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Regeneration of Mixed Solvent by Ion Exchange Resin: Selective Removal of Chloride and Sulfate

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Abstract: The selective extraction of sulfate and chloride ions from mixed solvent solutions was investigated. The mixed solvents consisted of water and 50 to 100%-w (salt-free solvent) ethylene glycol. The extraction was measured for mixed solvent solutions containing only sulfate and chloride, and mixed solvent solutions saturated with trona (sodium sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)$. Three anion exchange resins, Dowex 1X8-50, Dowex 21K-Cl, and Dowex MSA-1, were investigated for their chemical and physical resistance to the mixed solvent carbonate/bicarbonate solutions, for their swelling behavior in the different mixed solvents, and for their extraction efficiency for chloride and sulfate.

The loading of the ion exchangers was fitted to a Langmuir-type sorption model. While the extraction from trona-free mixed solvents was well reproduced, the loading of the ion exchangers with chloride and sulfate from trona-saturated mixed solvent solutions did not fit the sorption model. It appears, rather, that under these conditions chloride and sulfate are "salted out" of the bulk solution and driven into the ion exchangers.

Keywords: Ion exchange, organic solvent, mixed solvent, selective removal of chloride and sulfate

INTRODUCTION

Recrystallization, as well reactive recrystallization of soda (sodium carbonate), in a mixed solvent has been shown in related work (1–7) as

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energy-efficient, alternative process routes for the production of soda of higher physical quality and chemical purity than currently available soda. The mixed solvent used in these processes consists of water and ethylene glycol.

A vital factor for the economical feasibility of these processes is the recycle of the mixed solvent in the process. Inline purification steps are necessary to remove impurities from the mixed solvent recycle. Ion exchange resins may offer a possibility to selectively remove ionic impurities from the mixed solvent solution while not changing the solvent composition.

The globally most common sodium carbonate source is trona, sodium sesquicarbonate ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O(s)$, which occurs as a natural mineral in large, mostly subterranean deposits (8). It can be converted via the Mixed Solvent Reactive Recrystallization process (5–7) to high-quality soda.

Trona, recovered by solution mining (9), is a suitable starting material for the Mixed Solvent Reactive Recrystallization, as organic and insoluble particulate impurities have already been removed. This trona would still contain at least traces of soluble inorganic impurities: Traces of chloride and sulfate were found in samples of trona ore from Wyoming and California; see Gärtner et al. (5, 10).

Light soda ash used as starting material in the Mixed Solvent Recrystallization process by Oosterhof et al. (1, 2, 4) is commonly produced by the Solvay process from sodium chloride and contains measurable traces of sodium chloride.

These trace concentrations of sodium chloride and sodium sulfate remain in the mixed solvent after the recrystallization (10) and should be removed during the recycle. For these reasons, the inline removal of chloride and sulfate by different techniques has been investigated. Also membrane processes like electrodialysis, reverse osmosis, nano- and hyperfiltration offer feasible methods to remove dissolved ionic impurities from solutions. Especially electrodialysis appeared suitable for the outlined separation and has been tested in a related study (11).

In this work, three strongly basic anion exchange resins, Dowex 1X8-50, Dowex 21K-Cl, and Dowex MSA-1, were investigated for their resistance to the mixed solvent solutions, their swelling behavior, and their change in selectivity for sulfate and chloride with increasing ethylene glycol content and solution saturation with carbonate/bicarbonate.

THEORY

Ion exchangers usually consist of an inorganic or organic matrix structure, which links and immobilizes the active groups, which are usually ionic themselves. Cation exchangers usually contain anionic groups (e.g., sulfonate, carboxylate), while anion exchangers usually contain cationic groups (e.g., amine).

Most organic-polymer ion exchangers only achieve their ion exchange capability after swelling in solution, i.e., by taking up solution into their "pores" and hydrating (solvating) their ionic functional groups. All transport of ions in the ion exchanger resin takes place as diffusion through this pore solution. A high degree of swelling generally facilitates ion exchange processes, as more pore volume becomes available for diffusive transport. A lack of swelling, on the other hand, can decrease the (available) capacity of an ion exchange resin, as some of the active groups are not accessible by diffusion.

The degree of swelling, i.e., the amount of solution absorbed by the ion exchanger resin, in aqueous solution depends not only on the active ionic groups, but also on their counter ions in the pore solution and the general ionic strength of the surrounding bulk solution. Whereas highly hydrated counter ions result in an increased degree of swelling, a bulk solution of high ionic strength decreases the degree of swelling.

Phenomenologically, the degree of swelling is determined by the equilibrium of two forces (14):

a) The osmotic pressure between bulk and pore solution, i.e., the hydration (solvation) of the fixed active groups by the absorbed pore solution and the ionic interaction between the active groups and their counter ions.

b) The contractive force of the polymer matrix, which is stretched with the swelling. This force is a result of the tendency of polymer chains to rather take a folded or coiled shape (conformation) than a straight one.

This model not only explains the increase in swelling with more strongly charged and more heavily hydrated counter ions, but also the order of selectivity for strong ion exchangers, i.e., the preference for smaller, less charged and less hydrated counter ions.

Based on this theoretical consideration, organic co-solvents can have multiple effects on an ion exchange resin. First, they usually decrease the solubility (and increase the activity) of ionic species in solution, due to these solvents' lower dielectric constant [e.g., the dielectric constant of ethylene glycol (i.e., 41.4) is $\sim 1/2$ that of water (i.e., 80.1) at 20°C (13)], i.e., the decrease in dielectric shielding. The ionic charge is less buffered/distributed by the solvent, and the interactions between the ions become stronger in the bulk solution. This results usually in an increased ion sorption in the resin.

Second, since sorption/swelling is determined by the osmotic pressure (i.e. the chemical potential difference between resin and bulk solution) of each solvent component, the composition of the mixed solvent in the resin is usually not identical to the composition in the bulk solution. One of the solvents, either water or the organic solvent, is absorbed preferentially into the pores of the resin (14). For dilute solutions of ethylene glycol in water, water is taken up preferentially, resulting in a distribution coefficient for ethylene glycol of ca. 0.6 between resin and bulk solution for low ethylene glycol concentration (50 g/L) (14). At high ethylene glycol concentrations and in pure ethylene glycol, increased swelling was observed (16, 17). This increase in swelling was explained by the fact that the dielectric constant of ethylene glycol was high enough to allow dissociation of the ionic species, while it resulted at the same time in a significantly stronger repulsion between ions of the same sign—notably the fixed active groups.

