This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Ion-Exchange Kinetics for the Removal of Potassium from Crude Polyols on Strong Acid Resins

A. De Lucas[a]; P. Cañizares[a]; J. F. Rodríguez[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF CASTILLA-LA MANCHA CAMPUS UNIVERSITARIO, CIUDAD REAL, SPAIN

To cite this Article De Lucas, A. , Cañizares, P. and Rodríguez, J. F.(1997) 'Ion-Exchange Kinetics for the Removal of Potassium from Crude Polyols on Strong Acid Resins', Separation Science and Technology, 32: 11, 1805 — 1820

To link to this Article: DOI: 10.1080/01496399708000738

URL: http://dx.doi.org/10.1080/01496399708000738

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 32(11), pp. 1805–1820, 1997

Ion-Exchange Kinetics for the Removal of Potassium from Crude Polyols on Strong Acid Resins

ANTONIO DE LUCAS,* PABLO CAÑIZARES, and
JUAN F. RODRÍGUEZ
DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF CASTILLA-LA MANCHA
CAMPUS UNIVERSITARIO
S/N. 13004 CIUDAD REAL, SPAIN

ABSTRACT

Batch dynamics for the uptake of potassium from crude polyols on Amberlite 252, a strong acid ion-exchange resin, are obtained over a wide range of conditions. Experimental data have been analyzed using a homogeneous model with finite solution volume. An increase of diffusion coefficients with the resin weight used in the purification is observed. An asymptotic maximum value, approaching the value of the diffusion coefficient in bulk solution, is reached for high resin weights or low values of external concentration. The heterogeneous nature of the resin matrix and the large size of the diffusing molecule is proposed as an explanation of this behavior. The proposed purification procedure finds general applicability for other polyol types, being economically and technically feasible.

Key Words. Polyols; Ion exchange; Kinetic; Organic media

INTRODUCTION

Polyethers made from epoxides are produced throughout the world according to the same basic process, namely, polyaddition of basic structural units of epoxides (oxiranes) and, in most cases, according to an anionic mechanism. The discontinuous batch process is common practice (1).

---

* To whom correspondence should be addressed. E-MAIL: alucas@inqu-cr.uclm.es.

Potassium hydroxide is most often used as the basic catalyst. Because the quantity of catalyst added is small, at the end of the polymerization process most of the chains are terminated in hydroxyl groups with only a small amount of alcoholate endgroups.

The normal concentrations of catalyst in the crude polyols range from 1000 to 4000 ppm, but it is desirable to reduce this to a level below 5 ppm. The filtration processes, although used worldwide, have serious technical and economical disadvantages; for example, the filtration process is not always reliable due to different crystal size distributions and there are important polyol losses in the filter cakes (between 1–5%). The use of strongly acid cation-exchange resins can be an interesting alternative method for polyol purification. Taking into account that polyol production is a discontinuous process, polyol purification using cation-exchange resins could be carried out in a discontinuous way (2).

In contact with an H^+-type ion exchanger, potassium is retained on the resin by the following acid/base reaction (3):

$$\overline{R—H} + R'—CH_2OK \Leftrightarrow \overline{R—K} + R'—CH_2OH$$

where bars refer to the resin phase and R′ denotes the polyol chain.

Based on experimental evidence obtained from equilibrium data, it was demonstrated in a previous paper that the diffusing species is undissociated potassium polyalkoxide due to the low degree of dissociation of potassium in polyol media. The dissociation and the exchange of potassium for the hydrogen ions of the resin occur only in the vicinity of active sites. The above considerations imply that the Donnan exclusion effect is negligible in this case and that the rate of ion exchange is limited by the large size of the diffusing molecule (3).

The selection of the ion-exchange resin and the regeneration data for the purification of crude polyols have also been presented elsewhere (4, 5), showing that the process may be technically and economically feasible. Further experimental evidence about the diffusion of alcoholate was obtained from regeneration experiments.

Intraparticle diffusion is usually the rate-limiting step in the overall kinetics when a large organic molecule is involved in the diffusion process. Intraparticle diffusion is largely influenced by the nature of the resin matrix. Not only is part of the cross-sectional area of the resin bead blocked by the presence of the resin matrix, but diffusion around the matrix strands has to follow a tortuous and thus longer path. The rate of sorption may therefore decrease with progressive resin conversion, necessitating prolonged contact with sorbate to reach equilibrium (6). A practical example of this is the sorption of nitrogenated compounds from gasolines onto

Amberlite 15 which requires in excess of 72 hours to reach equilibrium (7).

