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CHLORIDE SULPHATE EXCHANGE ON ANION RESINS. KINETIC INVESTIGATIONS. III EXCHANGE RATES IN DILUTED SYSTEMS

As a continuation of a basic investigation related to the sea water desulphation process, the dependence of the $Cl^-/SO_4^=$ exchange rates of different anion resins on their main physico-chemical properties is investigated at low solution concentration, where ion diffusion through the liquid film is expected to be the rate determining step. As in previous investigations, the selectivity of the resins results to unfavourable effect on the exchange rates. Other important parameters appear to be the water content, the equivalent ratio and the stirring rate. These results agree with thermodynamic expectations and support the selection of a weak anion resin, with predominantly II^{ary} amino-type functional groups, as the best suited for the desulphation process.

1. INTRODUCTION

A basic investigation on the desulphation process [1], where sulphates are removed from sea water by means of a chloride form weak anion resin to prevent the formation of $CaSO_4$ scales in evaporation plants, has been carried out with special regard to the equilibrium and the kinetic aspects of the chloride/sulphate exchange on anion resins. The equilibrium measurements clearly demonstrated that a fundamental role in determining resin's affinity is played by the nature of the fixed charges of the resins, according to the "selectivity sequence" toward sulphates [2].

$$\text{quaternary} < \text{tertiary} < \text{secondary} < \text{primary amino-group resins} \tag{1}$$

Further investigations on the $Cl^-/SO_4^=$ exchange rate dependence on the main physico-chemical properties of the resins, in conditions where ion diffusion through the resin particles is the rate controlling step, again indicated a strong influence of the nature of the fixed charges of the resins [8]. In these conditions, however, an exactly opposite "kinetic sequence", as compared to (1), was obtained, strongly supporting a direct, unfavourable

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correlation between selectivity and kinetics in ion exchange processes. In this paper the rate determinations are extended to very low solution concentration (6×10^{-3}N), and the validity of the previous indications about the different resin parameters is investigated.

2. EXPERIMENTAL

The same apparatus previously described [3] has been employed, using the infinite batch-stirrer reactor technique. Few milligrams of resin, previously converted in chloride form by a 6.0×10^{-3}N mixed HCl/NaCl solution with a pH of 3.0, were added in each experiment to 0.8 dm³ of 6.0×10^{-3}N mixed Na_2SO_4/H_2SO_4 solution with the same pH. The chloride release was followed potentiometrically by chloride-selective electrodes and, by suitable "dynamically" determined reference curves, the Cl^- concentration variation with time recorded. For each resin, fraction of 16/18, 20/30 and 30/35 mesh were collected by liquid sieving with the same chloride solution used in resin conditioning, and the mesh size assumed as the average radius of each wet resin fraction, r_0.

After washing with pentane, the conditioned resins were brought to constant weight in a vacuum oven. The broken particles were then removed by rolling on a sloping plane. Before each experiment the dry weighed resin was allowed to re-hydrate standing all night in a 98% humidity box.

The exchange temperature was closely controlled to ±0.1°C. As usual, the exchange rates are expressed by the fractional attainement of equilibrium, $U = [Cl^-]_t/[Cl^-]_\infty$ where the amount of chlorides exchanged after an infinite time was calculated in each experiment by nomograms based on the equilibrium isotherms experimentally determined for each resin. As exemplified in fig. 1, using 0.3 g of dry resin/dm³ of solution, the 96.5% of the chlorides initially present in the resin will move to the solution at equilibrium. Knowing
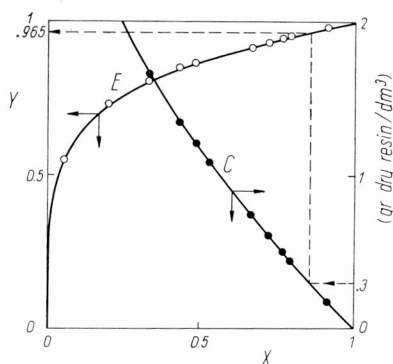

