Characterisation of surface modified polystyrene particles by microcalorimetry and liquid sorption

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Abstract

Different types of polystyrene particles were investigated by titration microcalorimetry and selective liquid sorption from 1-propanol(1)–water(2) mixtures. The first type of polymer particles is related to sulfonated polystyrene macrobeads of different surface charge. The other types are colloidal polystyrene particles: One of these is type-3-latices prepared by emulsion copolymerisation of styrene and sodium styrene sulfonate with potassium peroxodisulfate as the initiator. The second type of colloidal polystyrene particles is formed by a ground macroreticular ion exchange resin (Amberlyst 15). The adsorption measurements were performed in 1-propanol–water mixtures and were documented by composite isotherms.

The composite isotherms found for all three types of polystyrene particles are S-shaped in character. Water is preferentially sorbed up to water mole fractions $x_2 \approx 0.80$. The mole fraction of the adsorbed layer (x_2^s) was calculated from the surface excess and equilibrium diagrams (x_2^s/x_2) are presented.

The enthalpy effect accompanying the solvent exchange was determined by titration microcalorimetry. Changes in the conformation of the macromolecular frame were found to be an endothermic effect which is overlapped by the exothermic process of water displacement. The enthalpy of displacement isotherms fairly well reveal differences in the swelling ability of the particles surfaces. The change in free enthalpy was calculated from adsorption data from which entropy functions for the exchange process can be calculated.

In view of the thermodynamic potential functions structural changes in the adsorption layer and formation of alcohol water clusters on the surfaces of the colloidal polystyrene particles may play an important role in the dispersion stability. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Surface excess adsorption isotherms from binary liquid mixtures respond sensitively to the hydrophilic/ hydrophobic character of the adsorbent [1,2]. The composition of the adsorption phase changes with the character of the surface 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

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type of material the adsorption volume increases in two steps parallel with the interlamellar expansion of the mineral framework. When such an adsorbent is immersed in liquids or liquid mixtures, internal surface areas may become accessible to the liquids molecules (i.e., swelling and selective sorption [8,9]). Thus the interlamellar free volume which can be derived from the degree of swelling is often distinctly different from the sorption volume V^s determined from adsorption isotherms on the basis of the adsorption pore filling model [1,5–7].

In former studies we investigated the sorption of 1-propanol from water on polymer networks with different surface structure [10,11]. By a different polarity of the polymer frame an additional swelling ability had been introduced to the sorbents. We showed that the selective liquid sorption for the different polymer networks and the enthalpy of displacement as well was depending on the polarity and the extend of swelling.

In this study we investigated the selective liquid adsorption on colloidal polymer particles with different surface structure from 1-propanol(1)–water(2) mixtures. We have monitored the selective liquid sorption for the different polymer particles by the reduced surface excess and analysed the excess isotherm in order to determine the mole fraction of the adsorbed layer x_2^s and the adsorption volume V^s. For analysis of the energy balance of the adsorption process we have calculated the enthalpy of displacement from titration microcalorimetry.

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 [12–14]. If 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_2^0, to the equilibrium mole fraction x_2. The difference $\Delta x_2 = x_2^0 - x_0$ is measured by a suitable method. The experimental data are consequently expressed as composite isotherms, in which the excess amount adsorbed of one component is plotted as a function of its equilibrium concentration in the binary liquid mixture [14].

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:

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

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 $x_2^s = n_2^s/n^s$ 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 [5,15,16]

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

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

Here, $n_{2,0}^s$ is the adsorption capacity of the pure component 2 and $r = V_{m,2}/V_{m,1}$ 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). 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 [1,14,16]. 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 given by

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

and the adsorption capacity of the pure component 2 is then expressed as

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

Finally the mole fraction of component 2 in the adsorption layer x_2^s is calculated by

$$x_2^s = \frac{n_2^s}{n_1^s + n_2^s}, \tag{6}$$

which is suitable for determining $x_2^s = f(x_2)$, if n_1^s and n_2^s have been derived from the adsorption excess isotherms (Eqs. (2) and (3)).

