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Adsorption Isotherms for Oleic Acid Removal from Ethanol + Water Solutions Using the Strong Anion-Exchange Resin Amberlyst A26 OH

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Adsorption isotherms for the removal of oleic acid from ethanol + water solutions using a strong anion-exchange resin (Amberlyst A26 OH) were experimentally determined. The equilibrium data were correlated using the Langmuir model by adjusting the parameters q_m/(g of acid·g of dry resin^{-1}), maximum content that can be adsorbed on solid phase, and K_d/(g of acid·g of solvent^{-1}), the equilibrium constant. The Freundlich and Redlich−Petersen models were also used, but the Langmuir model shows the lower average deviations between experimental and calculated results. The behavior and the capacity of the resin to remove the fatty acid from the liquid phase were evaluated at different experimental conditions: the water content in ethanol was varied within the range (0 to 15) mass %, and two equilibrium temperatures were investigated: (298.15 and 313.15) K. It was observed that both variables, water content in ethanol and equilibrium temperature, do not significantly influence the equilibrium behavior. It was also observed that the strong anion-exchange resin (Amberlyst A26 OH) has a good performance in the removal of the fatty acid from the liquid phase. To determine exactly the mechanism for the uptake of oleic acid by the resin, equilibrium experiments were done with different oleic acid concentrations (7, 9, and 11) mass % in solution with water content in ethanol (0.57 ± 0.01) mass % at 298.15 K. In this way the concentration of oleic acid in resin phase was determined, and it was observed than the most important mechanism of uptake is the ion exchange.

Introduction

Crude vegetable oils are composed mainly by triacylglycerols, but they also contain lower amounts of partial acylglycerols, free fatty acids (FFA), and other minor components. The refining process of edible oils involves a series of steps in order to remove the undesirable contaminants, the most important step being the removal of FFA. The traditional refining methods, physical and caustic refinings, are not appropriate for crude oils with high FFA content. In the case of such oils, both processes cause high losses of neutral oil and nutraceutical compounds, the physical refining is energy intensive, and the chemical refining generates high amounts of soap stock.

For these reasons, several investigations are performed in order to develop alternative refining methods. The oil deacidification by liquid−liquid extraction with an appropriate solvent is one of those alternative methods.[1,2] Its advantages are the mild operational conditions concerning temperature and pressure, the possibility of restricting the loss of neutral oil and nutraceutical compounds by an adequate selection of the water content in the ethanolic solvent, and the easy stripping of the residual solvent from the refined oil as a consequence of the very high volatility difference between ethanol and neutral oil.[3,4]

But the recovery of the solvent from the extract phase was still not investigated. Although such a recovery could easily be performed by distillation, this option would certainly be energy intensive. In the present work, we investigated the possibility of using anion-exchange resins in order to adsorb fatty acids from the extract phase, allowing the recovery of the solvent for a new liquid−liquid deacidification step. In this case, the use of ion-exchange resins could be considered as a complement of the whole liquid−liquid extraction process, whose specific purpose is to perform the solvent recovery from the extract phase.

The use of resins in the processing of fatty systems has already been investigated in the literature. Resins were used in the chromatographic separation of unsaturated components, such as fatty acid methyl esters;[5] in the separation of crude palm oil carotene;[6] in the separation of mixtures of free fatty acids, of fatty esters, and of triglycerides;[7] and in the purification of polyunsaturated ω-3 free fatty acids present in the lipidic fraction of microalgas.[8]

Nowadays, the use of ion-exchange resins is very well established as a unit operation. The applicability of ion-exchange resins in industrial processes has steadily grown up, resulting in new techniques and processes that goes far beyond the water purification and demineralization that were the first and most important applications of ion-exchange resins.[9,10]

However, investigations using ion-exchange resins in organic media are still rare.[11−15] In this way, the study of adsorption isotherms and the ion-exchange mechanism in these conditions is important in order to develop new purification techniques for organic solutions.

