Potassium removal from water–methanol–polyol mixtures by ion exchange on Amberlite 252

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Abstract

Equilibrium isotherms for the uptake of potassium from polyol–water–methanol mixtures on Amberlite 252, a strong acid ion exchange resin, have been obtained in order to assess the possibility of using such a system to purify industrial polyether–polyols. The selectivity was very high. A two-step reaction scheme was proposed and equilibrium data were correlated by an equation derived according to the mass action law. Effective intraparticle diffusivities were obtained using a homogeneous model and the effects of the viscosity of the bulk solution and resin swelling on the exchange rate are discussed. A simple empirical equation correlating diffusivity with viscosity and resin swelling is suggested. Breakthrough curves were obtained under a wide range of conditions, being well correlated by the expression for breakthrough curves with rectangular isotherm. The proposed purification procedure is generally applicable to different polyol types, being economically and technically feasible. © 1997 Elsevier Science S.A.

1. Introduction

Polyurethanes are all around us, playing a vital role in many industries from shipbuilding to footwear, constructions to cars. Owing to the advantages of using polyethers for polyurethane production, nowadays polyethers have a worldwide production of 2.35 million tonnes. This clearly shows the leading role being played by polyethers in today's polyurethane industry.

The polyethers, commonly known as polyols, generally have an average molecular weight of between 200 and 10 000, depending on the application. They cannot be classified as high molecular weight compounds, though, because these generally refer to polymers with an average molecular weight exceeding 10 000 [1].

Polyether polyols are conventionally produced by the addition–polymerization reaction of an alkylene oxide with an organic compound, having at least one active hydrogen atom, in the presence of an alkaline catalyst. The operation of the process can be divided up into several steps. As a first step, the starter components (glycerin, ethylene glycol, butanediol, etc.) are mixed together with the basic catalyst, namely potassium hydroxide. An alcoholate is generally formed through removal of water by distillation. Next, the liquid epoxides

(propylene oxide and ethylene oxide are primarily used for the formation of polyethers) are continuously fed into the polymerization reactor. After reaching the desired degree of polymerization, a post reaction phase occurs. The catalyst is removed either by addition of an adsorbent or by neutralization with acids, whereby salts, which are insoluble in polyether, are formed. The solids are removed by filtration with chamber filters, precoat-type filters, or filter presses. A dewatering step must be performed before the filtration. Centrifugation, employing mixtures of polyol with different polar solvents, can also be employed for the removal of residual catalyst [2].

Although limited, some attempts have been made at using ion exchange resins as a means of polyether catalyst removal [3]. The key problems encountered in these past efforts have been the low ion exchange bed efficiency and regeneration problems. In other words, in order to reduce the catalyst level of a polyol to an acceptable concentration (<5 ppm), the amount of ion exchange resin required in a fixed bed operation would be quite large compared with the amount of polyol that the resin could treat; the total volume of the regeneration solutions was too high when effective.

In previous works dealing with the purification of flexible polyols with strong acid ion exchange resin, the mentioned difficulties were overcome. Amberlite 252 was selected for

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polyol purification [4], an improved regeneration process was developed [5], the equilibrium in crude polyol and in methanol–water–polyol mixtures was measured, and different schemes for the ion exchange process were established [6].

Nevertheless, the efficiency of direct crude polyol purification via ion exchange remained low. Therefore, the dilution of crude polyol with polar solvents seemed to be a suitable method to enhance the ion exchange capacity and the exchange rate [7]. The main drawback of this method is the cost of solvent removal after ion exchange purification. In the end, only an economic evaluation of both methods of polyol purification (pure or in ternary mixtures) will justify its application.

A major factor in this low capacity and exchange rate is the inhibition of mass transfer of the potassium polyalkoxide molecules through the mesh of a resin bead to the active ion exchange sites. This inhibition is due to the large size of the molecule containing the catalyst impurity to be exchanged. The use of water–methanol–polyol (WMP) mixtures allows the removal of catalyst via a greatly improved mass transfer rate by reducing the size of the solute that must access the active ion exchange sites. The presence of the polar solvents allows a certain degree of dissociation of potassium hydroxide, reduces the viscosity of the mixture and has a favorable effect on resin swelling, improving the mass transfer inside the resin [8].

No systematic investigation of intraparticle mass transfer in the ion exchange in organic mixed solvents appears to have been reported. In this paper, we address the equilibrium and kinetics of potassium uptake from water–methanol–polyol mixtures by the hydrogen form of Amberlite 252 in a batch system. Experimental uptake curves in batch system are analyzed in terms of a homogeneous model taking into account the resin structure and our previous experience. Experimental breakthrough curves in fixed bed and regeneration procedures are also presented to compare the performance of this method with the purification via ion exchange in crude polyol media.

2. Experimental work

2.1. 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 characterization of these products is shown in Table 1. The molecular weight distribution was determined by gel permeation chromatography. These polymers have a very narrow molecular weight distribution with polydispersity values under 1.25, as shown in Table 1.

2.2. Ion exchange resin

Amberlite 252 (Rohm and Haas, Co.), a macroreticular sulfonated polystyrene–divinylbencene resin, was selected in a previous paper [4] for polyol purification. The physical properties of the resin are summarized in Table 2. The void fraction, surface area, apparent density and pore size distribution were determined after dehydration using a Quantachrome Autoscan Porosimeter 2000 capable of operating to 60 000 psig, thereby measuring pores of radius 20–5000 Å.

The low percentage of void volume (7.3 versus 7.2% reported by Patell and Turner, [9]) and the absence of peaks 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^{-1}) is higher than in gel-type resins. These ion exchangers have been described by Yoshida et al. [10] 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, which cannot be described as agglomerates of microparticles.