2.2. Thermodynamic considerations

The integral enthalpy of displacement of component 2 by component 1 can be calculated from calorimetric data by Eq. (7), where the overall heat effect, $\Delta_{12}H_b$ is corrected for the mixing heat in the bulk phase, ΔH_{mix} [17–19]. On a molecular level 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:

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

Moreover, by integration of the well-known Gibbs equation, the free enthalpy for the adsorption process can be calculated from the excess data according to [6,20]:

$$\Delta_{21}G = -RT \int_{a_1=0}^{a_1} \frac{n_1^{\sigma(n)}}{x_2 a_1} \, da_1, \tag{8}$$

where x_2 is the mole fraction of component 2 in the bulk phase and a_1 is the activity of component 1 in the binary liquid mixture.

From the difference between the enthalpy of displacement and the free enthalpy of adsorption the

entropy term $-T\Delta_{21}S = \Delta_{21}G - \Delta_{21}H$ can be estimated [21], which possibly can rule out further details of the adsorption process.

3. Experimental

3.1. Materials

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

Macrobeads: Three polystyrene resins (PSS/L/5, PSS/L/6 and PSS/L/7) were prepared by suspension polymerisation of styrene and divinylbenzene (8%) in water as suspension medium and polyvinyl alcohol as stabilizer. The polymerisation was started by benzoyl peroxide [22]. The resulting gel like resins were sieved and the fraction of 0.25–0.5 mm was sulfonated with acetyl sulfate to different surface charges according to Zühlke et al. [23] (cf. Table 1).

Type-3-latices: Colloidal polystyrene particles were prepared by emulsion polymerisation of styrene and sodium styrene sulfonate as comonomer. The polymerisation reaction was initiated by potassium peroxodisulfate and performed by the seed and feed procedure according to Kim et al. [24]. By this process oligomeres of styrene and sodium styrene sulfonate are located in the outer sphere of the particles which results in a "hairy" surface [24].

Dispersion of a ground ion exchange resin (PS/KM/i): Amberlyst 15 (Fluka), macroreticular (30% divi-

Table 1
Surface charge (surface charge density σ_0; specific surface charge Σ_0), adsorption capacity, $n_{2,0}^s$, and volume of the adsorption layer, V^s, for the investigated resins and colloidal particles

Polymer material	Surface charge	Adsorption capacity	Sorption volume
Resins	Σ_0 [C g^{-1}]	$n_{2,0}^s$ [mmol g^{-1}]	V^s [ml g^{-1}]
PS/L/5	125.78	30	0.547
PS/L/6	192.0	17	0.310
PS/L/7	229.9	33	0.594
Latices	σ_0 [μC cm^{-2}]	$n_{2,0}^s$ [mmol g^{-1}]	V^s [ml^{-2}]
P(St/NaSS$_5$)1	15.29	12	2.61
P(St/NaSS$_3$)4	19.16	7.5	4.03
P(St/NaSS$_4$)1	19.74	12.5	4.72
NSS/2/2.1	33.87	10.8	5.18
NSS/3/1.1	304.14	47	8.15
Dispersion	σ_0 [μC cm^{-2}]	$n_{2,0}^s$ [mmol g^{-1}]	V^s [μl m^{-2}]
PS/KM/1	640.7	25	38.15

nylbenzene crosslink) cation exchange resin bearing sulfonate groups, was ground by wet milling. The resulting particles of 180–340 nm readily form a stable dispersion when immersed in distilled water.

All dispersions were cleaned by centrifugation and redispersion, subjected to dialysis for at least 4 weeks and converted to the proton form by mixed bed ion exchange [25]. The surface charge of the particles was determined by conductometric titration of the macrobeads and PCD measurements of the dispersions [25].

3.2. Methods

Adsorption measurements were performed in well sealed test tubes at room temperature. Amounts of approximately 3 cm^3 of the binary liquid mixture were added to approximately 0.15 g resin or sedimented latex sample, respectively. The change in the concentration of water in the bulk liquid (Δx_2) was determined by measuring the difference in the refractive index using a Zeiss liquid interferometer or a differential refractometer (Waters HPLC system), respectively. Usually, data were taken after equilibration periods of 48 h and centrifugation.