Third, the organic co-solvent can also absorb to the polymer matrix through London or dipole-dipole interactions (14). As these interactions are weaker than the electrostatic ones, this is usually a minor effect. For high concentrations of the organic co-solvent and a high affinity between it and the polymer matrix—such as for aliphatic hydrocarbon chains—this effect can become a major cause of (apolar) swelling. For ethylene glycol and the polystyrene matrix of the tested resins this affinity is not given and this effect is assumed irrelevant for the given ion exchangers despite the high ethylene glycol concentrations used in this work.

The equilibrium distribution of a solute *i* between resin and solution can be described by an expression similar to a Langmuir-adsorption isotherm:

$$\frac{q_i}{q_0} = \frac{k_i \cdot c_i}{1 + k_i \cdot c_i} \tag{1}$$

with q_i the loading of the resin with i, c_i the solute's concentration in the bulk solution and k_1 the Langmuir coefficient.

The Langmuir description is applicable to the ion exchange resin despite the fact that the solute, the counter ion, is not necessarily adsorbed (bound) to one specific active site, because all ionic species are—in the ideal case—assumed to be dissociated and the counter ions are therefore present in the pore solution as free species. But because of the electro-neutrality condition, every fixed charge of an active group has to be countered by an opposite charge from a counter ion in the pore solution. Therefore, the number of active site charges can be directly related to the number of opposite charges in the pore solution, which is similar to the adsorption described by the Langmuir expression, i.e., one solute molecule per sorption site.

Certain counter ions could draw additional co-ions (of the same charge as the fixed charges) into the pore solution. Under such conditions, the Langmuir expression would no longer properly describe the distribution behavior. A polymolecular-layer-adsorption expression like BET (Brunauer–Emmet–Teller) could be used to describe such a solute distribution between resin and solution.

Another complication of the description of the distribution of *one* solute species is the presence of *multiple competing* species, which definitely applies to our case. Not only chloride and sulfate are competing with each other for sorption into the pore solution, but they also have to compete with the other present anions, namely carbonate, bicarbonate, and the hydroxide ion.

In the ideal case, this could be described by an extended Langmuir expression:

$$\frac{q_i}{q_0} = \frac{k_i \cdot c_i}{1 + \sum_j k_j \cdot c_j} \tag{2}$$

The presence of the ethylene glycol, which decreases the electrostatic shielding between ionic species and promotes ionic association, adds another complication. Weak acid anions like carbonate and bicarbonate might be forced by this apolar environment to form bonds with the fixed charges, if the concentration of the ethylene glycol in the pore solution were sufficiently high. Such strong sorption could significantly slow the equilibration of the system.

The tested, strongly basic anion exchange resins consist of cross-linked styrene polymer-chains containing trimethyl-benzyl-amine as active groups. These groups give these ion exchangers the following order of (aqueous) selectivity for sorbed counter ions (12):

$$I^- > NO_3^- > Br^- > Cl^- > CH_3COO^- > OH^- > F^-$$

An overview of the properties of the three tested resins in aqueous solution is given in Table 1. The Dowex 1X8-50 and 21K-Cl resins are gel-type ion exchange resins, which implies that their porosity is dependant on their degree of swelling. Only in a sufficiently swollen state is their ion exchange capacity fully (and readily) accessible to the bulk solution. For this reason, these resins are described as *microporous.* The Dowex MSA-1 resin on the other hand is *macroporous*, i.e., its polymer matrix has wide pores, providing access to the full exchange capacity without dependency on swelling.

These resins were chosen for their high mechanical and chemical stability and their strongly basic character. They have not only to be resistant to the ethylene glycol in the mixed solvent as well as the increased swelling this might cause, but they also have to operate at a pH of 10 to 11, i.e., a trona (carbonate/bicarbonate) saturated solution. For the resin to be functional, its active groups have to be dissociated, which is only given in a strongly basic resin for this pH range.

EXPERIMENTAL

Previous to the experiments, the ion exchanger resins were transformed from their chloride form (Cl^-) into the hydroxide form (OH^-) by contacting 100 g of dry resin successively three times with app. 250 g of fresh 5M NaOH. This removed ca. 75% of the chloride from the resins and was sufficient for the experiments. See Addendum.

To investigate the ion exchange behavior of the three resins, the distribution of chloride and sulfate between resin and bulk solution was investigated for different compositions of the mixed solvent as well as with and without addition of trona.

In a first set of experiments, samples of the Dowex MSA-1 resin were contacted for 4 h with solutions containing app. 7500 ppm chloride ions and 4500 ppm sulfate ions at 25°C in resin to solution ratios of 1 : 2, 1 : 5, and

Table 1. Properties of the tested ion exchange resins according to supplier (12)

Resin	Dowex 1X8-50	Dowex 21K-Cl	Dowex MSA-1
Active group	Trimethyl amine	Trimethyl amine	Trimethyl amine
Matrix	Styrene-DVB, (Microporous) gel	Styrene-DVB, (microporous) gel	Styrene-DVB, macroporous
Shipped ionic form	Chloride (Cl^-)	Chloride (Cl^-)	Chloride (Cl^-)
Mean particle size	550 micron	580 micron	640 micron
Effective pH range	0–14	0–14	0–14
Exchange capacity			
Dry resin (meq/g)	3.5	4.5	4.0
Wet resin (meq/mL)	1.33	1.25	1.0
General properties	Excellent physical and chemical stability	Excellent mechanical stability, good kinetics, and high regeneration efficiency	Excellent mechanical and chemical stability, good kinetics, and high regeneration efficiency

1 : 10. Solutions containing app. 47, 62, and 80%-w (salt-free solvent) ethylene glycol were tested.

In a second set of experiments, the Dowex 21K-Cl and MSA-1 resins were contacted for 4 h with solutions containing app. 8500 ppm of chloride ions, 4000 ppm of sulfate ions. The resins were contacted in ratios of 1 : 2, 1 : 5, and 1 : 10 to the solution (by weight of wet resin to solution) at 50°C. Solutions containing app. 70, 90, and 100%-w (salt-free solvent) ethylene glycol were tested. Solutions saturated with trona and solutions without trona were tested to evaluate the impact of the high carbonate/bicarbonate on the extraction.

