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Flow microcalorimetry and competitive liquid sorption II. Liquid sorption and wetting on macroreticular hydrophilic/hydrophobic networks[1]

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Abstract

Three different types of polymer networks (polymer resins) were investigated by flow microcalorimetry and selective liquid sorption from 1-propanol(1)-water(2) mixtures. Type 1 network structure is formed by non-polar, non-swelling, macroporous resins (Amberlite XAD-2, Amberlite XAD-4). The composite isotherms for alcohol sorption were S-shaped. 1-Propanol is preferentially sorbed up to $x_1 \approx 0.5$. Macroreticular non-ionic resins, Amberlite XAD-7 and XAD-8, represent the second type of polymer structure. These particles have a considerable extent of swelling in the binary liquid mixture and 1-propanol was preferentially sorbed by the polymer. The composite isotherms were U-shaped and exhibit maxima and minima. The third type of network structure is attached to macroreticular polar, hydrophilic ion-exchange resins (Chelite-S, Amberlyste A-21). Depending on the composition range of the binary liquid mixture, the resins may swell to a different extent and water is preferentially embeded in the porous polymer network. The swelling of the polymer networks was monitored by the gravimetric technique in seperate experiments. The sorption capacity determined from the liquid uptake of the resins was related to the sorption capacity derived from the reduced surface excess. The enthalpy effect accompanying the sorption process was determined by flow and immersion microcalorimetry. The enthalpy of displacement isotherms reveals differences in polarity and swelling ability of the polymer network fairly well. Structural changes in the adsorption layers and formation of alcohol–water clusters on the surfaces play an important role. © 1998 Elsevier Science B.V.

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

1. Introduction

Surface excess adsorption isotherms from binary liquid mixtures respond with sensitivity to the hydrophilic/hydrophobic character of the adsorbent [1,2]. The composition of the adsorption phase changes with the character of the surface. Preceding studies with inorganic and organic adsorbents revealed that the mutual influence of the liquid molecules and the adsorbent structure rules the extent and composition of the surface phase. In the case of adsorption from different alcohol–water mixtures on carbon black and organophilic clay minerals very unusual adsorption isotherms with maxima and minima has been reported [3,4]. For the latter type of material, the adsorption volume increases in two steps in parallel with the

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interlamellar expansion of the mineral framework. Over a certain concentration range of the binary liquid mixture, the adsorption behaviour of the mineral adsorbents could be nicely modelled from combining the adsorption isotherms of non-polar carbon black and polar silica [3,4]. But an adsorbent susceptible to swelling or disaggregation will necessarily not maintain the definite structure, which had been characteristic of the dry state. When such an adsorbent is immersed in a liquid or a liquid mixture, internal surface areas may become accessible to the liquids molecules (i.e. swelling and selective sorption). In exteme cases, the material may even disaggregate (i.e. infinite swelling or dissolution of the sorbent structure) and selective liquid sorption is accompanied by the formation of a dispersion. Obviously, the sorbed liquid no longer occupy mono- or bimolecular surface layers but fill a more or less extended volume which had been termed as the sorption volume V^s [5–9]. At first glance, the sorption volume is almost identical with the total amount of liquid immobilized by the sorbent and can thus be determined from the degree of swelling of the network.

A well-discussed class of sorbents with limited swelling ability are clay minerals and their organic derivatives [3,4,9,10]. The sorption between the silicate layers can be followed by X-ray diffraction measurements to a high degree of accuracy. But the interlamellar free volume which can be derived from the degree of swelling is often distinctly different from the sorption volume V^s determined on the basis of the adsorption pore filling model [1,5–7]. If the liquid sorption by a polymer network is considerably large, only a part of the sorbed liquid is exposed to forces originated by the polymer material. Most of the liquid taken up is thus not bound by adsorption forces but can be described as free liquid mixture taken up upon swelling and pore filling. To account for these differences, a certain amount of the so-called bulk liquid mixture has been postulated [8,9].