2.3. Equilibrium experiments

The equilibrium experiments were carried out in 1 l flasks hermetically sealed and magnetically agitated, submerged in

Table 1
Characterization of polyols

Grade	Type	Density (g cm^{-3})	Viscosity (cP)	Potassium conc. crude form (ppm)	Av. mol Weight (GPC)	Polydispersity
F-135	Flexible	1.021	400	1348	4800	1.24
F-148	Flexible	1.010	300	2200	3550	1.09
F-155	Flexible	1.023	200	2450	3050	1.07

Table 2
Main properties of Amberlite 252

Active group	Average part size (mm)	Resin capacity n^∞ (meq/g dry resin)	Max. oper. temperature (°C)	Moisture content (%)	Surface area (cm^2 g^{-1})	Void fraction (%)	Apparent density (g l^{-1})
Sulfonic	0.494	4.83	135	54	24.87	7.2	1323

a temperature controlled thermostatic bath. 500 ml of the different WMP mixtures were added to each flask. Solution and resin were maintained at a fixed temperature under vigorous stirring, until equilibrium was achieved (one day). After that, the mixtures were filtered to remove the ion exchange resin and the filtrate was analyzed for potassium content by atomic emission spectrophotometry in a Thermo Jarrel Ash (Smith Hiejfe II) atomic absorption spectrophotometer. In order to take into account the matrix effect on the spectrophotometer measurements, different standard solutions had to be prepared to analyze each type of WMP mixture.

The resin phase composition was determined by mass balance from the initial and equilibrium compositions of the organic phase, according to Eq. (1):

$$n^* = \frac{V}{W}(C_0 - C^*)\qquad(1)$$

where C_0 and C^* are the initial concentration and equilibrium concentration of potassium in the liquid phase ($\text{meq}\,l^{-1}$ solution), respectively. n^* denotes the resin phase equilibrium concentration of potassium (meq/g dry resin). V is the mixture volume (l) and W is the dry ion exchange resin weight (g).

2.4. Rate experiments

The intraparticle diffusion dynamics was studied by measuring the rate at which potassium was taken up by the resin in a well-mixed tank. For a typical experiment, a weighed amount of ion exchange resin was mixed with 1 l of WMP mixture in a baffled glass mixing vessel. The mixture was then stirred for a period of time. Small aliquots (3 g) of the WMP mixture were periodically taken, and the potassium content analyzed. It was verified that the sample size was small enough not to change the polyol/solid ratio.

2.5. Breakthrough experiments

Breakthrough experiments were carried out in a stainless steel column of 22 mm i.d. and 600 mm length. The column was charged with a previously weighed amount of resin and the polyol was then pumped through the resin bed at different flow rates. Samples of the effluent WMP mixture were taken and analyzed for potassium content. After completion of a breakthrough curve, the spent resin was regenerated by a conventional method using HCl 0.5 M.

3. Results and discussion

3.1. Previous experiments

The ternary mixtures water–methanol–polyol F-148 are not soluble over the whole range of compositions. Methanol

has to be added to break up the emulsions formed by water and polyols. Fig. 1 shows in a triangular chart the solubility region for the ternary WMP mixtures, expressed in mass fractions. All the experimental work has been centered on the homogeneous phase region, to avoid mass transfer limitations caused by the presence of such emulsions.

3.2. Equilibrium

Fig. 2 shows the equilibrium isotherms of the ion exchange of potassium from WMP mixtures on Amberlite 252. The equilibrium isotherms are not affected by the composition of the monophasic mixtures over the range of conditions investigated, and the maximum value of n^* (meq/g dry resin) is the same as the exchange capacity n^∞ ($\text{meq}\,g^{-1}$) in all cases. On the contrary, only 75% of the exchange capacity is available when crude polyol is the external solution, as demonstrated by Lucas et al. [6]. A significant improvement in resin capacity is attained by using ternary mixtures.

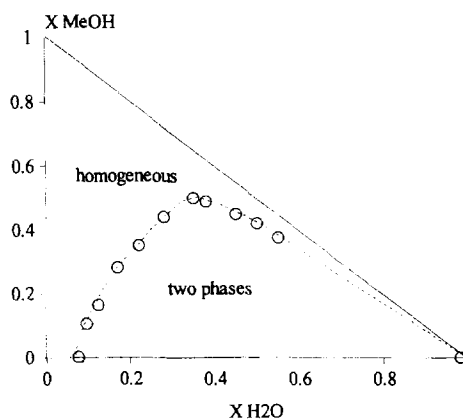The following reaction scheme can be proposed:

$$R' - CH_2OK + H_2O \overset{K_1}{\rightleftharpoons} R' - CH_2OH + K^+ + OH^-\qquad(2)$$

$$\overline{R - H} + K^+ + OH^- \overset{K_2}{\rightleftharpoons} \overline{R - K} + H_2O\qquad(3)$$
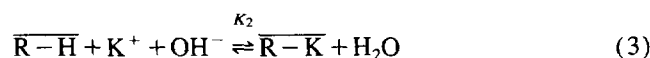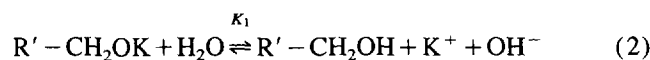

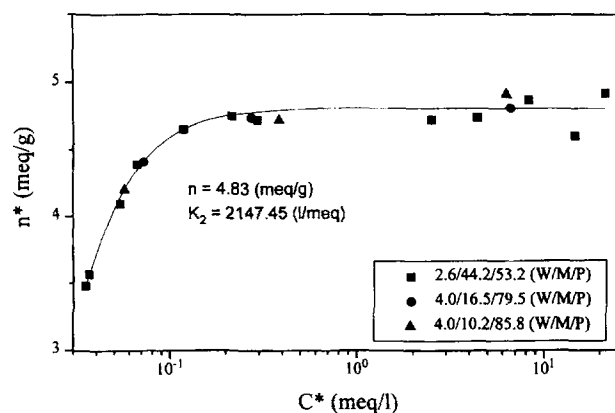Fig. 1. Solubility chart of water–methanol–polyol mixtures. $T = 333$ K.