To test the extraction of low concentrations of chloride and sulfate, 100 mL of mixed solvent solutions saturated with trona containing app. 60 ppm of chloride ions and 40 ppm of sulfate ions were contacted with the resins in their hydroxide form for 24 h at 25°C. The amount of resin in each in this last set of experiments corresponded to app. 2 g of dry resin in the original chloride form. Mixed solvents containing 0, 50, 70, and 90%-w (salt-free solvent) ethylene glycol were tested.

The concentrations of chloride and sulfate in solution were measured by ion chromatography before and after contacting with the resin. The loading of the resin with sulfate and chloride was then calculated by mass balance, i.e., the amounts of sulfate and chloride removed from the solution by the resin. As the resin was not completely stripped of chloride in the regeneration with NaOH, the remaining amount of chloride had to be added to the amount from the solution mass balance to obtain the total amount of chloride in the resin.

The swelling of the ion exchangers in trona-saturated solutions of solvents with ethylene glycol contents of 0, 50, 70, and 90%-w (salt-free solvent) was determined at 25°C. Two to 3 g samples of the NaOH regenerated (swollen) resin were contacted with 100 mL of solution for 24 h. Then the resin was filtered off, rinsed with distilled water, weighed and dried on the filter paper at 50°C for another 24 h, after which it was weighed again. The degree of swelling was calculated as the ratio between the weight increase through swelling in the test solutions and the dried weight at the end of the experiments.

$$\nu_s = \left(\frac{m_{IE,solution}}{m_{IE,dried}} - 1 \right) \cdot 100\% \quad [\%\text{-w dry resin}] \tag{3}$$

The trona was obtained 99.8%-w pure from Solvay, France. The mixed solvents were prepared from technical grade ethylene glycol and ultra-pure water. The saturation concentrations of trona in ethylene glycol–water mixed solvents can be found in Gärtner et al. (7). Sulfate and chloride were introduced to the samples as analytically pure sodium salts (Merck). The three ion exchange resins were obtained from Sigma Aldrich.

All experiments were executed in triple as shake tests in 50 ml Nalgene™ bottles in a thermostatic shaking bath.

RESULTS

Swelling in the Mixed Solvents

The results of the swelling experiments are summarized in Fig. 1. The degree of swelling v_s first decreased from about 40 to 50%-w in aqueous solution to 18 (Dowex 1X8-50) to 35%-w (Dowex MSA-1 and 21K-Cl) in 50%-w (salt-free solvent) ethylene glycol. Beyond 50%-w (salt-free solvent) ethylene glycol content the swelling increased almost linearly with increasing glycol content to reach 40%-w for Dowex 1X8-50 and app. 60%-w for Dowex MSA-1 and 21K-Cl in 90%-w ethylene glycol.

The Dowex 1X8-50 resin displayed a similar degree of swelling as the other two resins in the aqueous solution, but a ca. 15 to 20%-w lower degree of swelling in the mixed solvent solutions. Since Dowex 1X8-50 is a gel-type resin, its ion exchange capability (and even capacity, see above) requires a certain degree of swelling. Obviously, its affinity to the ethylene glycol is low, resulting in a decreased solvent sorption at middle ethylene glycol contents, where it preferentially absorbs water.

This is in good agreement with the observations of Helferich (14), Bodamer et al. (16) and Bonner et al., (17), who found preferential water sorption for low ethylene glycol contents, i.e., low swelling as the water distributes between the resin and the ethylene glycol containing bulk solution, and high swelling, most probably due to increased electrostatic repulsion of the fixed charges in the resin, for high glycol contents.

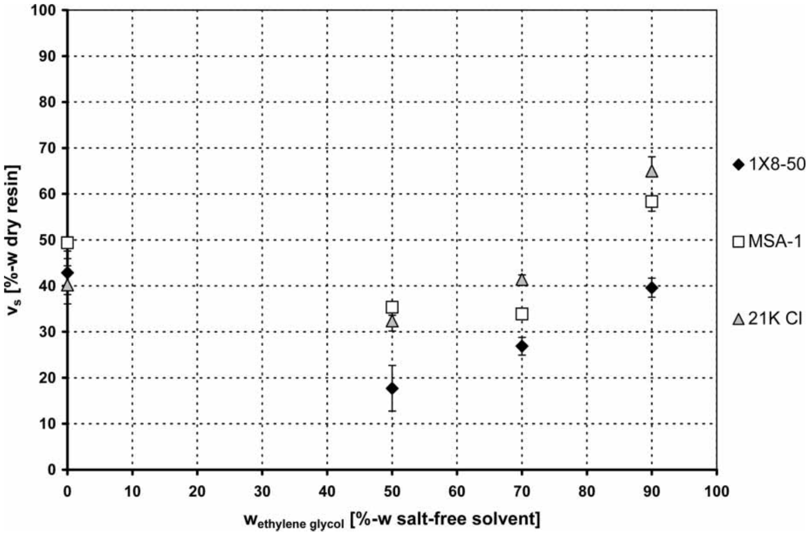

Figure 1. Swelling of the ion exchange resins in solvents of increasing ethylene glycol content at 25°C.

Chloride and Sulfate Sorption

The chloride and sulfate ions distributed between the resins' pore solution and the bulk solution in accordance with a Langmuir sorption isotherm, see Eq. (1). Based on the Langmuir model, the distribution coefficient of a solute species i, D_i, which is the ratio between resin loading q_i and bulk solution concentration c_i, can be expressed as a function of the resin loading q_i, see Eq. (6):

$$\text{Langmuir:} \quad \frac{q_i}{q_0} = \frac{k_i \cdot c_i}{1 + k_i \cdot c_1} \iff q_i + q_i \cdot k_i \cdot c_i = q_0 \cdot k_i \cdot c_i \tag{4}$$

$$\frac{q_i}{c_i} + q_i \cdot k_i = q_0 \cdot k_i \tag{5}$$

$$D_i = \frac{q_i}{c_i} \Longrightarrow D_i = -q_i \cdot k_i + q_0 \cdot k_i \tag{6}$$

Therefore, the distribution coefficient D_i is plotted vs. q_i to obtain the Langmuir coefficient k_i and the total exchange capacity q_0.

