_a^S / T$ versus $1 / T$.

Based on the values of ΔH_a^S for various polar molecules, Saint-Flour and Papirer⁶ proposed an empirical relationship to characterize a solid with an acid constant K_A and a basic constant K_D :

$$-\frac{\Delta H_a^S}{AN^*} = K_A \frac{DN}{AN^*} + K_D \quad (\text{S-8})$$

where DN and AN^* are the Gutmann donor and modified acceptor numbers,⁴ respectively, corresponding to the polar probes used to determine the specific interactions with the solid. Values of constants K_A and K_D of the adsorbent can be obtained by plotting $\Delta H_a^S/AN^*$ as a function of DN/AN^* , according to Eq. (S-8).

The K_D/K_A ratio is a measure of the surface acidity and basicity. Thus, for a ratio $K_D/K_A > 1$, the surface is considered to be alkaline, but acidic for $K_D/K_A < 1$.

Finite surface coverage

At finite coverage, when high quantities of probe molecules are introduced into the chromatographic system, the surface adsorption results in non-linear isotherms and asymmetrical peak shapes. Assuming that the recorded peak height is proportional to the partial pressure, the quantity adsorbed onto an adsorbent, α , can be calculated using the following expressions (S-9, S-10):¹

$$\alpha = \frac{1}{mRT} \int_0^p V_N dp \quad (\text{S-9})$$

$$p = \frac{RTnh}{F_f S} \quad (\text{S-10})$$

where p is the partial pressure of the adsorbate, n is the number of moles of probe injected, h is a height of the chromatographic peak and S is the area of the chromatographic peak. The definitions of R , T and m have been given previously.

The relationship between the amount of sample adsorbed in the column and the adsorbate vapour pressure is given by (S-11):⁷

$$\alpha = \frac{S_{\text{ads}} n}{mS} \quad (\text{S-11})$$

where S_{ads} is the chart area bounded by the axis of the time t_0 of the non-retained specimen and the adsorption envelope of the peak maxima.

The experimental isotherms can be converted to the linear form of the well-known BET isotherm:^{8,9}

$$\frac{p/p_0}{\alpha(1-p/p_0)} = \frac{1}{\alpha_m C} + \frac{(C-1)}{\alpha_m C} (p/p_0) \quad (\text{S-12})$$

where C is a constant related to the heat of adsorption, α_m is the amount of adsorbate adsorbed in a monolayer and p_0 is the vapour pressure of the adsorbate at the temperature of the measurement. If $(p/p_0)/\alpha(1-p/p_0)$ is plotted in the narrow range of applicability of BET theory ($0.05 \leq p/p_0 \leq 0.3$), the slope and the intercept allow an estimation of α_m and C .

In this paper, the p_0 values were calculated according to the Antoine equation using the literature data for n -C₆H₁₄,¹⁰ CHCl₃,¹¹ benzene¹¹ and THF¹².

The area occupied by the adsorbate in the monolayer, σ , can be calculated by assuming that the adsorbed molecules have a spherical shape in hexagonal close packing, arranged on the solid surface in the same way as on a plane surface immersed into bulk liquid of the adsorbate (S-13):¹³

$$\sigma = 1.091 \left(\frac{M}{N\rho} \right)^{2/3} \quad (\text{S-13})$$

where M is the molecular weight, ρ is the density of the probe, N is Avogadro's number and the constant 1.091 is a packing factor.

From σ and α_m data, the surface area of the adsorbent can be calculated using the following relation:

$$S_a = \alpha_m \sigma N \quad (\text{S-14})$$

The surface energetic heterogeneity of a solid may be described by the energy distribution function, χ , relating the number of adsorption sites having a given adsorption energy to the adsorption energy of the molecule. The experimental isotherm $\alpha(p, T)$ as the sum of the partial isotherms corresponding to the homogeneous adsorption segments, is given by the equation:

$$\alpha(p, T) = \alpha_m \int_0^\infty \chi(\varepsilon_E) \theta(\varepsilon_E, p, T) d\varepsilon_E \quad (\text{S-15})$$

where $\theta(\varepsilon_E, p, T)$ is the local isotherm of surface sites with the same ε_E .

To calculate χ , the terms derived by Rudzinski¹⁴ can be used:

$$\chi = -\frac{\partial \alpha}{\partial \varepsilon_E} + \frac{3.14^2}{6} R^2 T^2 \frac{\partial^3 \alpha}{\partial \varepsilon_E^3} \quad (\text{S-16})$$

where the ε_E function is estimated as:

$$\varepsilon_E = -RT \ln \frac{p}{K} - zu \frac{\alpha}{\alpha_m} \quad (\text{S-17})$$

using: $zu = H_L/4$,¹⁵ and $K = p_0 \exp(H_L/RT)$ ¹⁶, where z is the number of nearest neighbour adsorption sites, u is the interaction energy between molecules adsorbed on two neighbouring sites and H_L is the heat of evaporation of the probe.

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