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Studying of porous polymer surface properties changes by energetic heterogeneity function

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Abstract

In present work we try to detect changes on styrene-divinylbenzene microporous polymer surface by adsorption energy distribution function (heterogeneity function, χ). Polymer surface was modified by 0.1 – 10⁴ ppm of polyethylene glycol, polyethylene glycol adipate and tripropionitrilamine. Heterogeneity function was calculated from the inverse gas chromatography data. It is determined that function χ is capable to detect surface properties variations only at 10³ ppm and above modifier impregnation. If one use the first derivative of χ , it allows detecting surface properties changes after 0.1-1 ppm modifier impregnation.

Keywords: porous polymer; heterogeneity function; adsorption

В настоящей работе предпринята попытка обнаружить изменения свойств поверхности микропористого стирол-дивинилбензолного полимера с помощью функции распределения энергии адсорбции (функция неоднородности, χ). Поверхность полимера модифицировалась полиэтиленгликолем, полиэтиленгликолядипинатом и трипропилнитриламином с концентрациями 0.1-10⁴ ppm. Функция неоднородности рассчитывалась из данных обращенной газовой хроматографии. Установлено, что функция χ может быть применена для оценки изменения свойств поверхности только при количестве наносимого модификатора 10³ ppm и более. Использование первой производной функции χ позволяет детектировать изменение свойств поверхности пористого полимера при нанесении до 0.1-1 ppm модификаторов.

Ключевые слова: пористый полимер, функция неоднородности, адсорбция

Introduction

Surface heterogeneity is one of the fundamental properties of adsorbents. Nowadays many theoretical conceptions of adsorption and isotherms equations are based on adsorption energy distribution function χ [1-2].

At present there is exists a great deal of papers devoted to adsorption energy distribution function χ [3-4], including reviews [5-6]. Inverse gas chromatography is considered as major method for determining surface energy heterogeneity. It allows to rapidly and reliably investigating thermodynamic surface properties [7]. For heterogeneous materials an inverse gas chromatography at finite concentration is useful. It allows to estimate adsorbent properties at different degrees of surface coverage [1,8]. But unfortunately, despite all theoretical successes, heterogeneity function hasn't vast applications yet.

In this paper we suggest using heterogeneity function to detect any changes that take place on porous polymer surface after adsorption of polyethylene glycol (PEG), polyethylene glycol adipate (PEGA) and tripropionitrilamine (TPNA) molecules.

Experimental

Styrene-divinylbenzene polymer Dowex L-285 (Dow Chemicals) with a specific surface $800 \text{ m}^2/\text{g}$ and average pore size about 25 \AA was used. The modified samples were prepared by controlled impregnation of polymer with PEG, PEGA and TPNA amounting from 0.1 to 10^4 ppm.

Gas chromatograph Agat (Russia) with a thermal conductivity detector was used. Nitrogen of 60 ml/min flow rate was used a gas carrier. All columns were conditioned in nitrogen flow at $200 \text{ }^\circ\text{C}$ overnight. All analyses were carried at $200 \text{ }^\circ\text{C}$. As test-adsorbates n-propanol, n-butanol, and hexane were chosen. Samples amounting varied from 0.02 to $70 \text{ }\mu\text{l}$.

Calculations

From the experimental data specific retention volumes (V_g) and adsorbate concentrations in a gaseous phase (c) were calculated. Free energy of adsorption ε , kJ/mol was calculated from:

$$\varepsilon = -RT \ln V_g \quad (1)$$

The adsorption energy distribution function χ_1 was obtained by asymptotically correct condensation approximation method as the most widely used approach to surface heterogeneity estimating [5]:

$$\chi_1 = \frac{j \cdot p^2}{N_m (kT)^2} \cdot \frac{\delta \cdot V_g}{\delta p} \quad (2)$$

where j is a James–Martin coefficient, p is adsorbate pressure in a gaseous phase, N_m is the amount adsorbed in a monolayer, k is a Boltzman constant, T is measurement temperature. Taking into account that for polymeric adsorbents:

$$V_g = A \ln c + B \quad (3)$$

where A and B are constants, we use the following modification of the equation (2) [9]:

$$\chi_1 = \frac{A \cdot c}{a_m kT} \quad (4)$$

where a_m is a monolayer capacity, $\mu\text{mol/g}$.

Results and discussion

In literature χ vs. ε dependence is used to analyze heterogeneity. Such dependences for modified by PEG and non-treated polymers are shown in Fig. 1. As one can seen from the figures, there is no difference between a polymer with 1% PEG and a non-treated one. For 0.1% there is also observed no difference with a non-treated polymer, but for $10^{-2}\%$ and $5 \cdot 10^{-3}\%$ χ anomalously decreasing. Then, χ is close to a non-treated polymer for PEG $10^{-3}\%$ and less. Such phenomena can't be explained as in the case of 1% PEG modified sample the differences with a non-treated polymer should be maximum. It is clear, that χ_1 vs. ε dependence does not respond to surface variations. For samples modified by PEGA

and TPNA the results are similar. Thus, such dependences cannot be used to detect surface changes.

