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Flow microcalorimetry and competitive liquid sorption
I. Sorption behaviour of some polymer networks[1]

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Abstract

Three different polymer networks (polymer resins) are investigated by selective liquid sorption from 1-propanol/water mixtures. Network 1 is a non-polar, non swelling, macroporous resin. Networks 2 and 3 are macroreticular polar (hydrophilic) ion exchangers, which swell in the binary liquid mixture. The enthalpy of displacement isotherms accompanying the sorption processes are determined by flow microcalorimetry. The enthalpy isotherms reveal the differences in polarity of the polymer network.

Keywords :Polymers; Adsorption; Flow microcalorimetry; Networks; Macroreticular resins

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1. Introduction

Sorption by natural or synthetic polymer networks is often accompanied by specific interactions of the adsorptive with internal surfaces, which makes the sorption very selective [1,2]. If the volume of the polymer network increases considerably, one might consider this process as an example of three-dimensional swelling. The sorbed liquids then no longer occupy mono- or bimolecular surface layers but fill a more or less extended volume. The volume occupied by the sorbed liquid is called the sorption volume V^s. In the present study we investigate the sorption of water from 1-propanol/water mixtures on polymer networks of different polarity and swelling ability. The aim of our investigation was to examine the influence of the polymer particle structure and the polar-

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ity of the network on the adsorption excess isotherms and to illustrate the relation between the enthalpy of displacement (derived from microcalorimetric measurements) and the material content in the adsorption volume.

2. Theoretical

2.1. Surface excess isotherms

To obtain a suitable measure of adsorption from solution it is necessary to formulate definitions of surface excess quantities which contain only experimentally accessible quantities. Let us consider particles immersed in a binary liquid mixture. The composition of the bulk liquid usually changes from the initial mole fraction, x_2^0, to the equilibrium concentration, x_2. The difference $\Delta x_2 = x_2^0 - x_2$ is measured. The experimental data for adsorption from solution are usually expressed as composite isotherms, in which the excess amount of one component adsorbed is plotted as a function of its equilibrium concentration [3–6]. The excess amount adsorbed, $n_2^{\sigma(n)}$, is calculated from Δx_2 and is related to the composition of the adsorbed liquid (index s) by

$$n_2^{\sigma(n)} = \frac{n^0}{m}(x_2^0 - x_2) = n_2^s - n^s x_2 = n^s(x_2^s - x_2) = f(x_2) \qquad (1)$$

The total amount of binary liquid mixture per unit mass of adsorbent is n^0; $n^s = n_1^s + n_2^s$ is the material content of the sorbed phase, and $x_2^s = n_2^s / n^s$ is the corresponding mole fraction of component 2. According to Eq. (1) the excess isotherm $n_2^{\sigma(n)} = f(x_2)$ contains two individual isotherms, $n_1^s = f(x_2)$ and $n_2^s = f(x_2)$, which can be calculated by the expressions [7,8]

$$n_1^s = \frac{r n_{2,0}^s x_1 - r n_2^{\sigma(n)}}{x_1 + r x_2} \qquad (2)$$

$$n_2^s = \frac{n_2^{\sigma(n)} + r n_{2,0}^s x_2}{x_1 + r x_2} \qquad (3)$$

Here $n_{2,0}^s$ is the adsorption capacity of the pure component 2 and $r = V_{m,2}/V_{m,1} = n_{1,0}^s / n_{2,0}^s$ is the ratio of the partial molar volume of component 2 and component 1. The adsorption excess isotherms $n_2^{\sigma(n)} = f(x_2)$ are classified into five types (Schay-Nagy classification) [8]. Some isotherms have the common characteristic that a fairly long section can be approximated by a linear relationship. Thus the adsorption capacity of the pure component 2, which is required in Eqs. (2) and (3) can be obtained by the Schay-Nagy extrapolation method [1,5,7–9] The extrapolated values, $|n_1^s|$ and $|n_2^s|$, give the composition of the adsorbed phase within the range of x_2, for which the isotherm is linear. The volume occupied by the sorbed liquid is

$$V^s = |n_1^s| V_{m,1} + |n_2^s| V_{m,2} \tag{4}$$

The adsorption capacity of the pure component 2 is then

$$n_{2,0}^s = \frac{V^s}{V_{m,2}} \tag{5}$$

The volume fraction of component 2 in the polymer network (Φ_2^s) is given by

$$\Phi_2^s = \frac{n_2^s}{n_{2,0}^s} = \frac{V_2^s}{V^s} \tag{6}$$

which is suitable for determining $\Phi_2^s = f(x_2)$, if $n_{2,0}^s$ has been derived from the adsorption excess isotherms (Eq. (5)).