The enthalpy of displacement was recorded by a titration microcalorimeter (Thermometrics) at 298 K. 0.01–0.02 g of polymer was placed in the test tube and wetted with 0.15 ml water. Via a canula from a syringe (6110 lund syringe pump) 0.16 ml 1-propanol was added in small increments (usually 13 steps).

The integral displacement enthalpy isotherms, $-\Delta_{21}H$, 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 $\Delta_{mix}H$ was measured in the same equipment; by this means the necessary correction was made according to Eq. (7). The standard deviation for most of the calorimetric measurement by the above method varied between 2% and 5%.

4. Results and discussion

4.1. Surface excess isotherms

The selective liquid sorption on the polymer particles was studied first. The excess isotherms
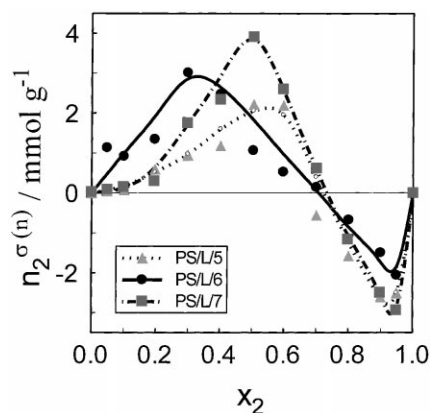

Fig. 1. Adsorption excess isotherms $n_2^{\sigma(n)}$ for the resins from 1-propanol(1)–water(2)mixtures.

$n_2^{\sigma(n)} = f(x_2)$ of sulfonated polystyrene resins with different surface charge are S-shaped (Fig. 1). Water is preferentially sorbed up to $x_2 < x_2^a$. The adsorption excess of water $n_2^{\sigma(n)}$ has positive values. The isotherm crosses the axis at the azeotropic point, $x_2^a \approx 0.75$. At the azeotropic point the adsorbed mixture is of the same composition as the liquid mixture in the bulk phase. For water mole fractions of $x_2 > x_2^a$ alcohol is preferentially adsorbed and adsorption excess of water $n_2^{\sigma(n)}$ has negative values. Moreover the surface excess of water at $x^2 < x_2^a$ and the surface excess of propanol at $x_2 > x_2^a$ increases with the specific surface charge, Σ_0, of the resins.

The adsorption excess isotherms on the colloidal particles are S-shaped too (Fig. 2). The adsorption excess isotherms in Fig. 2 are arranged in order of increasing surface charge density, σ_0, of the colloidal particles (cf. Table 1). The azeotropic point x_2^a of the isotherms is $x_2^a \approx 0.85$ for the particles with lower surface charge density and $x_2^a \approx 0.8$ for the highly charged particles. The extent of the adsorption excess of water up to the azeotropic point increases with the surface charge density of the particles.