To obtain more reliable data, we suggest using χ_1 vs. θ dependences, where θ is surface coverage. Fig. 2 presents such dependences for non-treated and PEG modified samples. As seen from Fig. 2, there is an appreciable difference between 1% and 0.1% PEG samples on the one hand and a non-treated sample on the other. The difference between a 1% PEG sample and a non-treated one is greater than between 0.1% PEG and non-treated samples. So, one can consider that χ_1 vs. θ dependence can reliably respond to some heterogeneity variations.

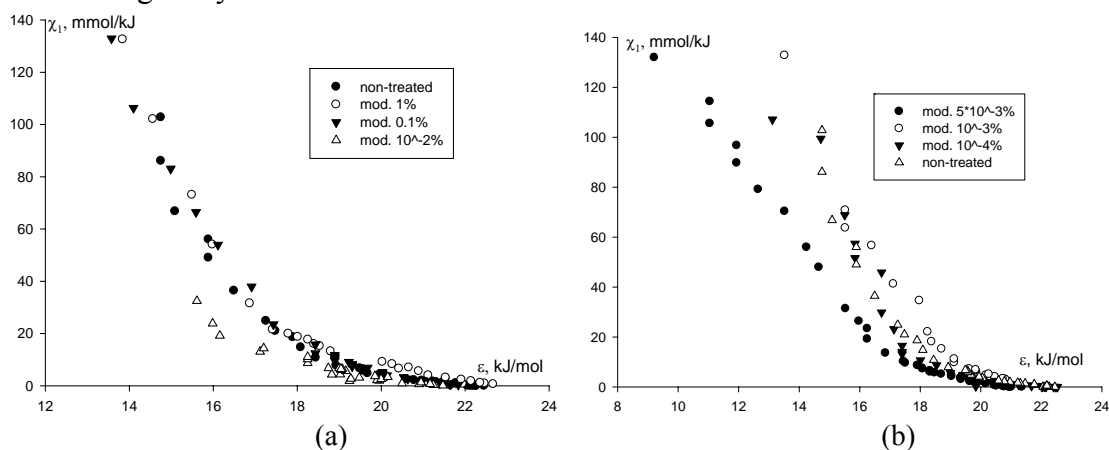


Fig. 1. Heterogeneity function χ_1 distribution on adsorption energy for non-treated and PEG modified samples

But for samples with PEG 10⁻²% and less there is no difference with a non-treated polymer. Consequently, χ_1 function is sensible to surface variations only after 0.1% and more PEG impregnation. The similar sensitivity to surface changes was observed in case of analyzing V_g vs. c dependences.

As one can see from Fig. 2, in any cases χ_1 value will rise with θ increasing. It can be suggested that physical meaning of χ_1 is the total adsorption centers amount at the given surface coverage. In order to obtain adsorption centers variations at different θ , we suggest using the first derivative of χ_1 as a heterogeneity function:

$$\chi_2 = \frac{d\chi_1}{d\theta} \quad (5)$$

χ_2 vs. θ dependences are shown in Fig. 3. Experimental curves for all samples were divided into two parts: from zero to 0.1 coverage and from 0.1 to 1.

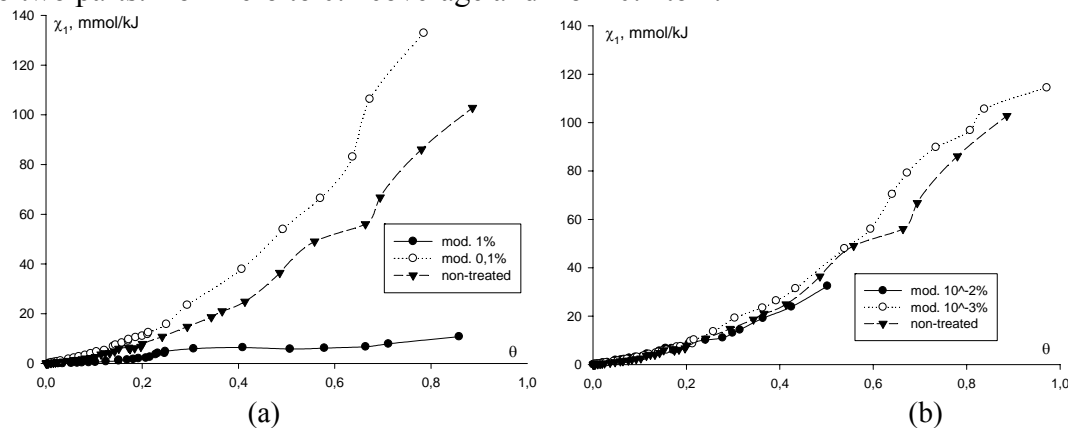


Fig. 2. Heterogeneity function distribution χ_1 on the surface coverage for non-treated and PEG modified samples