For the Dowex MSA-1 resin at 25°C in 47.4, 65.1, and 82.0%-w (salt-free solvent) ethylene glycol solution, the D vs. q plots are given in Fig. 2, while the derived Langmuir fits together with the experimental data points are given in Fig. 3. It can be noted from Fig. 2 that the distribution coefficients for both sulfate and chloride displayed a slight increase with increasing ethylene glycol content. This effect was more pronounced for sulfate than for chloride, where it was almost negligible. The reason for this was most likely that the more polar sulfate ion was more strongly affected by the increasingly apolar bulk

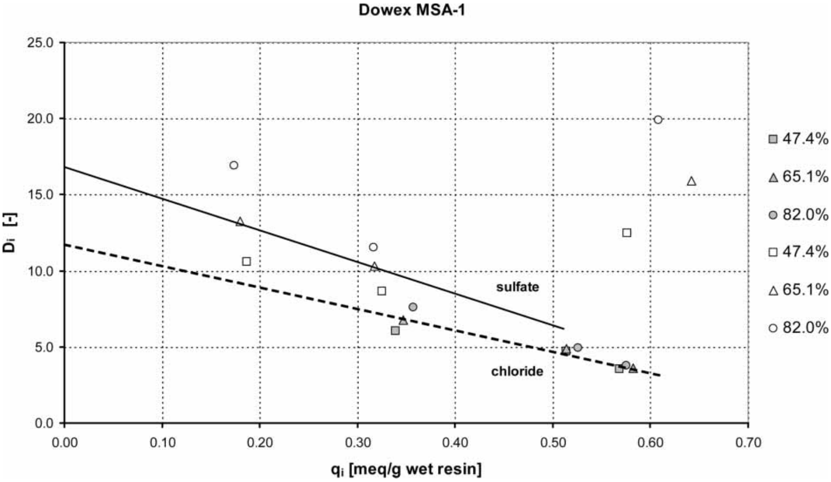

Figure 2. Distribution coefficient D vs. resin loading q for sulfate (white symbols) and chloride (gray symbols) loading of the MSA-1 resin at 25°C for 47.4, 65.1, and 82%-w (salt-free solvent) ethylene glycol in the mixed solvent (w/o trona).

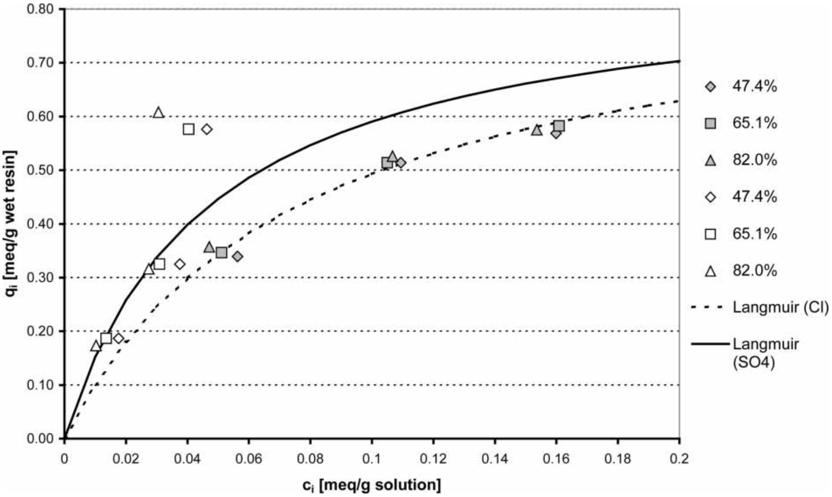

Figure 3. Resin load q vs. bulk concentration c for chloride (gray symbols) and sulfate (white symbols) sorption of Dowex MSA-1 resin at 25°C from solutions containing 47.4, 65.1, and 82.0%-w (salt-free solvent) ethylene glycol (w/o trona).

solution and was therefore more strongly drawn to the more polar pore solution.

The total exchange capacity of the wet Dowex MSA-1 resin, calculated from the exchange capacity of the dry resin, see Table 1, and the degree of swelling, was ca. 1.17 meq/g wet resin. From the plots of Fig. 2, an average Langmuir coefficient k_i of 13 g solution/meq for chloride and 21 g solution/meq for sulfate were obtained.

The Langmuir fit in Fig. 3 reproduces the distribution of chloride quite well, but the sulfate distribution shows a significant deviation for high sulfate loading. This effect was observed for all three ethylene glycol concentrations. For the deviant conditions, the sulfate loading q(SO4) was 0.60 meq/g wet resin, while the chloride loading q(Cl) was 0.57 meq/g wet resin, i.e., a combined total load of 1.17 meq/g wet resin, which corresponded exactly to the calculated total exchange capacity.

It is more likely, though, that sulfate was taken up in excess, i.e., together with a co-ion (sodium). The reason for this deviation from the Langmuir-behavior was probably the formation of $[NaSO_4]^-$ (or even $[Na_2SO_4]$) complexes (due to the apolar mixed solvent), which would be taken up in the pore solution, but would occupy less fixed-charges of the resin than the sulfate ions. As—due to the fixed charges—the pore solution is more polar than the mixed solvent bulk solution, it can also buffer such polar complexes better, resulting in an increased uptake of sulfate by the resin. The total capacity of the ion exchange resin was most probably not reached (or rather a fraction was still occupied by OH^-).

As can be seen from the experiments at 50°C with 70, 90, and 100%-w (salt-free solvent) ethylene glycol mixed solvents in Fig. 4, the distribution coefficients for sulfate and chloride strongly increased with temperature. In almost all experiments in solutions without trona, both Dowex 21K-Cl and MSA-1 were loaded to their total exchange capacity with sulfate and chloride at low bulk concentration. Therefore, it was not possible to obtain reliable Langmuir coefficients from these experiments.

Figure 4 shows, that sulfate was reduced to lower levels (max. 0.06 meq SO_4/g solution) in solution than chloride (up to 0.2 meq Cl/g solution) and that the maximum loading of chloride was app. 0.6 to 0.7 meq/g wet resin, while the maximum sulfate loading varied between 0.2 and 0.4 meq/g wet resin. Since these maximum loadings roughly correspond to the initial concentration of