The excess isotherms were analysed according to the Schay–Nagy extrapolation method. Then the mole fraction of the adsorbed layer x_2^s was calculated from the excess isotherms according to Eqs. (2), (3) and (6). In Fig. 3 the composition of the adsorbed layer x_2^s versus the composition of the bulk phase x_2 is depicted as equilibrium diagrams for the different adsorbents. For all particles water is bound preferentially from
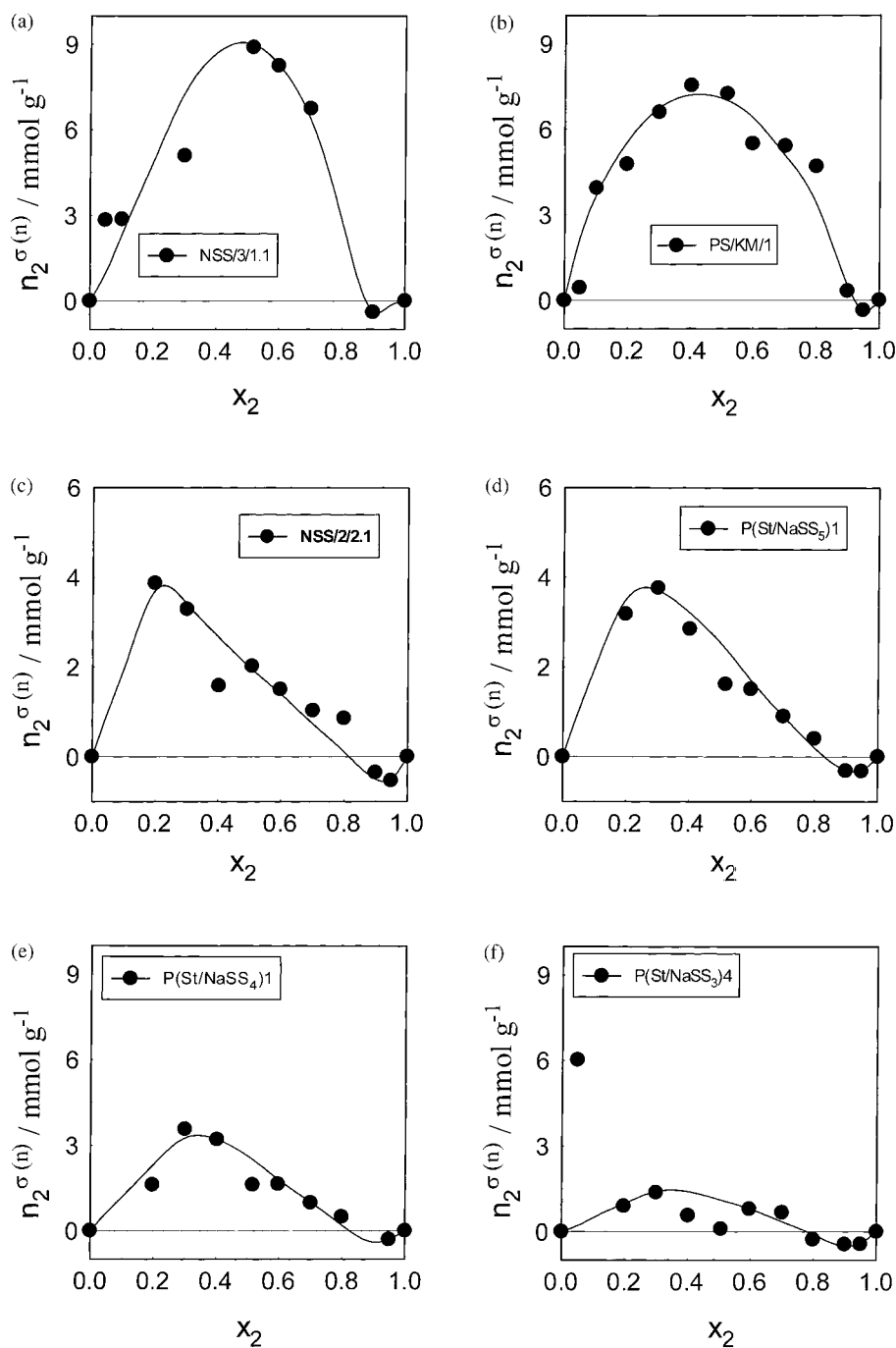
Fig. 2. (a)–(f) Adsoption excess isotherms $n_2^{\sigma(n)}$ for the colloidal particles from 1-propanol(I)–water(2)-mixtures.

