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Adsorption of Acidic Impurities From Organic Esters Using Basic Ion Exchange Resins as Functionalized Polymers

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Abstract: Sorption of acidic impurities from diethyl phthalate and butyl acetate using basic resins, bearing tertiary amino groups on a styrene-divinylbenzene macroporous matrix, has been investigated for purification of the esters. The equilibrium studies show selective sorption of the acidic impurities and a high loading capacity (in the range of 2.2–5.3 mol/kg of dry resin) even at millimolar acid concentrations. The uptake of the acids is assisted by specific Lewis acid-base interaction with the functional group of the resins. The interaction leads to formation of a hydrogen bonded complex between the acidic proton and the lone pair of electrons on the nitrogen of the amino group. The sorption studies have also been performed in ethanol and butyl alcohol to evaluate their use for the regeneration of the resins and recovery of the acids. The sorption data have also been analyzed using extended Flory-Huggin theory of polymer solutions to determine the interaction parameters between different components.

Keywords: Diethyl phthalate, butyl acetate, acetic acid, sorption, hydrogen bonding, purification, interaction parameters

INTRODUCTION

Organic esters, prepared by acid-catalyzed esterification of organic acids or anhydrides with alcohols, many times contain traces of the acid catalyst and/or the unreacted acid and intermediates as impurities. The presence of

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very small quantities of these impurities makes their removal difficult using conventional methods. Phthalate and acetate esters are used as intermediates and solvents for a variety of polymers. Existence of even trace amounts of acidic impurities, in such applications, can cause poor quality of products. Purification of diethyl phthalate, to remove the monoester and the acidic catalyst, is most commonly carried out by neutralization with aqueous alkaline solutions (1–3). Reactive methods using polyhydric alcohols to trap the acid catalyst (4), adsorption on calcium or magnesium oxide, carbon (5), γ-Al_2O_3, aluminosilicates, zeolites, clays (6–8), and reactive distillation (9–11) also have been reported.

Removal of acidic impurities from phthalate and acetate esters has been attempted in the present work using weak base resins carrying tertiary amino groups. Due to insignificant ionization of the acids in the non-aqueous phase, an ion exchange process is not possible and the uptake of the acids by the resins is attributed totally to sorption (12). The Lewis acid-base interaction between acidic hydrogen and the lone pair of electrons on the nitrogen of the amino group of the resin is responsible for the uptake of the acids by the weak base resin (13). The low energy of hydrogen bonding between the interacting centers ensures reversibility while the directionality and the short range of the bond confer useful selectivity for the separation (13–15). The loaded resins can be regenerated by treatment with polar solvents, such as alcohol. The regenerated solutions can be sent directly for esterification in the same plant, thereby reducing the cost of solvent recovery.

MATERIALS AND REAGENTS

Maharashtra Aldehydes and Chemicals Limited, Mahad, India, supplied diethyl phthalate. Butyl acetate, ethanol, n-butanol, and *p*-toluene sulfonic acid (*p*-TSA) were obtained from S. D. Fine Chemicals, Mumbai, India. Methanol, for high-performance liquid chromatography (HPLC) analysis of the ester phase, was obtained from Merck India Ltd. A weak base resin (Indion 850) and a strong anion exchange resin (Indion 810) were obtained from Ion Exchange Ltd., Mumbai, India. Both the resins have a macroporous matrix of polystyrene cross-linked by divinylbenzene. The Indion 850 resin carries tertiary amine functional groups, and the Indion-810 resin has quaternary ammonium groups with Cl^- counterions.

EXPERIMENTAL METHODS

Conditioning of the Resin

The resins were first washed with 5% (w/v) aqueous solution of sodium hydroxide followed by washing by a large volume of distilled water to make the resins completely alkali-free. The resins were then thoroughly washed with methanol and dried in an oven at 333 K and subsequently cooled to room temperature of 303 K.

Batch Adsorption Studies

The equilibrium sorption data were obtained by equilibrating a known amount of a resin (0.1–0.5 gms), in a constant temperature bath, with an ester phase (10–25 cm^3) containing varying concentrations of the acidic impurities (up to $0.1\,mol \cdot dm^{-3}$ in case of acetic acid and up to $0.052\,mol \cdot dm^{-3}$ in the case of *p*-TSA) in a specially designed adsorption cell. A period of 5 h was required to reach the equilibrium in the case of *p*-TSA/diethyl phthalate system and the same for the acetic acid/butyl acetate system was 8 h. The volume changes in the resins, because of the sorption of solvent/solute into the polymeric phase, were determined separately for each experiment. The volume of the resin was measured in calibrated glass tubes before and after the swelling by the solutions, and verified by visual observations under an optical microscope. The resin swelling was a slow process and took over an hour to reach the final volume. After the equilibrium was reached, the solution was separated from the resins, and the residual concentration of the acid was determined by a Knauer (Germany) high-performance liquid chromatography (HPLC) system for the *p*-TSA/diethyl phthalate system and titrimetrically for the acetic acid/butyl acetate system. No appreciable hydrolysis of butyl acetate was observed during the titration. The experiments were also repeated for the corresponding acid solutions in ethanol and butanol.

