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INTERPHASE MOBILITY AND MIGRATION OF HYDROPHOBIC ORGANIC METAL EXTRACTANT MOLECULES IN SOLVENT-IMPREGNATED RESINS

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ABSTRACT

Solvent-impregnated resins (SIRs) were made from polyvinyl pyridine and polyvinyl benzyl ammonium types of ionic polymers by impregnation of thiophosphoric acid type extractants. Morphological and nuclear magnetic resonance (NMR) studies were performed to observe the physical migration of the extractants under variation of two chemical factors: acidity and metal concentration. Morphological (surface area) measurements of the SIR-type polymer reveal surface area and pore-volume reduction upon metal-ion complexation and/or decreasing pH value. NMR measurements clearly show state variations of the

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extractant from a "solid" type state in the gel phase into a "liquid" state in the macropore phase. This phenomenon of migration of water-immiscible organic acids in response to pH changes of the external aqueous phase in SIRs, resembles a "smart" polymer in which large and sharp physical changes occur in response to a chemical stimulous. The discovery of the migration phenomena leads to a new unit operation definition, which is a hybrid between solid–liquid separation and liquid–liquid separation, and combines advantages of both technologies. SIRs can be used in remediation and other water treatment processes.

INTRODUCTION

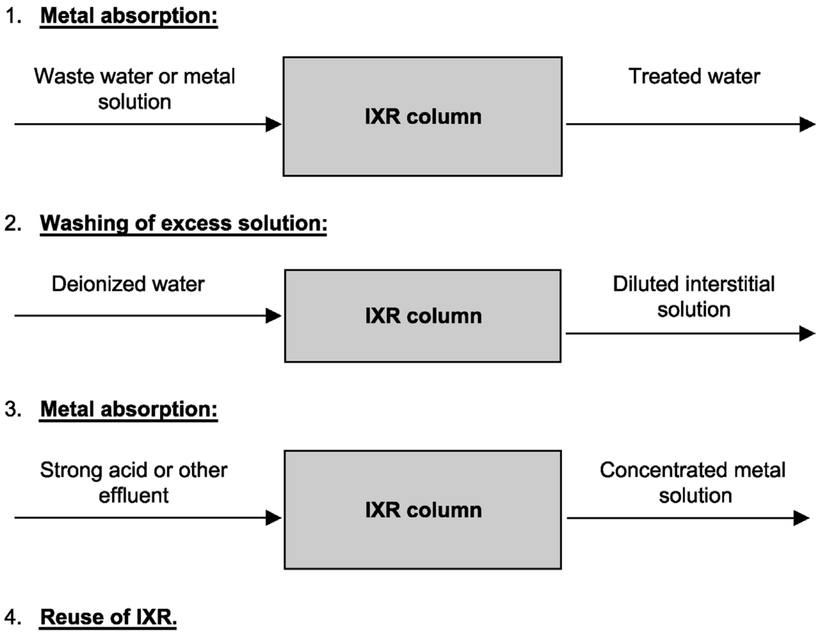
Excessive pollution of the earth's environment, air and water with heavy and transition metal ions is a serious threat to the inhabitants of this planet—plants, fish, animals, and humans. Synthetically engineered answers to this threat are metal binding molecules and macromolecules that can recognize and bind metal ions very specifically and strongly.

State-of-the-art methods include solvent extraction (SX) membranes (1), particularly liquid membranes (LM) (2–4), ion-exchange resins (IXR), and especially chelating ion-exchange resins (CIXR) (5,6). Solvent extraction and LM rely on a hydrophobic extractant immobilized in a liquid phase (SX) on polymeric porous membrane [supported liquid membranes (SLM)] (7). In CIXR, the ligand is fixed permanently. In SX, the chemical processes are fast and show good selectivity powers, since the process takes place on the interface between two liquid phases. In IX, the chemical processes are much slower and selectivity is usually lower. The advantage of IX is the simplicity of the solid–liquid separation processes. In CIXR, difficulties emanate from the high cost of chemical synthesis and low efficiency of metal regeneration from it.