Since a very slow rate of attainment of equilibrium sorption is related to the greater inaccessibility of sorption sites in the interior of resin beads and the longer diffusion path associated with progressive resin conversion, a significant decrease of diffusion coefficients must be observed for high resin conversion when large molecules are involved in the exchange process. The increase of inaccessibility of sorption sites toward the center of a styrene-divinylbenzene resin bead is related with the nature of the formation process. Much more divinylbenzene is incorporated into the copolymer at the beginning of the copolymerization than is expected based on the initial composition of the monomer mixture due to its greater reactivity. Thus, the divinylbenzene constituents, which at first are more tightly embedded into the polymer structure, induce the formation of nuclear regions with a narrow mesh, surrounded by material in which the amount of crosslinking agent progressively decrease. This causes an internal heterogeneity of the copolymer (8).

Amberlite 252, designated by the manufacturer as a macroporous strong acid resin, has been used in this work. Nevertheless, Patell and Turner (9) described Amberlite 252 as a quasi-gel-type resin. In that work, the bidispersed sphere model was rejected, and the diffusion behavior of the resin was analyzed in terms of the homogeneous sphere model.

In the present work, kinetic data for the removal of alkaline catalyst from polyols have been obtained by the batch method. The effects of the agitation speed, particle diameter, bulk concentration, temperature, and polyol grade on the ion exchange rate are reported. Taking into account the practical scope of this research, intraparticle effective diffusivities are calculated from the experimental uptake data by using a model from the bibliography: the homogeneous model with finite solution volume. The simplicity of the analytical solution will make simulation of the discontinuous industrial process easier. The behavior of the system is explained according to Buttersack's description of the distribution of active sites inside the resin bead (10).

EXPERIMENTAL SECTION

Polyol

Experiments were limited to the use of F-148, F-155, and F-135 grade polyols. Samples of these products were kindly supplied by Repsol Quimica Co. The product characterizations were given in previous works (3, 4). The molecular weight distribution was determined by gel permeation

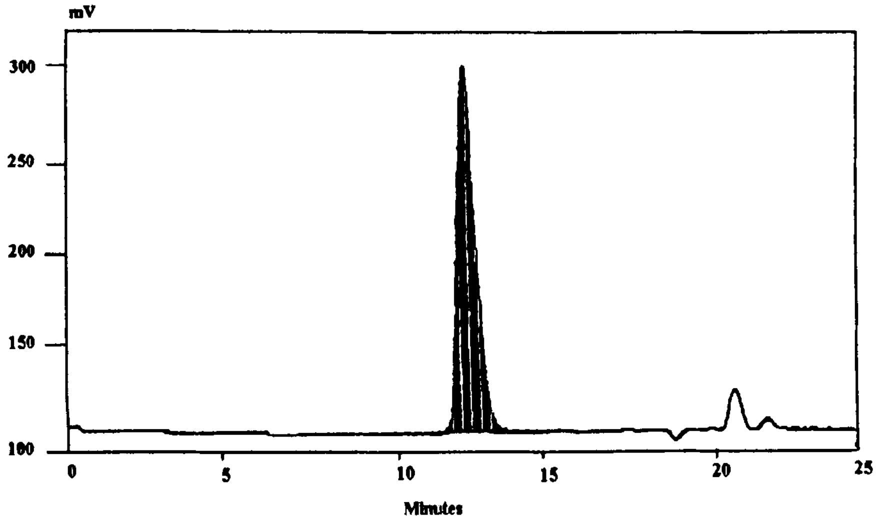

FIG. 1 Gel permeation chromatogram of polyol F-148.

chromatography (GPC). These polymers have a very narrow molecular weight distribution which will allow us to explain their kinetic behavior, as shown in Fig. 1 for polyol F-148.

Ion-Exchange Resin

Amberlite 252 (Rohm and Haas Co.), a macroreticular sulfonated polystyrene-divinylbenzene resin, was selected in a previous paper (4) for polyol purification. The physical properties of the resin are summarized in Table 1. The void fraction, surface area, apparent density, and pore size distribution were determined after dehydration by using a Quantacrome Autoscan Porosimeter 2000 capable of operating to 60,000 psig, thereby measuring pores in the range of 20 to 5000 Å in radius.

TABLE 1
Main Properties of Amberlite 252

Active group	Average particle size (mm)	Resin capacity n^{∞} (meq/g dry resin)	Maximum operating temperature (°C)	Moisture content (%)	Surface area (cm^2/g)	Void fraction (%)	Apparent density (g/cm^3)
Sulfonic	0.494	4.83	135	54	24.87	7.2	1.323