In the present study, we investigate the sorption of 1-propanol from water on porous polymer networks. The different networks have a considerable pore volume in the dry state. By a different polarity of the polymer frame, an additional swelling ability has been introduced to the sorbents. We have monitored the selective liquid sorption for the different polymer networks by the reduced surface excess and analysed the excess iotherm to determine the sorption volume V^s. To obtain an independent estimate of the material content of the adsorption volume, we measured the total liquid uptake by the porous sorbents. For an analysis of the energy balance of the sorption process, we have calculated the enthalpy of displacement from flow microcalorimetry. The aim of our investigations is to examine how sorption from binary liquid mixtures can be modified by the polymer structure and the polarity of the network, and to illustrate the relation between the mechanism of the exchange process and the enthalpy of displacement.

2. Theoretical

2.1. Surface excess isotherms

Adsorption from binary liquid mixtures is described by specific excess quantities which can be directly determined by experiment [11–13]. The mass m of sorbent particles is immersed in n^0 moles of the binary liquid mixture. The composition of the bulk liquid usually changes from the initial mole fraction, x_1^0, to the equilibrium mole fraction, x_1. The difference $\Delta x_1 = x_1^0 - x_1$ is measured by a suitable method. The experimental data are expressed as composite isotherms, in which the excess adsorbed amount of one component is plotted as a function of its equilibrium concentration [14]. The excess amount adsorbed, $n_1^{\sigma(n)}$, is calculated from Δx_1 and is related to the composition of the adsorbed liquid (index s) by:

$$\begin{aligned} n_1^{\sigma(n)} &= \frac{n^0}{m}(x_1^0 - x_1) = n_1^s - n^s x_1 \\ &= n^s(x_1^s - x_1) = f(x_1) \end{aligned} \tag{1}$$

Here n^0 is the initial amount of binary liquid mixture per unit mass of adsorbent, $n^s = n_1^s + n_2^s$ the material content of the sorbed phase, and $x_1^s = n_1^s/n^s$ the corresponding mole fraction of component 1. According to Eq. (1), the excess isotherm $n_1^{\sigma(n)} = f(x_1)$ contains two individual isotherms, $n_1^s = f(x_1)$ and $n_2^s = f(x_1)$, which can be calculated by the expressions in Refs. [5,14,15]

$$n_1^s = \frac{V_{m,2} n_1^{\sigma(n)} + V_{1,0}^s x_1}{V_{m,1}(x_1 + r x_2)} \tag{2}$$

$$n_2^{\mathrm{s}} = \frac{rV_{1,0}^{\mathrm{s}}x_2 - V_{\mathrm{m},1}n_1^{\sigma(n)}}{V_{\mathrm{m},1}(x_1 + rx_2)} \tag{3}$$

Here, $V_{1,0}^{\mathrm{s}}$ is the sorption volume of the pure component 1 and $r=V_{\mathrm{m},2}/V_{\mathrm{m},1}$ is the ratio of the partial molar volumes of component 2 and component 1. The sorption volume of the pure component 1, which is required in Eqs. (2) and (3) has to be determined by an additional procedure. Two procedures will be used here:

1. The Schay–Nagy extrapolation method [1,13,15]: Some adsorption excess isotherms $n_1^{\sigma(n)} = f(x_1)$ have a fairly long section that can be approximated by a linear relationship. The volume occupied by the sorbed liquid is deduced from the linear section of the isotherm. The extrapolated values give the composition of the adsorbed phase within the range of x_1, for which the isotherm is linear. The adsorption capacity of the pure component 1 is then given by:

$$|V_{1,0}^{\mathrm{s}}| = |n_1^{\mathrm{s}}|V_{\mathrm{m},1} + |n_2^{\mathrm{s}}|V_{\mathrm{m},2} \tag{4}$$

2. Measurement of swelling [16,24]: The gravitational determination the sorbed liquid is the straightforward way to estimate the adsorption capacity of a porous adsorbent. Assuming a quasi-ideal adsorption layer, the adsorption volume can be calculated from the total liquid uptake by the porous adsorbents.

$$V_{i,0}^{\mathrm{s}} = m_T^{\mathrm{s}}/\rho_i \tag{5}$$

Here m_T^{s} is the total amount of binary liquid mixture immobilized per weight of porous polymer particle and ρ_i the bulk density of component i. $V_{i,0}^{\mathrm{s}}$ is the apparent sorption volume of component i in cm^3 per gram of polymer particle. $V_{i,0}^{\mathrm{s}}$ truly reveals the sorption and swelling ability of the network structure.

