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Adsorption Isotherms for Removal of Linoleic Acid from Ethanolic Solutions Using the Strong Anion Exchange Resin Amberlyst A26 OH

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Adsorption isotherms for the removal of linoleic acid from aqueous ethanol were measured using a strong anion exchange resin (Amberlyst A26 OH). The data for linoleic acid were compared with previously published results for oleic acid. The equilibrium data were correlated using the Langmuir and Freundlich isotherms. Lower average deviations between experimental and calculated results were obtained with the Langmuir model. The capacity of the resin for adsorbing linoleic acid was evaluated at different water contents in ethanol, 100 $w = 0.50$ to 15.27, and at 298.15 K. The water content in ethanol does not influence significantly the equilibrium behavior, and the strong anion exchange resin has a good performance in the removal of linoleic acid from the liquid phase.

Introduction

Interest in the production of cottonseed oil has been growing because of its excellent performance in the frying process and its nutritional quality. Crude cottonseed and soybean oils contain essential fatty acids, the most important being linoleic acid, as well as vitamin E or tocopherols, natural antioxidants to which properties of preventing cardiovascular disease and cancer have been attributed.[1−5] Part of this nutritional value is lost during oil refining, either due to the occurrence of undesirable reactions, such as the transisomerization of fatty components, or due to the evaporation and degradation of nutraceuticals. As a consequence of its mild operational conditions, oil deacidification by solvent extraction with aqueous ethanol can preserve the quality of the final product and reduce the loss of nutraceutical components.[4,5] Nevertheless, the required recovery of the solvent from the extract phase generated during liquid−liquid extraction has still not been comprehensively investigated. In the present work we investigated the use of an anion exchange resin for adsorbing linoleic acid from the extract phase, allowing the solvent recovery for a new deacidification step. The use of resins in the processing of fatty acid systems has already been investigated in previous work,[6] but in the case for adsorbing oleic acid, the major fatty acid present in corn and rice bran oils. A comparison between the data obtained in the present work and in the previous one can then be made.

Experimental Section

Chemicals. Commercial grade linoleic acid was purchased from Merck. Anhydrous and azeotropic ethanol, both of analytical grade, were also supplied by Merck. Ethanolic solutions of different water contents were gravimetrically prepared, and their water concentrations (100 w, mass fraction) were: 0.50 ± 0.01 (anhydrous ethanol), 3.23 ± 0.06, 6.79 ± 0.03 (azeotropic ethanol), 8.22 ± 0.04, and 15.27 ± 0.27. Linoleic acid was analyzed according to the American Oil Chemists' Society (AOCS) methodology.[7] Its composition is given in Table 1, and the average molecular mass is 279.18 $g \cdot mol^{-1}$. The anionic resin Amberlyst A26 OH was kindly supplied by Rohm and Haas and has the same characteristics presented in our previous work.[6] The initial resin moisture content was 100 $w = 73.7 \pm 0.1$ on a wet basis, and the corresponding values for the resin prewetted with the different ethanolic solutions varied from 100 $w = 76.3$ to 77.3, on a wet basis too.

Table 1. Fatty Acid Composition of Merck Linoleic Acid

symbol	fatty acid		M^b/g·mol^{-1}	100 x	100 w
M	miristic	C14:0[a]	228.38	0.22	0.18
P	palmitic	C16:0	256.43	6.95	6.38
S	stearic	C18:0	284.48	3.22	3.28
O	oleic	C18:1	282.47	16.95	17.15
Li	linoleic	C18:2	280.45	72.09	72.42
Le	linolenic	C18:3	278.44	0.41	0.41
A	arachidic	C20:0	312.54	0.16	0.18