In the present work, adsorption isotherms for fatty acid removal from ethanol + water solutions, using the strong anion-exchange resin Amberlyst A26 OH, were determined. Fatty acids are long-chain monocarboxylic acids that can be considered very weak electrolytes with partially dissociated carboxylic groups in polar solutions, as those used in the present work. The adsorption of fatty acids in anionic

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Table 1. Resin Characteristics

adsorbent	resin	surface area ($m^2 \cdot g^{-1}$)	average pore diameter (Å)	harmonic mean size (mm)	concentration of sites ($eq \cdot L^{-1}$)	bulk apparent density ($g \cdot L^{-1}$)
Amberlyst A 26 OH	strong anionic	30	290	0.56−0.70	>0.80	675
Amberlyst A 21	weak anionic	35	110	0.49−0.69	>1.30	660
Amberlite XAD 4	adsorption	750	100	0.49−0.69	no sites	680

resins involves an ion-exchange equilibrium in which the hydroxyl ions OH^- initially present in the resin are partially replaced by counterions (dissociated fatty acids):

$$E^{\alpha+}OH_{\alpha}{}^{-} + \beta \cdot R - COO^{-} + \beta \cdot H^{+} \Leftrightarrow E^{\alpha+}OH_{\alpha-\delta}{}^{-}R - COO_{\delta}{}^{-} + (\beta - \delta) \cdot R - COO^{-} + \beta \cdot H^{+} + \delta \cdot OH^{-} \quad (1)$$

where $E^{\alpha+}OH_{\alpha}{}^{-}$ represents the anionic resin, in its OH^- form and containing α active sites, $R - COO^-$ indicates the dissociated fatty acid and $E^{\alpha+}OH_{\alpha-\delta}{}^{-}R - COO_{\delta}{}^{-}$ is the ion exchanger with δ active sites occupied by the fatty acid anion.

For most edible oils the main free fatty acid is oleic acid. For this reason, a commercial oleic acid was selected in the present work as the fatty acid source. The experimental results were fitted using Langmuir, Freundlich, and Redlich−Petersen models. The best fitting was obtained in the case of the Langmuir model, and the corresponding parameters, q_m/(g of acid·g of dry resin^{-1}) and K_d/(g of acid·g of solvent^{-1}), were reported.

Experimental Section

Chemicals. Commercial grade oleic acid was purchased from Merck. Anhydrous and azeotropic ethanol, sodium hydroxide, and sodium chloride (all analytical grade) were also supplied by Merck. Analytical grade chloridric acid was purchased from Vetec (Brazil). The ethanolic solutions were prepared, using an analytical balance (Adam, model AAA200, accurate to 0.0001 g), by adding demineralized water (Milli-Q Academic, model JBRQ 100 06) to anhydrous ethanol. The water contents in anhydrous and azeotropic ethanol and in the ethanolic solutions were determined by Karl Fisher titration using a Metrohm device (model 701 Kf Titrino and 703 Ti Stand).

The corresponding water concentrations were (0.57 ± 0.01) mass % (anhydrous ethanol), (3.09 ± 0.06) mass %, (7.06 ± 0.03) mass % (azeotropic ethanol), (9.03 ± 0.04) mass %, and (14.64 ± 0.27) mass %. The commercial grade oleic acid was analyzed by gas chromatography of fatty acid methyl esters according to the procedure of the AOCS Official Method (1-62).[16]

The strong anionic resin Amberlyst A26 OH and the other two types of resins tested, the weak anionic resin Amberlyst A 21 and the adsorption resin Amberlite XAD 4, were kindly supplied by Rohm and Haas. According to the manufacturer they have the characteristics shown in Table 1. All the resins tested have a styrene−divinylbenzene, hydrophobic matrix.

Procedures. The experimental setup consisted of equilibrium cells with an internal volume of 50 mL or 200 mL for conducting experiments with oleic acid initial concentrations in the solutions varying from (9.0 to 6.0) mass % or from (4.0 to 5.8) mass %, respectively. The equilibrium cells were hermetically sealed and connected to a thermostatic bath (Cole Parmer, model 12101-15), accurate to 0.1 K.

The suspensions formed by the resin and the solutions were vigorously stirred by solution recirculation in the cells with the help of a peristaltic pump (Cole Parmer, model masterflex 7521-40 and 7553-60).

Equilibrium data were generated for systems containing the resin and solution with different initial oleic acid concentrations ((4.0 to 9.0) mass %). These solutions were obtained by adding oleic acid to the previously prepared ethanol + water mixtures, and the uncertainty in their concentrations was estimated as $\pm 8.8 \cdot 10^{-4}$ mass %.