Solvent-impregnated resins (SIRs) were conceptually designed to act as a bridge between SX, IXR, and particularly, CIXR, combining solid–liquid separation technology with liquid–liquid extraction chemistry (8).

Until now, the application of SIRs was adapted to the unit operation of IXR, namely, first step: metal absorption; second: washing of excess solution; and third: recovery of metal ions by elution with a strong acid or other effluent, as depicted in Sch. 1 (9).

It is possible to divide SIRs into two types: extractants immobilized on regular polymer support, and extractants immobilized on ionic supporting resins. Usually, extractants are loaded onto macroreticular resins consisting of two phases: microporous gel phase with pore sizes up to 20 Å, and a macroporous phase with a



Scheme 1. Unit operation of IXR.

pore size of $10^3 - 10^4$ Å (10,11). The volumetric concentration of the ionic groups is therefore, much higher in the micropores than in the macropores (9).

In recent studies of the second type SIR, we discovered that the organic hydrophobic extractant migrates in a reversible fashion between the highly ionic microporous gel phase and the highly hydrophobic macroporous phase.

We will first describe the migration phenomenon and then the resulting conclusion and proposal for a new unit process, particularly suitable for SIR type II.

EXPERIMENTAL

Resins

Three types of macroreticular anion-exchange resins were used in this study: divinylbenzene (DVB)-crosslinked polyvinylpyridine (PVP) resins described as Reillex (Reily Chemicals S.A., Hautrage, Belgium), DVB-crosslinked polystyrene resins bearing strongly basic di-methyl-ethyl-ammonium groups (Lewatit MP600 Bayer A.G., Leverkusen, Germany), and DVB-crosslinked polystyrene resins bearing weekly basic tertiary amine groups (Lewatit MP62, Bayer A.G., Leverkusen, Germany). Their properties are summarized in Table 1, and defined designation of the resins are also used further in the text. The designations, PVP and LEW describe the resin type.

Extractants

The hydrophobic extractants di-(2-ethylhexyl)-thiophosphoric acid (D2EHTPA) obtained from Bayer A. G., Germany ^{31}P NMR: $\delta(CDCl_3) = 63.5$ (1P,s) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA) from BDH, Poole, UK, (A.R.) were used as water-immiscible organic acids for the impregnation of the anion-exchange resins. Solvent-impregnated resins were prepared according to methods described later.

Impregnation was performed by suspending a weighed amount of the resin (about 1 g) in a known amount of acetonitrile (5–6 g), containing various concentrations of the ligands. In our previous work, acetonitrile was found to be superior for this purpose to other alternative solvents, such as tetrahydrofuran (THF) (12). The polymer and solution were maintained at laboratory temperature with occasional stirring in a closed bottle for 12 hr. In separate parallel experiments, it was determined that this time is more than sufficient to achieve equilibrium. The residual equilibrium concentration of the extractant in the solution above the resin was determined in aliquot samples by titration, and/or by gravimetrically weighing the extractant residuum after evaporation of the solvent. The amount of the extractant supported on the resin was then determined from the material balance. The samples of the extractant-impregnated resins were drained on a glass frit and washed thoroughly with distilled water.

Measurements of Surface Area and Porosity

The surface area of the resins, both before and after impregnation, was determined after drying overnight at 110°C by nitrogen adsorption, using the Nelson–Eggertsen method (13), determining the nitrogen adsorption from changes of nitrogen concentration in the stream of mixture of nitrogen and a nonadsorbing gas over the sample. Evacuation of the sample container is not required and hence this method can be used for characterization of materials containing a liquid component.

Porosity of the resins was determined by inverse steric exclusion chromatography (ISEC) and by mercury porosimetry. The ISEC measurements were performed according to the procedure described in Ref. (14). For mercury porosimetry, the computer-operated apparatus AutoPore 9200 (Micromeritics, Norcross, GA, USA) was used.