Fig. 1. Nomogram for determination of equilibrium conditions

E— equilibrium curve, C— correlation curve. (Resin Amberlite IRA 93; 30/35 mesh; X— sulphate equivalent fraction in solution. Y — sulphate equivalent fraction in resin, at equilibrium; $6 \cdot 10^{-3}$N)

Rys. 1. Nomogram do określania warunków równowagi

E — krzywa równowagi, C — krzywa korelacji, (żywica Amberlite IRA 93; numer sita 30/35; X — równoważnikowa frakcja siarcza-nu w roztworze, Y — równoważnikowa frakcja siarczanu w żywicy w stanie równowagi $6 \cdot 10^{-3}$N)

the full exchange capacity of each mesh fraction of the resin, the calculation of U becomes an obvious tool.

As in previous investigations, the "infinite solution volume" condition, (i.e., negligible concentration in solution of the exchanged ion throughout the reaction, to prevent its appreciable back-diffusion) was also met in these experiments.

By reference to the "equivalent ratio", w, between the amount of exchangeable ions in the resin and the counter-ions in solution, the ISV condition is usually assumed for $w = 0.02$ eq$_r$/eq, according to TETENBAUM [10].

In a typical test, using 0.010 g of resin with full exchange capacity of 3.8 meq Cl/g dry resin and 0.8 dm^3 of 6.0×10^{-3} N sulphate solution, it resulted $w = 0.01 \times 3.8/0.8 \times 6 = 0.008$ meq$_r$/meq. Very small quantities of resin were necessary at this salinity to meet the ISV condition.
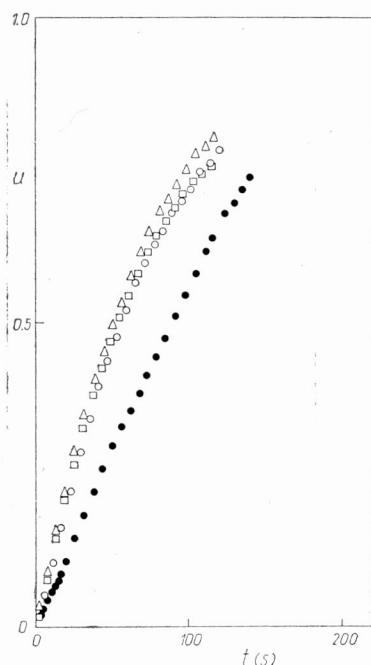

Fig. 2. Typical exchange kinetics

Rys. 2. Typowa kinetyka wymiany

Consequently, the reactor geometry had to be varied, in order to properly accomodate the sample amounts used in each test. Either the complete filling of the early described reactor with the resin mixed with equal mesh size glass beads (or with strong cation resin in sodium form), or the reduction of the reactor chamber proved satisfactory.

Unless otherwise specified, standard experiments were made at 25°C $w \simeq 0.008$ meq$_r$/ meq, stirring rate of 3000 rpm and reactor with internal chamber diameter of 5 mm. Even with this reduced geometry the superiority of the stirrer reactor technique over the simple batch procedure clearly appears from fig. 2.

The water content of the resins was evaluated by the centrifugation method [6], from the curves obtained by plotting the apparent water content of the sample versus the square of the speed of rotation of the centrifuge.

3. RESULTS AND DISCUSSION

At very low solution concentrations, the exchange rates appear to be extremely sensitive to the experimental conditions, particularly to the equivalent ratio and the stirrer-reactor speed. From the data in fig. 3 it can be seen that a linear increase of the exchange half
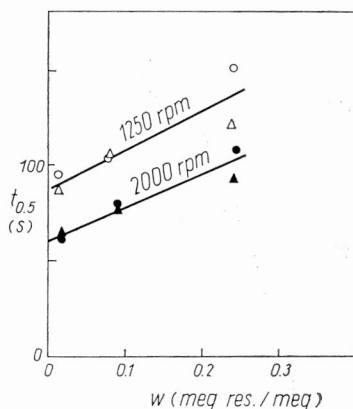

Fig. 3. Equivalent ratio influence on the exchange rates. (Resin Kastel A 500; 30/35 mesh)
Rys. 3. Wpływ równoważnikowego składu mieszaniny na szybkość wymiany (Żywica Kastel A 500; numer sita 30/35)

times with w occurs, quite independently of the stirring rate of the reactor. Proper amounts of samples had thus to be picked, according to resin exchange capacities, to have approximately the same w value in all the experiments, in order to meet the not-reversible exchange condition and to ensure the required reproducibility to the tests.