Two temperatures, (298.15 ± 0.1) K and (313.15 ± 0.1) K, were used in the experiments. To obtain the experimental data a constant proportion resin:solution, corresponding to 1:3 in a mass basis, was used in each cell. Before performing each equilibrium experiment, the resin was preconditioned in order to guarantee the removal of the excess moisture and the swelling of the resin. The preconditioning involved three steps: in the first step, the resins, especially the anionic ones, were pretreated with demineralized water in order to be activated in its OH^- form; in the second step, the resins were prewashed several times with the ethanolic solvent at the selected water concentration; and afterward they were immersed in the ethanolic solution with the same water content for at least 0.5 h. The pretreated resin samples and the oleic acid solutions, at the chosen initial concentrations, were weighed (Adam analytical balance, model AAA200, accurate to 0.0001 g) according to the proportion mentioned above and fed into each cell. The suspensions were maintained under vigorous stirring at fixed temperature until equilibrium was achieved (5 h). Prior experiments confirmed that this period guarantees the achievement of equilibrium.

At the end of this period, the solutions were removed from each cell with the help of a syringe. The oleic acid concentration in the solutions was determined using titration (modified AOCS method Ca 5a-40)[16] with an automatic titrator (Schott, model titroline easy). Measurements were made in triplicate.

As a consequence of the fact that the resins used in the experiments were prewetted, the amount of solvent carried by the resins in each set of experiments was determined by drying a sample between (3 and 5) g until constant mass in a vacuum oven (Napco model 5831) at 283.2 K for (8 to 9) h. These measurements were made in triplicate. The same procedure was also used for determining the initial moisture content of the resins before the preconditioning.

To compare the performances of the three different resins in the removal of oleic acid, a first set of experiments was conducted at (298.15 ± 0.1) K, using oleic acid solutions with 7.0 mass % dissolved in aqueous ethanol containing (7.06 ± 0.03) mass % of water. This first set of experiments clearly indicated that the strong anionic resin has a performance much better than the weak anionic and adsorption resins. The best one (Amberlyst A26 OH) was then selected to be used in the further set of equilibrium experiments described above.

As usual in experiments for determining adsorption isotherms, the equilibrium concentration in the solid phase was calculated by mass balance. The mass balance was performed on a solute (oleic acid) free basis, taking into account the initial and final oleic acid concentrations and the solvent carried by the resins into the cell. The equilibrium concentrations were also expressed on a solute free basis, as q^*/(g of oleic acid·g of dry resin^{-1}) versus C^*/(g of oleic acid·g of solvent^{-1}). Since the initial concentrations of the solutions were relatively high and they cannot be considered as dilute ones, the option for performing the mass balance as well as expressing the equilibrium concentrations on a solute free basis is the best one.

To validate the mass balance method for determining the solid phase composition, the resin concentration was directly measured for a limited set of equilibrium experiments performed at (298.15 ± 0.1) K, using solutions with (7, 9 and 11) mass % of oleic acid dissolved in ethanol with (0.57 ± 0.01) mass % of water and the strong anionic resin. First of all, equilibrium experiments were conducted at the three different initial concentrations to obtain the resin with adsorbed oleic acid. At the end of the equilibrium experiments, the liquid phase of each cell was analyzed in triplicate to determine the oleic acid concentration in the solutions, and the concentration of oleic acid in resin phase could be determined by mass balance, as usual. But in the present case the resin samples used in the experiments were carefully washed with ethanol containing (0.57 ± 0.01) mass % of water until no free acid could be detected in the solution. The wash procedure was repeated several times, and the total amount of ethanol used corresponds to 10 to 15 times the mass of resin. After each wash procedure, the acid content of the solution was determined by titration using the methodology already described. The wash procedure was interrupted only after two titration sequences indicating that there is no more free acidity to be washed out. This procedure was employed in order to remove the acid physically adsorbed in the resin. After that, the resin was contacted with a known excess of standard ethanol solution of sodium hydroxide (0.1 eq·L^{-1}), to promote the resin regeneration. The regeneration was performed in the equilibrium cells with stirring, until equilibrium was achieved (5 h), such as in the equilibrium experiments describe above. After this period a known aliquot of the liquid phase was analyzed by titration with a standardized ethanolic solution of chloridric acid (0.1 eq·L^{-1}) using an automatic buret (Dosimat 715, model from Metrohm). This analytical measurement allowed the direct calculation of the residual alkali in solution and, consequentially, the amount of sodium hydroxide used specifically in the resin regeneration. In this way the oleic acid concentration of the resin phase could be experimentally determined and compared with the results of the mass balance.