Table 1. Resin Description and Properties

Designation	Basicity	Ion Exchange Capacity (meq/g)	N Content by Elemental Analysis (meq/g)	Dry State Surface Area (m^2/g)	Swollen State Pore Volume (cm^3/g)	Divinylbenzene Content (mol %)	Trade Mark
PVP-M	Weak	5.2	6.0	76	0.872	25[a]	Reillex™ HP
LEW-Mw	Weak	5.2	5.5	14	0.270	n.s.	Lewatit MP62
LEW-Ms	Strong	4.0	4.1	23	0.428	n.s.	Lewatit MP600

[a] Information was supplied by manufacturer.

NMR Measurements

Two different measurements were made: cross-polarization magic angle spinning (CPMAS) mode on Bruker 200 spectrometer, and single-pulse sequence technique on Bruker AMX 250 (Bruker, Billerica, MA, USA) as presented in Ref. (15).

RESULTS AND DISCUSSION

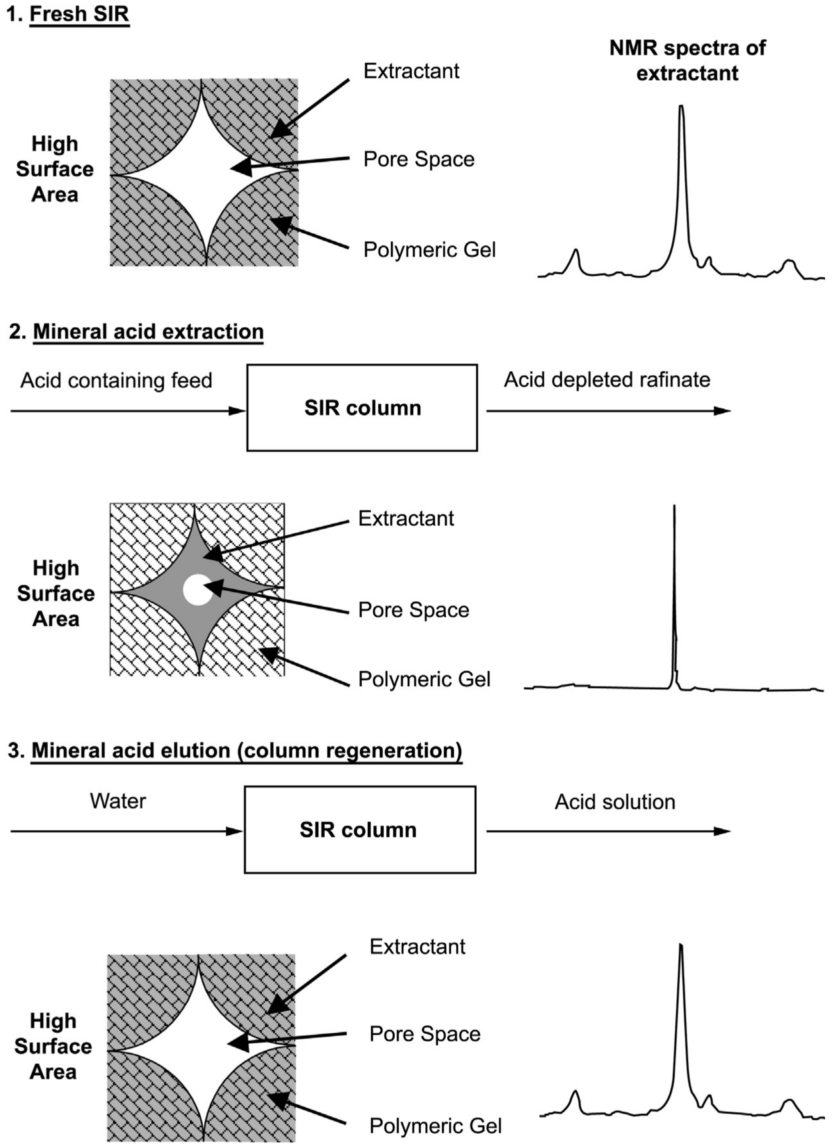
We observed the reversible migration of fatty water-immiscible organic acids between the gel (microporous) phase of macroreticular IXR and the macroporous phase of the resin upon variation of the pH in the external aqueous phase and the metal-ion concentration. The phenomenon was observed by morphological studies, namely, surface area and pore-volume measurements, and by solid and liquid state nuclear magnetic resonance (NMR).