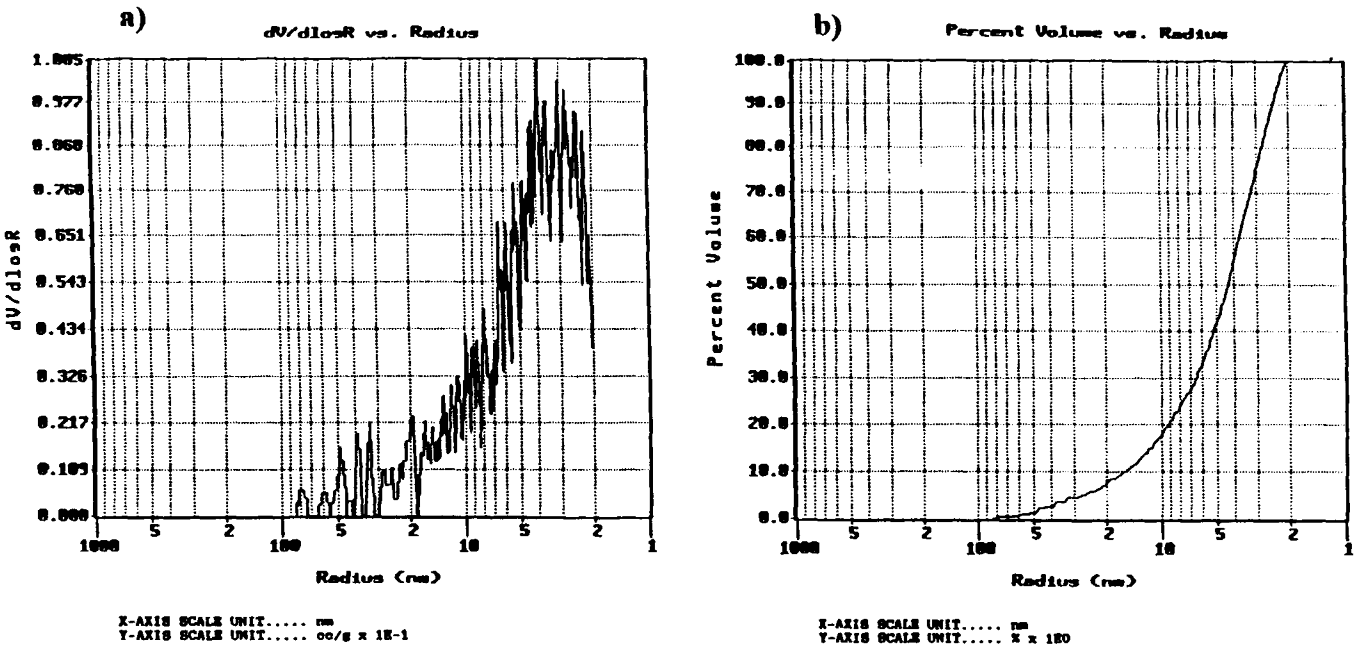

FIG. 2 Pore size distribution of Amberlite 252: a) differential mode, b) integral mode.

Figure 2 shows the distribution curve of the macropore diameter of Amberlite 252. The low percentage of void volume [7.2%; 7.3% was reported by Patell and Turner (9)] and the absence of a peak in the macropore size distribution corroborate that this resin is closer in appearance and behavior to conventional gel-type resins. Nevertheless, the surface area (24.87 m^2/g) is greater than in gel-type resins. These ion exchangers have been described by Yoshida et al. (11) as P-type resins. Instead of agglomerates of microspherical particles, their structure is constituted by holes of about 0.2 μm in diameter on the surface and a very complicated internal structure, not agglomerates of microparticles.

Rate Experiments

Intraparticle diffusion dynamics were studied by measuring the rate at which potassium was taken up by the resin in a well-mixed tank. For a typical experiment, a weighted amount of the ion-exchange resin, previously wetted with methanol, was mixed with 1000 g of polyol in a baffled glass mixing vessel. The mixture was then stirred for a period of time. Small aliquots (3 g) of the polyol were periodically taken, and the potassium content was analyzed. The sample size was considered small enough not to change the polyol/solid ratio. Potassium content in polyol samples was measured by atomic emission spectrometry in a Thermo Jarrel Ash (Smith Hiejfe II) atomic absorption spectrometer. The polyol samples were diluted with ethanol (1:5 by weight) to reduce their viscosity.

THEORY

The goal of this study is to use a simple, asymptotic model to describe the behavior of the resin Amberlite 252 in polyol media. Taking into account the practical scope of this work and the data available, the formulation of a detailed mechanistic model for the removal of potassium from polyols is not justified.

Amberlite 252 is described by the manufacturer as a macroporous resin. His data suggest that a biporous model might be accurate way of describing our system. Nevertheless, if we consider the internal structure of the Amberlite 252 matrix as described Patell and Turner (12), the kinetic behavior of the polyol–Amberlite 252 system should be represented by a homogeneous model.

