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Adsorptive Separation of *o*-/*p*-Aminoacetophenones using Acidic Ion Exchange Resins

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Abstract: Separation of *o*-/*p*-aminoacetophenones (*o*-/*p*-AAPs) is investigated by a two-step process: selective solubilization in an organic solvent followed by reactive adsorption on functionalized polymers. Since, *p*-AAP and *o*-AAP show inter- and intra-molecular hydrogen bonding, respectively, the former is solubilized to a much lesser extent than the latter in an organic solvent. For example, *o*-AAP dissolves completely while *p*-AAP shows only 1.8% saturation solubility in toluene. Selective solubilization of *o*-AAP in toluene, therefore, gives pure *p*-AAP as residual solid in high yields. In the subsequent adsorption step, a strongly acidic ion exchange resin removes selectively the trace amounts of *p*-AAP from the toluene phase giving pure *o*-AAP.

Keywords: Aminoacetophenones, separation, adsorption, ion exchange resin, selective solubilization

INTRODUCTION

Adsorption is gaining a greater acceptance for large-scale liquid phase separations, especially for removal of trace amounts of organic solutes from

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dilute aqueous solutions (1–3). Newer micro-porous and meso-porous adsorbents with different pore sizes, structures, and different surface properties have yielded more flexibility for selective adsorption of specific components (4). Adsorption on polymeric adsorbents has received special attention in this respect. Cross-linked polystyrene and polymethacrylate have frequently been used as the polymeric matrix backbone (5).

Sorption of different organic acidic/basic compounds, such as phenols, alcohols, and phenyl alkanols, etc., from non-polar solvents and aqueous media onto neutral polymeric (polycarboxylic) adsorbents has been extensively studied by Payne's group (6–9). For adsorption from an aqueous phase, hydrophobic interactions are predominant whereas for the adsorption from non-polar solvents the formation of a hydrogen bond between the proton donating group of a solute and the carbonyl group of the sorbent have been claimed to be responsible for the adsorption (6–9). Commercial ion exchange resins have recently assumed an important role in the adsorption processes due to the flexibility in their manufacture. The functional groups on the polymer matrix, the polymeric backbone itself and the pore size of the resin can be modified to suit the needs of the required separation. The larger pore size (~100–500 Å) of the ion exchange resins compared to those of molecular sieves and zeolites (3–10 Å) leads to higher rates of diffusion of solute molecules, and favorable operational equilibria. Our group has extensively studied adsorptive separations of different organic compounds from non-aqueous media on commercially available ion exchange resins, in recent years (10–16). In these applications, the resins act as sorbents and organic solvents are selected such that no significant ionization of the solute occurs. The presence of an organic solvent of low dielectric constant favors the association and formation of hydrogen bonded complexes. This interaction is reversible and sufficiently weak, so that the adsorbent can be easily regenerated with polar solvents (17). The differences in the properties of the solute molecules such as relative acidity/basicity and steric hindrances are exploited for selective sorption of a solute from the mixture onto the resin.

o-/*p*-Aminoacetophenones (*o*-/*p*-AAPs), manufactured by reduction of corresponding nitroacetophenones, find applications in the pharmaceutical and agrochemical industries (18). In the present work, an attempt has been made to separate these isomers by a two step process. Firstly, *o*-AAP is selectively solubilized in an organic solvent from its mixtures with *p*-AAP. Because of intermolecular hydrogen bonding, *p*-AAP shows a lower solubility in inert organic solvents than *o*-AAP, which shows an intramolecular hydrogen bonding. Pure *p*-AAP is thus isolated as a residual solid in this step. The trace amounts of *p*-AAP from the solution of *o*-AAP in the organic solvent then can be selectively adsorbed on an acidic ion exchange resin. A strong acidic resin and a weakly acidic ion exchange resin have been used in the present study, to investigate the capacity and selectivity of the resins for the separation of the AAP isomers.

MATERIALS AND REAGENTS

Hexane (petroleum fraction), toluene, and methanol, both AR grade, were obtained from s.d. Fine Chemicals Ltd., Mumbai. *p*-AAP was obtained from Garuda Chemicals Pvt. Ltd., Mumbai, and *o*-AAP was obtained from Rarco Research Lab., Mumbai. *p*-AAP was purified by recrystallization from water and *o*-AAP was used as such. A strong acidic ion exchange resin, Indion-190, with sulphonic acid as functional group on polystyrene cross-linked with divinyl benzene (particle size $= 0.42 - 1.2$ mm; exchange capacity $= 4.7$ meq/g dry resin) and a weak acidic ion exchange resin, Indion- 652, with carboxylic acid as functional group on polymethacrylic and divinyl benzene copolymer matrix (particle size range $= 1.2 - 2.9$ mm, exchange capacity $= 10$ meq/g dry resin) were obtained from Ion Exchange (India) Ltd. Mumbai. These resins were conditioned by washing with 5% (w/v) aq. HCl solution. The excess acid was removed by thoroughly washing the resins with a large volume of distilled water. The acid-free resins were then washed with methanol to remove excess moisture and then dried for 10 hours at 328 K and subsequently cooled to ambient temperature of 303 K in a desiccator.