The migration phenomena under pH-changes in the SIR type II polymers is described in Sch. 2. The acidic feed solution containing mineral acid ions is fed through an SIR column. This forces accumulation of the organic extractant in the macropores (step 2), and the gel phase becomes extractant-deficient. In step 3, the water rinse of the SIR column forces the mineral acid out of the resin pores with concurrent migration of the extractant from the macropores to the inner gel phase rendering the macropores free of the extractant. In the case of creation of metal–extractant complex, the extractant is not bound to the functional groups of the resin anymore, but creates its own phase in the macropores (Sch. 3).

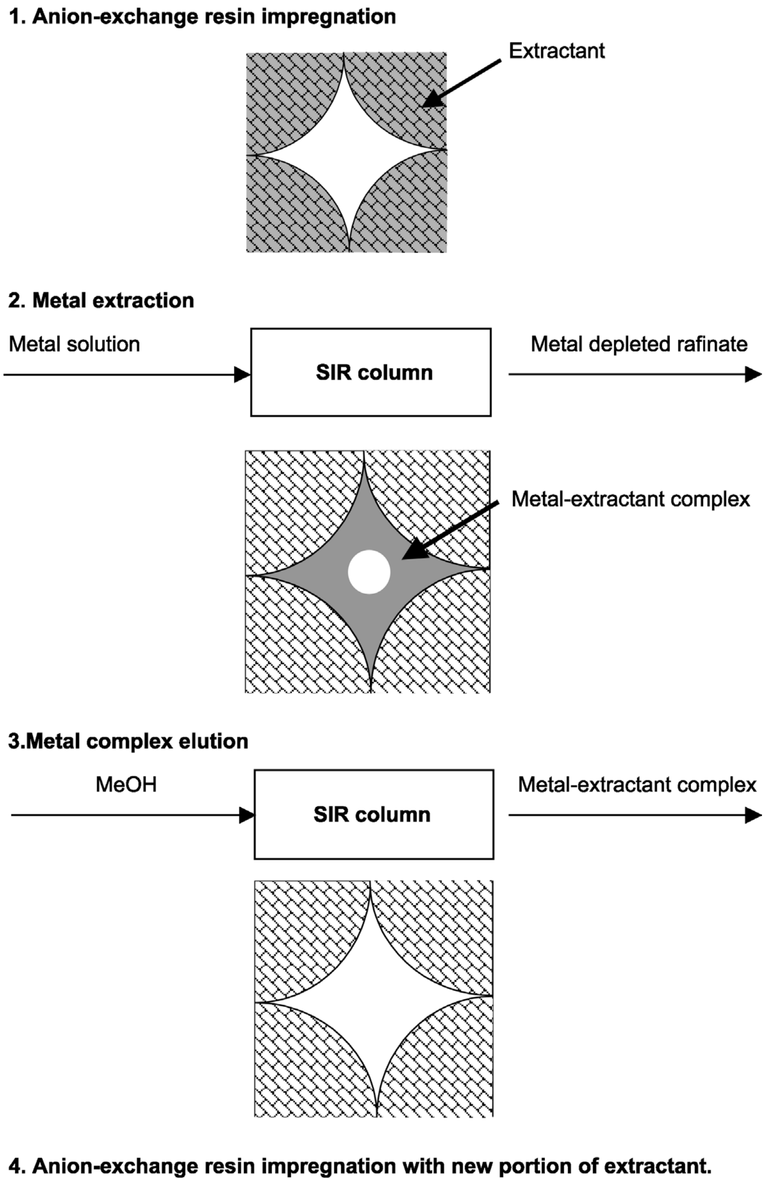
Morphological Study

The results of specific surface area measurements dependence on the pH are presented in Table 2. The experiments were performed in columns. Phosphorous elemental analysis of the polymer samples before and after treatments with acid solutions showed that polymer loading can be kept at an almost constant level (Table 3).