The homogeneous model assumes that there exists a quasi-homogeneous phase inside the solid particle (13, 14). Furthermore, the same solution is also valid, as a limiting case, for biporous models assuming that the entire mass transfer resistance lies in microspheres (15). The most general solution for intraparticle controlled diffusion from a well-stirred solution of limited volume was given by Crank (16) as the relation between the total amount of potassium M_t in the particles after time t and the corresponding quantity after infinite time M_∞

$$\frac{M_t}{M_\infty} = \frac{C_0 - C}{C_0} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\exp(-p_n^2 D_{\text{eff}} t/R^2)}{9 + 9\alpha + 9p_n^2\alpha^2} \tag{1}$$

where the p_ns are the nonzero roots of

$$\tan p_n = \frac{3p_n}{3 + \alpha p_n^2} \tag{2}$$

and $\alpha = V\rho/KW$, where K is the molar distribution coefficient calculated as $K = n/C_0$.

Similar mathematical expressions have been obtained by other authors for intraparticle diffusion control in spherical particles (17–19).

RESULTS AND DISCUSSION

Influence of Agitation Speed

Five runs were made at various agitation speeds between 100 and 700 rpm. As shown in Fig. 3, the film resistance to mass transfer begins to be significant below 300 rpm, leading to decreasing ion-exchange rates.

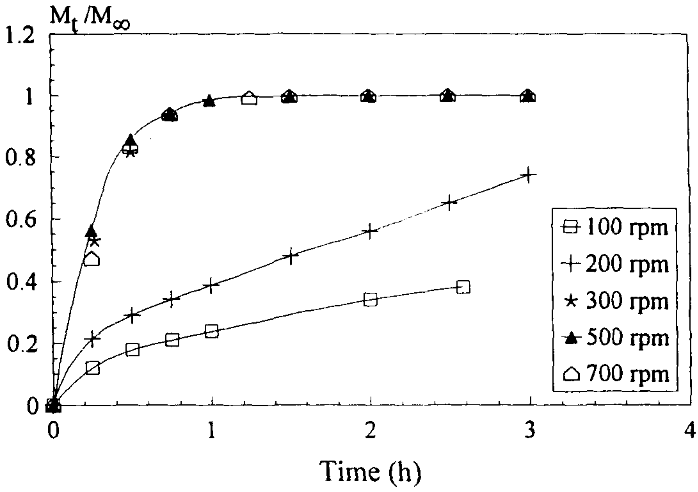

FIG. 3 Normalized average solid concentration of potassium versus time. Influence of agitation speed on the uptake rate of potassium from crude polyol F-148. $V = 1000$ cm^3, $W = 35$ g, $d_p = 0.550$ mm, $C_0 = 0.055$ meq/g, $T = 373$ K.

The decrease of the ion-exchange rate below 300 rpm is too large to be solely due to external mass transfer resistance. This fact indicates that bulk mixing or suspension of the particles is deficient, making the rate of sorption unusually low. An agitation speed of 500 rpm was selected for the rest of the experiments because the film resistance could be considered negligible and no significant cracking or attrition of the resin beads was observed.

Influence of Particle Diameter

The ion-exchange rates were also measured for five particle size fractions at 100°C and using 35 g of resin (dry basis). A plot of half time versus bead radius, given in Fig. 4, shows that the rate of ion exchange is inversely proportional to the square of the bead radius. This inverse relationship is predicted by the homogeneous model.

According to the assumptions of the model, the diffusion coefficients should be independent of particle size and inversely proportional to the square of the bead radius, as can be confirmed in Table 2, thus providing evidence that the model is essentially correct under these conditions.

It is also important to remark that the homogeneous model can be used to correlate the kinetic data obtained in nonaqueous media, which show that the fundamental mechanism of diffusion must be basically the same in aqueous and nonaqueous media. The differences in behavior are neces-

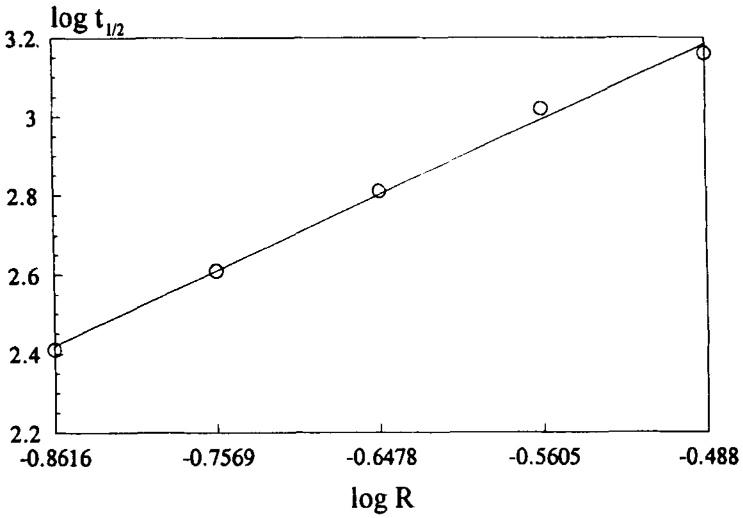

FIG. 4 Logarithmic plot of $t_{1/2}$ (seconds) of sorption of potassium from crude polyol versus average radius of sorbent particle, R. V = 1000 cm^3, W = 35 g, C_0 = 0.055 meq/g, agitation speed = 500 rpm, T = 373 K.