Column Studies

A glass column was packed with the preconditioned Indion 850 resin. To minimize the dead volume and the mass transfer effects in the column, the top and bottom zones of the column were packed with small glass beads. An ester phase of known acid concentration was pumped through the column at a constant flow rate, in upward direction to minimize any channeling within the bed. Samples were withdrawn from the outlet stream at regular time intervals and analyzed for the acid content. This was done till the bed was exhausted as indicated by the same inlet and outlet acid concentrations. Desorption of the adsorbed acid from the loaded resin bed was conducted using ethanol, at the same flow rate as adsorption, in the case of the *p*-TSA/diethyl phthalate system and n-butanol in the case of the acetic acid/butyl acetate system, to regenerate the resin.

RESULTS AND DISCUSSIONS

Equilibrium sorption was investigated using Indion 850 resin for the systems: *p*-TSA/diethyl phthalate, *p*-TSA/ethanol, acetic acid/butyl acetate, and acetic acid/n-butanol. Indion 850 is a weakly basic resin with tertiary amino groups on the polystyrene-divinylbenzene matrix. It is not strictly an ion exchange resin because of the presence of a very small number of quaternary ammonium groups on the matrix and should be treated as a weakly basic functionalized polymer. Indion 810 resin has, however, the same polymer matrix but with quaternary ammonium groups, and the ion exchange mechanism may be possible with this resin.

The sorbed amount of the acid (q, mol/kg) was determined from the mass balance given the initial and final bulk liquid phase acid concentrations. The acids were strongly sorbed, particularly from all the esters at all liquid phase concentrations. Figure 1(i) shows the uptake of p-TSA from diethyl phthalate and from ethanol on both, Indion 850 and Indion 810, resins. Figure 1(ii) shows the uptake of acetic acid from butyl acetate and butanol on both the resins.

p-TSA is selectively and strongly sorbed from diethyl phthalate and poorly from ethanol on Indion 850 resin. Similarly, selective sorption of acetic acid from butyl acetate and its relatively poor sorption from butanol on the same resin are evident. The strong base resin, Indion 810, however, shows a much-reduced sorption of the sulfonic acid.

Poor sorption from the alcohol phases indicates the possibility of regenerating the resin using alcohols. An additional advantage can be gained if the alcohol phase, used for the regeneration, can be sent directly for esterification in the same plant, thereby reducing the cost of solvent recovery.

The maximum uptake of p-TSA from diethyl phthalate was 3.1 mol/kg adsorbent and that of acetic acid from butyl acetate was 5.3 mol/kg, on the Indion 850 resin. Although, p-TSA and acetic acid were also selectively sorbed from the alcohol phases, the uptake was significantly lower on the same resin. The uptake of p-TSA reduced by a factor of 2 to 1.46 mol/kg from ethanol. The sorption of acetic acid also reduced by similar extent to 2.3 mol/kg from butanol. The reported uptakes of acetic acid from ethyl acetate are 11 mol/kg on Indion 850 resin and 5 mol/kg on Indion 810 resin (19). Similarly, sorption of acetic acid from ethanol on Indion 850 resin has been reported at 8.5 mol/kg and on Indion 810 resin at 4.0 mol/kg (19). Considering these large sorption values, the high loading capacities of the resins for the acids from the esters in the present studies are not surprising.

The strong anion exchange resin, Indion 810, showed a much-reduced sorption capacity as compared to the weak base Indion 850 resin from the respective ester phases and in the alcohols, the loading capacities reduced further. The uptake of acetic acid by the resin from butyl acetate was 2.23 mol/kg and that of p-TSA from diethyl phthalate was 1.3 mol/kg. The resin also showed selective sorption of the acids from the alcohols phase with capacities, 2.3 mol of AcOH/kg from butanol and 1.3 mol of p-TSA/kg from ethanol. We can term this uptake selective with respect to the solvent because the concentration of the acid in the ester phase is much less as compared to the ester itself in contact with the resin. The interaction of