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EXPERIMENTAL METHODS

Solubility Measurements

For the determination of solubility of AAPs, an excess amount of an aminoacetophenone was added to a known amount of an organic solvent in a stoppered cell and then kept in a constant temperature water bath. The contents of the mixture were intermittently mixed using a cyclo-mixer. After giving a sufficient time (4–5 hr) for equilibration, the solution was analyzed for the dissolved aminoacetophenone concentration by a UV-visible absorption spectrometry using a UV-visible attachment on a JASCO spectrofluorometer (FP-6200), by absorption at their characteristic wavelengths. *p*-AAP showed the absorption maxima at 296, 300, and 325 nm in hexane, toluene and methanol, respectively, whereas the corresponding values for *o*-AAP were 356, 361, and 367 nm, respectively. These experiments were repeated at different temperatures.

Batch Adsorption Equilibrium Studies

The equilibrium adsorption studies were conducted by adding known amounts of the resins to solutions of aminoacetophenones in a given organic solvent in specially fabricated glass adsorption cells to avoid loss of the solvent during the equilibration process. The cells were then well stoppered, sealed, and kept in a shaker incubator at a preset temperature to attain the equilibrium.

It was determined separately by analyzing the solutions after every hour that nearly seven hours were needed to attain the equilibrium. The residual concentration of the amine was obtained by analyzing the solution by UV-visible absorption spectroscopy. To measure the swelling of the resin, the volume of the dry resin and that of the wet resin at equilibrium were also measured. The experiments were also carried out with the mixtures of amines in toluene at 303 K.

Column Studies

A glass column (internal diameter = 1 cm; length = 21.5 cm) was filled with Indion 190 resin, by settling the resin beads in toluene for uniform packing of the resin beads in the column. The bulk void fraction of the bed was 0.33. In order to minimize dead volume and end effects of mass transfer, the top and bottom zones of the column were packed with 1 mm dia. glass beads. A solution containing AAPs in toluene (concentrations of *p*-AAP and *o*-AAP = 0.046 and 0.115 $\mathrm{mol/dm^3}$, respectively) was pumped through the column using a peristaltic pump at a flow rate of 4 $\mathrm{cm^3/min}$, in the upward direction to minimize channeling within the bed. Samples were withdrawn from the outlet stream at regular time intervals and analyzed by UV-visible spectroscopy. The operation was continued until the bed was saturated and then desorption of the amines was carried out by pumping pure methanol through the column in the upward direction at a flow rate of 3 $\mathrm{cm^3/min}$. The samples from the outlet were again analyzed for the amine content.

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RESULTS AND DISCUSSION

Selective Solubilization

For an efficient separation process a solvent should selectively solubilize one of the isomers, thus achieving the maximum degree of separation and thereby minimize the amount of the resin in the subsequent adsorptive separation. In search for the selective solvent, the solubilities of both, *o*- and *p*-AAPs, were determined in three organic solvents, i.e. hexane, a non-polar solvent; toluene, an aromatic solvent with medium polarity; and a polar solvent, methanol. The intermolecular hydrogen bonding in *p*-AAP makes its solubilization difficult in a non-polar solvent. The solubility values of *o*-/*p*-AAPs in different solvents at 301 K are given in Table 1.

p-AAP shows almost no solubility in hexane. Hexane, being a non-polar solvent, cannot overcome the intermolecular attractive forces between *p*-AAP molecules. However, *o*-AAP, with intramolecular hydrogen bonding, shows a comparatively higher solubility in hexane. Toluene, which is slightly polarizable because of its π-electron clouds, interacts to a significant extent

Table 1. Solubilities of aminoacetophenones in different solvents at 301 K

	p-AAP			*o*-AAP		
Solvent	Solubility (g solute/ kg solvent)	Mole fraction (x_i)	γ_i	Solubility (g solute/ kg solvent)	Mole fraction (x_i)	γ_i
Hexane	0.45	3×10^{-4}	1432	69.8	4.3×10^{-3}	27.8
Toluene	17.9	1.2×10^{-2}	34.3	Very high	—	—
Methanol	539.4	0.11	3.6	Very high	—	—

Temperature: 301 K.

with aromatic solutes. Thus, *p*-AAP has a much higher solubility in toluene than that in hexane. The interaction of toluene with *o*-AAP is so significant that *o*-AAP is completely soluble in toluene. In methanol, the solubility of both the isomers is very high. Methanol, because of its own −OH group is a good hydrogen-bond donor as well as an acceptor and forms strong H-bonds with both -NH_2 and carbonyl groups of the aminoacetophenones. The solubility of *o*-/*p*-AAPs in these solvents at different temperatures is shown in Fig. 1. Note that *p*-AAP's solubility in methanol is higher than *o*-AAP's solubility in n-hexane. In other solvents it is substantially lower.