2.2. Thermodynamic considerations

The integral enthalpy of displacement of component 1 by component 2 can be obtained by Eq. (7), where the overall heat effect, $\Delta_{12}H_b$, is corrected for the mixing heat in the bulk phase, $\Delta_{mix}H$ [10–13]. The enthalpy of displacement can also be written in terms of the molar enthalpies of the components in the sorption volume, h_1^s and h_2^s. In this equation $\Delta_{12}H^{se}$ denotes the excess enthalpy of the sorbed phase.

$$\Delta_{12}H = \Delta_{12}H_b - \Delta_{mix}H = (n_1^s h_1^s + n_2^s h_2^s) + \Delta_{12}H^{se} \tag{7}$$

The function $\Delta_{12}H = f(x_2)$ or $f(\Phi_2^s)$ is determined by the composition of the sorbed phase (Φ_2^s), the molar adsorption enthalpies of the components (h_i^s) and the excess enthalpy of the sorbed phase, $\Delta_{12}H^{se}$ [14]:

$$\Delta_{12}H = \Phi_2^s n_{2,0}^s (h_2^s - r h_1^s) + \Delta_{12}H^{se}(\Phi_2^s) \tag{8}$$

3. Experimental

3.1. Materials

The adsorption of propanol (index 1) and water (index 2) was studied with different networks.

Network 1: Non-ionic adsorbent Amberlite XAD-2 (Serva, Germany), porous styrene/divinylbenzene copolymer; particle size 0.05–0.1 mm.

Networks 2 and 3: Chelite-S and Chelite-C (Serva, Germany), copolymers of styrene and divinylbenzene, highly crosslinked macroporous material with hydrophilic mercapto groups (Chelite-S) and aminodiacetic acid groups (Chelite-C); particle size 0.05–0.1 mm.

The polymer samples were washed with alcohol and water, dried with acetone and stored in a vacuum desiccator.

3.2. Methods

Adsorption measurements were performed in well sealed test tubes at room temperature. Amounts of 5–10 cm^3 of the binary liquid mixture were added to 0.2–0.5 g of vacuum dried (353 K) polymer samples. The change of concentration of water in the bulk liquid (Δx_2) was measured by a Zeiss liquid interferometer after equilibration periods of 48 h.

The enthalpy of displacement was recorded by a flow microcalorimeter (LKB 2107) at 298 ± 0.01 K. Prior to the calorimetric experiment, prewetting and swelling of the polymers in pure 1-propanol was necessary. This immersion process was established in a special vacuum device described in detail in earlier publications [2,14,15]. The flow cell of the microcalorimeter was filled with the vacuum dried polymer sample (50–200 mg), carefully sealed and mounted in the glass apparatus. The equipment was then evacuated and pure 1-propanol was introduced from a reservoir. The flow cell was then quickly transferred to the calorimeter, which had been previously filled with the given liquid.

The flow rate of the liquid mixtures was almost constant during measurements; depending on the degree of swelling of some samples, its value varied from 15 to 18 $cm^3\ h^{-1}$. The integral displacement enthalpy isotherms, $\Delta_{12}H = f(x_2)$, were determined by the cumulative method. Beginning with the pure component 1, with stepwise change of the mixture composition, the heat effects were summed. In a separate experiment, the enthalpy of mixing ($\Delta_{mix}H$) was measured with the same flow cell filled with teflon powder as an inert material; by this means the necessary correction was made according to Eq. (7). The standard deviation of the calorimetric measurement by the above method varied between ±9% and ±12%, depending on the composition of the mixture and the polymer network.