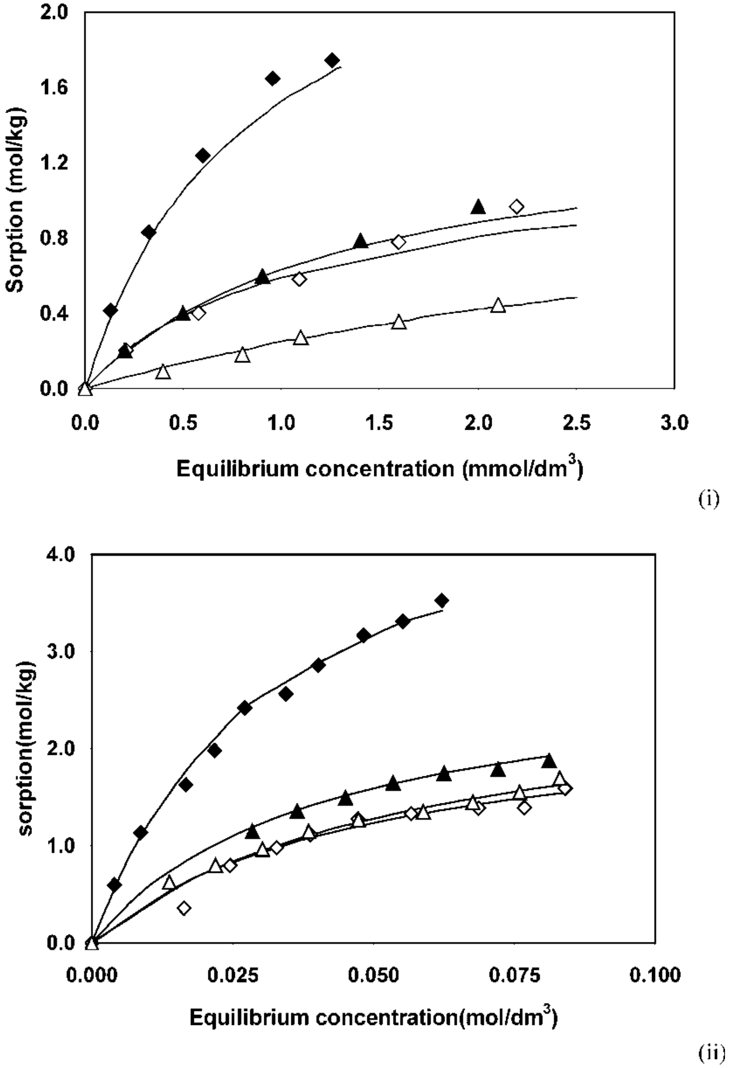

Figure 1. Sorption of acids from organic esters and alcohols. (Hollow symbol: Alcohol Filled symbol: Ester) (i) *p*-TSA solvent: Diethyl phthalate, Ethanol (ii) AcOH solvent: Butyl acetate, n-Butanol ◇ Indion-850; △ Indion-810.

quaternary ammonium groups of the Indion 810 resin with acetic acid is affected by the steric hindrance of three bulky methyl groups on the quaternary nitrogen. The OH$^-$ counterion associated with the resin may form an anion from the corresponding acid which then remains associated with the positively charged ammonium group. However, in such a case, the amount of the sorbed acid should be equivalent to the exchange capacity of the resin, i.e.,

~2.0 mol/kg on dry resin weight basis. Although, the sorption capacity of Indion 810 resin matched the same for acetic acid in butanol, for sorption of *p*-TSA from diethyl phthalate it was lower. The sorption of *p*-TSA was, however, much stronger than that of acetic acid on both the resins as is evident from the adsorption constants.

It appears that a mechanism other than ion exchange could be responsible for the uptake of the acids from the non-aqueous phases on the weak base resin. If molecular interaction through hydrogen bonding or even charged ion-dipole interaction is responsible for the sorption, the ease at which such interactions are allowed between the molecules should decide the extent of sorption and also the selectivity in separation. A resin with an easy access to its functional group should show higher sorption and probably lower capability in discerning different types of molecules. A tertiary amino group allows relatively easier access to its lone pair of electrons on the tertiary amino nitrogen as compared to positively charged nitrogen of the quaternary ammonium group. The latter may, however, show better selectivity in such sorption processes.

Effect of Solution Phase Non-Ideality on Sorption

The solutions of the acids, in either the ester or alcohol phase, exhibit a non-ideal behavior because of strong intermolecular interactions. The presence of polar groups on these molecules would give rise to these molecular interactions. This behavior should also have a significant impact on their sorption behavior from their corresponding solutions. The difference in the sorption behaviors from different solvents originates from the difference in the solvations of the acid(s) in their respective phases. The sorption has to compete with solvation and/or relative interactions of the acid with the solvent. If the solute is preferably solvated by the solvent, its adsorption tendency becomes weaker, while in poorly solvated conditions, the tendency of the solute to get out of the solution phase is stronger (16). The preference of solvation in a liquid phase can be quantitatively estimated from the activity coefficient (γ) of the acids which are the measures of their interaction with the solvent. Poor solvation should give a γ value far greater than unity, which also indicates low solubility of the solute in the solution phase. A smaller value of γ, on other hand, indicates a strongly favored solvation of the solute and higher solubility of the solute.