In the preparation of the SIRs, the extractant concentration was carefully controlled so that the extractant volume in the resin pores matches, as close as possible, the swollen state resin pore volume as measured by ISEC (Table 1). The volume of macropores for LEW-Mw is 0.270 cm^3/g and for LEW-Ms 0.428 cm^3/g. Since the columns are not overloaded with the extractant, i.e., the extractant volume is equal but not higher than the pore volume, the specific surface area changes may be attributed to the extractant migration between the resin macropores and the resin gel phase. When the SIR polymer is treated with a



Scheme 2. Description of the migration phenomena under pH change in SIR resins.



Scheme 3. Description of the migration due to variation in metal concentration and a new unit operation recommended for water remediation.

Table 2. Specific Surface Area, m^2/g of the Solvent-Impregnated Resin Type Polymers Used in the Solid State ^{31}P NMR Experiments. The High Difference Between Values of Water Washed and Fresh Surface Areas of SIR on LEW-Mw Support Are Explained by Incomplete Collapse of the Morphology of Nonrigid Resin During Drying

			Consequent SIR Treatments		
Resin	Extractant	Fresh Solvent-Impregnated Resin	1st HCl 2 *M* Wash	Water Wash	2nd HCl 2 *M* Wash
LEW-Mw	D2EHPA	10.7	4.1	23.6	4.3
LEW-Ms	D2EHPA	20.4	7.5	21.4	4.7
PVP-M	D2EHDTPA	45.8	21.0	40.5	not measured
LEW-Ms	D2EHTPA	21.1	3.8	22.8	3.9

strong mineral acid solution, the extractant (a weaker organic acid) is displaced and excluded from the polymeric gel phase into the pore space; this phenomena is expressed by the drop in the specific surface area of the SIR samples. Then, extensive water wash shifts the equilibrium to the left and the mineral acid is washed out from the resin. The water-immiscible organic acid forms a salt with the polymeric base group and reenters the polymer gel phase, increasing the specific surface area back to the values measured for fresh SIRs. Upon subsequent HCl treatment, the extractant is again expelled into the pore space and the surface area diminishes. This process may be repeated several times.

The equilibrium process can be described in the following equilibrium Eq. (1):

$$-\mathrm{NR_2H^+L^-_{res,gel}} + \mathrm{H^+_{aq}} + \mathrm{H^-_{aq}} \rightarrow -\mathrm{NR_2H^+X^-_{res,gel}} + \mathrm{HL_{res,pore}}, \qquad (1)$$

where $-NR_2$ is a polymeric amine site, HL is water-immiscible organic acid, and X is a mineral acid anion.

Table 3. Extractant Loading on Polymer Support, g Extractant/g Support, as Determined by Phosphorus Elemental Analysis

			Consequent SIR Treatments		
Resin	Extractant	Fresh Solvent-Impregnated Resin	1st HCl 2 *M* Wash	Water Wash	2nd HCl 2 *M* Wash
LEW-Mw	D2EHPA	0.21	0.20	0.20	0.21
LEW-Ms	D2EHPA	0.39	0.31	0.28	0.29
LEW-Ms	D2EHTPA	0.43	0.39	0.40	0.39