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

Procedure. The experimental runs were performed in the same way described in our previous work, including the analytical methods and corresponding equipment for measuring water and fatty acid contents as well as resin moisture.[6] The experiments were conducted using ethanolic solutions containing five different water contents and initial fatty acid compositions varying from (10.0 to 6.0) % (by mass). A temperature of (298.15 ± 0.1) K was used in the whole set of experiments. Linoleic acid solutions were obtained by adding the solute to the previously prepared ethanol + water mixtures, and the maximal uncertainty in the initial compositions was ± 0.16 % (by mass). The equilibrium liquid-phase composition was measured in triplicate, with standard deviations in the range of ($5.65 \cdot 10^{-7}$ to $1.69 \cdot 10^{-3}$) g of acid·g of solvent^{-1}, being the lower figures obtained for the lower concentration values. The equilibrium composition in the solid phase was calculated by

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Table 2. Adsorption Isotherms for Commercial Linoleic Acid[a]

C^*/(g acid·g solvent^{-1})	q^*/(g acid·g dry resin^{-1})	C^*/(g acid·g solvent^{-1})	q^*/(g acid·g dry resin^{-1})	C^*/(g acid·g solvent^{-1})	q^*/(g acid·g dry resin^{-1})
Ethanol + Water		Ethanol + Water		Ethanol + Water	
(100 w_{ws} = 0.50)[b]		(100 w_{ws} = 3.23)		(100 w_{ws} = 6.79)	
T/K = 298.15		T/K = 298.15		T/K = 298.15	
100 w_{sr}[c] = (76.5 ± 0.3)		100 w_{sr} = (76.4 ± 0.2)		100 w_{sr} = (76.3 ± 0.3)	
$1.29\cdot10^{-4}$	1.045	$5.00\cdot10^{-5}$	0.935	$2.60\cdot10^{-5}$	0.873
$1.34\cdot10^{-4}$	0.977	$5.10\cdot10^{-5}$	0.837	$2.80\cdot10^{-5}$	0.894
$1.40\cdot10^{-4}$	0.907	$5.50\cdot10^{-5}$	0.856	$3.40\cdot10^{-5}$	1.032
$1.43\cdot10^{-4}$	1.057	$5.90\cdot10^{-5}$	0.875	$3.60\cdot10^{-5}$	0.981
$1.62\cdot10^{-4}$	0.933	$6.60\cdot10^{-5}$	0.936	$8.40\cdot10^{-5}$	0.946
$1.74\cdot10^{-4}$	0.962	$6.90\cdot10^{-5}$	0.721	$1.70\cdot10^{-4}$	1.019