The stirring speed has an intuitive influence on the exchange rates, as it contributes the (ideal) liquid film surrounding the resin bed to reach its limiting thickness. As indicated in fig. 4, a speed of 3000 rpm could be satisfactorily used for that purpose. Higher speeds, which could probably produce a closer approach to the minimum film thickness, were unpracticable, due to excessive vibrations of the apparatus.

Table 1 lists the main physico-chemical characteristics of all the investigated resins. In table 2 there are reported the exchange half times and the corresponding (apparent) interdiffussion coefficients, $D_{0.5}$. The latter are calculated by the well known rate equation
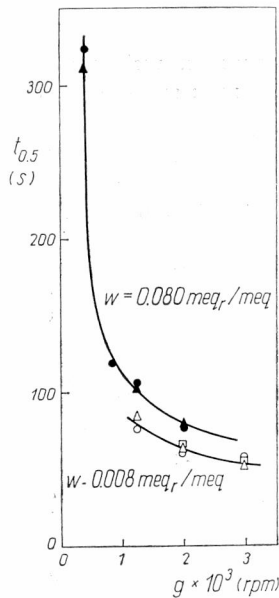
Fig. 4. Stirring rate influence on the exchange rates. (Resin Kastel A 500; 30/35 mesh)

Rys. 4. Wpływ szybkości mieszania na szybkość wymiany (Żywica Kastel A 500; numer sita 20/35)

Table 1

Main physico-chemical properties of the investigated resins. (NaCl/HCl 6×10^{-3}N; pH $= 3.0$; $25°$C)

Resin	Predominant functional group	Matrix	Porosity	Exchange capacity (eq/Kg dry resin)		
				16/18 mesh	20/30 mesh	30/35 mesh
Kastel A 500	IV^{ary} (type 1)	Styrenic	gel	3.05	3.22	3.48
Lewatit M 500	IV^{ary} ,,	,,	,,		3.68	
Amberlite IRA 400	IV^{ary} ,,	,,	,,		3.50	
Kastel A 300	IV^{ary} (type II)	,,	,,		3.14	
Lewatit M 600	IV^{ary} ,,	,,	,,		3.02	
Relite 2 A	IV^{ary} ,,	,,	,,		3.31	
Kastel A 101	III^{ary} ,,	,,	,,		3.76	
Amberlite IRA 93	III^{ary} ,,	,,	macroreticular	3.77	3.80	2.98
Relite A MS	III^{ary} ,,	,,	gel		3.81	
Lewatit MP 60	III^{ary} ,,	,,	macroporous		3.91	
Amberlite IRA 68	III^{ary} ,,	Acrylic	gel		4.23	
Kastel A 105	III^{ary} ,,	,,	,,	4.78	4.96	3.79
Lewatit Ca 9222	III^{ary} ,,	,,	,,	4.26	4.26	
Wofatit AK 40	II^{ary} ,,	Styrenic	macroporous	4.82	4.80	4.20
Kastel A 102	II^{ary} ,,	Acrylic	gel	5.98	5.98	5.98
Relite MG-1	II^{ary} ,,	,,	,,		5.82	
Duolite A 366	II^{ary} ,,	,,	,,		6.46	
Duolite S 2002	I^{ary} ,,	Styrenic	porous		33.13	

Table 2

Kinetic data for the $Cl^-/SO_4^=$ exchange on various anion resins. (6.0×10^{-3}N; pH 3.0; 25.0°C; 3000 rpm; $w = 0.008$ meq$_r$/meq)