Figure 2 shows the variation of activity coefficient of acetic acid with its concentration in the ester and alcohol phases. The activity coefficient of p-TSA in the diethyl phthalate phase, calculated by regular solution theory, was very high at 7 and was almost independent of the acid concentration. On the other hand, as observed for acetic acid in the alcohol phase, the activity coefficient of p-TSA in the alcohol phase was constant close to unity. The activity coefficients were estimated using UNIFAC group

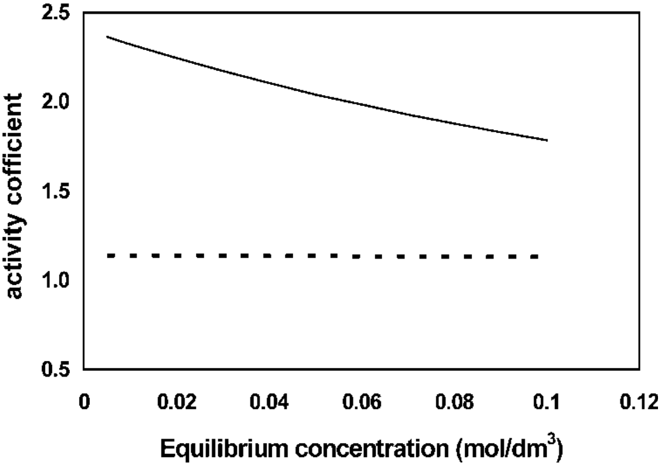

Figure 2. Activity coefficient of acetic acid in butyl acetate and butanol. solid line: Ester; dotted line: Alcohol.

contribution method for the systems involving acetic acid (17, 18). In both the alcohols, the activity coefficients of the respective acids are nearly unity. The activity coefficients of *p*-TSA in diethyl phthalate and that of acetic acid in butyl acetate are, on the other hand, considerably higher than unity. The activity coefficient of *p*-TSA did not vary much, because of its low concentrations in the ester phase, with the acid concentration. The activity coefficient of acetic acid decreases in butyl acetate showing improved solvation with increase in the acid concentration. The activity coefficient remains still higher than unity and, therefore, indicates still less solvated acid which should show greater affinity for the resin phase. A solvent showing poor affinity for the acid forces it out of the solution and promotes its sorption on a solid surface, in this case on the resin. Strong solvation of both the acidic impurities in ethanol and butanol, as indicated by their respective activity coefficients, should reduce their sorption tendency from the alcohol phases.

The sorption of acid increases rapidly at low acid concentrations and approaches a limiting value at higher concentrations of the acids. The uptake of the acid by the resins follows the Langmuir isotherm

$$\frac{q}{q_{\max}} = \frac{KC_{eq}}{1 + KC_{eq}} \tag{1}$$

where q and q_{max} are the adsorbed amount and the maximum loading capacity, respectively, on a dry resin weight basis, K is the equilibrium constant, and C_{eq} is the equilibrium liquid phase concentration. The interaction responsible for the adsorption can be viewed as a Lewis acid-base interaction between the lone pair of electrons on the resin's nitrogen and the acidic hydrogen, which leads to the formation of a hydrogen bond between the two interacting centers. The sorbed amounts of the acids were fitted into the Langmuir isotherm. The lines in Fig. 1 are the fitted curves.

The adsorption equilibrium constants (Table 1) for adsorption of acids from respective diethyl phthalate and butyl acetate phases are higher, showing greater affinity of the acids toward the resins. With ethanol and butanol, the solute-solvent interactions are stronger due to the polar nature of the alcohols which results in lower adsorption equilibrium constants.

In order to include the solvent effect on the adsorption the activity coefficient (γ) of the solute can be incorporated in the adsorption isotherm (19). If the concentration terms in the Langmuir equation are replaced by the product of activity coefficient and concentration, then a modified equilibrium constant, K_m, may represent the interaction between the resin and the solute, in the absence of non-ideality in the adsorbed phase. The modified Langmuir isotherm in the semi-empirical form is

$$\frac{q}{q_{max}} = \frac{K_m C_{eq} \gamma}{1 + K_m C_{eq} \gamma} \tag{2}$$

Table 1 also reports the modified isotherm parameters for both the systems. If the adsorption is influenced by solvation of solute in the solution phase only, then K_m in the modified isotherm should be the same or at least similar in two different solvents. This indeed is the observation in the case of adsorption of acetic acid from butyl acetate and butanol where the K_m values are closer, indicating that solution phase non-ideality is responsible for different uptakes from two different solvents. The K_m values of adsorption of *p*-TSA from diethyl phthalate and ethanol are not, however, the same. This indicates that factors, in addition to the solution phase non-ideality, could also play a significant role in the uptake of *p*-TSA. Such factors may include