Fig. 2. Equilibrium isotherm for potassium from WMP mixtures on Amberlite 252. Stirring speed = 600 rpm, $T = 333$ K, $V = 0.5$ l.
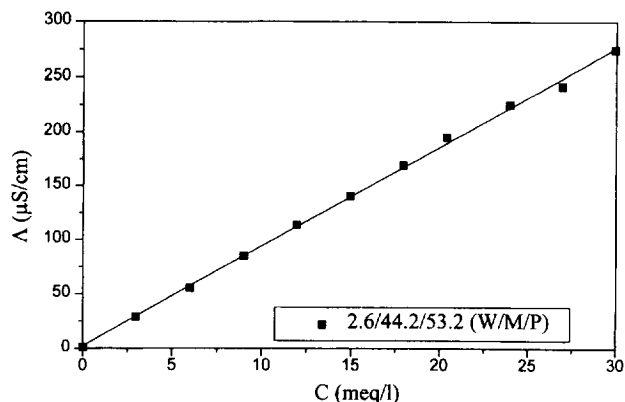
Fig. 3. Relation between conductivity (μS) and potassium concentration (meq l^{-1}) for a (2.6/44.2/53.2) WMP mixture. $T = 333$ K.

where R' denotes the polyol chain, R refers to the polymeric resin matrix and overbar represent the resin phase.

First of all, water brings about the hydrolysis of the alkoxide, neutralizing the crude polyol (Eq. (2)). Since the polyol and water are not miscible, methanol has to be added to break the resulting emulsion, thus forming a homogeneous mixture. Moreover, the presence of methanol (a polar solvent) and water allows the dissociation of potassium hydroxide, reduces the viscosity and has a favorable effect on resin swelling, therefore improving the ion exchange process inside the resin bead.

According to Eq. (3), the process of ion exchange in these mixed systems is similar to conventional ion exchange followed by neutralization reaction of an alkaline solution.

Although Eq. (2) has been written as a reversible reaction, conductivity measurements demonstrate that it is completely displaced to the right-hand side, K_1 being very high. As shown in Fig. 3, there is a linear relationship between conductivity and potassium content over the whole range of possible concentrations (from zero up to the potassium content of crude polyol). This means that potassium is completely and equally dissociated at all the concentrations studied and hence Eq. (2) can be considered as irreversible in practice [11].

This behavior can be easily explained: polyether–polyols, like other alcohols, are very weak acids with a low degree of dissociation in aqueous solution [12], whereas alkoxides are strong alkaline compounds in aqueous solution showing a low degree of dissociation in the absence of water. Therefore, equilibrium Eq. (2) should be completely displaced to the right-hand side because the polyalkoxide has a strong tendency to pass into the alcohol form, whereas the polyol does

not show any tendency to change into the alkoxide form owing to its higher stability [13].

Considering Eq. (2) as irreversible and taking into account the very high value of K_1, Eq. (3) will be the main process responsible for the equilibrium behavior of the system, from which the following equation can be derived according to the mass action law:

$$C^{*2} = \frac{n^*}{K_2(n^\infty - n^*)} \text{ or } n^* = \frac{n^\infty K_2 C^{*2}}{1 + K_2 C^{*2}} \qquad (4)$$

where K_2 (l^2 meq^{-2}) denotes the equilibrium constant of Eq. (3).

The solid line in Fig. 2 represents the results calculated with Eq. (4). The values of K_2 given in Table 3 were found by matching the experimental isotherms obtained for three different WMP mixtures. The large value of K_2 indicates that the reaction (Eq. (3)) is displaced to the right-hand side, so that it can be considered as irreversible for practical purposes.

Eq. (3) is the conventional neutralization reaction of the hydroxyl ions forming water. The low degree of dissociation of water ($K_w = 9.616 \times 10^{-14}$ at 60 °C) explains the displacement of Eq. (3) to the right-hand side.

Further, the experimental data have been fitted to Langmuir and Freundlich equations in dimensionless form, as follows.

$$\text{Langmuir: } Y^* = \frac{X^*}{R + (1 - R)X^*} \qquad (5)$$

$$\text{Freundlich: } Y^* = X^{*\beta} \qquad (6)$$

where $X^* = C^*/C_0$ and $Y^* = n^*/n^\infty$

Yoshida et al. [14] suggest that for $R < 0.05$ or $\beta < 0.1$, the isotherms can be taken as irreversible. The fitted values, shown in Table 3, clearly fulfill these conditions, and the analytic solution proposed by the mentioned authors for irreversible isotherms can then be applied in the simulation of the breakthrough curves in this case.