To better characterize the strong anionic resin Amberlyst A26 OH, the concentration of its acid sites was experimentally determined. This determination was performed by conducting breakthrough experiments in a small glass column. An amount of approximately 20 mL of resin, in its activated OH$^-$ form, was carefully weighed (with accuracy of ±0.0001 g) and packed in the glass column. Aqueous solution of sodium chloride, (15.00 ± 0.02) mass %, was continuously pumped through the resin bed at a flow rate of (16 mL·min^{-1}), with the help of a peristaltic pump (Cole Parmer, model masterflex 7553-60). In this way the OH$^-$ form of the activated resin sites was converted into the Cl$^-$ form. Samples of the effluent solution were monitored by pH and refractometry index measurements to confirm the end of the ion-exchange process between OH$^-$ and Cl$^-$ and to guarantee the completion of the breakthrough curve. At the end of the process, the whole effluent solution was analyzed by titration against a standardized solution of chloridric acid (0.1 eq·L^{-1}) using an automatic buret (Dosimat 715, model from Metrohm). The determination of the alkali amount in solution corresponds exactly to the OH$^-$ quantity generated by the ion-exchange process, allowing the calculation of the resin capacity. This procedure was performed in triplicate, so that the average resin capacity and the corresponding standard deviation were estimated.

Table 2. Fatty Acid Composition of Merck Oleic Acid

symbol	fatty acid		M^b/g·mol^{-1}	mol %	mass %
M	miristic	C14:0[a]	228.38	0.55	0.45
P	palmitic	C16:0	256.43	5.89	5.39
S	stearic	C18:0	284.48	1.57	1.59
O	oleic	C18:1	282.47	80.18	80.76
Li	linoleic	C18:2	280.45	11.81	11.81

[a] In Cx:y, x = number of carbons, and y = number of double bonds. [b] M = molecular mass.

Results

The fatty acid composition of the commercial oleic acid is given in Table 2, and its corresponding average molecular mass is 280.43 g·gmol^{-1}. As can be seen, oleic acid is the major component, but the commercial fatty acid also contains significant amounts of linoleic and palmitic acids.

Tables 3, 4, and 5 show the equilibrium results: in the first table the performances of the three different resins tested are presented, the second table contains the comparison between the solid-phase concentrations in the strong anionic resin obtained by mass balance and by the direct measurement of its composition, and the third table gives the set of equilibrium results for the strong anionic resin.

The uncertainties of the solution equilibrium concentrations (C^*) can be estimated on the basis of the standard deviations of the analytical measurements, and their values varied within the range ($3.1 \cdot 10^{-8}$ to $1.2 \cdot 10^{-4}$) g of oleic acid·g of solvent^{-1}, being the lower figures obtained for the lower concentration values. The variation coefficients for these measurements were lower than 3 % for the majority of the experimental data. Fewer measurements had values around 10 %, particularly those performed at lower concentrations. The uncertainties of the solid-phase concentrations (q^*) were calculated by error propagation and their values varied always in the range ($1.5 \cdot 10^{-2}$ to $2.7 \cdot 10^{-4}$) g of oleic acid·g of dry resin^{-1}, being the lower figures obtained for the lower concentration values.

As can be seen in Table 3, the strong anion-exchange resin (Amberlyst A26 OH) was the best one for removal of oleic acid once the values of the equilibrium concentration of oleic acid in the resin phase (q^*) and (C^*) equilibrium concentration in solution phase are larger and lower, respectively, than the correspondent values for the other two resins tested. The Amberlyst A26 OH resin had the best performance because it contains strong ionic groups with high dissociation capacity that improves the possibility of ion exchange. For this reason, the strong anion-exchange resin (Amberlyst A26 OH) was selected to be used in the subsequent equilibrium experiments. In the case of the other two resins tested, the capacity of removing oleic acid was much lower. This occurs particularly in the case of the adsorption resin that contains no ionic groups, so that only physical adsorption is possible. Considering that fatty acids are very weak electrolytes, the comparison between the three resin types seems to suggest that the

Table 3. Equilibrium Concentration in Solid and Liquid Phases for Three Different Types of Resin[a]

adsorbent	C^* (g of acid·g of solvent^{-1})	q^* (g of acid·g of dry resin^{-1})	X_i (mass %)[b]	X_p (mass %)[c]
Amberlyst A 26 OH	$1.06 \cdot 10^{-4}$	1.275	73.7 ± 0.1	83.3 ± 0.4
Amberlyst A 21	$3.72 \cdot 10^{-2}$	0.278	54.3 ± 0.2	76.4 ± 0.4
Amberlite XAD 4	$4.57 \cdot 10^{-2}$	0.172	50.4 ± 0.1	73.7 ± 0.4

[a] Solvent: ethanol (7.06 ± 0.03) mass % of water; T/K = 298.15. Initial fatty acid concentration = ($6.99 \pm 8.8 \cdot 10^{-4}$) mass %. [b] Initial resin moisture (before preconditioning), on wet basis. [c] Moisture after preconditioning, on wet basis.