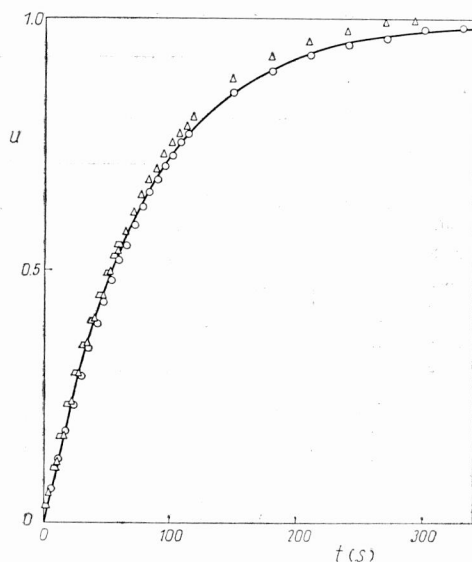| Resin	16/18 mesh		20/30 mesh		30/35 mesh	
	$t_{0.5}$ (s)	$D_{0.5}$ (cm²/s) × 10⁵	$t_{0.5}$ (s)	$D_{0.5}$ (cm²/s) × 10⁵	$t_{0.5}$ (s)	$D_{0.5}$ (cm²/s) × 10⁵
Kastel A 500	93	2.24	56	2.85	38	3.71
Lewatit M 500			69	2.63		
Amberlite IRA 400			53	3.60		
Kastel A 300			61	2.95		
Lewatit M 600			88	2.03		
Relite 2 A			50	2.75		
Kastel A 101			105	1.65		
Amberlite IRA 93	525	0.34	203	0.65	90	0.93
Relite 4 MS			91	2.57		
Lewatit MP 60			95	2.53		
Amberlite IRA 68			53	3.97		
Kastel A 105	143	2.39	70	3.67	40	3.59
Lewatit Ca 9222			55	3.82		
Wofatit AK 40	575	0.48	235	0.84	116	1.11
Kastel A 102	172	2.23	81	3.42	59	3.94
Relite MG 1			68	4.63		
Duolite A 366			153	2.09		
Duolite S 2002			152	1.26		

Fig. 5. Predicted and experimental exchange kinetics (Resin Kastel A 105; 30/35 mesh; □, △, ○ — experimental points; curve calculated according to eq. (2), with $D = 2.66 \times 10^{-5}$ cm²/s)

Rys. 5. Przewidywana i doświadczalna kinetyka wymiany (Żywica Kastel A 105; numer sita 30/35; □, △, ○ — punkty doświadczalne; krzywa obliczona z równania (2) przy $D = 2.66 \times 10^{-5}$ cm²/s)

for film diffusion controlled, infinite solution volume, isotopic exchanges [4, 5]

$$U = 1 - \exp\left(\frac{3DCt}{\delta r_0 \overline{C}}\right) \tag{2}$$

which, for $U = 0.5$ gives

$$D_{0.5} = 0.23 r_0 \delta \overline{C} / C t_{0.5}. \tag{3}$$

The total ion concentration in solution and ion exchanger, C and $\overline{C}$, have been used, considering the substantially total conversion of the resin in each experiment. The limiting value of 10^{-3} cm for throughly mixed systems has been assumed for the film thickness, δ, in our experimental conditions [7].

It must be noticed that equation (2) is theoretically valid only for isotopic (or trace) exchanges, while the hypothesis of a strict film diffusion control does not appear to be unambiguously supported by the present experiments.

However, due to its ability to satisfactorily correlate the experimental data (see for instance fig. 5), it has been used in this case to provide a semi-quantitative way for the different resins to be characterized on the basis of their (apparent) interdiffusion coefficients.

Among the several physico-chemical parameters considered in an attempt to correlate the exchange rates to resin properties (basicity, crosslinking, type of matrices, porosity, etc.), the following appeared to be controlling at a greater extent: selectivity and water content of the resins.

3.1. SELECTIVITY

As indicated by fig. 6, the same "kinetic sequence" previously demonstrated in particle diffusion conditions has been found in these experiments, with exchange rates decreasing in the order

$$\text{quaternary} > \text{ternary} > \text{secondary} > \text{primary amino-group resins.} \tag{4}$$

This, compared with reverse "selectivity sequence" (1), definitely confirms that lower kinetics have to be expected when the more selective resins are used.

Such unfavourable correlation between selectivity and kinetics suggests that specific interactions between fixed charges and counterions inside the resin, which are obviously stronger with the more selective resins, should control the exchange kinetics even at these low concentrations.