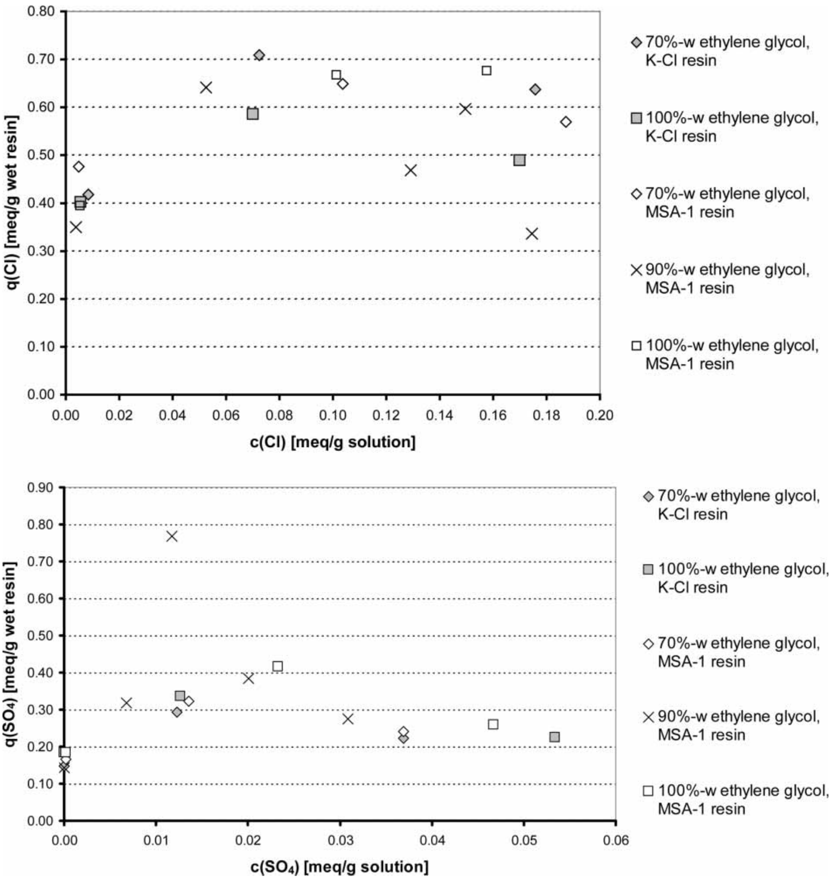

Figure 4. Resin loading q vs. bulk solution concentration c for chloride (above) and sulfate (below) for Dowex 21K-Cl and MSA-1 resin in 70, 90, and 100%-w (salt-free solvent) ethylene glycol solutions (without trona) at 50°C.

8500 ppm chloride and 4000 ppm sulfate, the maximum loadings might actually be reversed for reversed initial concentrations. It can still be concluded that both ion exchange resins show a slightly higher affinity to sulfate than chloride.

In the experiments at 50°C with Dowex 21K-Cl and MSA-1 with solutions saturated with trona, the resins were occupied to a significant fraction by carbonate and bicarbonate, resulting in a decrease in the loading with sulfate and chloride. While the sulfate loading dropped to app. constant 0.1 meq/g wet resin (irrespective of bulk concentration), the chloride loading varied between 0.1 and 0.3 meq/g wet resin, see Fig. 5.

Exceptions were the conditions in the 90%-w (salt-free solvent) ethylene glycol solution, where both chloride and sulfate obtained a maximum in their

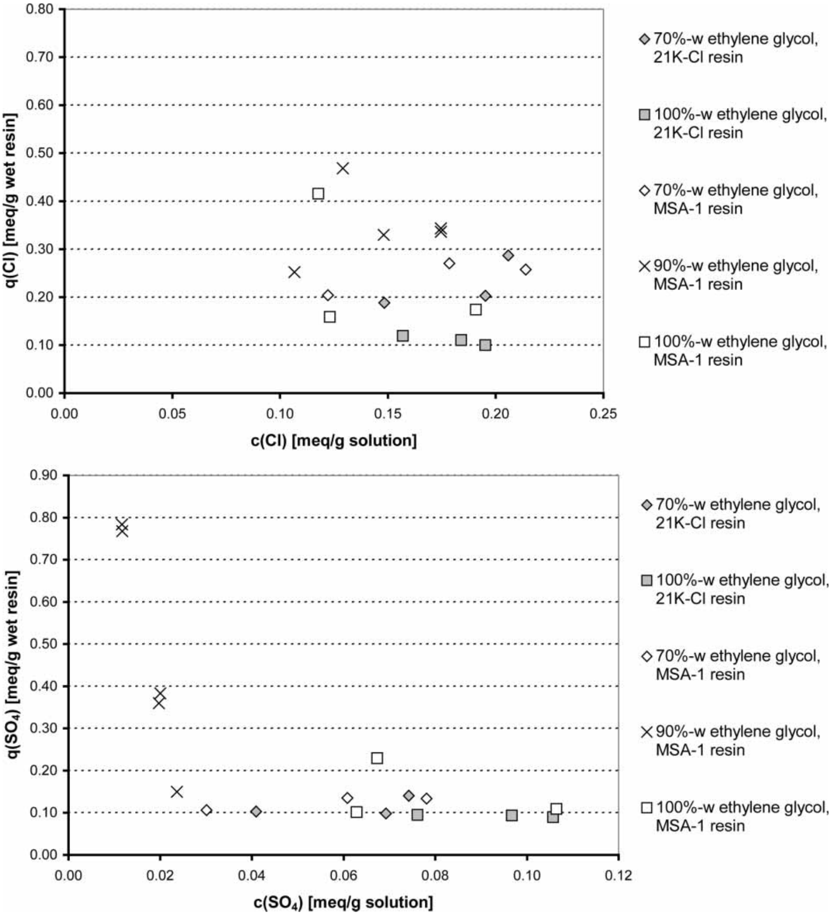

Figure 5. Resin loading q vs. bulk concentration c for chloride (above) and sulfate (below) for Dowex 21K-Cl and MSA-1 resin at 50°C in 70, 90, and 100%-w (salt-free solvent) ethylene glycol solutions saturated with trona.

loadings. This minimum in carbonate and bicarbonate loading of the resin coincides with the solubility minimum of bicarbonate in the mixed solvent solutions, see Gärtner et al. (7).

The distribution coefficient of sulfate and chloride did depend significantly on the ethylene glycol content of the solution, as can be seen in Fig. 6. Even though no distribution was measured for the Dowex 21K-Cl resin in 90%-w (salt-free solvent) ethylene glycol solution, the values in 70 and 100%-w ethylene glycol are identical enough to assume also a maximum in chloride and sulfate extraction at 90%-w ethylene glycol for Dowex 21K-Cl.

It should be noted for the peak at 90%-w ethylene glycol, that while the distribution coefficient of chloride remained rather low with maximally 3.6, the distribution coefficient for sulfate reached exceptionally high levels with a value of 65 to 70. This indicates, that the sulfate ions are almost driven out of the bulk solution into the resin.