Table 1. Langmuir and modified langmuir isotherm parameters

Resin	K (cm^3/mmol)	K_m (cm^3/mmol)	q_{max} (mol/kg)
Solvent = butyl acetate, solute = acetic acid, temperature = 303 K			
Indion 850	31	15.2	5.3
Indion 810	24.7	16.9	2.23
Solvent = diethyl phthalate, solute = *p*-TSA, temperature = 313 K			
Indion 850	1079	162	3.1
Indion 810	876	131	1.3
Solvent = butanol, solute = acetic acid, temperature = 303 K			
Indion 850	20.4	21.2	2.25
Indion 810	20	23.2	2.03
Solvent = ethanol, solute = *p*-TSA, temperature = 313 K			
Indion 850	759	761	1.46
Indion 810	222	225	1.3

specific solvent-resin interactions and the non-ideality in the adsorbed phase due to interaction amongst the adsorbed molecules.

Swelling of the Resins

The polymeric network of the resin is strongly influenced by organic solvents. A certain amount of solvent/solution penetrates into the polymeric network of the resin, and swells it depending upon the affinity of the solvent for the polymer structure. The driving force for the solvent uptake is the solvation tendency of the ionic groups and the tendency of the highly concentrated polymer phase to dilute itself (20). The elastic polymer matrix expands until the swelling equilibrium is attained as a balance of osmotic and electrostatic forces and the resistance to expansion due to cross-linking. The swelling of the resins makes more volume available in the resin phase, and particularly, the adsorption sites are more easily accessible to the solute. Swelling further facilitates penetration of the solution into the resin matrix (21). In fact, the swelling of the resin may become a prerequisite for appreciable sorption.

The swelling ratio (SR) is defined as ratio of swollen resin volume to dry resin volume. The SR of Indion 850 resin for the butyl acetate/AcOH system was 1.6 while for the BuOH/AcOH system it was 1.3. Indion 810 resin showed a much lower SR at 1.1 indicating insignificant swelling. A higher degree of cross-linking in the latter could be responsible for its poor swelling. The relaxation of the polymer matrix helps in accommodating the acid/base complex. At lower concentrations, the adsorption mechanism is predominant in accord with the hypotheses that the solute must first be concentrated on the surface before it can penetrate the matrix.

For the systems involving acetic acid, the swelling ratio was almost constant but in the case of *p*-TSA/DEP, the SR increased nonlinearly from 1.2 to 1.32 in DEP and from 1.1 to 1.2 in ethanol, even at very low acid concentrations. At higher acid concentrations the SR remained constant at these values. The increase in the swelling ratio with the increase in *p*-TSA concentration shows that the solute is also partly responsible for the swelling of the resin.

The swelling was more in the esters than that in the alcohols. Certain solvents may enhance swelling by London dispersion interactions with the organic constituents of the resin matrix. The higher swelling in the esters is a result of their more favorable interaction with the resin's backbone. The solvation of the resin matrix by the solvent is responsible for enhanced swelling in the non-aqueous phases. The resins carry organic tertiary amine groups fixed on the backbone. The affinity of such groups for polar organic solvents like alcohols is also relatively strong. At the same time bulky substituents guarantee a considerable minimum distance between the two interacting centers. In the presence of less polar esters, this type of interaction is further reduced. If some quaternary ammonium groups are present on the resin, they may also contribute toward the swelling.

Equilibrium Sorption Model

The Langmuir isotherm, used earlier to represent the sorption data, has certain limitations. Particularly, the high sorption capacity of the resin, far above the exchange capacity of the resin, is not explainable within the framework of the Langmuir isotherm which takes into account only the interaction of the solute with the functional groups on the surface. The simultaneous sorption of a solvent into the resin structure also has to be identified to ascertain the true sorption of the acidic impurities. We, therefore, also analyzed the sorption data of the acids in the resins in terms of an equilibrium partitioning model.

If the acid uptake by the resins is viewed as an equilibrium partitioning of the solute between the external solution and the solvent-swollen resin phase, the equilibrium can be analyzed by a thermodynamic sorption model. This type of consideration involves not only the functional groups but the entire body of the resin and does not need the framework of Langmuir isotherm. The swollen resin phase is considered as a *pseudo*-homogeneous phase composed of the polymer, the solute and solvent and the acid is partitioned between this phase and an external solution, which does not include the polymer.