$1.83\cdot10^{-4}$	0.987	$7.10\cdot10^{-5}$	0.969	$2.58\cdot10^{-4}$	0.944
$2.33\cdot10^{-4}$	1.097	$9.80\cdot10^{-5}$	1.096	$2.63\cdot10^{-4}$	1.092
$2.59\cdot10^{-4}$	1.133	$9.90\cdot10^{-5}$	1.037	$2.68\cdot10^{-4}$	1.102
$6.14\cdot10^{-4}$	1.117	$1.26\cdot10^{-4}$	0.907	$3.51\cdot10^{-4}$	1.043
$6.36\cdot10^{-4}$	1.097	$1.62\cdot10^{-4}$	0.959	$5.87\cdot10^{-4}$	0.953
$8.42\cdot10^{-4}$	1.102	$1.68\cdot10^{-4}$	0.979	$6.75\cdot10^{-4}$	0.921
$2.47\cdot10^{-3}$	1.129	$2.08\cdot10^{-4}$	1.118	$6.95\cdot10^{-4}$	0.893
$2.95\cdot10^{-3}$	1.127	$2.37\cdot10^{-4}$	1.039	$1.18\cdot10^{-3}$	1.020
$6.41\cdot10^{-3}$	1.140	$7.40\cdot10^{-4}$	1.125	$1.29\cdot10^{-3}$	1.009
$9.88\cdot10^{-3}$	1.124	$1.35\cdot10^{-3}$	1.121	$7.91\cdot10^{-3}$	0.975
$1.58\cdot10^{-2}$	1.117	$1.44\cdot10^{-3}$	1.191	$1.00\cdot10^{-2}$	1.001
$1.78\cdot10^{-2}$	1.111	$2.92\cdot10^{-3}$	1.126	$1.68\cdot10^{-2}$	1.091
$2.24\cdot10^{-2}$	1.107	$4.63\cdot10^{-3}$	1.173	$2.48\cdot10^{-2}$	1.070
		$1.09\cdot10^{-2}$	1.161		
		$1.32\cdot10^{-2}$	1.250		
		$1.70\cdot10^{-2}$	1.190		
		$2.01\cdot10^{-2}$	1.034		
		$2.09\cdot10^{-2}$	1.224		
Ethanol + Water		Ethanol + Water			
(100 w_{ws} = 8.22)		(100 w_{ws} = 15.27)			
T/K = 298.15		T/K = 298.15			
100 w_{sr} = (77.3 ± 0.1)		100 w_{sr} = (77.2 ± 0.3)			
$2.55\cdot10^{-5}$	0.894	$2.45\cdot10^{-5}$	0.728		
$2.70\cdot10^{-5}$	0.814	$2.70\cdot10^{-5}$	0.775		
$2.95\cdot10^{-5}$	0.770	$1.77\cdot10^{-4}$	0.892		
$1.77\cdot10^{-4}$	1.012	$1.88\cdot10^{-4}$	0.857		
$1.83\cdot10^{-4}$	0.811	$1.90\cdot10^{-4}$	0.804		
$2.20\cdot10^{-4}$	0.952	$2.55\cdot10^{-4}$	0.961		
$2.22\cdot10^{-4}$	0.903	$3.09\cdot10^{-4}$	0.982		
$2.51\cdot10^{-3}$	0.867	$3.46\cdot10^{-4}$	0.908		
$3.27\cdot10^{-4}$	0.977	$3.62\cdot10^{-4}$	1.008		
$3.55\cdot10^{-4}$	0.852	$5.87\cdot10^{-4}$	0.875		
$1.22\cdot10^{-3}$	1.133	$8.11\cdot10^{-4}$	0.976		
$1.75\cdot10^{-3}$	1.067	$3.39\cdot10^{-3}$	1.114		
$2.13\cdot10^{-3}$	1.092	$7.06\cdot10^{-3}$	0.990		
$8.74\cdot10^{-3}$	1.016	$1.57\cdot10^{-2}$	1.044		
$1.06\cdot10^{-2}$	0.995	$1.78\cdot10^{-2}$	0.998		
$2.21\cdot10^{-2}$	0.944				