Another noteworthy effect is the almost linear increase of the chloride and sulfate distribution coefficient with the respective chloride and sulfate loading; see Fig. 7, which is actually inverse of what was expected according to the Langmuir expression.

A similar behavior could be observed in the tests with 60 ppm chloride and 40 ppm sulfate at 25°C. The distribution coefficients of sulfate and chloride increased with increasing glycol content, see Fig. 8.

The development of the sulfate distribution coefficient in Fig. 8 matched the one in Fig. 6 quite well. While in 25°C and far lower sulfate initial concentration, the increase of the distribution coefficient with increasing glycol content was more gradual, in both cases the maximum distribution coefficient at 90%-w (salt-free solvent) glycol was in the range of 60 to 70. This illustrates that the influence of sulfate concentration on the distribution coefficient is

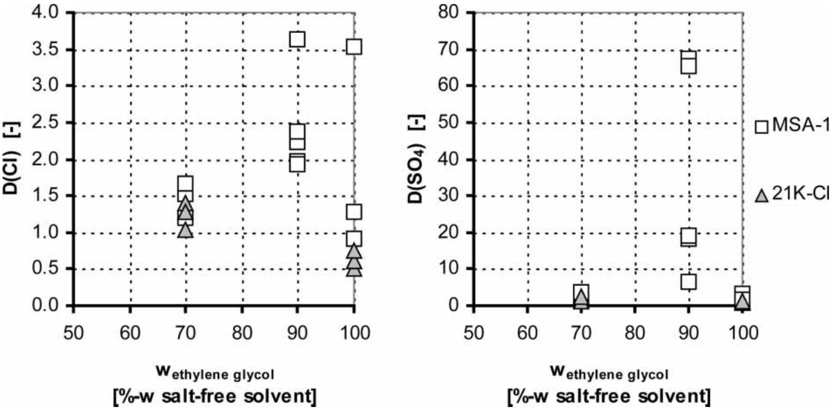

Figure 6. Dependence of the distribution coefficients for chloride and sulfate of Dowex 21K-Cl and MSA-1 resin on the ethylene glycol content for trona-saturated solutions for 50°C.

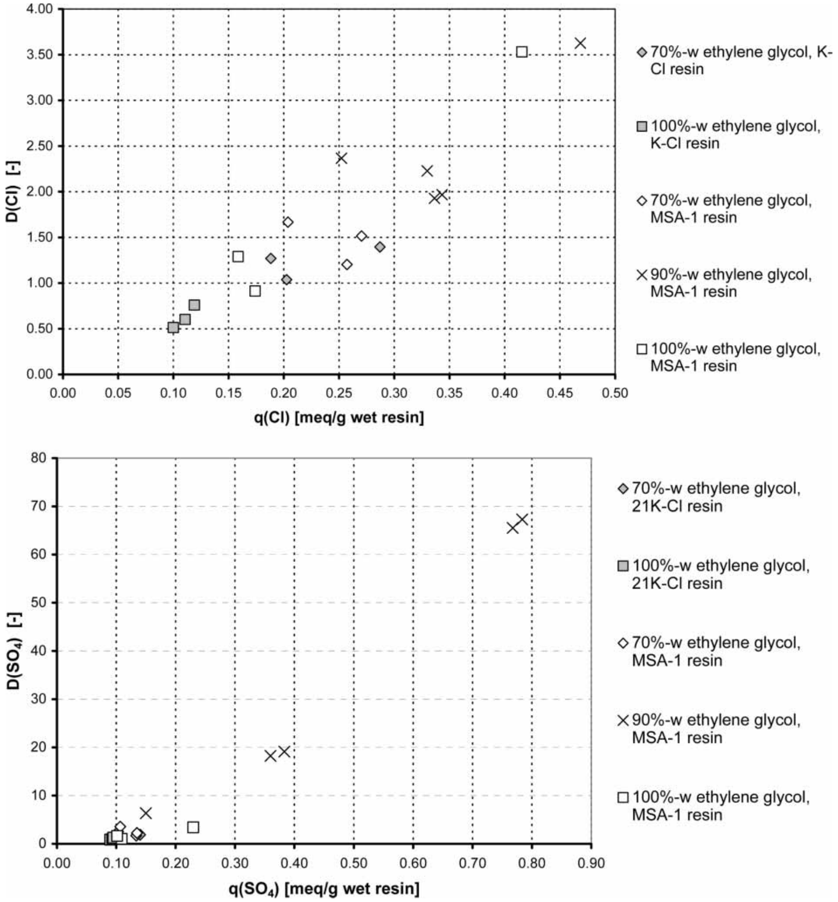

Figure 7. Distribution coefficient D_i vs. resin loading q_i of chloride (above) and sulfate (below) for Dowex 21K-Cl and MSA-1 resin at 50°C in 70, 90, and 100%-w (salt-free solvent) ethylene glycol solutions saturated with trona.

negligible compared to the influence of the glycol content *in saturated-trona solution.*

The development of the chloride distribution coefficient (at 25°C and low chloride concentration) in Fig. 8 differed significantly from the one observed in Fig. 6 at 50°C. Not only were the distribution coefficients at the lower temperature and concentration by more than factor of magnitude higher, i.e., 30 to 90 at 25°C compared to 1.0 to 3.6 at 50°C. Also the maximum distribution coefficient at 25°C was found at 70%-w (salt-free solvent) glycol, while at 50°C the maximum coincided with the one of sulfate at 90%-w (salt-free solvent) glycol.