TABLE 2
Diffusion Coefficients Obtained for Different Mean Particle Diameters (d_p)

d_p (mm)	$D_{eff} \times 10^8$ (cm^2/s)	Average deviation (%)
0.275	4.16	5.4
0.350	4.52	7.9
0.450	4.25	3.9
0.550	4.17	3.9
0.650	4.08	5.8

sary consequences of the special characteristics of the solvent and the solute involved in the exchange process.

Influence of Resin Weight

In order to determine the influence of the polyol/resin ratio on the ion-exchange rate in crude polyol media, three series of runs were carried out using resin weights ranging from 35 to 55 g/kg of crude polyol and temperatures of 80, 100, and 120°C. As an example, Fig. 5 shows the

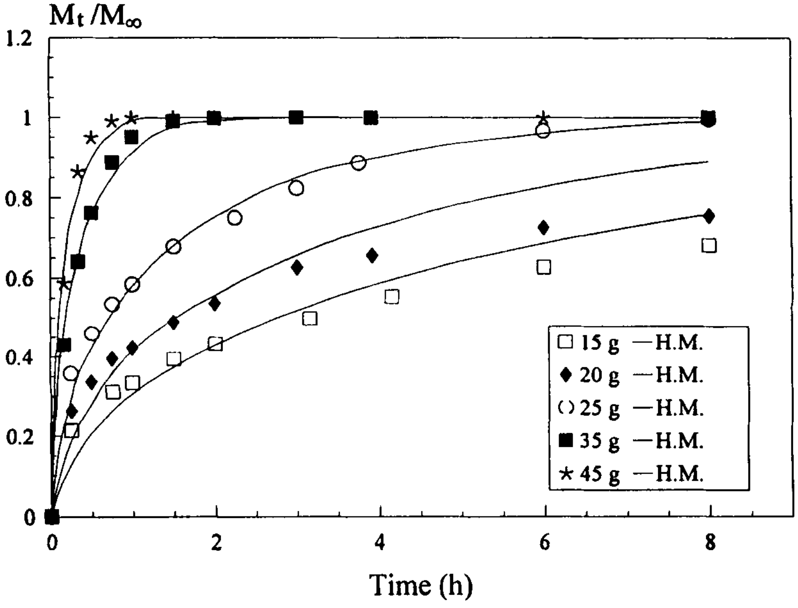

FIG. 5 Normalized average solid concentration of potassium versus time. Influence of resin weight. Comparison of experimental points and predicted profiles. $V = 1000$ cm^3, $d_p = 0.550$ mm, $C_0 = 0.055$ meq/g, agitation speed = 500 rpm, $T = 373$ K.

concentration histories for a temperature of 100°C and the theoretical curves obtained from the model.

As shown in Table 3, the diffusion coefficients increase with the amount of resin, a tendency not usual in aqueous ion-exchange systems. This peculiar behavior of our system can be explained using Buttersack's (10) description of the accessibility of active sites inside the resin matrix.

Regarding a styrene-DVB sulfonic acid exchanger with a certain degree of crosslinking, one has to keep in mind this is an average value of nearly Gaussian distribution. In this case, Amberlite 252 would be made up of a superficial part with large holes and a inner part that can be considered as a polymeric sieve consisting of different local mesh sizes.

Regarding a penetrating ion or molecule, a fraction with meshes larger than the size of the substrate exists (the superficial part), leading to a diffusion coefficient nearly equal to that in the bulk phase. When the size of the substrate is similar to that of the mesh, the diffusion coefficient must decrease. Finally, a nonaccessible fraction is characterized by meshes smaller than the size of the substrate with a local diffusion coefficient of zero. The nonaccessible fraction should consist of isolated highly crosslinked regions located in the inner part of the resin. Their diameter (diffusion length) is relatively small compared with the size of the diffusing molecule or ion (10). This explanation of active site accessibility is based on previous works (7, 20) which report a decrease of the diffusion coefficients similar to that observed in this work.