Table 4. Comparison between the Value of Equilibrium Concentration in Solid Phase Determined by Mass Balance and Experimentally after Resin Regeneration[a]

initial fatty acid concn (mass %)	q^* (g of acid·g of dry resin^{-1}) mass balance	q^* (g of acid·g of dry resin^{-1}) exptl
$7.61 \pm 2.98 \cdot 10^{-7}$	1.296	1.275
$9.59 \pm 2.02 \cdot 10^{-6}$	1.323	1.307
$11.63 \pm 1.64 \cdot 10^{-5}$	1.326	1.301

[a] Solvent: ethanol (0.57 ± 0.01) mass % of water; T/K = 298.15; resin: Amberlyst A26 OH.

most important mechanism of oleic acid removal in the strong anionic resin is by ion exchange.

As can be seen in Table 4, the q^* values obtained by mass balance and by the analytical measurements after resin regeneration were very close. In fact, the average deviation between both values is 1.6 % and the values obtained by mass balance were always slightly higher, indicating that only a small amount of oleic acid was retained by physical adsorption. In the experimental determination of q^* after the resin regeneration, the solid phase was washed with ethanol several times, so that all oleic acid physically adsorbed were removed with only the fatty acid remaining that effectively participated in the ion-exchange process. This last result confirms that in the case of Amberlyst A26 OH the main mechanism of adsorption is ion exchange. The very low differences in the q^* values obtained by both methods indicate that the mass balance allows a very good estimation of the equilibrium concentrations in the resin phase.

The q^* values shown in Table 4 are close to the maximal resin capacity. Taking into account the resin initial moisture (see Table 3), its maximal capacity can be converted to a wet basis, as it is usually reported in the literature. In this case a q^* value of 1.300 g of acid·g of dry resin^{-1} corresponds to 0.342 g of acid·g of wet resin^{-1}. Considering the bulk apparent density of the resin (675 g·L^{-1}, see Table

Table 5. Adsorption Isotherms of Oleic Acid[a]

ethanol + 0.57 mass % of water T/K = 298.15 X_p = (83.0 ± 0.3) mass %[b]		ethanol + 3.09 mass % of water T/K = 298.15 X_p = (83.9 ± 0.2) mass %		ethanol + 7.06 mass % of water T/K = 298.15 X_p = (83.3 ± 0.3) mass %	
C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})	C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})	C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})
$1.11 \cdot 10^{-5}$	1.039	$1.18 \cdot 10^{-5}$	1.105	$1.22 \cdot 10^{-5}$	1.021
$9.96 \cdot 10^{-6}$	1.053	$1.26 \cdot 10^{-5}$	1.154	$1.71 \cdot 10^{-5}$	1.127
$1.75 \cdot 10^{-5}$	1.131	$1.00 \cdot 10^{-5}$	1.086	$1.91 \cdot 10^{-5}$	1.135
$3.28 \cdot 10^{-5}$	1.180	$4.71 \cdot 10^{-5}$	1.201	$2.37 \cdot 10^{-5}$	1.168
$3.32 \cdot 10^{-5}$	1.169	$7.13 \cdot 10^{-5}$	1.265	$3.17 \cdot 10^{-5}$	1.206
$3.42 \cdot 10^{-5}$	1.147	$1.49 \cdot 10^{-4}$	1.296	$6.25 \cdot 10^{-5}$	1.279
$5.18 \cdot 10^{-4}$	1.257	$2.49 \cdot 10^{-4}$	1.308	$1.04 \cdot 10^{-4}$	1.303
$2.25 \cdot 10^{-3}$	1.269	$4.69 \cdot 10^{-3}$	1.376	$3.98 \cdot 10^{-4}$	1.322
$3.24 \cdot 10^{-3}$	1.334	$8.29 \cdot 10^{-3}$	1.386	$7.10 \cdot 10^{-4}$	1.339
$5.42 \cdot 10^{-3}$	1.258	$1.25 \cdot 10^{-2}$	1.419	$2.12 \cdot 10^{-3}$	1.342
$2.69 \cdot 10^{-3}$	1.313			$4.38 \cdot 10^{-3}$	1.357
				$6.18 \cdot 10^{-3}$	1.362
				$1.33 \cdot 10^{-2}$	1.370