2.2. Thermodynamical considerations

The integral enthalpy of displacement of component 2 by component 1 can be obtained by Eq. (6), where the overall heat effect, $\Delta_{21}H_{\mathrm{b}}$, is corrected for the mixing heat in the bulk phase, $\Delta_{\mathrm{mix}}H$ [17–19]. 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}:

$$\Delta_{21}H = \Delta_{21}H_{\mathrm{b}} - \Delta_{\mathrm{mix}}H = n_1^{\mathrm{s}}\left(h_1^{\mathrm{s}} - \frac{1}{r}h_2^{\mathrm{s}}\right) + \Delta_{21}H^{\mathrm{se}} \tag{6}$$

In this equation, $\Delta_{21}H^{\mathrm{se}}$ denotes the excess enthalpy of the sorbed phase. The function $\Delta_{21}H=f(x_1)$ is determined by the composition of the sorbed phase (n_1^{s}), the molar adsorption enthalpies of the components (h_i^{s}) and the excess enthalpy of the sorbed phase, $\Delta_{21}H^{\mathrm{se}}$ [20].

3. Experimental

3.1. Materials

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

Networks 1 and 2: Non-ionic sorbent Amberlite XAD-2 and Amberlite XAD-4 (Serva, Germany), a porus styrene/divinylbenzene copolymer, particle size 0.05–0.1 mm.

Networks 3 and 4: Non-ionic sorbent Amberlite XAD-7 and Amberlite XAD-8 (Serva, Germany), a porus copolymer with an aliphatic matrix consisting of cross-linked polymethacrylates, particle size 0.05–0.1 mm.

Networks 5 and 6: Chelite-S and Amberlyste A-21 (Serva, Germany), highly cross-linked macroporous material (aromatic matrix, styrene/divinylbenzene copolymer) with hydrophilic mercapto groups (Chelite-S) and dimethyl amino groups (Amberlyste A-21); 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.

1-Propanol (Renal, Hungary) was of p.a. purity. The water was freshly bidistilled.

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_1) was measured by a Zeiss liquid interferometer after equilibration periods of 48 h.

Swelling was determined as the weight of water (or 1-propanol–water mixture) sorbed per gram of dry resin. The liquid that clings to the surface of the resin was removed by centrifugation in a tube provided with a filter disk (10 min at 2000 rpm).

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 is necessary. This immersion process is astablished in a special vacuum device described in detail in earlier publications [21]. 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 is then evacuated and pure 1-propanol is introduced from a reservoir. The flow cell is then quickly transferred to the calorimeter. 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 $\mathrm{cm^3\,h^{-1}}$. The integral displacement enthalpy isotherms, $\Delta_{21}H=f(x_1)$, were determined by the cumulative method. Beginning with the pure component 2, with stepwise change of the mixture composition, the heat effects were summed. In a separate experiment, the enthalpy of mixing ($\Delta_{\mathrm{mix}}H$) 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. (6). The standard deviation for most of the calorimetric measurement by the aforementioned method varied between ±9 and ±12%, depending on the composition of the mixture and the polymer network. It should be pointed out that, especially in the water rich concentration region and for the hydrophobic adsorbents, the detector signal became very unstable and the accuracy of the calorimetric measurement is decreased considerably.