3.3. Kinetic experiments

Based on the experiences reported in previous works using Amberlite 252, the diffusion behavior of the solutes (molecules or ions) inside this "quasi-geliform" resin must be analyzed in terms of the homogeneous intraparticle diffusion model [15]. In the same way, Saunders et al. [16] found that the main resistance to mass transfer inside the mentioned

Table 3
Equilibrium constants determined from WMP mixtures

Composition W/M/P (% weight)	K_2 (l^2 meq^{-2})	n^∞ (meq g^{-1})	Av. dev. (%)[a1]	$R \times 10^4$	Av. dev. (%)[a2]	$\beta \times 10^2$	Av. dev. (%)[a2]
3/43/54 4/16/80 4/10/85	2147 ± 40	4.83 ± 0.1	7.5	4.5 ± 0.1	3.4	2.1 ± 0.1	7.74

[a]Average deviation has been calculated as: $1, \frac{1}{m}\sum_{i=1}^{m}\frac{|n^*_{i\exp} - n^*_{i\text{fit}}|}{n^*_{i\exp}} \times 100$; $2, \frac{1}{m}\sum_{i=1}^{m}\frac{|Y^*_{i\exp} - Y^*_{i\text{fit}}|}{Y^*_{i\exp}} \times 100$.

resin would lie in the gel microparticles. Thus, a homogeneous model was employed in a previous work to obtain the effective diffusion coefficients in crude polyol using Amberlite 252, with satisfactory results [17]. Further, the solutions of the homogeneous model are basically the same as those obtained, as a limiting case, for biporous models if we replace the radial coordinate in the microspheres (all of them with the same concentration profile) by the radial coordinate in the particle, assuming that the mass transfer resistance lies entirely in the microspheres [18].

The homogeneous model assumes that a quasi-homogeneous phase exists inside the solid particle, which is quite true for a quasi-geliform resin [19,20].

Intraparticle transport in ion exchange resins is generally controlled by the interdiffusion of counterions. Since the exchanged species are charged, their diffusion will be described by the Nernst–Planck equations, with the following additional assumptions. The presence of co-ions in the ion exchanger is neglected, the ionic diffusivities of each counterion are assumed to remain constant and the ion fluxes within the resin are subject to the restrictions imposed by the conditions of electroneutrality and no net electric current. With these assumptions, making use of the Nernst–Planck equations, the conservation equation for the potassium ion in the spherical resin particles may be written as

$$\frac{\partial n_K}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{KH}\frac{\partial n_K}{\partial r}\right) \tag{7}$$

where r is the radial coordinate inside the resin particle (cm), t is the time variable (s) and the effective interdiffusion coefficient D_{HK} (cm^2 s^{-1}) is given by

$$D_{KH} = \frac{D_K D_H (n_K + n_H)}{D_K n_K + D_H n_H} \tag{8}$$

Since the external concentration of potassium is very low and the amount of resin in the hydrogen form is very large, the concentration of potassium inside the resin bead remains very low during the experiment and hence the following simplification can be made:

$$D_{KH} = D_K \text{ if } n_K \ll n_H \tag{9}$$

i.e. the effective diffusion coefficient is that of the less concentrated ion and can be considered for simplicity as constant [19].

The initial and boundary conditions are the following:

$$t = 0, \quad r < R_p, \quad n_K = 0 \tag{10}$$

$$t > 0, \quad r = 0, \quad \frac{\partial n_K}{\partial r} = 0 \tag{11}$$

$$t > 0, \quad r = R_p, \quad \frac{dC_K}{dt} = -\frac{3W}{VR_p}D_{KH}\left(\frac{\partial n_K}{\partial r}\right) \tag{12}$$

where R_p is the particle radius (cm).

The most general solution for the previous model which supposes intraparticle controlled diffusion from a well-stirred

solution of limited volume was given by Crank [21] as the relation between the total amount of potassium M_t in the particles at time t and the corresponding quantity at infinite time M_∞:

$$\frac{M_t}{M_\infty} = \frac{C_{K0} - C_K}{C_{K0} - C_{K\infty}}$$

$$= 1 - \sum_{n=1}^{\infty}\frac{6\alpha(\alpha+1)\exp(-p_n^2 D_{KH}t/R_p^2)}{9 + 9\alpha + 9p_n^2\alpha^2} \tag{13}$$

where p_n are the non-zero roots of

$$\tan p_n = \frac{3p_n}{3 + \alpha p_n^2} \tag{14}$$

and $\alpha = VC_0 / Wn^\infty$

The diffusion coefficients were determined by fitting the experimental data to Eq. (13) using a non-linear regression method based on the Marquardt algorithm [22]. The swelling radii of the resin beads in each kind of WMP mixture were used for calculations.

The effect of agitation on ion exchange kinetics was measured for different WMP mixtures (from crude polyol to the most diluted mixture), performing experiments at different stirring speeds ranging between 200 and 700 rpm. The results showed that agitation influences the exchange rate below 300 rpm while above this speed the kinetics are independent of the degree of agitation and hence are not influenced by film diffusion. 500 rpm was selected as the stirring speed for this investigation.

In a previous work dealing with the purification of crude polyol via ion exchange, it was demonstrated that prewetting of the resin particles with methanol allowed an increase in the capacity and ion exchange rate [4]. Based on the equilibrium conclusions that describe the reaction of exchange as similar to a conventional neutralization in aqueous media, it might be expected that the prewetting of the resin will have no influence in this kind of system.

A set of comparative experiments were done using prewetted and dry resin for two different compositions of the bulk solution. As shown in Fig. 4, kinetic curves for the prewetted and dry resin are identical, demonstrating that prewetting has
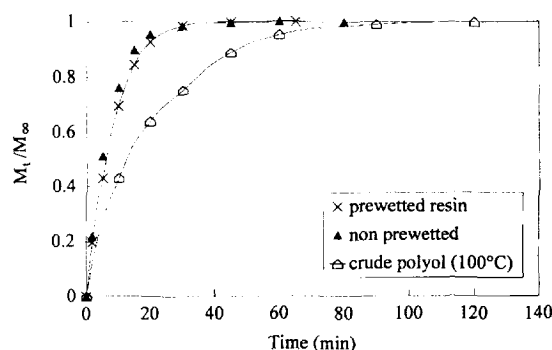