The phase equilibria involve the entire body of the resin which, when swollen, is assumed to constitute a homogeneous phase including the polymer and the other chemical species. The equilibrium partitioning of the solute between the polymer and an external liquid phase is described by equating the activities of the involved components

$$a_i^p = a_i^l \tag{3}$$

where superscripts '*p*' and '*l*' indicate the polymer and the liquid phases, respectively, and N is the number of the components, excluding the polymer (22). The model is completed by the following mass balance equations

$$n_i^p + n_i^l = n_i^0 \tag{4}$$

where, n_i is the number of moles of the ith component and the index 0 refers to the value at the beginning of the experiment. From these, one can compute the compositions of the two phases, and in particular the volume fractions v_i in the polymer phase.

$$v_i = \frac{n_i^p V_i}{V_p^0 + \sum_{i=1}^{N} n_j^p v_j} \tag{5}$$

where v_i is the molar volume of the ith component (198 cm^3/mol for diethyl phthalate, 13.54 cm^3/mol for PTSA, 58.5 cm^3/mol for ethanol, 57.63 cm^3/mol for acetic acid, 51.65 cm^3/mol for butyl acetate and 98 cm^3/mol for butanol). V_p^0 is the volume of the dry resins. The denominator of Eq. (5) represents the total volume of the swollen polymer particles.

The activities in the swollen polymer phase can be evaluated using the extended Flory-Huggins model.

$$\ln a_i^p = 1 + \ln v_i - \sum_{j=1}^{N+1} m_{ij} v_j + \sum_{j=1}^{N+1} \chi_{ij} v_j - \sum_{j=1}^{N+1} \sum_{k=1}^{j-1} m_{ik} v_j v_k \chi_{kj} + \eta v_i \left(\frac{5}{3} v_p^{1/3} - \frac{7}{6} v_p \right) \tag{6}$$

The index $j = N + 1$ refers to the polymer, $V_p = V_{N+1}$ is the polymer volume fraction in the polymer phase, and $m_{ij} = V_i/V_j$ is the ratio of molar volumes, χ_{ij} represents the molecular interaction between components, i and j. The first term of Eq. (6) accounts for the entropic contributions (23, 24). The entropy effect is due to the ability of the sections of a long chain molecule to act more or less independently of one another as kinetic units and occupy different orientations in the lattice. The next two terms describe the energetic interactions among the molecules through the binary interaction parameters (χ_{ij}) and account for the enthalpy of mixing. The heat of mixing can be considered to originate in the replacement of some of the contacts between like species in the solution. The last term represents the elastic deformation contribution which is responsible for keeping the swelling of the resin finite.

The activity of each component in the liquid phase, in equilibrium with the polymer phase, was evaluated using the Regular Solution Theory for the system involving diethyl phthalate and by the UNIFAC group contribution method for butyl acetate. The interaction parameters (χ_{ij}) of the model were evaluated by fitting the experimental sorption data in the previous equations. The interaction parameter between the resin and diethyl phthalate is 1.16 while that between the resin and ethanol is -5.89. Thus, the interaction between the ester and resin is less favorable while that of resin with ethanol is more, leading to comparatively poorer sorption of the acid from ethanol. The values for interaction parameter between resin with butyl acetate and butanol are 0.93 and 1.41, respectively.

The negative values of interaction parameters indicate attractive interaction whereas their positive values show repulsive tendency. The interaction parameters were evaluated at three different temperatures for adsorption from the esters and their values are reported in Table 2.

Figure 3 shows the fitted sorption data from diethyl phthalate and butyl acetate systems, respectively, as $X^l - X^s$ diagram representing mole fractions of the acid in the two phases at equilibrium. The $X^l = X^s$ line represents equal mole fractions of the acids in both, liquid and adsorbed, phases. In the region above this line, the acid is selectively sorbed by the resins in comparison to the solvent, and below the diagonal line the solvent is preferentially taken up by the resins (25).

The negative interaction parameters of the acids with the resins indicate attractive interaction whereas those between the resin and diethyl phthalate

Table 2. Interaction parameters of sorption model

Temperature	$\chi_{P\text{-}pTSA}$	$\chi_{DEP\text{-}pTSA}$	$\chi_{pTSA\text{-}DEP}$	$\chi_{DEP\text{-}P}$
p-TSA/diethyl phthalate/polymer				
303 K	−8.85	−2.56	11.5	1.2
313 K	−6.2	−1.25	0.47	1.16
323 K	−0.88	2.41	18.2	1.09
	$\chi_{AcOH\text{-}P}$	$\chi_{BuOAC\text{-}AcOH}$	$\chi_{AcOH\text{-}BuOAC}$	$\chi_{BuOAC\text{-}P}$
AcOH/butyl acetate/polymer				
303 K	−3.10	−2.31	−0.34	0.92
313 K	−2.95	−2.52	−0.26	0.93
323 K	−2.85	−2.89	−0.22	0.93

or butyl acetate are positive showing their poorer affinity for the resin. We also observe that the affinity of the resins for the acid decreases at higher temperatures. This difference is very significant in the case of diethyl phthalate whereas the effect of temperature is less in the case of butyl acetate. The points shift toward the diagonal line on increasing temperature thus showing a decreasing separation efficiency. This is also in accordance with the experimental observations that sorption decreases with increase in temperature.