As in previous experiments [8], the retardation effect of selectivity on exchange rate can be explained by means of the collision theory, according to the lower frequency by which highly energetic interactions are disrupted in selective resins (like those with II[ary] or I[ary] amino groups), so that a lower over-all rate for the site-to-site transport of ions through the particle channels occurs.
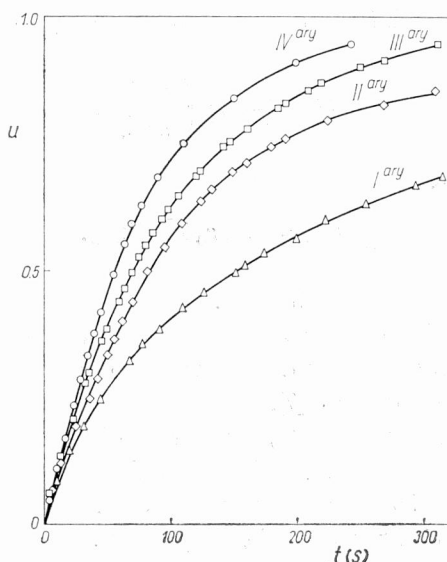
Fig. 6. Experimental exchange kinetics of some typical anion resins with different aminotype functional groups; 20/30 mesh

○ — Kastel A 500, □ — Kastel A 105, ◇ — Kastel A 102, △ — Duolite S 2002

Rys. 6. Doświadczalna kinetyka wymiany niektórych typowych żywic anionitowych o różnych aminowych grupach funkcyjnych; numer sita 20/30;

○ — Kastel A 500; □ — Kastel A 105; ◇ — Kastel A 102; △ — Duolite S 2002

3.2. WATER CONTENT

As a well known statement of ion diffusion in polymers, a high content of water is often assumed to facilitate ion diffusion through the solid phase.

Hydrophilic resins with new kind of matrices (poly or metacrylic, other than the older epoxy and phenolic resins), with real porosity (macro or homo-porous, macroreticular), have been developped in recent years on the assumptions that faster kinetics (and better resistances to organic fouling) could be achieved with these products compared to conventional, though physically more resistant, styrenic resins of the gel type.

Our data seem to agree with this general rule as far as gel type resins with various matrices are compared (fig. 7, curve A). Exchange rates and water content appear to be less easily related when the porous structure of the resin is modified. According to the data in fig. 7, curve B, where the styrenic resins with different porosity are compared, the higher water content associated with macroporosity is not sufficient to appreciably improve the exchange rates of conventional resins, while definitely lower kinetic rates occur with the investigated macroreticular products.

Owing to the physical structure of macroreticular resins, consisting of conglomerates of microspheres with pores between them, the high cross-linking of the microspheres is expected to lead to microsphere diffusion coefficients up to ten order of magnitude lower
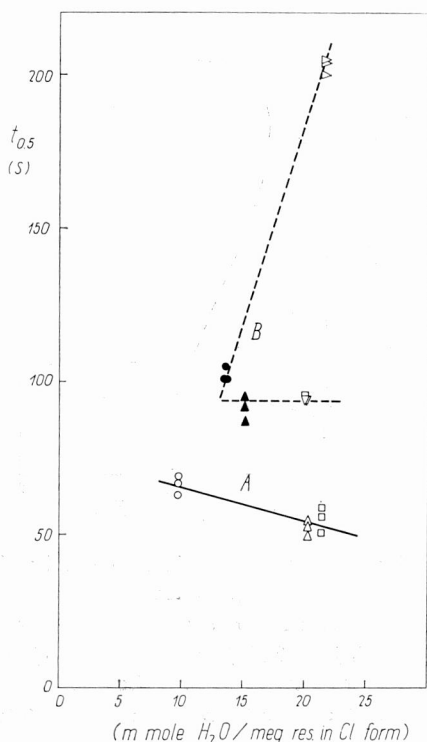
Fig. 7. Half exchange times of III^{ary} amino group resins with different water content