Specific surface area measurements of a series of SIRs of varying loadings of metals (copper, nickel, and lead) are shown in Fig. 1. The "packing" of the resin pore structure with metal-dithiophosphoric complex (in this case, any of the three studied metals having similar behavior) caused a remarkable decrease in the specific surface area. Increasing the amount of sorbed metal ion causes an exclusion of the extractant from the gel phase and migration into the free pore space. The pore volume of PVP-M resin is sufficiently high to accommodate the entire excluded metal–extractant complex. In one case, that of LEW-Mw, we have even observed (at the highest levels of metal uptake) an appearance of liquid droplets of the extractant outside the resin beads and the specific surface area reached practically zero. LEW-Mw—a macroreticular resin showing a relatively substantial difference in the morphology of the dry and swollen state, imbibes higher volumes of the extractant than does PVP-M. The surface area of the original LEW-Mw support is only 7.0 m^2/g while the surface area of the SIR loaded with 0.649 g D2EHDTPA/g SIR is 20 m^2/g. The pore volume of this resin is so small (0.3 mL/g of the dry resin in a water-swollen state). Hence, it is not surprising that this resin cannot accommodate the entire metal–extractant complex in its inner volume, and the extractant is forced to exit.

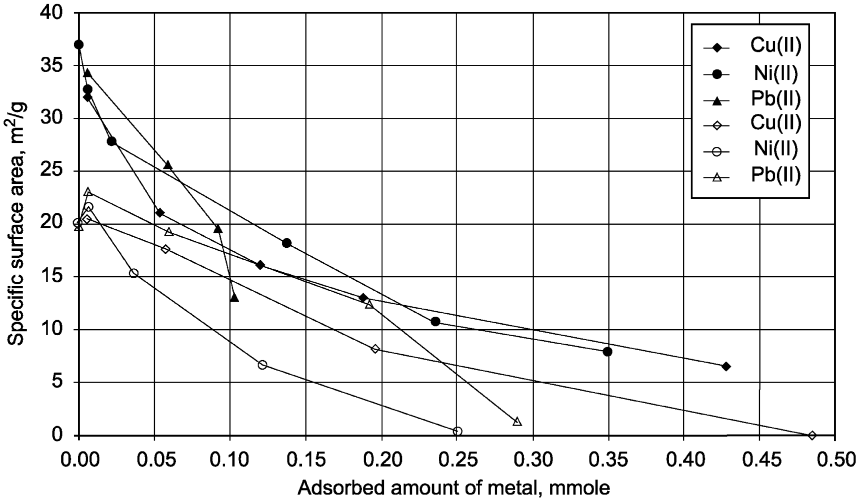


Figure 1. PVP-M based SIR (filled symbols) and LEW-Mw based SIR (open symbols) surface area dependence on adsorbed amount of metal. SIR loadings 0.35 g/g of SIR and 0.45 g/g of SIR, respectively.

The results obtained so far show that the extraction of metals by PVP-M–D2EHDTPA SIR leads to the following process: Eq. (2).

$$2(-NR_2H^+L^-_{res,gel}) + MeX_{2aq} \rightarrow 2(-NR_2H^+X^-_{res,gel}) + MeL_{2\,res,pore}, \qquad (2)$$

where X is anion of metal salt and $-NR_2$ is a polymeric amine site.

Two experimental facts point out to this metal extraction mechanism: (1) D2EHDTPA exclusion from the resin–gel phase as a result of amine–D2EHDTPA complex decomposition. This contention is supported by the dramatic decrease in the SIR's specific surface area upon an increase in metal binding. (2) The fourier transform infrared spectra (FTIR) of SIRs, following elution of the metal complexes, show the presence of absorption bands pertaining to protonated pyridine groups in the absence of D2EHDTPA characteristic peaks.

The same process of metal–D2EHDTPA complex transfer from polymer gel into pore volume is observed in SIRs prepared from weak base (LEW-Mw) or strong base anion-exchange resins.

