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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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Abstract. 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 with the adjusted parameters q_m , maximum content that can be adsorbed on solid phase (g acid/g dry resin), and K_d , equilibrium constant (g acid/g solvent). In this way the behavior and the capacity of the resin to remove the fatty acid from the liquid phase was evaluated. The influences of water content in ethanol (0 to 15) mass % and equilibrium temperature (298.15 and 313.15) K were investigated. 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.

Keywords: Ion Exchange Resins, Adsorption Isotherms and Fatty Acids.

1. Introduction

Crude vegetable oils are composed mainly by triacylglycerols, but they also contain lower amount 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 the 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 soapstock.

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 (Gonçalves and Meirelles, 2004; Rodrigues et al., 2004).

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 (Rodrigues et al., 2003; Gonçalves et al., 2002).

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

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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 (DeJarlais et al., 1983), in the separation of crude palm oil carotene (Latip et al., 2001), in the separation of mixtures of free fatty acids, of fatty esters and of triglycerides (Adlof and Emken, 1981) and in the purification of polyunsaturated ω -3 free fatty acids present in the lipidic fraction of microalgas (Ibáñez González et al., 2001).

Nowadays, the use of ion exchange resins is very well established as an 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 (Miers, 1995; Utsunomiya, 1995).

However, investigations using ion exchange resins in organic media are still rare (Cao et al., 2002; Antonio de Lucas et al., 1997; Anasthas and Gaikar, 1999; Gaikar and Maiti, 1996; Antonio de Lucas et al., 2001). In this way, the study of adsorption isotherms and 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.

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 well fitted by the Langmuir model and the corresponding parameters, q_m (g acid/g dry resin) and K_d (g acid/g solvent), were reported.

2. Material and Methods

Material. Commercial grade oleic acid was purchased from Merck. Anhydrous and azeotropic ethanol, both analytical grade, were also supplied by Merck. The ethanolic solutions were prepared, using an analytical balance (Adam, model AAA200, accurate to 0.0001g), 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 analysed by gas chromatography of fatty acid methyl esters according to the procedure of the AOCS (1988) Official Method (1-62). Its composition is given in Table 1 and the corresponding average molecular mass of the commercial fatty acid is 280.43 g/gmol.

Table 1. Fatty acid composition of Merck oleic acid

Symbol	Fatty acid	M ^b (g/gmol)	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 C_x : y, x = number of carbons, and y = number of double bonds, ^b M = molecular mass

The anionic resin Amberlyst A26 OH was kindly supplied by Rohm and Haas and according to the manufacturer it has the following characteristics: spherical beads with mean size in the range (0.56 to 0.7) mm, average pore diameter 290 Å, adsorption capacity ≥ 0.8 eq/l and bulk apparent density 675 g/l.

The initial resin moisture content was determined by drying until constant mass in a vacuum oven (Napco model 5831) and the obtained value was (73.66 ± 0.12) mass % in a wet basis. The resin was pretreated with demineralized water to be activated in its OH⁻ form.

Methods. The experimental set up 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 (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).

Ion exchange 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 $\pm 8.8 \times 10^{-4}$ 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 pre-conditioned in order to guarantee the removal of the excess moisture and the swelling of the resin. The pre-conditioning involved two steps: in the first one the resin, in its OH⁻-form, was pre-washed several times with the ethanolic solvent at the selected water concentration, and afterwards the resin was immersed in the ethanolic solution with the same water content for at least half an hour. The pretreated resin samples and the oleic acid solutions, at the chosen initial concentrations, were weighed (Adam analytical balance, model AAA200, accurate to 0.0001g) 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 (1988) Method Ca 5a-40) with an automatic titrator (Schott, model titroline easy). Measurements were made in triplicate, with standard

deviations in the range of (3.1×10^{-8} to 1.2×10^{-4}), 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.

By the fact that the resin used in the experiments was prewetted, the amount of solvent carried by the resin was determined by drying a sample between (3 to 5) g until constant mass in a vacuum oven (Napco model 5831) at 283.2 K for (8 to 9) h. Such measurements were made in triplicate, and the obtained values for the solvent content in the prewetted resin with different ethanolic solutions varied in the range (83.0 ± 0.3 to 84.0 ± 0.1) mass % in a wet basis.

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 resin into the cell. The equilibrium concentrations were also expressed on a solute free basis, as q^* (g of oleic acid/g of dry resin) versus C^* (g of oleic acid/g of solvent).

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. 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 (3.1×10^{-8} to 1.2×10^{-4}) g of oleic acid/g of solvent. The uncertainties of the solid phase concentration, q^* , were calculated by error propagation and their values were always lower than 3.0×10^{-3} g of oleic acid/g of dry resin.

3. Results

The experimental equilibrium data obtained for each system investigated, corresponding to the counterion (oleic acid) concentration in the solution (C^*), and the concentration of counterion (oleic acid) adsorbed in the resin (q^*), are shown in Figure 1 and Figure 2.

As can be observed in these Figures, high amounts of oleic acid can be adsorbed by the resin. In fact, the equilibrium concentrations in the liquid phase are in most cases very low, indicating that most part of the oleic acid dissolved in the initial solutions was transferred to the solid phase. In some cases, specially 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 acid·g 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 the data obtained at low oleic acid concentration.