A — poly-acrylic; gel resins — *B* — poly-styrenic, $\bigcirc, \triangle$ — gel, $\triangledown$ — macroporous or $\triangleright$ — macroreticular resins — ($\bigcirc$ — Kastel A 105, $\triangle$ — Amberlite IRA 68, $\square$ — Lewatit Ca 92222, $\bigcirc$ — Kastel A 101, $\blacktriangle$ — Relite 4 MS, $\triangledown$ Lewatit MP 60, $\triangleright$ — Amberlite IRA 93 — 20/30 mesh

Rys. 7. Czas połowicznej wymiany żywic trzeciorzędowych grup aminowych, o różnej zawartości wody

A — poliakrylowe; żywice żelowe — *B* — polistyrenowe, $\bigcirc, \triangledown$ — żelowane, $\triangledown$ — makroporowate lub $\triangleright$ — makroretikulinowe ($\bigcirc$ — Kastel A 105, $\triangle$ — Amberlite IRA 68, $\square$ — Lewatit Ca 92222, $\bigcirc$ — Kastel A 101, $\blacktriangle$ — Relite 4 MS, $\triangledown$ — Lewatit MP 60, $\triangleright$ — Amerlite IRA 93 — numer sita 20/30

than those in the macrospheres, according to the bi-disperse structure model WEATHERLEY and TURNER [10].

This obviously leads to lower over-all kinetics even if more water is present in the macropores of these resins.

On the other hand, no appreciable water transport seems to be associated to the ion fluxes within the resin during the exchange. As can be seen by fig. 8, where the water content as a function of the composition of the external solution is reported for some of the investigated resins, in no case the variations exceeded the 15% of the average value of the water content for each resin.

It seems thus likely, at least in the investigated conditions, to neglect the water flux and to assume the $Cl^-/SO_4^=$ exchange as a strictly binary system, so that the Nernst–Plank diffusion treatment previously used to describe such process [3] appears sufficiently justified.
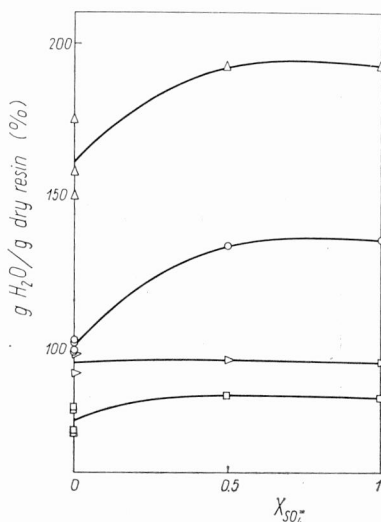
Fig. 8. Water content of the resins as a function of sulphate equivalent fraction in the external solution
20/30 mesh

6×10^{-3}N, O — Kastel A 500; △ — Amberlite IRA 93; ▷ Relite MG 1; □ — Duolite S 2002

Rys. 8. Zawartość wody w żywicach jako funkcja równoważnikowej frakcji siarczanu w roztworze
zewnętrznym numer sita 20/30

6×10^{-3}N,^{3}O — Kastel A 500; △ — Amberlite IRA 93; ▷ Relite MG 1; □ — Duolite S 2002

3.3. INDICATIONS FOR PROCESS DESIGN

From an application point of view, the adverse influence of a strong selectivity on the exchange rates (other than on resin regenerability, obviously), support the use of an acrylic, gel, intermediately basic anion resin for the desulphation process. With a resin of this type, like the Kastel A 102, previously selected on the basis of mass balance considerations for a pilot plant evaluation of this process [1], half exchange times lesser than 90 s are obtained in these conditions. These figures favourably compare with the pilot plant data, where, at a column flow rate of about 0.8 cm/s, an exchange zone height of about 36.0 cm for the exhaustion step was calculated, so that an over-all resin-solution contact time within the zone of 45 seconds resulted.

The about 10 times higher concentration of sulphates in sea water than in this investigation (60×10^{-3} eq $SO_4^=$/dm^3 sea water) clearly accounts for the noticeably lower reaction times found in pilot plant operations compared to bath experiments.