4. Results and discussion

4.1. Excess isotherms and swelling

The adsorption excess isotherm on the two non-polar polystyrene adsorbents, Amberlite XAD-2 and XAD-4, are S-shaped with an extended linear portion (Fig. 1(a)). They are of type IV (sigmoid, Schay–Nagy classification) with an azeotropic point at $x_1\approx0.5$–0.6. $n_1^{\sigma(n)}=f(x_1)$ for middle polar Amberlite XAD-8 (Fig. 1(a)) is slightly negative at $x_1\geq0.7$, and the excess isotherm is S-shaped with an azeotropic point at $x_1\approx0.6$–0.7. The negative values of $n_1^{\sigma(n)}$ simply means that, in this concentration range, there is a preferential sorption of water relative to 1-propanol by the polymer network. The sorption of alcohol by the middle polar resin Amberlite XAD-7 is preferential over the entire composition range (Fig. 1(b)). For the hydrophilic modified styrene/divinylbenzene resins (Chelite-S, Amberlyste A-21) and 1-propanol(1)–water(2) mixtures the azeotropic composition occurs at low 1-propanol mole fractions and the excess isotherm is now inverted S-shaped with an azeotropic point at $x_1\approx0.1$. The networks preferentially accumulate water from almost any 1-propanol-water mixture. It should be clearly understood that the isotherms in Fig. 1 are composite isotherms and both components of the binary liquid mixture contribute to them. In physical terms, it means that both components 1 and 2 can be sorbed at the same time by the network. The total liquid uptake by the different resins had been determined by the gravimetric technique. The experimental data are plotted in Fig. 2 as a function of the liquid composition. The hydrophobic polymer networks of Amberlite XAD-2 and XAD-4 (Fig. 2(a)) have the lowest liquid uptake and in the region below $x_1\approx0.2$ the wetting of the porous styrene/divinylbenzene networks is not sufficient to fill the porous network structure completely [16]. Even for the middle polar Amberlite XAD-8, the complete filling of the pore volume could not be achieved, whereas the more hydrophilic polymers Amberlite XAD-7, Chelite-S and Amberlyste A-21 (Fig. 2(b)) took up liquid in excess of the pore volume, determined from gas adsorption and intrusion porosimetry [16,22,24]. In fact, the latter sorbents swell considerably and we could detect much larger thermal effects in the calorimetric experiments (see Section 4.2).

4.2. Displacement enthalpy isotherms

The displacement of water by 1-propanol is illustrated by the enthalpy changes $-\Delta_{21}H=f(x_1)$ in Fig. 3. The shape of $-\Delta_{21}H$ suggests that the dis-

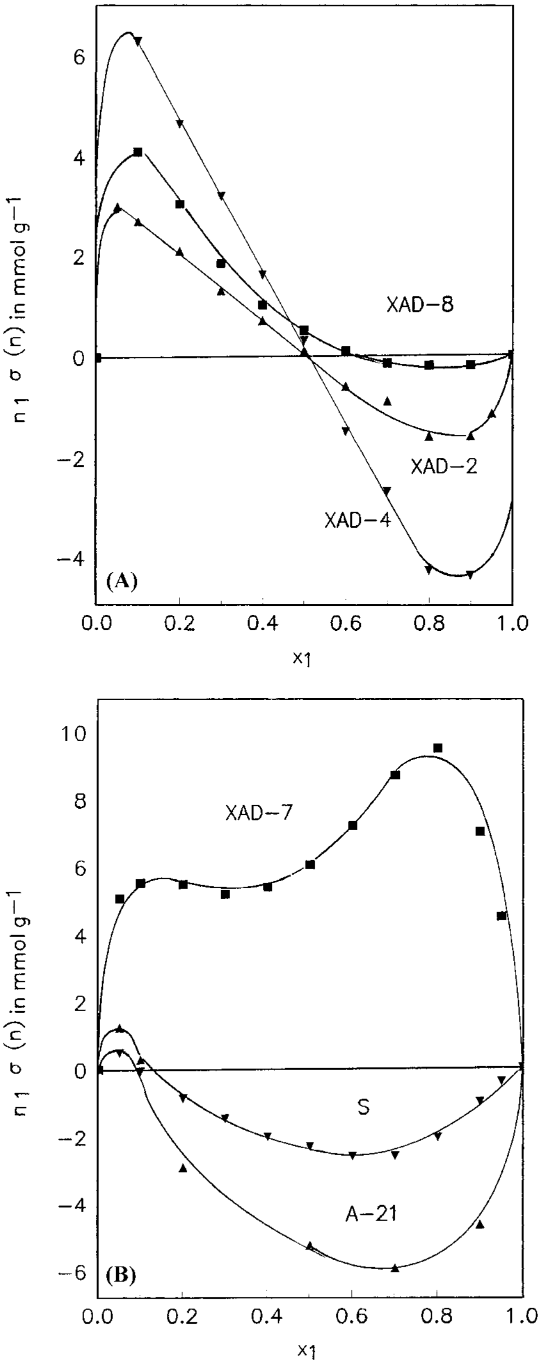

Fig. 1. (a) Surface excess isotherms $n_1^{\sigma(n)}=f(x_1)$ for (□) Amberlite XAD-8, (▽) Amberlite XAD-4 and (△) Amberlite XAD-2. x_1: equilibrium mole fraction of water. (b) Surface excess isotherms $n_1^{\sigma(n)}=f(x_1)$ for (□) Amberlite XAD-7, (▽) Chelite-S and (△) Amberlyste A-21; x_1: equilibrium mole fraction of water.