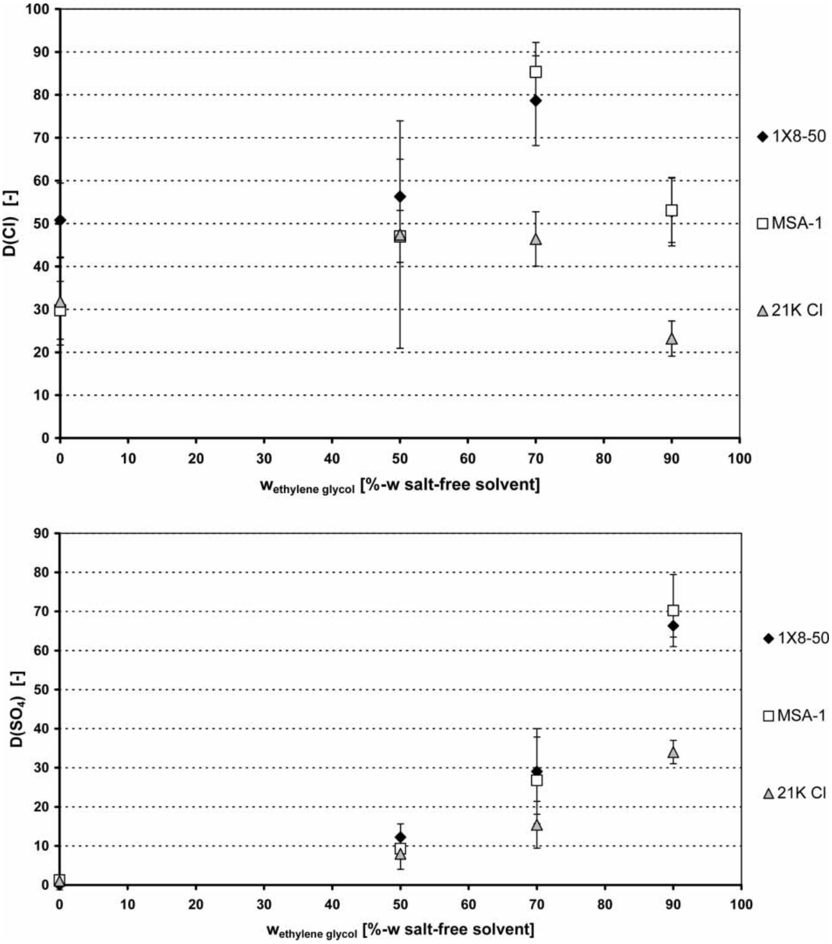

Figure 8. Dependence of the distribution coefficients for chloride and sulfate of Dowex 1X8-50, 21K-Cl, and MSA-1 resin on the ethylene glycol content for trona-saturated solutions at 25°C.

It can be noted from Figs. 6 and 8, that the distribution coefficients for Dowex MSA-1 and 1X8-50 were noticeably higher than the ones for Dowex 21K-Cl for both sulfate and chloride, indicating that the two first resins had a higher affinity for sulfate and chloride in the trona-saturated solution. Since this affinity was not noted for Dowex MSA-1 and 21K-Cl in trona-free solution (see Fig. 4), this suggests that Dowex 21K-Cl might have a higher affinity to carbonate/bicarbonate ions.

The linear relationship between the distribution coefficient D_i and the resin loading q_i of Fig. 7 was also found in the 25°C experiments with trona-saturated solutions; see Fig. 9. The surprisingly good fit between D_i

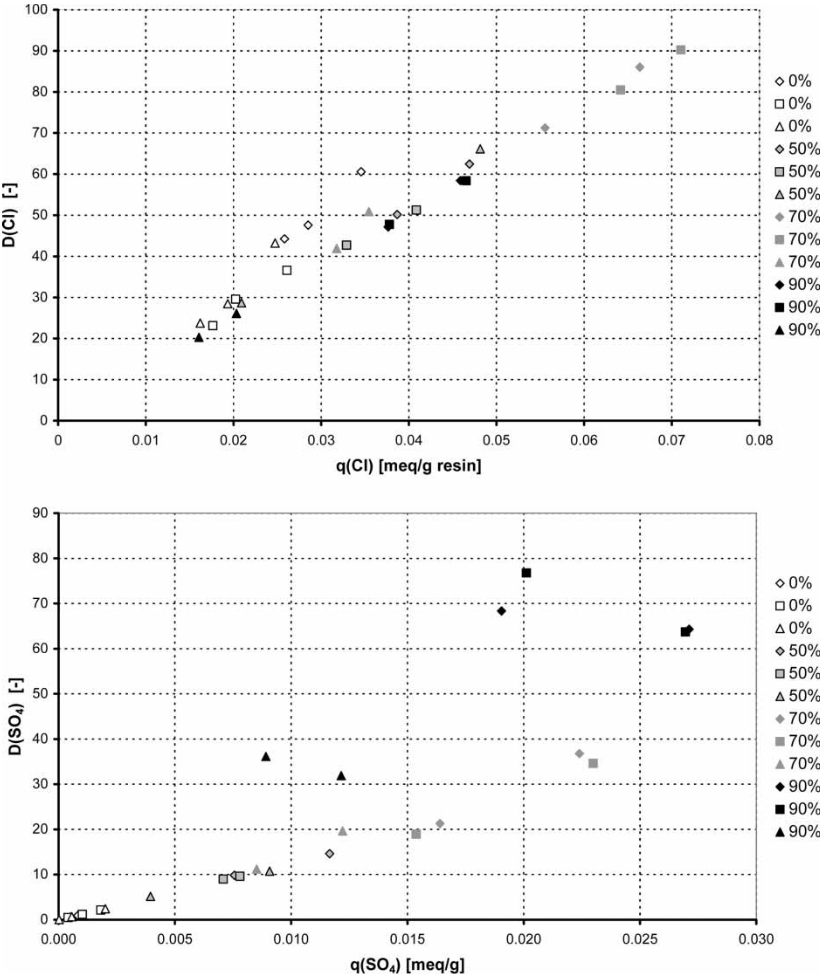

Figure 9. Apparent distribution coefficient D_i vs. resin loading q_i of chloride (above) and sulfate (below) for Dowex 1X8-50 (diamond symbols), MSA-1 (square symbols) and 21K-Cl (triangle symbols) resin at 25°C in 0, 50, 70, and 90%-w (salt-free solvent) ethylene glycol solutions saturated with trona.

and q_i can be explained by the mass balance, as the amount of solute Δn_i taken from the solution was simply added to the loading of the resin, resulting in the following relationship:

$$D_i = \frac{q_i}{c_i} = \frac{q_{i,1} + \Delta q_i}{c_{i,1} - \Delta c_i} = \frac{1}{c_{i,1} - \Delta q_i \cdot m_{\text{resin}}/m_{\text{solution}}} \cdot q_i$$

$$= \frac{1}{c_{i,1} - (q_i - q_{i,1}) \cdot m_{\text{resin}}/m_{\text{solution}}} \cdot q_i \tag{7}$$

Eq. (7) can be simplified into

$$D_i = \frac{\text{const.}}{\text{const.} - q_i} \cdot q_i \tag{8}$$

A slight hyperbolic tendency, as implied by Eq. (8), can be seen in the sulfate plot of Fig. 9 and is noticeable in the chloride plot of Fig. 7. This indicates, that the bulk solution concentration did not (directly) influence the distribution coefficient for the trona-saturated solutions. Therefore, the distribution in trona-saturated solutions can apparently not be described by a Langmuir fit or another sorption-isotherm expression (as in the experiments without trona).