1-propanol/water mixtures at smaller mole fraction of water. At larger water mole fraction, 1-propanol is partitioned in preference towards the particles. The shape of the curves in Fig. 3 indicate that the composition of the adsorption layer in the plateau region is almost independent of the surface charge.
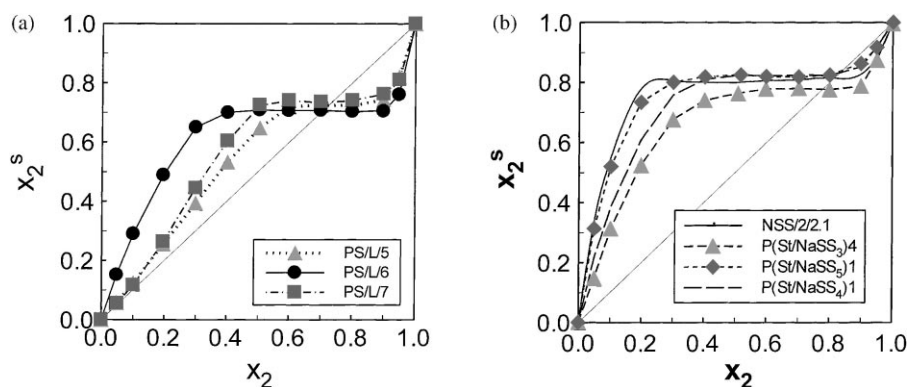
Fig. 3. Mole fraction of the adsorption layer x_2^s: (a) for the resins as a function of the bulk composition x_2; (b) for the latices as a function of the bulk composition x_2.

The volume of the adsorption layer V^s for type-3-latices increases with the surface charge density σ_0 (cf. Table 1). For the polymer resins have very different surface areas, as determined by N_2 adsorption in BET measurements, the values of the sorption volume V^s cannot be compared with each other.

4.2. Displacement enthalpy isotherms

The displacement of water by 1-propanol is illustrated by the enthalpy change $-\Delta_{21}H = f(x_2)$ of the colloidal particles (Fig. 4). For the lattices in Fig. 4a the accuracy of measurements is reached and no reliable detector signal was obtained. The displacement enthalpy given in Fig. 4b and c is slightly exothermic for the first increment of added 1-propanol. As the calorimetric titration proceeds the latex dispersions behave quite different.

For particles with higher surface charge density the endotherm at $x_2 = 0.97$–0.95 and the increase of the enthalpy for $x_2 < 0.95$ (i.e., at higher 1-propanol concentrations) is becoming stronger (Fig. 4b and c). The particles of the latex NSS/3/1.1 have the highest surface charge of all (cf. Table 1) and the isotherm presented in Fig. 4c has a clearly endothermic section at low 1-propanol concentrations around $x_2 \approx 0.95$ but an exothermic branch is created upon further addition of alcohol for $x_2 < 0.9$.

The dispersion PS/KM/1 is formed from finely ground Amberlyst 15. The endotherm at low mole fractions of 1-propanol is very small (Fig. 4c) and is within the accuracy of the detection limit. The cumulative enthalpy of displacement has negative values over the entire range of $x_2 = 1$–0.8.

The shape of the displacement enthalpy isotherm is further sensitive on the shape of the particles and its surfaces. The particles of the dispersion of the ground ion exchange resin have a really high adsorption capacity but a relatively smooth surface if compared to the hairy layer of the latex particles. The displacement (Fig. 4c) is exothermic and accompanied by only small endothermic effects. For type-3-latices, the endothermic effects increase with the volume of the adsorption layer (which vice versa increases with the number of sulfonated units on the surface of the particles). Thus, the structure of the surface layer and the shape of the polymer particles will play a decisive role for the mechanism of the displacement reaction.

For further analysis of the displacement processes in the adsorbed layer, we will compare the enthalpy of displacement measured for the colloidal particles with those for the sulfonated polystyrene resins.