Fig. 4. Normalized resin uptake M_t/M_∞ versus time. Influence of prewetting on the rate of uptake of potassium from different WMP mixtures and from crude polyol. $V = 1$ l, stirring speed = 500 rpm, $T = 333$ K (WMP), $T = 373$ K (crude polyol).
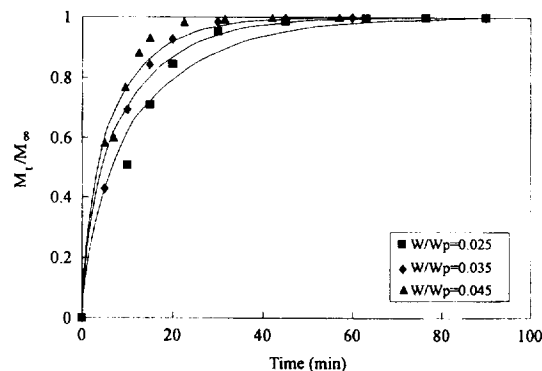
Fig. 5. Normalized resin uptake M_t/M_∞ profiles during the uptake of potassium from (2.6/44.2/53.2) WMP mixtures for different resin weights. Comparison of experimental points and predicted results. $V = 1$ λ, stirring speed $= 500$ rpm, $T = 333$ K.

no influence in this case and can be discarded as a previous step in the discontinuous operation procedure. The presence of polar solvents in the mixture makes the resin swelling almost instantaneous. Thus, the prewetting of the resin has a negligible influence on the exchange rate. Nevertheless, in crude polyol the methanol filling the pores of the prewetted resins plays an important role in the exchange process, swelling the resin matrix and allowing the diffusion of polyalkoxide.

Comparing the exchange rates in crude polyol and WMP mixtures, it can be seen that mass transfer can be greatly improved by using mixtures of non-polar and polar solvents as shown in Fig. 4, where the resin uptake of potassium from crude polyol is also represented for comparison.

In order to measure the influence of the polyol/resin ratio on the ion exchange rate in these mixed solutions, three runs were carried out using resin weights ranging between 25 and 45 g/kg of crude polyol in the mixture. Fig. 5 shows the concentration histories and the theoretical lines calculated with the homogeneous model. As shown in Table 4, the fit of the model was within 8% of the observed values and the diffusion coefficients do not change with the different resin/ polyol ratios. Both facts seem to support the proposed ion exchange scheme (the behavior is quite similar to a conventional aqueous system) being the major part of the active sites of the resin equally accessible for the potassium ions, with constant diffusion coefficients for different resin conversions.

Taking into account the practical scope of this work, it was important to determine the influence of mixture composition on the ion exchange rate. The final objective was to select a mixture composition with an optimal relation between cost

Table 4
Influence of resin weight on the diffusion coefficients

W/W_p	$D_{KH} \times 10^7$ (cm^2 s^{-1})	Av. dev. (%)
0.025	1.55	8.1
0.035	1.54	5.5
0.045	1.60	7.1

of solvent removal and time of purification for its industrial application.

The ion exchange rates were also measured for various mixture compositions. Figs. 6 and 7 show the effect of the bulk solution composition on the uptake of potassium from the external solution. As the dilution of polyol with methanol and water increases, so does the ion exchange rate, and vice versa.

According to Marcus [8], the degree of swelling is the major factor for anhydrous or mixed solvents, and the viscosity is also important in determining the diffusion coefficients in the resin. The homogeneous particle diffusion model was used to obtain the diffusion coefficients for each system. It is evident from Figs. 6 and 7 that the theoretical curves are in reasonable agreement with the experimentally observed behavior.

Table 5 shows the experimental values of intraparticle diffusivities, mean deviation, resin swelling, and viscosity of bulk solution. Viscosity measurements were done in a rotating digital viscometer Brookfield model DV-II and resin swelling was measured using the microscope.

Typical values of the diffusion coefficient of potassium in aqueous systems are at least one order of magnitude higher
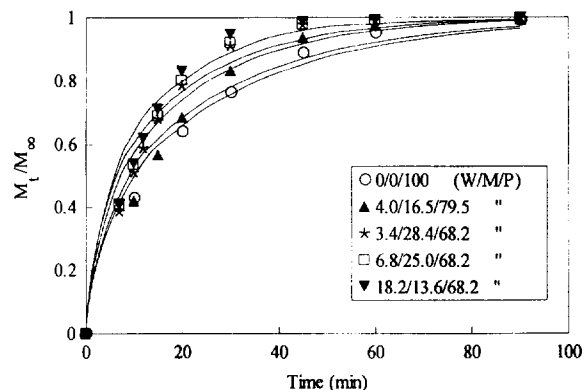

Fig. 6. Normalized resin uptake M_t/M_∞ versus time. Effect of mixture composition on the ion exchange rate. Concentrated solutions. Comparison of experimental points and predicted results. $V = 1$ 1, $W = 35$ g/kg polyol, Ag. Speed $= 500$ rpm, $T = 333$ K.
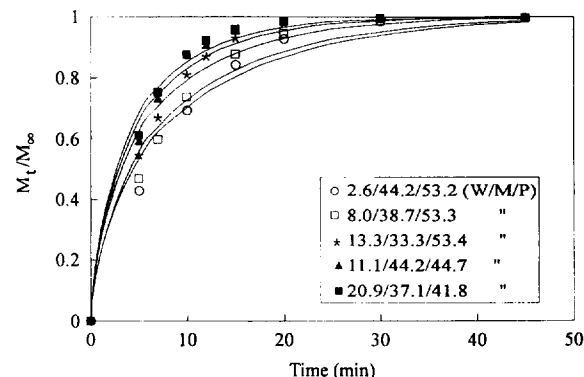

Fig. 7. Normalized resin uptake M_t/M_∞ versus time. Effect of mixture composition on the ion exchange rate. Diluted solutions. Comparison of experimental points and predicted results. $V = 1$ 1, $W = 35$ g/kg polyol, Ag. Speed $= 500$ rpm, $T = 333$ K.