The previous description based on diffusion measurements is in good agreement with the morphological description based on the data obtained from the copolymerization process of resin bead production. At the beginning of copolymerization the large reactivity of divinylbenzene makes its rate of polymerization faster, leading to an inhomogeneity of crosslinking

TABLE 3
Influence of Resin Weight on the Diffusion Coefficients

T (°C)	W (g)	$\bar{n}$ (meq/g)	$D_{\mathrm{eff}} \times 10^8$ (cm^2/s)	Average deviation (%)
80	35	1.60	0.92	9.9
	45	1.25	4.39	8.8
	55	1.01	4.65	7.7
100	15	3.78	0.26	10.2
	20	2.85	0.47	10.3
	25	2.28	1.04	3.5
	35	1.60	4.17	3.9
	45	1.25	7.75	8.5
120	35	1.66	4.38	1.8
	45	1.24	10.50	4.1

distribution in the particle. The nuclei are regions of relatively high crosslinking density, while there is a gradation of crosslinking density through the bead (21).

In a previous paper (3) dealing with the equilibrium in polyol media it was demonstrated that only 80% of the active sites of the resin are available for exchange in pure polyol media, confirming that a part of the resin is not accessible to exchange. This lack of capacity was explained by taking into account the large size of the diffusing molecule and the inaccessibility of the nuclei of the resin particles.

The observed reduction of diffusion coefficients is related to the increment of inaccessibility of sorption sites in the interior of resin beads and the longer diffusion path associated with progressive resin conversion. As the potassium concentration inside a resin particle grows, the polyalkoxide has to diffuse deeper into the resin beads where there are gradually greater diffusional limitations.

This fact produces a decrease of the diffusion coefficients that can be correlated with the final potassium concentration inside the ion-exchange resin. The following empirical relation between the final conversion ($\bar{n}/n^{\infty}$) and the diffusion coefficients could be obtained for each temperature:

$$D = D_{\infty}\left(\frac{\bar{n}}{n^{\infty}}\right)^{s}, \qquad 1.1 < \bar{n} < 3.6 \tag{3}$$

The values of D_{∞} and s obtained from Eq. (3) are shown in Table 4.

Furthermore, based on the preceding explanations, it is to be expected that a maximum value of the diffusion coefficient nearly equal to that of the polyalkoxide in crude polyol media will be obtained for high resin weights and low external concentrations.

Influence of Bulk Concentration and Temperature

In order to confirm the last supposition, three series of experiments were carried out with different bulk concentrations, resin weights, and temperatures. Since a certain grade of crude polyol from the petrochemi-

TABLE 4
Empirical Constants of Eq. (3) for the Homogeneous Model

T (°C)	$D_{\infty} \times 10^9$	s
80	0.56	
100	1.01	−3.22
120	1.31	

cal plant always has a constant potassium content, dilution of a crude polyol with purified polyol had to be done to obtain samples of polyol with different concentrations.

Experimental data were analyzed using the homogeneous model. As expected, the homogeneous model fits the experimental data fairly well, and the diffusion coefficients reach an asymptotic maximum value for each temperature, as predicted above. Figure 6 shows the effective diffusion coefficients obtained from the homogeneous model versus the value of the mean capacity used at the end of the experiment.

The physical behavior of the system can now be described. As the first stage of the exchange, polyalkoxide invades the peripheral region of the resin bead, which is very accessible to diffusing molecules. Diffusion coefficients obtained under these conditions must be very similar to the diffusion coefficient of polyalkoxide in bulk solution. A value of 2.8×10^{-6} cm^2/s was estimated from Wilke and Chang's equation (22) for the liquid phase diffusivity of potassium alcoholate.

If ion exchange progresses beyond this superficial point, the polyalkoxide has to diffuse into the inner part of the resin matrix where the mesh openings are narrow. The diffusional constraints in this part of the resin

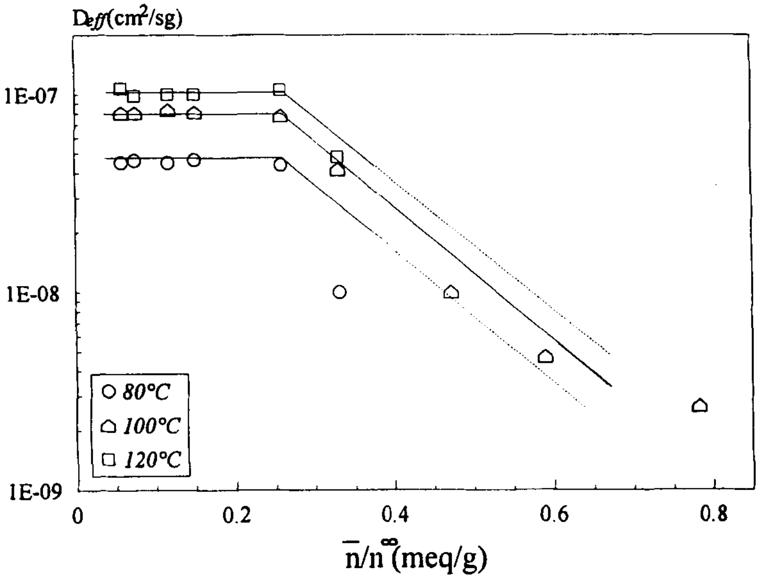

FIG. 6 Influence of final mean concentration of potassium in the resin beads on effective diffusion coefficient at different temperatures. $V = 1000$ cm^3, $d_p = 0.550$ mm, agitation speed = 500 rpm.

cause the mentioned reduction of the diffusion coefficients. The absence of real macropores in the resin matrix is not as important as the existence of a polymer network that prevents the accessibility of molecules to the exchange sites. The inner part of the resin is not available for ion exchange due to its high degree of crosslinking and entanglement.