Column Studies

The breakthrough curves were obtained by plotting the dimensionless concentration of the acidic solute(s) in the effluent against the number of bed volumes of the solution passed through the column. Figure 4 shows the breakthrough curves for the adsorption and desorption of *p*-TSA and acetic acid, respectively. For *p*-TSA, ethanol was used as a desorbent, and for experiments involving acetic acid, butanol was used as the desorbent. At the experimental conditions, 5 bed volumes of the feed solution were required to arrive at the breakpoint in the case of adsorption of *p*-TSA from diethyl phthalate. About 43 bed volumes were required to completely saturate the bed. The breakpoint in the case of adsorption of acetic acid from butyl acetate occurred at 2.6 bed volumes. The saturation occurred at 25 bed volumes.

In the desorption studies of *p*-TSA, about 90% of the acid was eluted in the first 20 bed volumes of ethanol. However, around 40 bed volumes were required for complete regeneration. Both sorption and desorption, as discussed next, showed a strong intraparticle resistance to mass transfer steps, which would become a controlling factor in the application of the

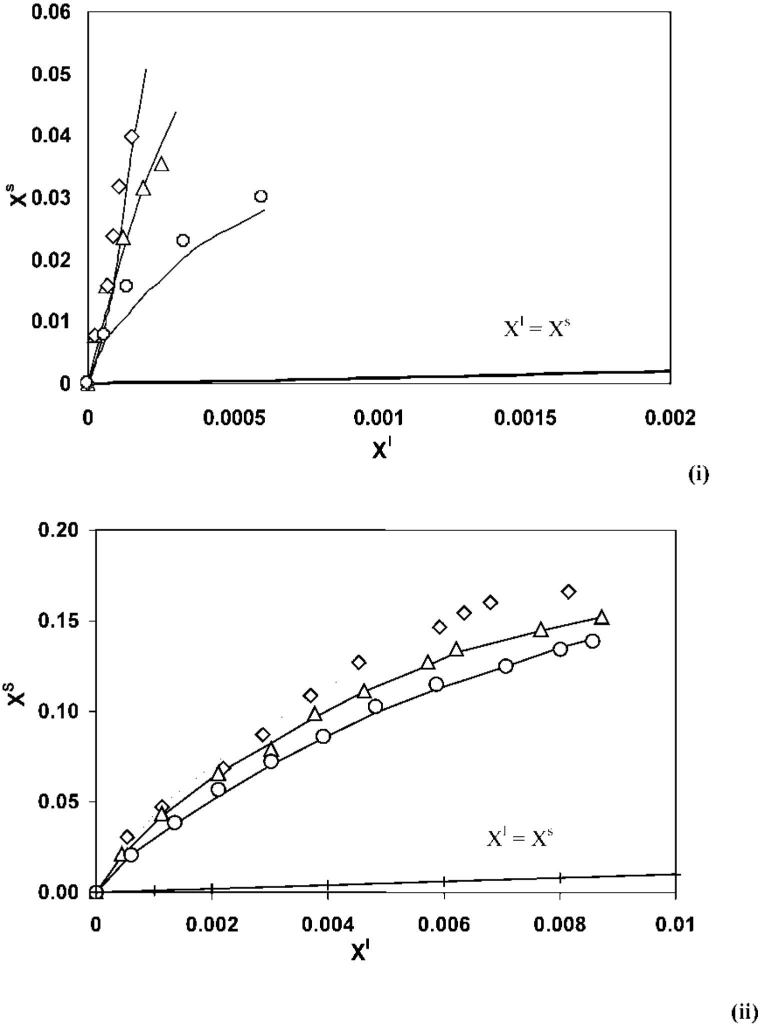

Figure 3. Equilibrium sorption model for acids into Indion 850 resin at different temperatures. (i) *p*-TSA solvent: Diethyl phthalate (ii) AcOH solvent: Butyl acetate (◇) 303 K; (△) 313 K; (○) 323 K.

resin. The use of the regenerated bed for the second cycle of adsorption showed no significant loss of the resin's adsorptive capacity.