[a] Solvent: ethanol + water solutions; resin: Amberlyst A26 OH. [b] w_{ws} represents the mass fraction of water in the solvent. [c] w_{sr} represents the mass fraction of solvent (ethanol + water) in the resin phase after the preconditioning with ethanolic solutions (wet basis moisture of the resin).

mass balance performed on a solute-free basis.[6] The uncertainties in the solid-phase composition, calculated by error propagation, were always lower than $3.0\cdot10^{-3}$ g of acid·g of dry resin^{-1}. To check the mass balance approach, the solid-phase composition was also directly measured for a specific equilibrium experiment performed at (298.15 ± 0.1) K, using a solution with 100 w = 9.72 of linoleic acid dissolved in ethanol with 100 w = 0.50 ± 0.01 of water. This measurement followed the procedure described in detail in our previous work.[6]

Results

The experimental equilibrium data, expressed in terms of the solution composition C^*/(g linoleic acid·g solvent^{-1}) and the resin composition q^*/(g linoleic acid·g dry resin^{-1}), are given in Table 2. Figure 1 shows a comparison between the whole set of equilibrium data obtained for linoleic acid and the corresponding values for oleic acid.[6] As can be observed in

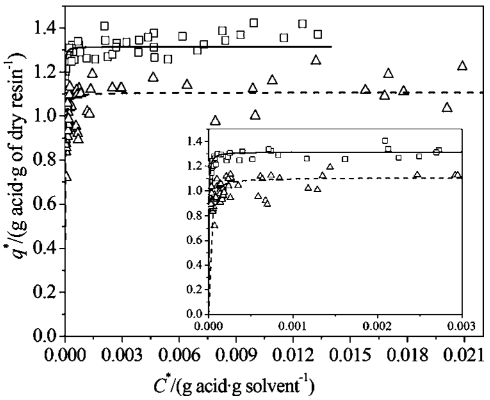

Figure 1. Equilibrium isotherms for fatty acids at 298.15 K: □, experimental data for oleic acid;[6] △, experimental data for linoleic acid; — and ---, Langmuir model.

Table 2 and Figure 1, high amounts of linoleic acid were adsorbed by the resin, but the resin saturation was reached in a solid-phase composition lower than the saturation value attained in the case of oleic acid. Nevertheless, the equilibrium concentrations in the liquid phase were in most cases very low, because the major part of the linoleic acid dissolved in the initial solutions was transferred to the solid phase. In case of the experiment conducted for checking the mass balance approach, the deviation between the q^*-value obtained by direct measurement (1.033 g of acid·g of dry resin^{-1}) and that calculated by mass balance (1.057 g of acid·g of dry resin^{-1}) was only 2.4 %, confirming that the mass balance calculation allows a good estimation of the equilibrium compositions in the resin phase. On the other hand, the value obtained by mass balance was slightly higher, indicating that a small amount of linoleic acid was possibly retained in the solid phase by physical adsorption. In fact, in the experimental run performed for checking the mass balance approach, the solid phase was washed with ethanolic solutions several times after equilibrium was attained, so that all linoleic acid physically adsorbed was removed, with fatty acid only remaining that effectively participated in the ion exchange process and whose concentration in the solid phase was then measured.

The Langmuir and Freundlich isotherms are frequently used in the literature for representing the adsorption equilibrium with ion exchange and adsorptive resins.[8−12] Both models were tested in the present case on the basis of the Langmuir and Freundlich equations published in our prior work.[6] At first, a specific set of parameters was adjusted to each experimental isotherm. The best results were obtained for the Langmuir equation, with an average absolute deviation (AAD)[6] between calculated and experimental q^* values of each isotherm varying within the range (3.5 to 11.7) %. The corresponding range for the Freundlich model is (4.6 to 12.6) %, always larger than the values obtained with the Langmuir model. The Langmuir parameters specific for each isotherm varied within the following ranges: the maximal adsorption capacity of the resin, q_m/(g acid·g dry resin^{-1}), from (1.104 ± 0.033) to (1.141 ± 0.018) and the equilibrium constant, K_d/(g acid·g solvent $^{-1}$), from $(1.00 \pm 0.36)\cdot 10^{-5}$ to $(1.50 \pm 0.31)\cdot 10^{-5}$. Taking into account the parameter values and their standard deviations, the water content in the aqueous ethanol does not have a significant influence on the equilibrium behavior. For this reason a unique set of parameters can be adjusted to the whole set of experimental data. In this case the following results were obtained: q_m/(g linoleic acid·g dry resin^{-1}) = (1.107 ± 0.022), K_d/(g linoleic acid·g solvent^{-1}) = $(1.00 \pm 0.23)\cdot 10^{-5}$, AAD = 8.6 %. A similar behavior was obtained for oleic acid in our prior work.[6] Figure 1 shows the linoleic and oleic acid experimental data and the Langmuir curves calculated with the corresponding unique sets of parameters.