Finally, the influence of temperature on the asymptotic maximum values of effective diffusion coefficients were correlated according to the following relation (22):

$$\frac{D_{\text{eff}}}{T} = 2.083 \times 10^{-7} e^{-2604/T}, \qquad \bar{n} < 1.1 \text{ meq/g} \tag{4}$$

Influence of Polyol Grade

Several runs were made using different polyol grades (Fig. 7). The main properties of polyol and the diffusion coefficients are shown in Table 5. Based on Eq. (3), it would be expected that F-155 with the higher potassium content would show the smallest diffusion coefficient and F-135 with the lowest concentration of potassium would show the highest diffusion coefficient. However, the low molecular weight of F-155 make its diffusion

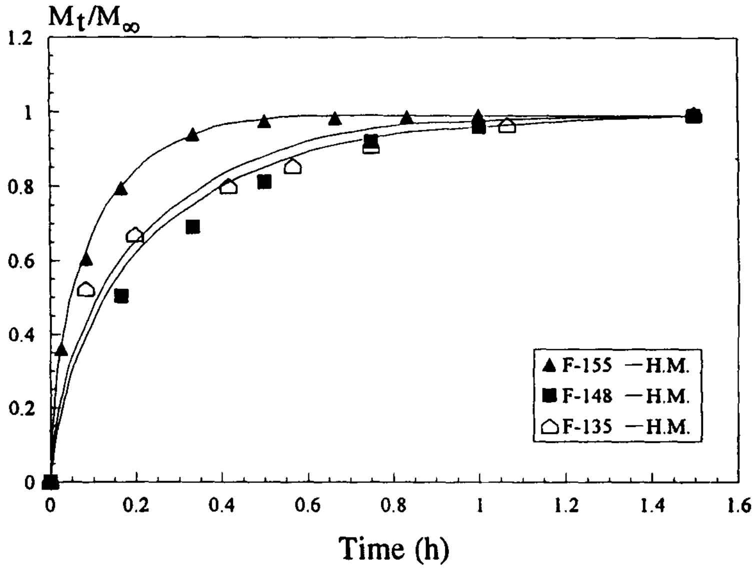

FIG. 7 Normalized average solid concentration of potassium versus time. Influence of polyol grade on exchange rate. $V = 1000$ cm^3, $W = 35$ g, $d_p = 0.550$ mm, agitation speed $= 500$ rpm, $T = 373$ K.

TABLE 5
Influence of Polyol Grade on the Diffusion Coefficients

Grade	Average molecular weight (GPC)	Viscosity (cP), 40°C	C_0 (ppm)	$\bar{n}$ (meq/g)	$D_{eff} \times 10^8$ (cm^2/s)	Average deviation (%)
F-135	4800	400	1348	0.985	4.40	4.0
F-148	3550	300	2200	1.602	4.17	3.9
F-155	3050	200	2450	1.791	10.00	1.0

inside the resin easier, thereby showing a higher diffusion coefficient. On the other hand, F-135 shows a diffusion coefficient very similar to F-148, although it has the highest molecular weight. This is due to its lower potassium content which results in a shorter diffusion length of polyalkoxide inside the bead and consequently an increased diffusion coefficient.

These experiments demonstrate the general applicability of this discontinuous ion-exchange method to other flexible polyol grades. A Spanish patent has been developed on the basis of the results reached during this research project (23).

CONCLUSION

The removal of potassium from impurified polyols using Amberlite 252, a strong cation-exchange resin, can be carried out in a discontinuous way.

The homogeneous model with finite solution volume can fit the kinetic data obtained in nonaqueous systems, showing that the fundamental mechanism of diffusion must be basically the same in aqueous and nonaqueous media.

Three regions can be distinguished inside the resin particle: (a) an outer region, covering 10% of the resin radius, with large macropores (holes) in its structure and allowing easily accessibility to potassium polyalkoxide; (b) a central region, ranging between 10 and 60% of the resin radius, that exhibits a progressive reduction of accessibility; and (c) an inner core of the particle, inaccessible to large diffusing molecule.

This purification process finds general applicability for flexible polyols and is economically competitive with other purification methods currently used. A Spanish patent has been developed based on this research project.