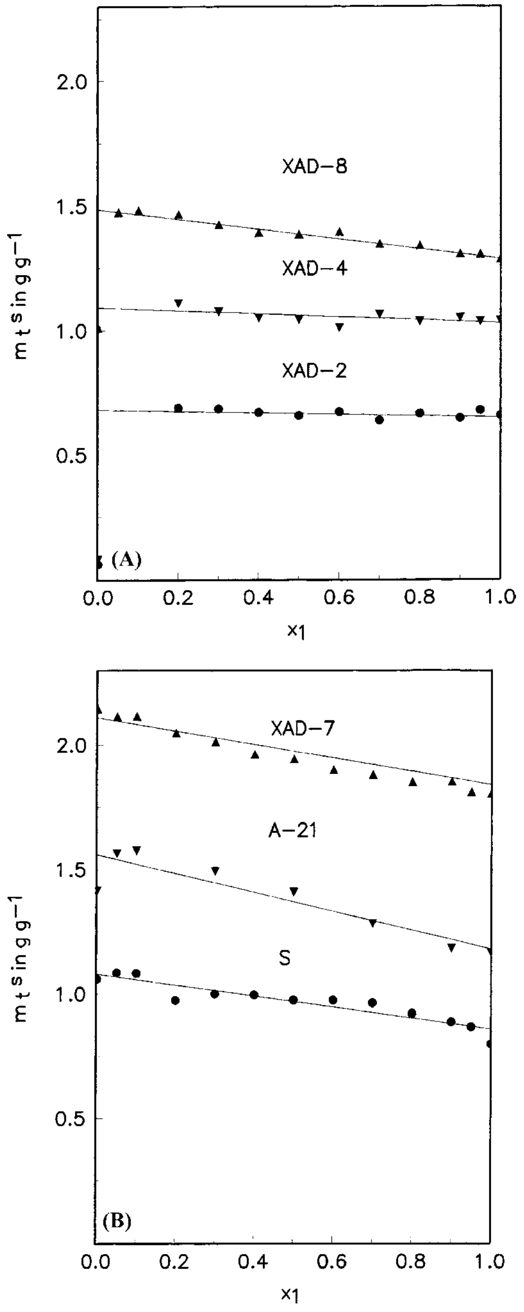

Fig. 2. (a) $m_t^s=f(x_1)$ – diagrams for (○) Amberlite XAD-2, (▽) Amberlite XAD-4 and (△) Amberlite XAD-8; x_1 is the equilibrium mole fraction of 1-propanol in the binary liquid mixture. (b) $m_t^s=f(x_1)$ – diagrams (○) for Chelite-S, (▽) Amberlyste A-21 and (△) Amberlite XAD-7; x_1 is the equilibrium mole fraction of 1-propanol in the binary liquid mixture.