ethanol + 9.06 mass % of water T/K = 298.15 X_p = (83.9 ± 0.1) mass %		ethanol + 14.64 mass % of water T/K = 298.15 X_p = (83.5 ± 0.3) mass %		ethanol + 7.06 mass % of water T/K = 313.15 X_p = (83.3 ± 0.3) mass %	
C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})	C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})	C^*/(g of acid·g of solvent^{-1})	q^*/(g of acid·g of dry resin^{-1})
$1.29 \cdot 10^{-5}$	1.082	$6.29 \cdot 10^{-6}$	1.028	$8.43 \cdot 10^{-6}$	0.980
$1.32 \cdot 10^{-5}$	1.158	$2.49 \cdot 10^{-5}$	1.159	$7.05 \cdot 10^{-6}$	1.010
$1.90 \cdot 10^{-5}$	1.221	$3.66 \cdot 10^{-5}$	1.193	$1.22 \cdot 10^{-5}$	1.059
$4.32 \cdot 10^{-5}$	1.242	$3.31 \cdot 10^{-5}$	1.203	$1.76 \cdot 10^{-5}$	1.112
$2.29 \cdot 10^{-4}$	1.276	$8.61 \cdot 10^{-5}$	1.215	$1.50 \cdot 10^{-5}$	1.115
$8.24 \cdot 10^{-4}$	1.289	$1.16 \cdot 10^{-3}$	1.262	$6.81 \cdot 10^{-5}$	1.211
$7.38 \cdot 10^{-4}$	1.325	$2.49 \cdot 10^{-3}$	1.280	$2.11 \cdot 10^{-4}$	1.247
$2.72 \cdot 10^{-3}$	1.331	$3.86 \cdot 10^{-3}$	1.288	$3.63 \cdot 10^{-4}$	1.248
$2.09 \cdot 10^{-3}$	1.408	$4.69 \cdot 10^{-3}$	1.311	$1.62 \cdot 10^{-3}$	1.258
$9.25 \cdot 10^{-3}$	1.368	$7.32 \cdot 10^{-3}$	1.325	$4.72 \cdot 10^{-3}$	1.265
$9.95 \cdot 10^{-3}$	1.423	$8.45 \cdot 10^{-3}$	1.343	$3.91 \cdot 10^{-3}$	1.344
				$6.98 \cdot 10^{-3}$	1.298
				$1.15 \cdot 10^{-2}$	1.355

[a] Solvent: ethanol + water solutions; resin: Amberlyst A26 OH. [b] Wet basis moisture of the resin after preconditioning with ethanolic solutions.

Table 6. Parameter Values of Langmuir Model

T / K	solution	q_m / (g of acid·g of dry resin^{-1})	K_d / (g of acid·g of solvent^{-1})	AAD (%)[a]
298.15	ethanol + 0.57 mass % of water	1.311 ± 0.033	(2.84 ± 0.28)·10^{-6}	2.55
	ethanol + 3.09 mass % of water	1.329 ± 0.021	(2.26 ± 0.43)·10^{-6}	2.65
	ethanol + 7.06 mass % of water	1.329 ± 0.037	(2.88 ± 0.19)·10^{-6}	1.68
	ethanol + 9.03 mass % of water	1.329 ± 0.031	(2.32 ± 0.41)·10^{-6}	2.93
	ethanol + 14.64 mass % of water	1.309 ± 0.024	(2.26 ± 0.40)·10^{-6}	2.92
313.15	ethanol + 7.06 mass % of water	1.302 ± 0.021	(2.55 ± 0.22)·10^{-6}	2.73

[a] Calculated according to eq 5.