Table 5
Influence of viscosity and resin swelling on the diffusion coefficients

Composition W/M/P (% weight)	Viscosity μ (cP)	Resin swelling (%)	Swelled radius $R_p \times 10^2$ (cm)	$D_{KH} \times 10^7$ (cm² s⁻¹)	Av. dev (%)
0/0/100 [a]	56.0	6.6	2.81	0.446	4.6
4.0/16.5/79.5	40.0	86.8	3.38	0.659	8.0
3.4/28.4/68.2	19.50	78.0	3.33	0.876	7.8
6.8/25.0/68.2	20.45	93.4	3.42	0.949	7.8
18.2/13.6/68.2	20.58	105.5	3.49	1.090	8.3
2.6/44.2/53.2	8.50	78.0	3.33	1.535	6.3
8.0/38.7/53.3	8.82	97.8	3.45	1.772	5.7
13.3/33.3/53.4	8.91	110.9	3.52	2.220	5.0
11.1/44.2/44.7	5.50	103.3	3.48	2.746	3.8
20.9/37.1/41.8	4.71	124.7	3.60	3.102	3.3
18.6/44.2/37.2	3.62	135.1	3.65	3.831	2.3

[a] Values obtained at 100°C.

Table 6
Influence of polyol type on the diffusion coefficients in a (2.6/44.2/53.2) WMP mixture

Polyol type	Mol. weight	Viscosity (cP)	Resin swell (%)	$D_{KH} \times 10^7$ (cm² s⁻¹)	Av. dev. (%)
F-135	4800	9.21	74.81	1.390	4.5
F-148	3550	8.50	78.02	1.535	6.3
F-155	3050	7.81	75.05	1.990	3.2

than in WMP mixtures [23], and the diffusion coefficients for crude polyols are at least one order of magnitude smaller than in the mixtures [17].

As indicated above, resin swelling has a major influence on the ion exchange rate in non-aqueous media. Up to now, only a qualitative explanation has been proposed based on the half-reaction times for different mixed and non-aqueous systems [8]. An exponential relation between resin swelling and the diffusion coefficients was proposed by Kataoka et al. [24]. However, according to Reid et al. [25], a relation also exists between viscosity and the diffusion coefficients in solution.

Summing up, the following useful and accurate empirical equation for estimating the diffusion coefficients including both influences (viscosity and resin swelling) can be written:

$$D_{KH}(cm^2 s^{-1}) =$$

$$4.506(10^{-6})\mu^{-0.64} \exp(5.06 \times 10^{-3} S) \qquad (15)$$

where S is the resin swelling calculated as $s = $ [(Vol. wet resin − Vol. dry resin)/Vol. dry resin] × 100 and μ denotes the viscosity of the WMP mixture in cP.

The parameters of Eq. (8) were found out by fitting the diffusion coefficients to the equation using a non-linear regression method also based on the Marquardt algorithm. All data coincide with the estimated values within an error band of 10%, except the value for crude polyol which exhibits a 20% deviation between the predicted and experimental values.

Although the previous correlation can only be used for viscosity values between 3 and 56 cP, it covers all the range

of possible one-phase WMP mixtures, for its industrial application.

These diffusivity values have been derived from the analysis of a very specific system (WMP mixtures). Therefore, the applicability of the parameters of Eq. (8) will be very limited. Validation of these parameters for other non-aqueous systems should be confirmed experimentally, in order to extend their range of applicability.

An economical evaluation of each mixture, on the basis of total purification times and the costs of solvent removal, allowed us to select the (WMP) mixture composition 2.6/44.2/53.2 as optimal. This composition was used for the rest of the experimental work.
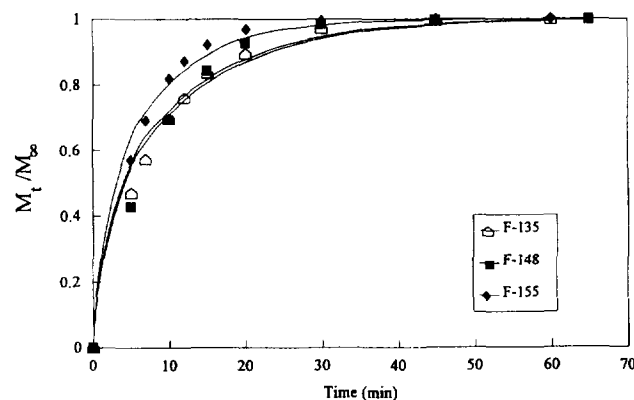

Fig. 8. Normalized resin uptake M_t/M_∞ versus time. Effect of polyol grade on the rate of uptake of potassium from a (2.6/44.2/53.2) WMP mixture. Comparison of experimental points and predicted results. $V = 1$ l, Ag. Speed = 500 rpm, $T = 333$ K.
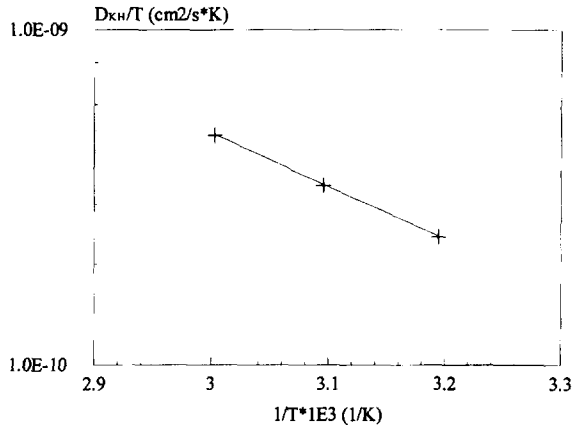
Fig. 9. Relation between temperature and D_{eff} for a (2.6/44.2/53.2) WMP mixture. $V = 1$ l, Ag. Speed = 500 rpm, $T = 333$ K.