Since a large number of bed volumes of butanol was required for the desorption of acetic acid, the desorption was tried at higher temperatures. As expected, a lesser number of bed volumes of the solvent was required for the complete regeneration of the bed at higher temperatures. The desorption profiles at three different temperatures also are shown in Fig. 4. Here, the

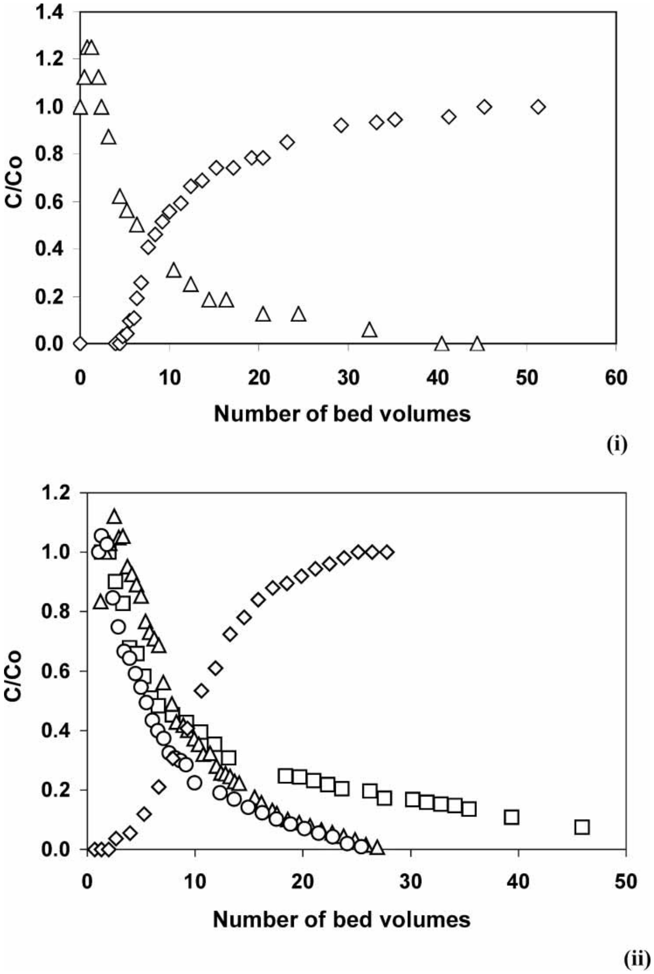

Figure 4. Breakthrough curves for adsorption and desorption. (i) ◇: Adsorption of *p*-TSA from diethyl phthalate. △: Desorption of *p*-TSA using alcohol (column i.d., 1.0 cm; resin: Indion 850; packed length: 15 cm; initial acid concentration: 0.05 mol/dm^3; flow rate: 4.0 cm^3/min). (ii) ◇: Adsorption of AcOH from butyl acetate desorption of AcOH using n-butanol (◇) 303 K; (△) 313 K; (○) 323 K (column i.d., 1.0 cm; resin: Indion 850; packed length: 22 cm; initial acid concentration: 0.052 mol/dm^3; flow rate: 6.5 cm^3/min).

adverse effect of temperature on the adsorption was used advantageously for faster and complete regeneration of the resin bed.

The adsorption breakthrough curves were analyzed to estimate the overall transfer coefficient to characterize external and internal mass transfer processes, by standard calculation procedure available in the literature (26).

At breakthrough point, the fractional ability of the resin bed to adsorb the solute was ~0.57. The degree of saturation of the bed was 44% in case of butyl acetate, and for the DEP it was 50% at the same point.

The overall mass transfer coefficient was estimated to be 7.06×10^{-6} m/sec for acetic acid in the case of butyl acetate/AcOH system and for the sulfonic acid, it was 1.4×10^{-6} m/sec, in the case of DEP/sulfonic acid system. The magnitude of the overall transfer coefficients in both the cases, when compared to the external mass transfer coefficient in a packed bed (27), indicates a strong influence of intraparticle resistance to the mass transfer of the acids into the resin structure. The reported external mass transfer coefficient of acetic acid in a packed bed of the same resin under similar conditions are an order of magnitude higher (27). The relative magnitude of the effective mass transfer coefficient indicates that diffusion inside the particle should control the adsorption kinetics and, therefore, the rate of sorption into the resin.

CONCLUSION

The sorption of acetic acid from butyl acetate and that of *p*-TSA from diethyl phthalate are influenced strongly by non-ideality in the solution phase which is reinforced by specific Lewis acid-base interaction with weak base resins, Indion 850 and Indion 810 resins. The uptake of the acids by the basic resins is highly selective with equally high capacity ($\sim 2.5-5.0\,\text{mol}\cdot\text{kg}^{-1}$). The weak base resin gave a better performance in the sorption of the acids than the strong base resin. The resin's swelling affects the capacity of the resins to sorb the acids and plays a significant role in enhancing the sorption.

The equilibrium sorption model, as partitioning of the acids between the organic solvent phase and resin polymer phase, provides a better representation of the sorption process.

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