The enthalpy of displacement $-\Delta_{21}H$ for the sulfonated polystyrene resins was determined from titration calorimetry and is presented in Fig. 5a–c. Additional, the free enthalpy of the adsorption process $-\Delta_{21}G$ calculated according to Eq. (8) and the entropy term $-T\Delta_{21}S$ for the displacement of water by 1-propanol is also shown in Fig. 5a–c. The positive values of the enthalpy of displacement function $-\Delta_{21}H$ is indicative for an overall exothermic displacement reaction. With increasing specific surface charge of the polymer particles (PS/L/5 < PS/L/7) the
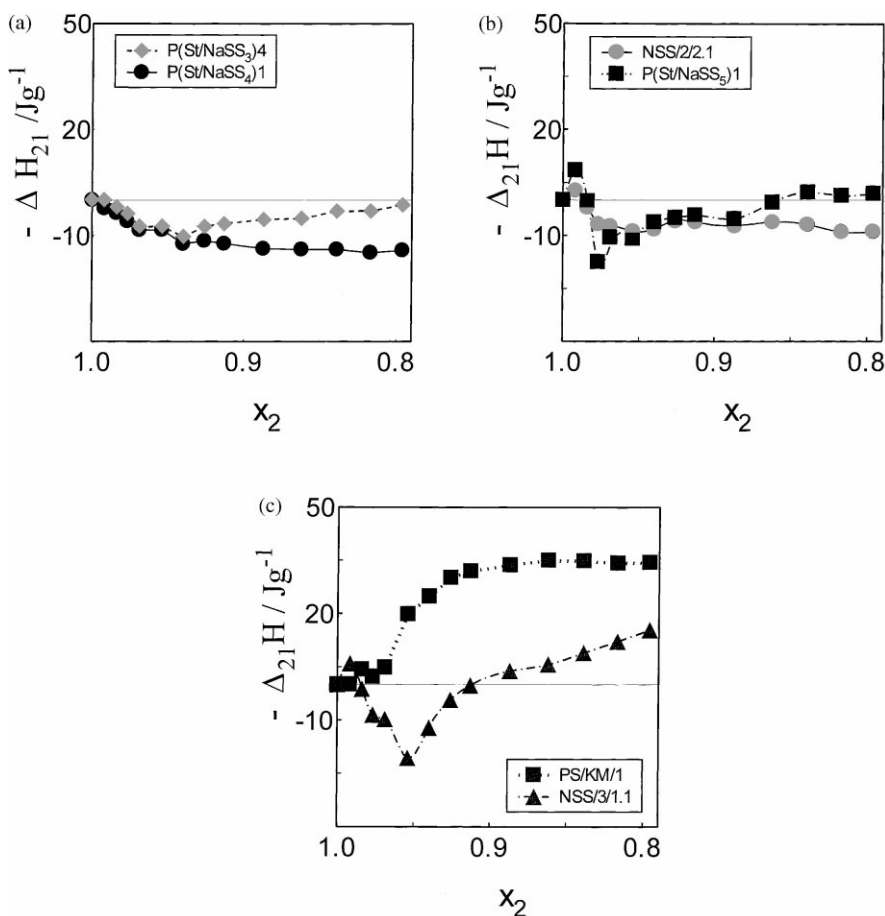
Fig. 4. (a) and (b) Displacement enthalpy isotherms $-\Delta_{21}H$ for type-3-latices. (c) Displacement enthalpy isotherms $-\Delta_{21}H$ for a type-3-latex and the dispersion PS/KM/1.

displacement process of water by 1-propanol becomes apparently less exothermic. Even so the entropy term $-T\Delta_{21}S$ decreases for low 1-propanol concentrations as the specific surface charge increases. The decrease in the entropy function results from a shoulder in the isotherm of the enthalpy of displacement which is more pronounced for the particles with higher specific surface charge. For the relative degree of swelling, which had been measured in separate experiments, is the same for the three resins we suspect that conformational changes in the adsorption layer of the gel-like resins may be the reason for these endothermic terms. The hairy surface of type-3-latices is supposed to have a gel-like character too and may be compared with the investigated gel-like resins. The endotherm for the type-3-latices which increase with

the volume of the adsorbed layer, V^s, thus results from swelling and conformational changes in the adsorbed layer.