NMR Study

A more direct, method is ^{31}P MAS solid-state NMR. The extractant migration from the polymeric gel to the polymer pore space and back may be followed using the difference in the chemical shifts in the ^{31}P solid-state NMR spectra of the extractant molecule inside the SIR resin. In the gel phase, the extractant is chemically associated with the polymeric amine groups while in the macropores, the extractant exists as a "liquid" occupying the pore volume. The acidic extractant, forming a salt with the polymeric amine group in the polymer gel phase, is part of the solid polymeric matrix, so that the corresponding phosphorous peak must be accompanied by sidebands and has a quite substantial line width, HHFW (half height full width, ca. 500 Hz, "solid" type peak). The solid type peak is shifted slightly to strong field, similar to the peaks of salts. On the other hand, the liquid extractant in the macropores shows a narrow peak without sidebands (liquid type peak).

The results of solid state ^{31}P NMR measurements of the LEW-Ms impregnated with D2EHPA are shown in Fig. 2.

Two different measurements were made: CPMAS mode [presented in Fig. 2(a)], and single-pulse sequence technique presented in Fig. 2(b). Figure 2(a) (1) shows the spectrum of a fresh SIR polymer sample recorded directly after impregnation. Figure 2(a) (2) shows the same sample after treatment with 2 *M* of HCl acid solution and Fig. 2(a) (3) shows the sample after washing with water. The ^{31}P signal in Fig. 2(a) (2) is clearly a superposition of two peaks of different origin. One is a solid type peak and the other a liquid type peak. So, evidently, a portion of the extractant migrated from the gel phase into the pore space after the HCl washing step. As cross-polarization suppresses the signal intensity from the liquid extractant, the ratio of solid and liquid peaks in the spectrum does not correspond to the real ratio of the extractant concentrations in the gel and in the macroporous phases. Indeed, the single-pulse excitation experiment with a

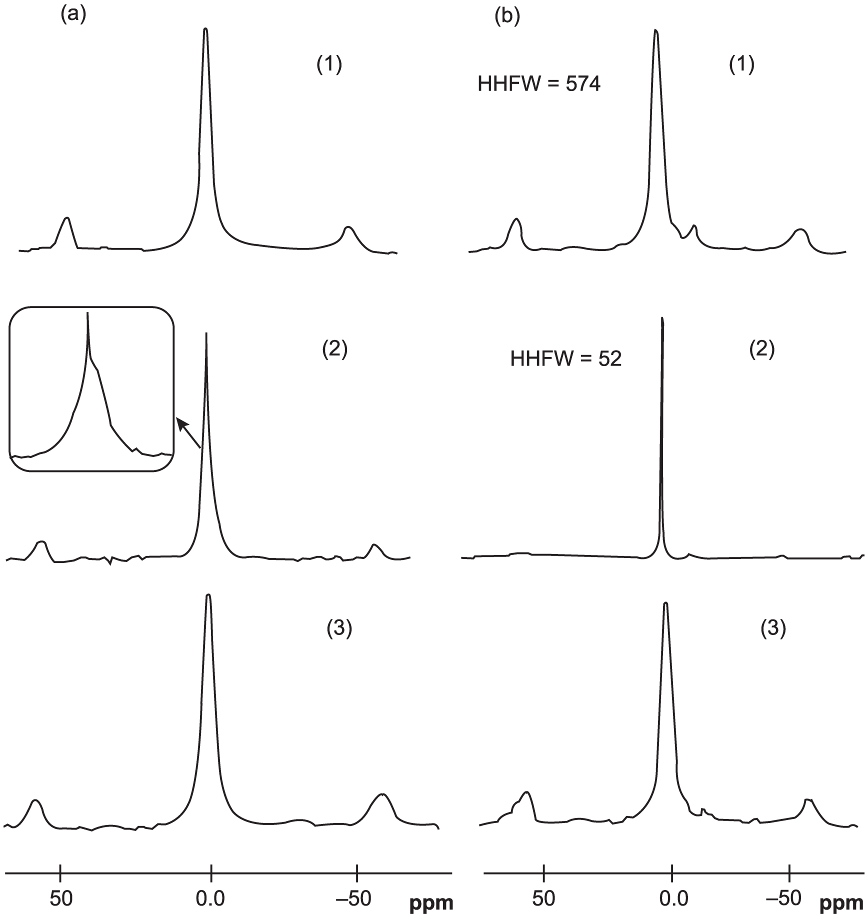


Figure 2. ^{31}P MAS solid state NMR spectra of the SIRs composed of D2EHPA and LEW-Ms as polymeric support recorded in (a) cross-polarization mode; (b) single pulse sequence technique.