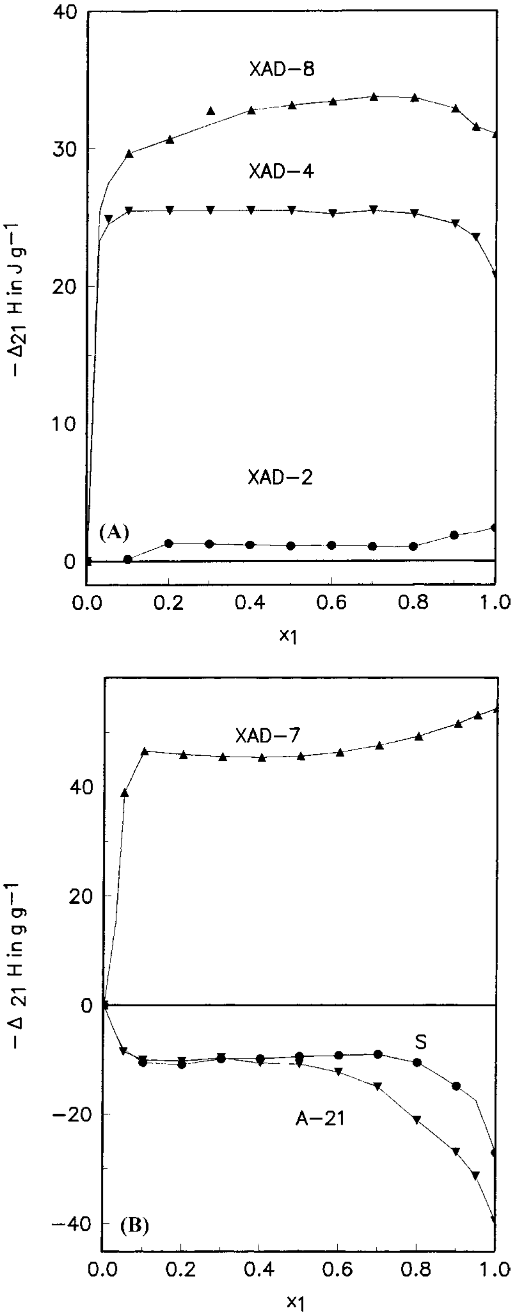

Fig. 3. (a) Integral enthalpy of displacement, $-\Delta_{21}H=f(x_1)$ for (○) Amberlite XAD-2, (▽) Amberlite-4 and (△) Amberlite XAD-7. $x1$: equilibrium mole fraction of water in the binary liquid mixture. (b) Integral enthalpy of displacement, $-\Delta_{21}H=f(x_1)$ for (▽) Amberlyste A-21, (○) Chelite-S and (△) Amberlite XAD-7; x_1: equilibrium mole fraction of water in the binary liquid mixture.

placement of water by 1-propanol for the non-polar networks Amberlite XAD-2 and XAD-4 is accompanied by an increase in the enthalpy function (Fig. 3(a)). For the middle polar sorbents Amberlite XAD-8 (Fig. 3(a)) and Amberlite XAD-7 (Fig. 3(b)), the heat effect is appreciable and the majority of heat evolution is due to the first steps of the displacement process (up to $x_1\approx0.2$). The enthalpy of displacement for the non-polar network of Amberlite XAD-4 and the middle polar Amberlite XAD-8 is exothermic and the isotherm has a plateau value from $x_1\approx0.2$–0.8 of ≈-25 and -33 J g^{-1}, respectively. Both isotherms have a noticeable downward section of larger mole fractions of alcohol but the overall displacement process remains exothermic (Fig. 3(a)). The bending back of the curves at mole fractions $x_1\geq0.8$ is a typical feature for sorbents having S-shaped excess isotherms [20,21].

The increase of the enthalpy function, $-\Delta_{21}H=f(x_1)$, is also very pronounced for the middle polar acrylic ester network Amberlite XAD-7 (Fig. 3(b)). The plateau value in the enthalpy of displacement isotherms (from $x_1\approx0.2$ to 0.5) is ca. -45 J g^{-1}. For the more hydrophilic polymer networks Chelite-S and Amberlyste A-21, the enthalpy of displacement isotherm decreases from $x_1=0$ up to $x_1\approx0.1$ (Fig. 3(b)). The plateau value in the enthalpy of displacement isotherms (from $x_1\approx0.1$ to 0.5) is ca. -10 J g^{-1} for both hydrophilized polystyrene networks. At higher mole fraction of 1-propanol, the enthalpy function starts to decrease again (as it is expected for inverted S-shaped excess isotherms [20,21]) and this secound endotherm is larger for the hydrophilic polystyrene network Amberlyste A-21 ($\Delta_{21}H\approx40$ J g^{-1}) and smaller for Chelite-S (Δ_{21}H$\approx$25 J g^{-1}).

5. Discussion

Before discussing the results presented in the foregoing section, it may be helpful to give some comments related to the sorbent structure. The non-polar networks of amberlite XAD-2 and Amberlite XAD-4 represents true macroreticular resins (aerogels). Each bead may be considered to be composed of a large number of microspheres with average pore diameters from hundred to several thousand picometers. After