1), this value can be further expressed as 0.823 eq·L^{-1}, a result that is in agreement with the capacity reported by the manufacturer (>0.8 eq·L^{-1}). The resin capacity determined by the breakthrough experiments was 0.85 eq·L^{-1}, with standard deviations of ± 7.5·10^{-5} eq·L^{-1}, a value consistent with the capacity reported by the manufacturer and the q^* values shown in Table 4

The experimental equilibrium data shown in Table 5, corresponding to the counterion (oleic acid) concentration in the solution (C^*) and the concentration of counterion (oleic acid) in the solid phase (q^*), indicated that high amounts of oleic acid can be adsorbed by the strong anionic resin. In fact, the equilibrium concentrations in the liquid phase are in most cases very low, demonstrating that most part of the oleic acid dissolved in the initial solutions was transferred to the solid phase. In some cases, especially for solutions with initial concentration lower than 6.0 mass %, the liquid phase equilibrium concentration were so low that it could not be precisely determined. Considering the titration technique used in the present work, it was estimated that concentrations lower than 3.8·10^{-6} (g of acid·g of solvent^{-1}) (3.8 ppm) could not be determined with the necessary precision. Figure 1 shows the whole set of experimental data, and Figure 2 shows the data obtained at low oleic acid concentrations.

The experimental data were correlated by three different equilibrium models, Langmuir, Freudlich, and Redlich−Petersen isotherms, given in eqs 2−4:[17]

$$q^* = \frac{q_m C^*}{K_d + C^*} \tag{2}$$

$$q^* = K_f (C^*)^n \tag{3}$$

$$q^* = \frac{K_r q_m C^*}{1 + (K_r C^*)^\beta} \tag{4}$$

where C^*/(g of oleic acid·g of solvent^{-1}) is the equilibrium concentration of the counterion in the liquid phase; q^*/(g of oleic acid·g of dry resin^{-1}) is the equilibrium concentration of the counterion adsorbed in the resin; q_m indicates the maximal adsorption capacity of the resin; K_d represents the equilibrium constant; K_f and n are parameters of the Freundlich model; K_r/(g of solvent·g of oleic acid^{-1}) is a constant of the Redlich−Petersen model; and β is denominated degree of heterogeneity, a parameter that usually should be restrained within the range $0 < \beta < 1$. In the case of the Langmuir model, K_d is usually interpreted as the ratio of the desorption (k_2) and adsorption (k_1) rate constants, the constants of the reversible equilibrium reaction on which the Langmuir model is based. Most works in the literature use the Langmuir and Freundlich model for description of the equilibrium behavior using ion-exchange resins.[8,11−14]

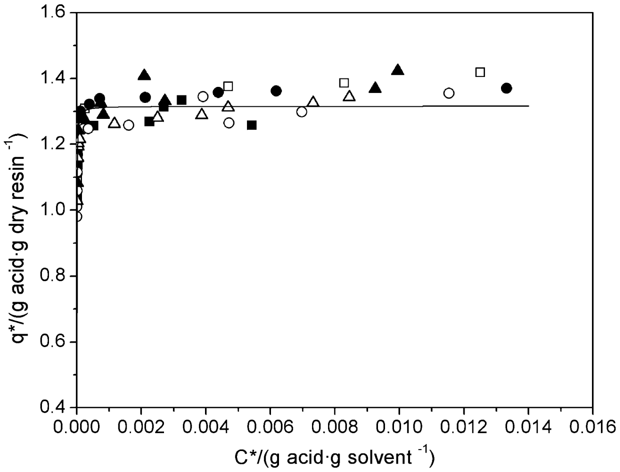

Figure 1. Equilibrium isotherms at 298.15 K: ■, 0.57 mass % of water; □, 3.09 mass % of water; ●, 7.06 mass % of water; ▲, 9.06 mass % of water; △, 14.64 mass % of water. At 313.15 K: ○, 7.06 mass % of water; —, Langmuir model.

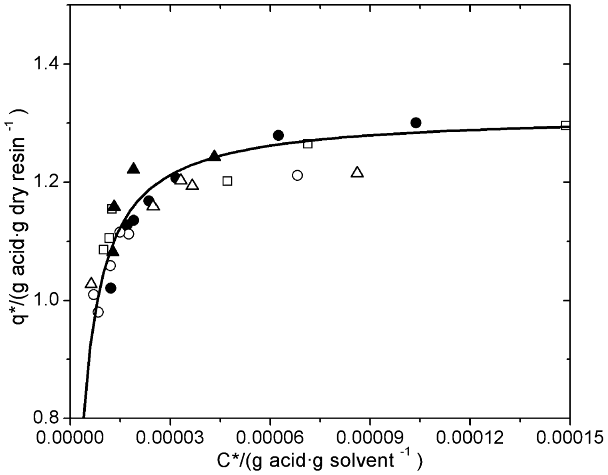

Figure 2. Equilibrium isotherms at low oleic acid concentrations.