CONCLUSION

Kinetic investigations on the $Cl^-/SO_4^=$ exchange on anion resins in very diluted systems showed, by an even larger evidence than found when the process was of the particle diffusion type, that the rates of exchange are strictly dependent on resin selectivities.

Experimental results suggest that energetic interactions between mobile and fixed charges inside the resin must be more properly accounted in ordinary, strongly selective exchanges up to a point that the resistance to ion diffusion in the solid phase should eventually become the rate determining step even when a "film" controlled mechanisms could be expected.

Further investigations on the role of selectivity on the mechanisms of ion diffusion are thus required.

ACKNOWLEDGEMENTS

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WYMIANA JONÓW Cl⁻/SO₄⁼ NA ANIONITACH. BADANIA KINETYCZNE. SZYBKOŚCI JONOWYMIENNE W ROZTWORACH ROZCIEŃCZONYCH

W trakcie podstawowych prac dotyczących procesu odsiarczania wody morskiej, zbadano szybkość wymiany jonów Cl⁻/SO₄⁼ w zależności od głównych właściwości fizyko-chemicznych różnych anionitów w roztworze o niskim stężeniu, przyjmując, że dyfuzja jonowa przez ciekłą warstwę jest czynnikiem determinującym szybkość. Podobnie jak i w poprzednich badaniach, stwierdzono, że selektywność żywic wpływa niekorzystnie na szybkości jonowymienne. Innymi ważnymi parametrami są zawartości wody, równoważny stosunek, i szybkość mieszania. Wyniki te są w zgodzie z przewidywaniami termodynamicznymi i potwierdzają wybór słabej żywicy anionitowej, z przewagą drugorzędnych grup funkcyjnych typu aminowego, jako najodpowiedniejszej do procesu odsiarczania.

DER AUSTAUSCH VON CL⁻/SO₄⁼-IONEN MITTELS ANIONENAUSTAUSCHERN. KINETISCHE UNTERSUCHUNGEN. AUSTAUSCHGESCHWINDIGKEITEN IN VERDÜNNTEN LÖSUNGEN

Bei Weiterführung der Versuche zur Entschwefelung von Meerwasser, wurde die Austauschgeschwindigkeit von $Cl^-/SO_4^=$ in Abhängigkeit von den physikalischen und chemischen Eigenschaften verschiedener Anionenaustauschern in verdünnten Lösungen getestet, wobei angenommen wurde, daß die Ionendiffusion durch den Flüssigkeitsfilm für die Reaktionsgeschwindigkeit verantwortlich ist. Ähnlich wie in vorangehenden Versuchen wurde festgestellt, daß die Selektivität der Harze sich ungünstig auf die Austauschgeschwindigkeit auswirkt.

Weitere wichtige Parameter des Austausches sind: der Wassergehalt, das Gleichgewichtsverhältnis und die Geschwindigkeit des Vermischens. Die Ergebnisse stimmen mit der thermodynamischen Voraussicht gut überein und bestätigen die Auswahl eines schwachen Anionenharzes, in dem sekundäre, aminenartige Funktionsgruppen vorherrschen; solche Harze sind für die Entschwefelung bestgeeignet.

ОБМЕН ИОНОВ $Cl^-/SO_4^=$ НА АНИОНИТАХ. КИНЕТИЧЕСКИЕ ИССЛЕДОВАНИЯ. ИОНООБМЕННЫЕ СКОРОСТИ В РАЗБАВЛЕННЫХ РАСТВОРАХ

В ходе работ по процессу обессеривания морской соли исследовалась скорость обмена ионов $Cl^-/SO_4^=$ в зависимости от главных физико-химических свойств разных анионитов в растворах с низкой концентрацией, причем принято, что фактором, определяющим скорость, является ионная диффузия сквозь жидкий слой. Подобно предыдущим исследованиям, обнаружено, что селективность смол неблагоприятно влияет на ионообменные скорости. К другим важным параметрам относятся содержание воды, эквивалентное отношение и скорость перемешивания. Эти результаты находятся в соответствии с термодинамическими расчетами и подтверждают выбор слабой анионитной смолы, с перевесом второстепенных функциональных групп аминотипа, наиболее соответствующей для процесса обессеривания.