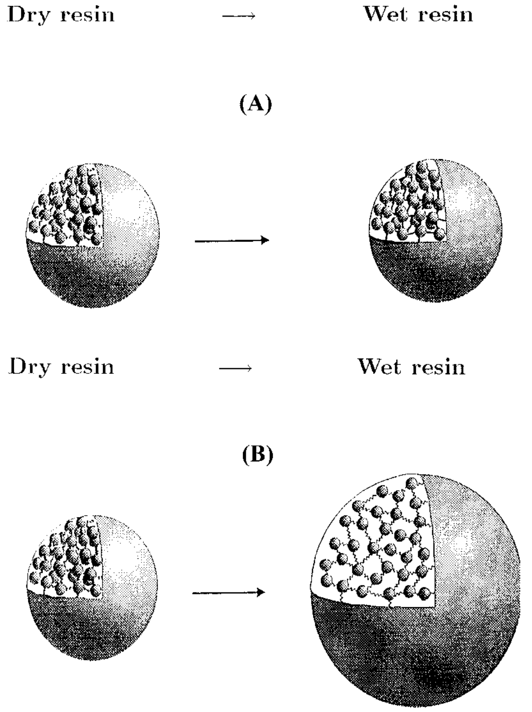

Fig. 4. (a) True macroreticular type of polymer network: dry and wet resins retaining the same porosity. (b) Macroreticular polymer network with a certain degree of gel porosity: the apparent pore volume increase upon wetting.

drying these particles, retain all or most of their porosity (Fig. 4(a)). This contrasts with the structure of conventionally polymerized sorbents which have only gel porosity in the swollen state and no permanent dry porosity. The middle polar macroporous resins (Amberlite XAD-8 and Amberlite XAD-7) and the hydrophilic network of Chelite-S and Amberlyste A-21 can be better described as a macroreticular type of polymer network with a certain degree of gel porosity. Thus, the particles may form swollen xerogels with the binary liquid mixture (Fig. 4(b)) and combine the feature of macroreticular and gel-type resin. By assuming a quasi-ideal adsorption layer, the apparent adsorption volume can be calculated from the experimental data of the total liquid uptake by the porous adsorbents according to Eq. (5). The data can be related to the values of the pore volume cited in the literature [16,22] to confirm the different swelling ability of the networks (Table 1). It is evident from Table 1 that for Amberlite XAD-7, Amberlite XAD-8 and Amberlyste A-21 the apparent sorption volume exceed the pore volume determined on the dry resins.

The excess isotherms with linear sections had been analysed according to the Schay–Nagy extrapolation (Eq. (4)) and Table 1 include the sorption volume derived therefrom [1]. It can be deduced from the data presented in Table 1 that only a part of the absorbed liquid is exposed to forces originated by the sorbent material. To account for the difference a certain amount of bulk like liquid mixture must have been taken up by the sorbent [8,9].

The shape of the enthalpy function is largely influenced by the extensive sorption of bulk-like liquid and swelling of the polymer particles. Thus, the sorption volume of the polymer networks is far from ideal, i.e. $\Delta_{21}H^{se}\neq 0$ in Eq. (6). Moreover, clustering and association behaviour is well-established for alcohol–water mixtures [25] and it is not astonishing that

Table 1
Porosity and swelling of the macroreticular polymer networks

Polymer network	Helium porosity [a] $cm^3\ g^{-1}$	Mercury intrusion [b] $cm^3\ g^{-1}$	Apparent sorption [c] $cm^3\ g^{-1}$	Schay-Nagy extrapolation [d] $cm^3\ g^{-1}$
Amberlite XAD-2	0.69	≈0.6	0.7	0.30
Amberlite XAD-4	0.99	≈1.0	1.1	0.70
Amberlite XAD-7	1.08	≈1.1	2.2	n.d.
Amberlite XAD-7	0.82	≈0.8	1.5	0.49
Amberlyste A-21	n.d.	≈0.5	1.6	0.37
Chelite-S	n.d.	≈0.8	1.1	0.21

[a] Data taken from Ref. [22].
[b] Data extrapolated from Ref. [22].
[c] Eq. (5), data extrapolated from Fig. 3(a) and (b).
[d] Eq. (4), data taken from Ref. [1].

the enthalpy of displacement even for the rigid macroreticular resins is shifted from its ideal value. The effect is largest for the sorbents with a high sorption capacity. Here, the non-ideality of the sorption volume is observed in the sorption of 1-propanol water clusters, which may cause larger heat effects [3,4,23,24]. The curves in Figs. 2 and 3 indicate that the liquid uptake in the plateau region of the enthalpy isotherms differ significantly with the nature of the polymer networks. According to this classification, we may, a priori, speculate on the sorption mechanisms.