The parameter values of the Langmuir model are given in Table 6. The average absolute deviations (AAD) between the experimental (q^*_{exp}) and calculated (q^*_{calc}) data were evaluated according to eq 5 and are also shown in Table 6:

$$\text{AAD} = \frac{1}{m} \sum_{i=1}^{m} \left| \frac{q^*_{\text{exp},i} - q^*_{\text{calc},i}}{q^*_{\text{exp},i}} \right| \times 100 \tag{5}$$

where m is the total number of experimental data. As can be seen in Table 6, the AAD values varied within the range (1.6 to 3.0) %. The corresponding range for the Freundlich model is (3.0 to 5.1) %, always larger than the deviations obtained with the Langmuir model. In the case of the Redlich−Petersen model, the AAD values varied within the range (1.1 to 4.9) %. These deviations are slightly lower than the corresponding results for the Langmuir model only in the case of ethanolic solutions containing (3.09 and 9.03) mass % of water. Such results for the Redlich−Petersen model were obtained restraining the degree of heterogeneity within the recommended range ($0 < \beta < 1$), and its adjusted value tends to be equal to 0.98 for each one of the isotherms. Without this restriction, the parameter β tends to assume the value 1, so that the Redlich−Petersen model becomes identical to the Langmuir model with $K_r = 1/K_d$. The fitting results indicate that the Langmuir model was the best option to correctly describe the experimental data. The K_d values are much lower than 1, reflecting the fact that the equilibrium isotherms are favorable to the removal of the oleic acid by the ion-exchange resin and that their curvatures are convex-upward.[18]

Taking into account the q_m and K_d values and their standard deviations (see Table 6), it can be concluded that the solvent water content and the temperature do not have a significant influence on the equilibrium behavior, at least in the range of values selected for the present work. For this reason a unique set of parameters can be adjusted to the whole set of experimental data. The following results were obtained: q_m/(g of oleic acid·g of dry resin^{-1}) = (1.316 ± 0.007), K_d/(g of oleic acid·g of solvent^{-1}) = $(2.57 \pm 0.16)\cdot 10^{-6}$, AAD = 3.0 %. The same procedure was applied using the Freundlich and Redlich−Petersen models with the following results, respectively: $K_f = (1.600 \pm 0.027)$, $n = (0.0303 \pm 0.0020)$, AAD = 3.6 %; K_r/(g of solvent·g of oleic acid^{-1}) = $(7.5 \pm 0.30)\cdot 10,^5$ q_m/(g of oleic acid·g of dry resin^{-1}) = (1.183 ± 0.024), $\beta = (0.98 \pm 0.03)$, AAD = 3.8 %. Figures 1 and 2 show the experimental data and the Langmuir curve calculated with the unique set of parameters given above.

The small value obtained for the equilibrium constant (K_d) indicates that the adsorption rate constant (k_1) is much higher than the desorption rate constant (k_2), expressing the preference of the solute for the solid phase. Such a result is also reflected in the high slope of the curve in the first part of the isotherm (Figures 1 and 2).

The q_m values indicate the maximal resin capacity. The value of q_m/(eq·L^{-1}) mentioned above as compared with the experimental capacity reflect once more the efficient behavior of the resin in removal of oleic acid by ethanolic solutions. The value of q_m/(eq·L^{-1}) was a slightly lower than the capacity value obtained experimentally, probably because some restriction of oleic acid to contact the activated sites of the resin, caused by the fact that the acid has a large molecular mass and, as seen before, by the fact that little physical adsorption is involved in the mechanism of oleic acid removal.

Conclusions

The strong anion-exchange resin Amberlyst A26 OH had the best performance in the removal of oleic acid from ethanolic solutions, in comparison with the weak anionic resin Amberlyst A 21 and the adsorption resin Amberlite XAD 4.

Adsorption isotherms for the removal of oleic acid from ethanol + water solutions were determined using the strong anion-exchange resin Amberlyst A26 OH. The equilibrium isotherms were not significantly influenced by the water content in the solvent, varied within the range (0.57 to 14.64) mass %, and by the two selected temperatures, (298.15 and 313.15) K. The experimental data were well-correlated by the Langmuir model, with low deviations between experimental and calculated data. The anionic resin presented a very good performance in the removal of oleic acid from ethanolic solutions. The experimental data indicate that the most important mechanism for the uptake of oleic acid is the ion exchange one, although small amounts of acid seems to be physically adsorbed by the anionic resin.

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