4 Results and discussion

4.1. Surface excess isotherms

First the selective sorption of 1-propanol/water mixtures on the three networks was studied. The surface character of the adsorbents is hydrophilic (Chelite-S, Chelite-C) or hydrophobic (Amberlite XAD-2). The excess isotherm $n_2^{\sigma(n)} = f(x_2)$ for the hydrophilic resin (Chelite C) and 1-propanol(1)/water(2) mixtures is U-shaped, and water is preferentially adsorbed over the entire range of concentrations (Fig. 1). For Chelite-S, $n_2^{\sigma(n)}$ is slightly negative at $x_2 \geq 0.9$ and the excess isotherm is S-shaped with an azeotropic point at $x_2 \approx 0.89$. The negative values of $n_2^{\sigma(n)}$ simply means that in this concentration range there is a preferential adsorption of component 1 on the polymer network. The difference between the initial and equilibrium concentrations of component 2 is, therefore, a negative value.

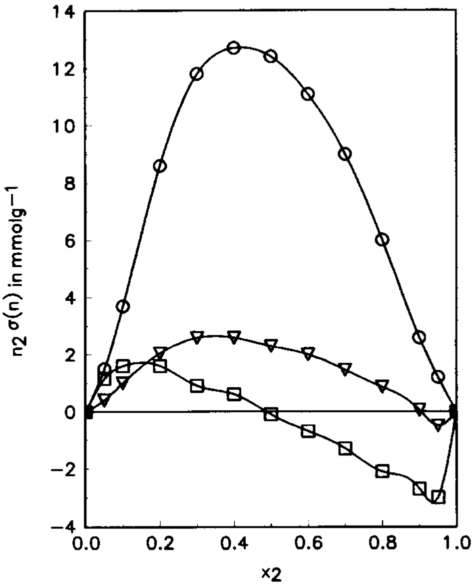

Fig. 1. Surface excess isotherms $n_2^{\sigma(n)} = f(x_2)$ for Chelite-C (○), Chelite-S (▽) and Amberlite XAD-2 (□); x_2 = equilibrium mole fraction of water.

The adsorption excess isotherm on non-polar polystyrene adsorbent Amberlite XAD-2 is S-shaped with an extended linear portion (Fig. 1). It should be clearly understood that the isotherms in Fig. 1 are composite isotherms and both components 1 and 2 of the binary liquid mixture contribute to them. In physical terms this means that both components 1 and 2 are sorbed at the same time by the non-polar network and that the composition of the sorbed phase is almost constant in the linear part of the excess isotherm.

The excess isotherms were analysed according to the Schay-Nagy extrapolation method (Chelite-S was analysed by a modified procedure described in Refs. [1,15]). The plot of Φ_2^s, the volume fraction of water in the network, versus x_2, the mole fraction of water in the immersion liquid (Fig. 2), revealed that water is bound preferentially from n-propanol/water mixtures at low water mole fractions for all networks. At higher water mole fractions, n-propanol is partitioned in preference towards the non-polar polystyrene particles. The curves in Fig. 2 indicate that the uptake of water in the plateau region differs significantly with the nature of the polymer networks. The amounts of water adsorbed are a function of surface structure and polarity of the polymers.

We have attempted to fit our results to a variety of equations which have been derived for the presentation of data on small molecule binding. However none of these approaches explain in a satisfactory way the variations in the water uptake.

4.2. Displacement enthalpy isotherms

The displacement of 1-propanol by water is illustrated by the enthalpy changes $-\Delta_{12}H = f(x_2)$ of the three polymer networks (Fig. 3). For the hydrophilic polymer net-

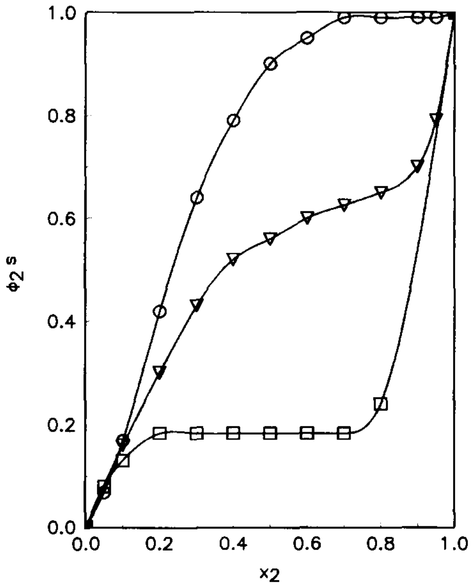

Fig. 2. $\Phi_2^s = f(x_2)$ diagrams, calculated in analogy to Eq. (6) for Chelite-C (O); Chelite-S (▽) and Amberlite XAD-2 (□); x_2 = equilibrium mole fraction of water.