The only parameter directly affecting the distribution coefficients in the trona-saturated mixed solvents was the ethylene glycol content: The driving force for the sulfate and chloride loading of the resin was apparently dominated by the effect of the glycol content on the activities of the different ionic species in solution. Chloride and sulfate were "salted out" of the bulk solution and "salted into" the more polar resin by the combined effect of the glycol and the high carbonate/bicarbonate concentration in the experiments with 90%-w ethylene glycol.

An explanation for the "salting out" effect is that polar but uncharged (or less charged) Na-Cl and Na-SO4 complexes formed in the apolar mixed solvent solution and distributed preferentially to the more polar ion exchanger pore solution, which provides better charge buffering. The "salting out" is in fact a partitioning effect between two liquid phases, the pore solution and the bulk solution—and not limited to specific sorption sites, i.e. the fixed charges. Therefore the Langmuir sorption model does not apply.

As can be seen from Figs. 6 and 8, the distribution coefficients were approximately constant for a given ethylene glycol content and the presented measured values can be used to extrapolate it for different ethylene glycol contents. For a different temperature, it appears most feasible to measure the distribution coefficient of interest, as—especially for chloride—the distributions coefficients vary significantly with temperature.

CONCLUSIONS

The mixed solvent alone did not strongly affect the chloride and sulfate loading of the ion exchangers. While the sulfate and chloride loadings slightly increased with increasing glycol content, the loading in trona-free solutions can still be described reliably by Langmuir isotherms, i.e., as functions of the bulk solution concentration.

In the trona-saturated mixed solvent solutions, on the other hand, the loading was no longer controlled by the chloride/sulfate concentration in the bulk solution, but rather by a "salting out" effect of the trona-saturated mixed solvent. The distribution coefficients between resin (pore solution) and bulk solution were here very strongly affected by the ethylene glycol content. Maximal extraction was achieved in solutions containing app. 90%-w (salt-free solvent) ethylene glycol.

Despite the strong effect of the high carbonate/bicarbonate concentration, satisfactory degrees of chloride and sulfate extraction could be achieved from the trona-saturated solutions. Especially the Dowex MSA-1 and 1X8-50 resins showed good affinities for chloride and sulfate.

The swelling of the resins in trona-saturated solutions was also significantly influenced by the glycol content and was found to drop from purely aqueous solutions till app. 50%-w (salt-free solvent) ethylene glycol, and to increase from there by app. the same amount till 90%-w (salt-free solvent) ethylene glycol.

The extraction of chloride and sulfate from mixed solvent solutions saturated with trona was found possible, but further tests are required to evaluate the influence of temperature and initial chloride and sulfate concentration on the degree of extraction.

For the application of ion exchange for the regeneration of mixed solvent in the Mixed Solvent Recrystallization and Mixed Solvent Reactive Recrystallization processes, not only economical methods for the resin regeneration have to be found, but also loading and regeneration tests with the mixed solvent solutions in actual ion exchange columns are required. From the obtained results, the biggest economical obstacle appears to be the co-extraction of carbonate/bicarbonate, which reduces the available exchange capacity of the resins for chloride and sulfate by up to 70%.

NOTATION

c_i	concentration of i in solution (meq/g solution)
$c_{i,1}$	initial concentration of i in the solution (meq/g solution)
D_i	distribution coefficient between pore and bulk solution (−)
k_i	Langmuir coefficient (g solution/meq)
q_0	total exchange capacity of the resin (meq/g wet resin)
q_i	loading of the resin with solute i (meq/g wet resin)
$q_{i,1}$	initial loading of the resin with i (after regeneration) (meq/g wet resin)
v_s	mass-based swelling of resin (%-weight dry resin)
w	weight fraction ethylene glycol in mixed solvent [%-weight (salt-free)]

Indices

i	solute i
j	solute j
resin	in the resin
solution	in the solution

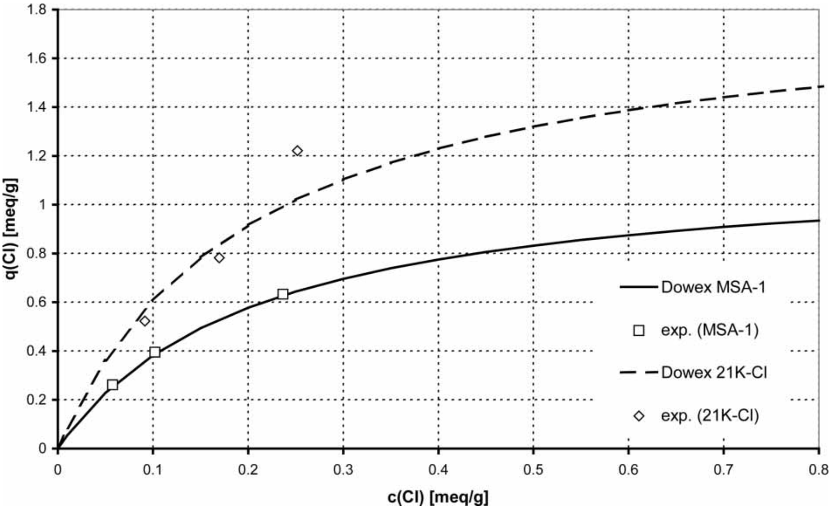

Figure 10. Langmuir fits for the chloride loading of Dowex 21K-Cl and Dowex MSA-1 and the experimentally observed points during stripping of the resins with 5M NaOH at 50°C.

ADDENDUM

For the stripping of the ion exchange resins in preparation for the experiments, it was tested, whether the distribution between resin and solution could be described by a Langmuir-expression according to Eq. (1). The total capacity of the wet resin was calculated from the dry capacity and the degree of swelling in the 5M NaOH used for chloride stripping. The total capacity q_0 of Dowex 21K-Cl was app. 1.86 meq/g wet resin and app. 1.17 meq/g wet resin for Dowex MSA-1.

The Langmuir-coefficient was fitted from the experimental data and was found to be ca. 4.8 g solution/meq chloride for both resins. The resulting fits are given in Fig. 10.

$$\frac{q(Cl)}{q_0} = \frac{4.8 \cdot c(Cl)}{1 + 4.8 \cdot c(Cl)} \tag{9}$$

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