This work was part of a research project funded by a petrochemical company, and hence there was interest in demonstrating that this purification method could be generally applied to all polyol types. Fig. 8 shows the experimental points and theoretical lines obtained from the homogeneous model.
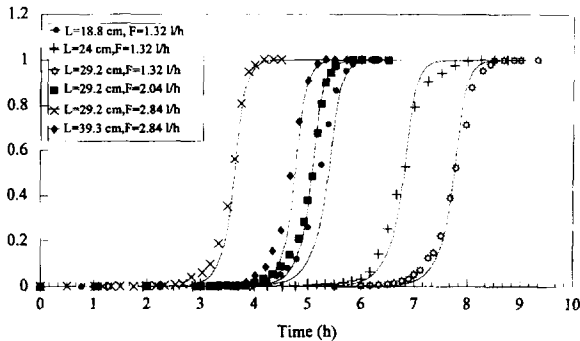

Fig. 10. Breakthrough curves of uptake of potassium from a (2.6/44.2/53.2) WMP mixture. $T = 333$ K. ——— theoretical lines.

As expected, diffusion coefficients are only slightly affected by the type of polyol, since polyol does not play any significant role in the exchange process (Table 6). As the resin swelling is the same for the three kinds of polyol investigated, only a small increase in solution viscosity with the molecular weight of the polyol can justify the small changes in the diffusion coefficients.

These experiments demonstrate the general applicability of this batch ion exchange method to different kinds of rigid and flexible polyol grades.

Finally, the influence of temperature on the exchange rate for the selected WMP compositions was investigated (Fig. 9). The effective intraparticle diffusion coefficients could be correlated with temperature according to the following relation [25]:

$$D_{KH}/T = 1.597(10^{-7})e^{-1944/T} \qquad (16)$$

Correlation coeff.: 0.997.

3.4. Breakthrough curves

Representative experimental breakthrough curves obtained using four resin weights and three different flow rates are shown in Fig. 10.

The expression for the breakthrough curve for a rectangular isotherm system, in which the mass transfer rate is controlled by the combined effects of external film and internal homogeneous diffusional resistance, has been given by Yoshida et al. [26].

For simplicity, axial dispersion was neglected and the intraparticle mass transfer was represented by a linear driving force. The part of the general analytic solution ($\delta \geq 1$) used for the prediction of the breakthrough curves is shown in Table 7. τ, δ and ξ are dimensionless parameters with respect to contact time, bed height, and the ratio of external to intra-

Table 7
Summary of the analytic solution of the breakthrough curve for a rectangular isotherm and a single-component system in a homogeneous model

General solution	Range of τ and ξ	
$\delta \geq 1$		
$x = 1 - \dfrac{\xi}{\delta}\exp(-\tau/\delta),\ \bar{y} = 1 - \exp(-\tau/\delta)$	$\tau \geq 0, 0 \leq \xi \leq (\delta - 1)$	(17)
$x = \dfrac{1}{\delta}\exp(\delta - 1 - \xi),\ \bar{y} = \tau\exp(\delta - 1 - \xi)$	$0 \leq \tau \leq \left(\dfrac{1}{\delta}\right),\ \xi \geq (\delta - 1)$	(18)
$x = \bar{y} = 1 - \left[1 - \dfrac{1}{\delta}\exp(\delta - 1 - \xi)\right]\exp\left[\left(\left(\dfrac{1}{\delta} - 1\right)\right)/\delta\right]$	$\tau \geq \left(\dfrac{1}{\delta}\right),\ (\delta - 1) \leq \xi \leq \delta - 1 + \ln\left(\dfrac{\delta - 1}{\delta}\right)$	(19)
$x = \bar{y} = \dfrac{1}{\delta}\exp\left(\tau - \xi + \delta - 1 - \dfrac{1}{\delta}\right)$	$\dfrac{1}{\delta} \leq \tau \leq \xi - \delta + 1 + \dfrac{1}{\delta} - \ln\left(\dfrac{\delta - 1}{\delta}\right),\ \xi \leq \delta - 1 + \ln\left(\dfrac{\delta - 1}{\delta}\right)$	(20)
$x = \bar{y} = 1 - \dfrac{\delta}{\delta - 1}\exp\left\{\left[-\tau + \xi - \delta + 1 + \dfrac{1}{\delta} - \ln\left(\dfrac{1}{\delta} - 1\right)\right]/\delta\right\}$	$\tau \geq \xi - \delta + 1 - \dfrac{1}{\delta} - \ln\left(\dfrac{\delta - 1}{\delta}\right),\ \xi \geq \delta - 1 + \ln\left(\dfrac{\delta - 1}{\delta}\right)$	(21)

Table 8
Influence of bed height and flow rate on the resin capacity used in breakthrough experiments

W (g)	z (cm)	F ($l\,h^{-1}$)	n_s (meq/g dry resin)	Total capacity (%)	W_p/W (g polyol/g resin)
36	18.8	1.32	3.09	64.6	57.4
46	24.0	1.32	3.49	73.0	64.9
56	29.2	1.32	3.46	72.3	64.3
56	29.2	2.04	3.15	65.8	58.5
56	29.2	2.84	2.91	60.8	54.2
76	39.3	2.84	3.37	70.5	62.9

particle mass transfer resistance, respectively. The time dimensionless variable τ and the parameters ξ and δ are defined as

$$\tau = \frac{C_0 k_f\left(t - \frac{z}{v}\right)}{n_0}, \quad \xi = \frac{(1-\epsilon)k_f z}{\epsilon v}, \quad \delta = \frac{k_f C_0}{k_p n_0}$$

where k_f (s^{-1}) and k_p (s^{-1}) are mass transfer coefficients in the external film and inside the solid phase, respectively.