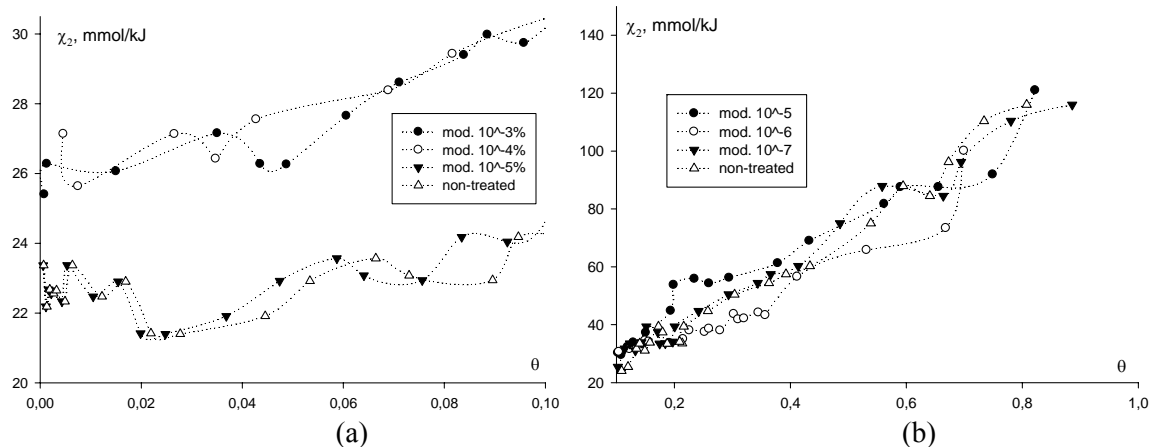


Fig. 3. Heterogeneity function distribution χ_2 on the surface coverage for non-treated and PEG modified samples: (a) from 0 to 0.1; (b) from 0.1 to 1

So, a heterogeneity function up to 0.1 coverage's to be constant. It is noticeable that up to 0.1 coverage χ_2 on modified sorbents from $10^{-4}\%$ of impregnated PEG will be more than on a non-treated sample. So, χ_2 function allows to trace surface changes from ppm level of the adsorbed substances. Its sensibility is in 10^3 higher than for χ_1 function.

It should be mentioned, that at low coverages χ_2 of modified samples is greater that on a non-treated polymer due to stronger intermolecular interactions between n-butanol and PEG.

To prove reliability of the results obtained we have modified the initial polymer again by $10^{-5}\%$ and $10^{-4}\%$ PEG and undergone it with a non-treated sample by an described in 2. chromatographic investigation using hexane as a probe.

Fig. 4 represents χ_2 vs. θ dependence. As one can see, in the case of hexane as a probe a valuable χ_2 difference between modified and non-treated samples is observed even after $10^{-5}\%$ PEG impregnation. χ_2 on modified sorbents have less values than on non-treated ones due to hexane nonpolarity.

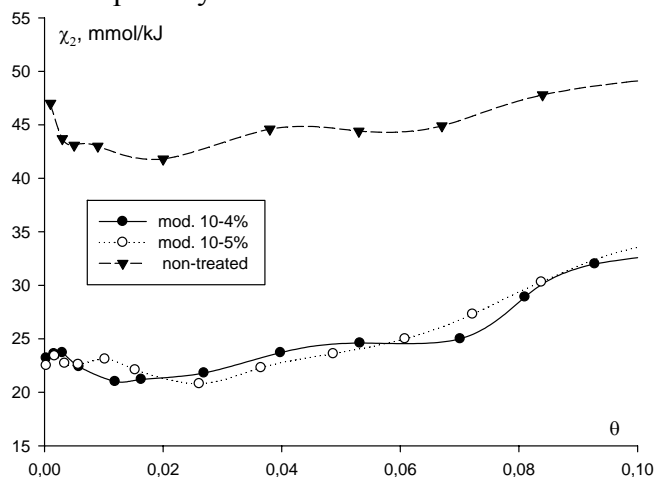


Fig. 4. Heterogeneity function distribution χ_2 on the surface coverage for non-treated and PEG modified samples

However, χ_2 of up to 0.1 coverage will be unsatisfactory as a quantitative parameter. So, χ_2 for 1% and 0.1% impregnated PEG samples will be virtually equal, as well as for $10^{-3}\%$ and $10^{-4}\%$ PEG samples, although χ_2 will generally rise with PEG increasing.

Conclusions

For porous polymer sorbent investigated χ_1 vs. ε dependences didn't show any reliable results. Using of χ_1 vs. θ dependences revealed the similar sensitivity of V_g vs. c dependence – its sense only if 0.1% and more PEG had been impregnated. The χ_2 parameter of up to 0.1 coverage allows to see surface changes for 10⁻⁴%-10⁻⁵% PEG impregnated. Such an approach could be used to detect any impurities on various surfaces. Adsorbed molecules of different polarity are possible to be identified on sorbent surfaces as well.

The analysis of χ_2 vs. θ dependence slopes shows that as quantitative characteristics they are more reliable than χ_2 vs. ε slopes. However, surface heterogeneity and χ_{tg}^θ correlation remains quite ambiguous and unexplored, and will be investigated in further researches.

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