The equilibrium constant K_d is usually interpreted as the ratio of the desorption and adsorption rate constants, the constants of the reversible equilibrium reaction on which the Langmuir model is based. The small value of K_d points out that the adsorption rate constant is much larger than the desorption rate constant and indicates the fatty acid preference for the solid phase. Such a result is also reflected in the almost vertical slope of the curve in the first part of the isotherm (see insert in Figure 1). The q_m value indicates the maximal resin capacity. Taking into account the resin initial moisture, this capacity can be converted to a wet basis, as it is usually reported in the literature. In this case the q_m value (1.107) corresponds to 0.296 g acid·g wet resin^{-1}. Considering the bulk apparent density of the resin, this value can be further expressed as 0.695 eq·L^{-1}, a result that is around 13 % lower than the capacity reported by the manufacturer (> 0.8 eq·L $^{-1}$). This value is also lower than the previous result reported for commercial oleic acid (0.821 eq·L^{-1}).[6] Considering that the presence of oleic acid in the commercial fatty acid used in the present work is not higher than 17 % (by mol), such a lower maximal resin capacity must be attributed to its high content of linoleic acid (see Table 1). Nevertheless, it cannot be a consequence of any hindrance related to the size of the resin pores. The projected length of oleic acid molecules is (18 to 19) Å, and in the case of linoleic acid the corresponding value is 18 Å.[13] The oleic acid molecule is slightly bent because of the *cis* configuration at its double bond, and linoleic acid has a U-shaped conformation caused by its two *cis* double bonds. The two U-shaped linoleic acid conformers reported in the literature have lengths of approximately (12 and 14) Å.[13] Taking into account that Amberlyst A26 OH has pore sizes of 290 Å, the difference in the molecule sizes of oleic and linoleic acids is not relevant for explaining the different q_m values.

The pK_a values of oleic and linoleic acids are 9.85 and 9.24, respectively.[14] Although these values cannot directly explain the observed differences in the maximal resin capacity, it should be noted that the pK_a values of fatty acids are correlated with the values of area per molecule and intermolecular distance estimated for these compounds in spread monolayers. In fact, saturated fatty acids, with their straight alkyl chains, pack closer in adsorbed monolayers than fatty acids with *cis* double bonds. The kinks in the molecules caused by the *cis* double bonds prevent the unsaturated fatty acids from packing closely in these monolayers. In the case of linoleic acid the typical two *cis* double bonds make such an effect even more pronounced than that observed for oleic acid. This justifies the following limiting areas of the monolayer, as reported by Kanicky and Shah:[14] (20, 41, and 48) Å^2 for stearic, oleic, and linoleic acids, respectively. The intermolecular distances in monolayer follow the same trend: (4.47, 6.40, and 6.93) Å for stearic, oleic, and linoleic acids, respectively.[14] When fatty acids are packed closer, the hydrogen atom from the carboxyl group may be shielded between oxygen atoms belonging to carboxyl groups from adjacent acids in the monolayer. This makes it more difficult to strip away this hydrogen atom from the carboxyl group, causing the increase in the pK_a values.

On the other hand, adsorption of fatty acids can occur as a consequence of van der Waals interactions and, in the case of unsaturated ones, of $\pi-\pi$ interactions between the acid double bonds and the resin unsaturations, whose structure is based on a styrene and divinylbenzene copolymer. Nevertheless, results reported in our prior work, comparing oleic acid adsorption in Amberlyst A26 OH, in a weak anionic resin, and in an adsorptive one, strongly suggest that the main contribution in the present case is due to ion exchange.[6] This means that the carboxylic groups from the fatty acid molecules must be available for dissociating and establishing Coulombic attractive interactions with the strongly basic quaternary ammonium groups, which represent the Amberlyst A26 OH active sites. As indicated above, in the case of linoleic acid this availability requires an intermolecular distance higher than for oleic acid, a behavior that can explain the lower q_m value obtained in the present work. In fact, this can limit the resin saturation level mainly in the case of those adjacent active sites separated by a distance lower than or in the order of the required intermolecular distance.

Conclusions

Adsorption isotherms for the removal of linoleic acid from aqueous ethanol using the anion exchange resin Amberlyst A26 OH were determined and compared to previous published data for oleic acid. The isotherms were not significantly influenced by the water content in the solvent. The experimental data were well-correlated by the Langmuir model. The anionic resin has a very good performance in the removal of fatty acids from ethanolic solutions.

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