The experimental equilibrium coefficients shown in Table 3 are small enough to justify the assumption of a rectangular isotherm [14]. Intraparticle effective diffusivity values, D_{KH}, were experimentally obtained as indicated in the previous section. First of all, the external mass transfer coefficient k_f (s^{-1}) was estimated from the following correlation [27]:

$$\left(\frac{1-\epsilon}{\epsilon}\right)^{1/3}\frac{k'_f Sc^{2/3}}{v} = 1.85\,Re^{-2/3} \tag{22}$$

$$k_f = 6k'_f/2R_p \tag{23}$$

The diffusivity of the potassium ions in the WMP mixture was estimated from the Wilke–Chang equation [28]. The value obtained for the free diffusivity of potassium in a WMP mixture was 2.44×10^{-6} cm^2 s^{-1}. Although this correlation is basically applicable for non- electrolyte solutions, the mentioned value is within the range that would be expected from extrapolation of the value in aqueous solution (1.96×10^{-5} cm^2 s^{-1}). The values of τ and ξ can be calculated according to the definitions and the estimated values of k_f. In order to match the theoretical breakthrough curve with the experimental breakthrough, the value of δ is calculated from the experimentally obtained value of D_{KH}, taking into account that k_p is calculated from $k_p = 15D_{KH}/R_p^2$.

Experimental behavior is usually well predicted by theoretical curves (as derived from Fig. 10). Thus, the effective interdiffusion coefficients and the proposed model are accurate enough to describe the behavior of the system for its industrial application.

Although the diffusivity values were derived from the Wilke–Chang equation, they may be considered acceptable for practical purposes, taking into account the good fit of the model to the experimental curves.

It is also significant that a WMP mixture allows the use of almost the entire resin capacity compared with the poor results reached when crude polyol is passed through a cation exchange bed [4,5]. For its practical application, the potassium content of polyol must be 5 ppm or less. Table 8 shows the useful capacity n_5 (meq g^{-1}), the percentage of total capacity ($n_5/n^{\infty} \times 100$) and the weight of polyol per gram of dry resin (W_p/W) that can be purified in each experiment before the concentration of potassium in the effluent exceeds 5 ppm. As the height of the bed increases or the flow rate decreases, the useful capacity increases, reaching 73% versus the 54% reported in a previous work dealing with this purification method [7].

Finally, 15 operation–regeneration cycles were carried out using a conventional regeneration method (H_2O, HCl 0.5 M, H_2O). The breakthrough curves remained identical thereafter, demonstrating efficient and simple regeneration. This regeneration technique is effective and economical compared with the resin regeneration method used for the purification of crude polyol without dilution [5].

4. Conclusion

The removal of potassium from crude polyols using ternary water–methanol–polyol mixtures on Amberlite 252, a strong cation exchange resin, can be carried out in a discontinuous or semicontinous way.

The equilibrium for the uptake of potassium from these mixtures is very favorable and can be considered as irreversible for practical purposes. A two-step reaction scheme was proposed and equilibrium data were correlated by an equation derived according to the mass action law.

Effective intraparticle diffusivities were fitted using a homogeneous model. The effects of the viscosity of the bulk solution and of resin swelling on the diffusion coefficients could be correlated by a simple and accurate empirical equation.

Breakthrough curves were obtained under a wide range of conditions, being well correlated by the expression for breakthrough curves with a rectangular isotherm. A conventional aqueous regeneration technique can be used for the regeneration of spent resin.

This purification process is generally applicable to flexible and rigid polyols, being economically competitive with other purification methods currently used.

5. Nomenclature

C_i	bulk liquid phase concentration of species i, meq l^{-1}
C_{i0}	initial bulk liquid phase concentration of species i, meq l^{-1}
$C_{i\infty}$	bulk liquid phase concentration of species i after infinite time, meq l^{-1}
C_i^*	equilibrium bulk liquid phase concentration of species i, meq l^{-1}
D_{HK}	effective intraparticle interdiffusion coefficient, $cm^2 s^{-1}$
D_i	effective intraparticle diffusion coefficient of component i, $cm^2 s^{-1}$
F	volumetric flow, $l h^{-1}$
k_f	liquid phase mass transfer coefficient, s^{-1}
k'_f	liquid phase mass transfer coefficient, $cm s^{-1}$
k_p	resin phase mass transfer coefficient, s^{-1}
K_2	equilibrium constant for Eq. (3), $kg meq^{-1}$
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
n_i	local solid phase concentration, $meq g^{-1}$
n_i^*	equilibrium solid phase concentration, $meq g^{-1}$
n_0	resin phase concentration in equilibrium with feed in breakthrough curves, $meq l^{-1}$
n^∞	saturation capacity, $meg g^{-1}$
p_n	non-zero roots of Eq. (14)
R	parameter of Eq. (5)
R_p	radius of resin particle, cm
Re	$2R_p v \rho \epsilon / \mu (1 - \epsilon)$
S	resin swelling, Eq. (15)
T	temperature, K
t	time, s
v	interstitial fluid velocity, $cm s^{-1}$
V	volume of bulk solution, l
W	weight of resin particles, g
W_p	weight of polyol in the mixture, g
X^*	ionic fraction in solution at equilibrium
Y^*	ionic fraction in the resin phase at equilibrium
z	distance through the bed, cm

5.1. Greek symbols

α	dimensionless variable, Eq. (14)
β	dimensionless variable, Eq. (6)
δ	$k_f C_0 / k_p n_0$
ϵ	void fraction of bed
μ	viscosity, $g cm^{-1} s^{-1}$
ξ	$(1 - \epsilon) k_f z / \epsilon v$

ρ	apparent density of resin particles, $g l^{-1}$
τ	$C_0 k_f (t - z/v) / n_0$

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