ACKNOWLEDGMENTS

This investigation was supported by Repsol Química S.A. through of Foundation for the collaboration of University and Enterprise (F.U.E. C-1170/90). We would like to thank Mariano Malaga of the research center of Repsol Química S.A. for their help in the GPC determinations, and Professor A. Rodrigues of the Department of Chemical Engineering of the University of Porto for his useful suggestions.

NOMENCLATURE

C	bulk liquid phase concentration (meq/cm^3)
C_0	initial bulk liquid phase concentration (meq/cm^3)
d_p	particle diameter (mm)
D_{eff}	intraparticle effective diffusivity (Eq. 1) (cm^2/s)
D_∞	constant factor in Eq. (3)
K	molar distribution coefficient
M_t	total amount of potassium inside the resin particles after time t (meq)
M_∞	total amount of potassium inside the resin particles after infinite time (meq)
$\bar{n}$	mean final solid phase concentration (meq/g)
n_∞	saturation capacity in aqueous media (meg/g)
p_n	nonzero roots of Eq. (2)
R	radius of resin particle (cm)
s	exponent in Eq. (3)
T	temperature (K)
t	time (s)
V	volume of bulk solution (cm^3)
W	weight of resin particles (g)

Greek Symbols

α	parameter of Eq. (2)
ρ	apparent density of resin particles (g/cm^3)

REFERENCES

1. Z. Wirpsza, *Polyurethanes: Chemistry, Theory and Applications. Polymers Science Series*, Ellis Horwood PTR Prentice-Hall, Chichester, Great Britain, 1993, Chap. 1.
2. K. Schauerte, M. Dahm, W. Diller, and K. Uhlig, "Raw Materials," in *Polyurethanes Handbook* (G. Oertel, Ed.), Hanser Publishers, Munich, Germany, 1985, Chap. 3.

3. A. Lucas, P. Cañızares, J. F. Rodríguez, and A. Nuñez, *Solv. Extr. Ion. Exch.*, *14*, 141–159 (1996).
4. A. Lucas, P. Cañızares, and J. F. Rodríguez, *Sep. Sci. Technol.*, *30*(1), 125–140 (1995).
5. A. Lucas, P. Cañızares, and J. F. Rodríguez, *Ibid.*, *30*(6), 949–962 (1995).
6. M. Chanda and G. L. Rempel, *Ind. Eng. Chem. Res.*, *33*, 623–630 (1994).
7. M. E. Prudich, D. C. Cronauer, R. F. Voguel, and J. Solash, *Ind. Eng. Chem., Process Des. Dev.*, *25*, 742–746 (1986).
8. C. M. Cheng, J. W. Vanderhoff, and M. S. El-Aasser, *J. Polym. Sci., Part A: Polym. Chem.*, *30*, 245–256 (1992).
9. S. Patell and J. C. R. Turner, *J. Sep. Proc. Technol.*, *2*, 21–30 (1980).
10. C. Buttersack, *Reactive Polym.*, *10*, 143–164 (1989).
11. H. Yoshida, T. Kataoka, and S. Sikeda, *Can. J. Chem. Eng.*, *63*, 422–429 (1985).
12. S. Patell and J. C. R. Turner, *J. Sep. Proc. Technol.*, *2*, 31–39 (1980).
13. F. G. Helfferich, *Ion Exchange*, McGraw-Hill, New York, NY, 1962, Chap. 5.
14. T. Huang and K. Li, *Ind. Eng. Chem. Fundam.*, *1*, 50–55 (1973).
15. B. G. Neeru Anand, B. G. R. Manoja, and K. Gupta, *Chem. Eng. Sci.*, *19*, 3277–3290 (1994).
16. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1975, Chap. 9.
17. E. Costa, A. Lucas, and M. E. González, *Ind. Eng. Chem. Fundam.*, *23*(4), 400–405 (1984).
18. S. Goto, M. Goto, and H. Teshima, *Ibid.*, *20*(4), 368–371 (1981).
19. K. S. Knaebel, D. D. Cobb, T. T. Shih, and Pigford, *Ibid.*, *18*(2), 175–180 (1979).
20. G. S. Libinson, E. M. Savitskcaya, and B. P. Bruns, *Russ. J. Phys. Chem.*, *37*, 329 (1963).
21. K. Jerabek, K. J. Shea, D. J. Sasaki, and G. J. Stoddard, *J. Polym. Sci., Part A: Polym. Chem.*, *30*, 605–611 (1992).
22. C. R. Reid, J. M. Prausnitz, and E. B. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York, NY, 1987.
23. A. Lucas, P. Cañızares, J. F. Rodríguez, and E. Costa, Spanish Patent 9,401,514 (July 12, 1994).

Received by editor June 25, 1996
Revision received November 1996