5. Summary and conclusions

We have measured the adsorption surface excess for sulfonated polystyrene resins and colloidal polystyrene/polystyrene sulfonate particles from 1-propanol/water mixtures. The results of our investigations can be summarized as follows:

1. The composition of the adsorbed liquid mixture does not depend on surface charge of the investigated polymers.
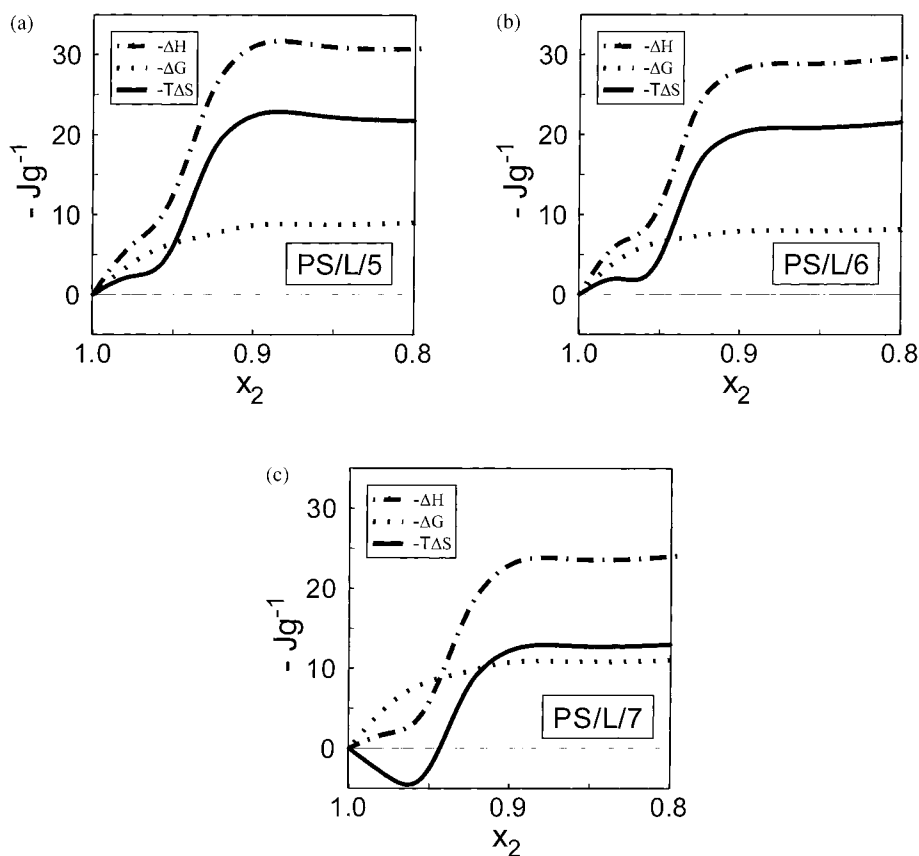
Fig. 5. Displacement enthalpy $-\Delta_{21}H$, free enthalpy of adsorption $-\Delta_{21}G$ and the entropy term $-T\Delta_{21}S$: (a) PS/L/5, (b) PS/L/6, (c) PS/L/7.

2. The adsorption capacity increases with increasing surface charge of the latex particles. This results in a larger volume of the adsorption layer V^s for the particles with higher surface charge density σ_0 (cf. Table 1).

3. The gel-like resins and the hairy surface of the latex particles is able to swell in 1-propanol/water mixtures [10,11]. Swelling of the surface layer of colloidal particles can not be followed by common methods. By the aid of titration microcalorimetry the enthalpic effects accompanying the displacement reaction can be determined. The precise and careful analysis of the enthalpy of displacement isotherm may provide further information about the different processes involved.

4. For sulfonated polystyrene resins the displacement of water by 1-propanol is exothermic and accom-

panied by an endothermic effect which increases with the specific surface charge of the particles. For the colloidal particles with a hairy surface, thus having a gel-like character too, the overlapping endothermic effect increases with the volume of the adsorption layer of the latices. We again suppose that this is due to structural changes in the adsorption layer and it shall be the topic for further research work.

Finally it is really worth to note that the composition of the liquid mixture adsorbed by the colloidal particles in the range of $x_2 = 0.5$–0.95 reminds us of the composition of 1-propanol–water clusters observed in 1-propanol–water mixtures [26]. Probably the structural changes are caused by the formation and adsorption of 1-propanol–water clusters, swelling the outer sphere of the investigated latices. Again, further

investigations are necessary to undermine this view and will be published soon.

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