30 sec repetition time [Fig. 2(b) (2)] shows the presence of a liquid peak only. The single pulse method can provide the real solid–liquid extractant ratio if the lattice relaxation time (T_1) for solid extractant molecules is much shorter than the time span between two successive excitation pulses. The T_1 was measured using the inversion recovery method and was found to be 8.9 sec for the D2EHPA–polymeric amine complex and 5.3 sec for the D2EHTPA–polymeric amine complex. Therefore, the amount of solid extractant (in the gel phase) in the resin sample after HCl washing is very small. Examination of the sample after treatment with water by single-pulse excitation gives one solid peak spectrum, excluding the presence of liquid extractant in the polymeric pores.

Similar experiments were performed with LEW-Mw and LEW-Ms based resins containing D2EHTPA. Freshly prepared SIR of LEW-Ms has solid ^{31}P peak at 61.3 ppm on CPMAS spectrum. After a treatment with 2 *M* HCl, only one liquid peak at 65.7 ppm appeared on the CPMAS spectrum, and at 63.2 ppm, on single-pulse spectrum. The CPMAS spectrum made after water treatment shows solid type peak that is shifted back to 61.3 ppm. The SIR prepared from LEW-Mw showed the same behavior. Freshly prepared SIR has solid ^{31}P peak at 60.3 ppm on CPMAS spectrum. After a treatment with 2 *M* HCl, only one liquid peak at 66.9 ppm appeared on the CPMAS spectrum, and at 64.6 ppm, on single-pulse spectrum. The CPMAS spectrum made after water treatment shows solid type peak that is shifted back to 60.3 ppm.

Therefore, transformations of the phosphorous peak from solid to liquid and again to solid, following the change of the aqueous pH solutions, appear in all the spectra of all those SIR polymer samples.

Distribution Constant

The expression of a distribution constant for both (change in acidity and metal complexing) processes can be evaluated under the following simple assumptions:

1. simple ion exchange as described in Eqs. (1) and (2),
2. aggregation of an extractant or its metal complex into a separate phase due to their extremely low solubility in water.

Therefore, the distribution constant at equilibrium is defined as:

$$K_\mathrm{d} = \frac{[\mathrm{LH}_\mathrm{loaded}] - [L^-_\mathrm{gel}]}{[L^-_\mathrm{gel}]}, \tag{3}$$

where $[L^-_\mathrm{gel}]$ is the concentration of the extractant that remained in the gel phase after the reaction reached its equilibrium. The value of the distribution constant depends on the initial extractant loading, initial concentration of mineral acid or metal, and on the resin morphology and capacity. The exact dependence is under further research.

CONCLUSIONS

The newly discovered interesting phenomenon of migration of water-immiscible organic acids inside solid IXRs (type II SIRs) in response to pH and metal concentration variations in the external solution, shows SIRs that resemble "intelligent" polymers (16,17) in which large and sharp physical changes occur in response to some chemical stimuli. The discovery of the migration phenomena leads to a new unit operation definition which is a hybrid between solid–liquid separation and liquid–liquid separation, and combines advantages of both technologies, such as easy handling of solid phase with the high selectivity of small molecular organic extractants. We have shown that SIRs may be used in the treatment of very dilute metal solutions such as in groundwater remediation and other water treatment processes (M. Vilensky Ph.D. thesis work in preparation). The novel unit operation is described in Sch. 3.

We have noticed that pH and metal concentration changes cause considerable variation in the distribution constant of the extractant and its metal complex between the gel and macropore resin phases. Those variations may be correlated to the morphological properties of the polymeric support. More accurate work is underway.

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