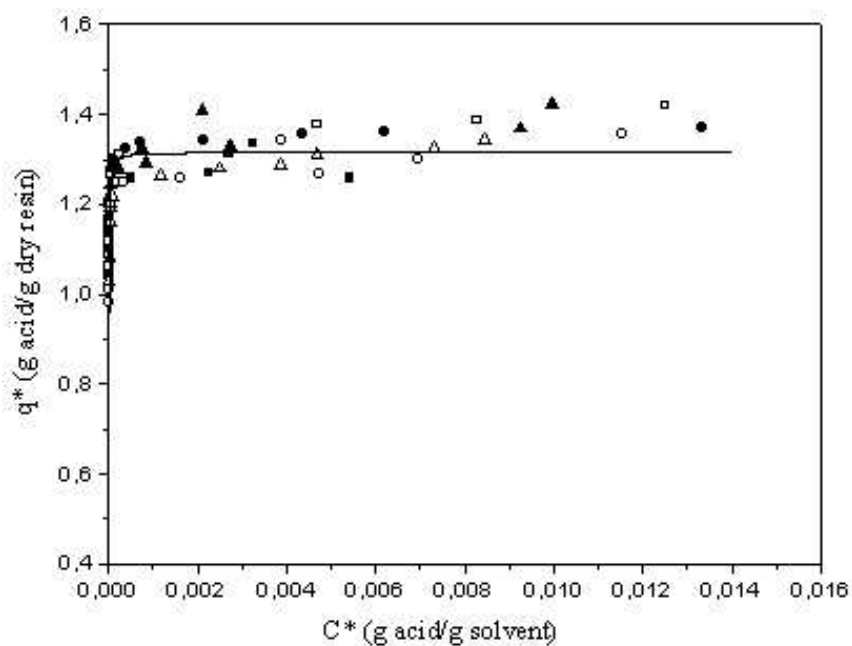


Fig. 1. Equilibrium isotherms at 298.15 K: (■) 0.57 mass % of water; (□) 3.09 mass % of water; (●) 7.06 mass % of water; (▲) 9.06 mass % of water; (Δ) 14.64 mass % of water; and at 313.15 K: (○) 7.06 mass % of water; (—) Langmuir model.

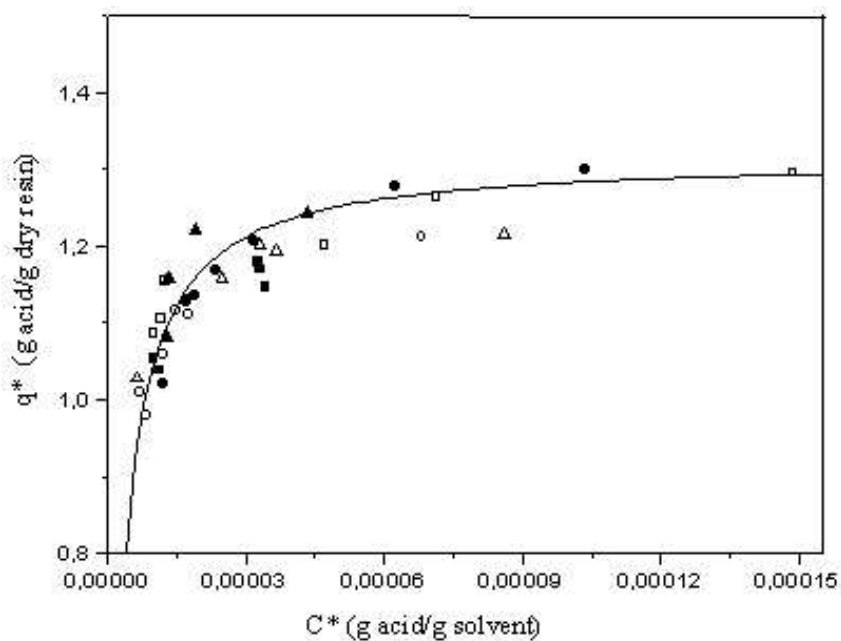


Fig. 2. Equilibrium isotherms at low oleic acid concentrations.

The experimental data were correlated by the Langmuir equilibrium model, given in Eq. (1) below:

$$q^* = \frac{q_m \cdot C^*}{K_d + C^*} \quad (1)$$

Where C^* (g oleic acid/g solvent) is the equilibrium concentration of the counterion in the liquid phase, q^* (g oleic acid/g dry resin) 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_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 (Ibáñez Gonzalez et al., 2001; Cao et al., 2002; Antonio de Lucas et al., 1997; Anasthas and Gaikar, 1999; Gaikar and Maiti, 1996).

The parameter values of the Langmuir model are given in Table 2. The Average Absolute Deviations (AAD) between the experimental (q_{exp}^*) and calculated (q_{calc}^*) data were evaluated according to Eq. (2) below and are also shown in Table 2.

$$AAD = \frac{1}{m} \cdot \sum_{i=1}^m \left| \frac{q_{exp, i}^* - q_{calc, i}^*}{q_{exp, i}^*} \right| \times 100 \quad (2)$$

Where m is the total number of experimental data. As can be seen in Table 2 the AAD values varied within the range (1.6 to 3.0) %.

Table 2. Parameters values of the Langmuir model

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

The fitting results indicate that the Langmuir model describe very well 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 (Brunauer et al., 1940).

Taking into account the q_m and K_d -values and their standard deviations (see Table 2), it can be concluded that the water content in the solvent 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 oleic acid/g dry resin) = (1.316 ± 0.007) , K_d (g oleic acid/g solvent) = $(2.57 \pm 0.16) \times 10^{-6}$, AAD = 3.0 %. This generalized Langmuir curve is shown in Figures 1 and 2.

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 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. Taking into account the resin initial moisture, its maximal capacity can be converted to a wet basis, as it is usually reported in the literature. In this case the q_m (g acid/g dry resin) value (1.316) corresponds to 0.347 (g acid/g wet resin). Considering the bulk apparent density of the resin, this value can be further expressed as 0.834 eq/l, a result that is in agreement with the capacity reported by the manufacturer (> 0.8 eq/l).

4. Conclusions

Adsorption isotherms for the removal of oleic acid from ethanol + water solutions were determined, using the 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.

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