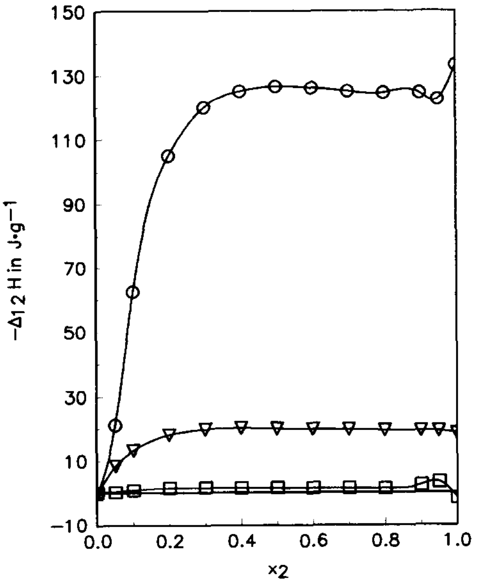

Fig. 3. Integral enthalpy of displacement, $\Delta_{12}H = f(x_2)$ for Chelite-C (O), Chelite-S (▽) and Amberlite XAD-2 (□); x_2 = equilibrium mole fraction of water.

works (Chelite-C, Chelite-S) the enthalpy of displacement increases monotonously up to $x_2 \approx 0.9$. The enthalpy of the hydrophilic polystyrene network (Chelite-C) increases monotonously as expected for U-shaped excess isotherms [13]. As the excess isotherm of sample S is S-shaped, the curve decreases slightly at mole fractions of water $x_2 \geq 0.8$. For the non-polar network of sample XAD-2, $-\Delta_{12}H$ has a noticeable upward section at higher mole fractions of water but the overall displacement process is endothermic.

The general shape of $-\Delta_{12}H$ suggests that the preferential sorption of water on the polar networks is accompanied by a significant enthalpy decrease. Unfortunately the cumulative displacement enthalpy of 1-propanol by water can be measured with reliable accuracy only up to $x_2 \approx 0.9$. At higher water concentration the mixing heat effect, $\Delta_{mix}H$, is too high in comparison with the heat of displacement for accurate flow calorimetric measurements, specially for the very low heat effects on the non-polar sample Amberlite XAD-2.

5. Conclusions

Hydrophilic macroporous resins Chelite-C represents a rather classical type of polymer network but with a certain degree of permanent porosity. In the water rich region these particles are highly swollen xerogels and consists of two components: water acts as the dispersion medium and the charged polymer network is the dispersed component. The macromolecular network of the resin is contracted during drying and loses a part of its porosity. When the dried resins are contacted with 1-propanol/water mixtures, swelling and selective adsorption of water occurs. In the region of low water mole fraction the expansion of the network increases with increasing x_2, and water is strongly preferred over the entire concentration range [16].

The less hydrophilic network (Chelite S) and much more the hydrophobic network (Amberlite XAD-2) represents true macroreticular resins (aerogels). After drying these particles retain their porosity. In 1-propanol/water mixtures the pore volume is filled with bulk liquid. The hydrophobic macroreticular resin adsorbs water preferentially only up to the azeotropic point. The middle polar macroporous sample (Chelite-S) exhibits an intermediate state. Water is preferentially adsorbed over a wide range of concentrations but there is also a very modest enrichment of 1-propanol for $x_2 \geq x_2^a$.

The network structure of the particles is well reflected in the enthalpy isotherms. The large negative (exothermic) values of the enthalpy function observed for the hydrophilic network (Chelite-C) is a consequence of the extensive water sorption and swelling of the polymer particles. For the middle polar macroporous sample (Chelite-S) the preferential sorption of water is accompanied by an intermediate heat effect. The sorption volume is far from ideal at larger water mole fraction ($\Delta_{12}H \neq 0$ in Eq. (8)). This non-ideality of the sorption volume is observed in the sorption of water clusters, which causes higher heat effects [2,16,17]. On the other hand clustering and association behaviour is well established for alcohol/water mixtures [17] and it is not astonishing that the enthalpy of displacement even for the hydrophobic macroreticular resin is shifted to a slight but measurable exothermic value.

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