The macroreticular resin Amberlite XAD-2 and Amberlite XAD-4 absorb 1-propanol in excess of the concentration in the bulk up to the azeotropic point $x_1^a \approx 0.5$ to 0.06. In the lower x_1-region, i.e. at $x_1 \ll 0.1$, the non-polar polymer framework must first be wetted by 1-propanol molecules. Once the polymer is covered by alcohol molecules, the pore volume can be readily filled with bulk liquid. For the brittle- and porous-structured resins Amberlite XAD-2 and Amberlite XAD-4, we could not detect sgnificant swelling in the 1-propanol–water mixtures by the crude gravimetric analysis. The microcalorimetry clearly indicates that the preferential sorption of 1-propanol is accompanied by an exothermic heat effect. For Amberlite XAD-4 and the middle polar Amberlite XAD-8, the preferential sorption of 1-propanol has really large values at $x_1 \leq x_1^a$ and is slightly endothermic from $x_1 \geq x_1^a$ to $x_1=1$.

On the other hand, we can see that the thermal effect for the displacement of water by 1-propanol is drastically reduced for the hydrophilised macroporous samples Chelite-S and Amberlyste A-21. Both samples are readily wetted by the 1-propanol–water mixtures. They not only differ in the amount and in the structure of the polar functionalities, but also in their swelling ability. Changes in the state of swelling causes an aditional heat effect manifested in the enthalpy isotherms.

The middle polar macroporous sample Amberlite XAD-7 exhibits an intermediate behaviour. Alcohol is preferentially adsorbed over a entire range of concentration and the increase in the enthalpy function is very pronounced with a second increase at a 1-propanol mole fraction $x_1 \geq 0.4$. In the same region of alcohol mole fraction, a second increase in adsorption is observed. Thus, 1-propanol is strongly preferred over the entire concentration range and the enthalpy function remains exothermic over the whole concentration region.

It had been mentioned in Section 1 that unusual adsorption isotherms with maxima and minima have already been reported in the literature. For the 1-propanol–water system on Printex GP-80 Marosi et al. [4] measured an U-shaped excess isotherm with a secondary shallow maximum at a molar fraction of 1-propanol $x_1 \approx 0.8$. The appearance of the secondary maximum had been interpreted as the result of a strong structure-forming effect of the alcohol–water mixtures. In other publications, layered materials such as 2/1 layer silicates have been investigated by selective liquid sorption and microcalorimetry in parallel with the interlamellar expansion of the mineral framework [9]. In methanol–water mixtures, the adsorption behaviour of the hydrophobised mineral adsorbents could be nicely modelled from combining adsorption isotherms of non-polar carbon black and polar silica [3,4]. Adsorption isotherms with two maxima have been obtained.

When the molecules of the liquid mixture, as in the case of 1-propanol–water, are strongly associated, the structuring influence of he polymer surface, especially of a complex sorbent like that of a macroreticular network structure, has to compete with the self-association of the liquid molecules. Swelling and clustering is a function of surface structure and polarity of the polymers. Therefore, it is not astonishing that our results will not fit to a variety of equations which have been derived for the presentation of enthalpy of displacement of binary liquid mixtures on solid surfaces [11,12,14,20,21].

6. Conclusions

Wetting, liquid uptake and sorption from 1-propanol–water mixtures was studied on three types of networks. The surface character of the two polar copolymers made of styrene and divinylbenzene (Chelite-S, Amberlyste A-21) and the middle polar adsorbent Amberlite XAD-7 are hydrophilic, i.e. the polymer particles could be easily wetted by pure 1-propanol, 1-propanol–water mixtures and pure water as well. The middle polar adsorbent Amberlite XAD-8 and the two non-polar styrene/divinylbenzene copolymers (Amberlite XAD-2, Amberlite XAD-4) were completely wetted only at an alcohol mole fraction $x_1 \geq 0.1$, i.e. the polymer matrix of the sorbents is at least partly hydrophobic in character.

The total liquid uptake is not only a measure of the wetting of the different polymer particles. Comparing the actually determined sorption volume with the theoretical values based on the simple pore filling model and the values determined in an earlier publication by the Schay–Nagy extrapolation method, we can deduce an appreciable estimate of the swelling characteristic of the network.

The enthalpy of displacement isotherms fairly-well reveal differences in polarity and swelling ability of the polymer network. Moreover, structural changes in the adsorption layers and formation of alcohol–water clusters on the surfaces will play an important role in determining the shape of the enthalpy function. Further investigation is in progress now.

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