Activity coefficient (γ) of a solute in a saturated solution is a measure of its interaction with the solvent. The higher the solvation of a solute in a given solvent, the greater will be its interaction with the solvent and thus lower will be its 'γ' values. For a poorly solvated solute 'γ' values are substantially higher than unity. The activity coefficient of a solute in a given solvent at saturation is given by Equation (1)

$$\gamma_2 = \frac{f_{2,\mathrm{puresolid}}}{x_2 f_2^0} \tag{1}$$

where γ_2 is activity coefficient of the solute in the solvent, $f_{2,\ \mathrm{puresolid}}$ is the fugacity of the pure solid, f_2^0 is the fugacity of the solute at a standard state to which the activity coefficient refers to.

The activity coefficient of a solute at saturation in a given solvent can be estimated using Equation (2) and physiochemical properties of the solute (19).

$$\gamma_2 = \frac{1}{x_{2,\mathrm{sat}}} \exp\left\{ \frac{\Delta h_f}{\mathrm{R}} \left[\frac{1}{T_m} - \frac{1}{\mathrm{T}} \right] + \frac{1}{\mathrm{RT}} \int_T^{T_m} \Delta C_p \mathrm{dT} - \frac{1}{\mathrm{R}} \int_T^{T_m} \frac{\Delta C_p}{\mathrm{T}} \mathrm{dT} \right\} \tag{2}$$

The heat of fusion (Δh_f), specific heat capacity (C_p) and melting point (T_m) of *p*-AAP estimated from correlations in the literature (20–23) are 18.6 kJ/mol, 0.19 kJ/mol · K and 379 K, respectively, whereas the corresponding values for *o*-AAP are 14.4 kJ/mol, 0.27 kJ/mol · K and 293 K, respectively. These values were used to estimate γ values for both the amines in different solvents at

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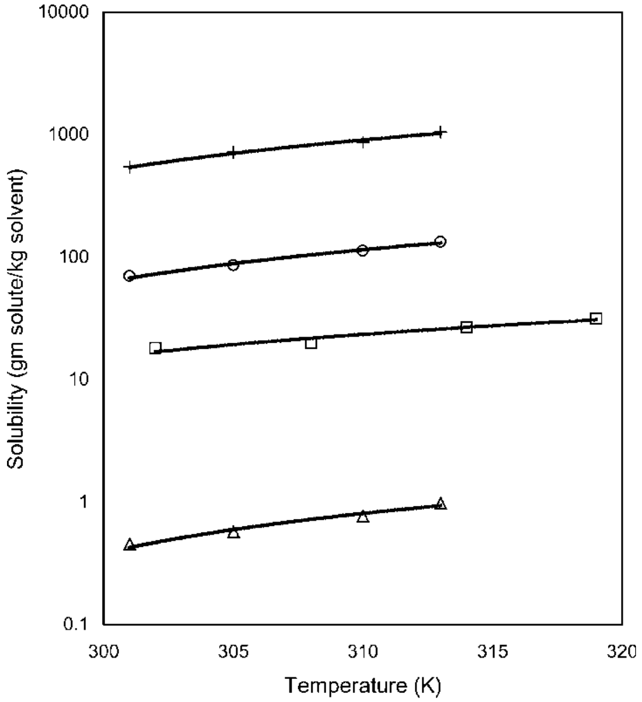

Figure 1. Solubility of aminoacetophenones in different solvents. △: *p*-AAP in hexane; ○: *o*-AAP in hexane; □: *p*-AAP in toluene; +: *p*-AAP in methanol.

saturation (Table 1). Predictably, γ is the highest for *p*-AAP in hexane which indicates its lowest solubility, followed by γ of *o*-AAP in hexane which, however, shows a comparatively higher solubility. The solubility of *p*-AAP in methanol is the highest and its γ value is the lowest. *p*-AAP in the toluene phase, shows an intermediate γ value. The γ values, calculated from the solubility of these solute-solvent pairs at four different temperatures, were fitted into UNIQUAC liquid phase model (24), to estimate the optimum values of interaction parameters using a least square technique, which are reported in Table 2.

To investigate the effect of the presence of *o*-AAP on the solubility of *p*-AAP in different organic solvents, the solubility of *p*-AAP was also determined in the presence of the other isomer. At an *o*-AAP concentration of 0.125 kg/kg of toluene (which is not its saturation solubility), the solubility of *p*-AAP increased to about 2.5 times its solubility in toluene when present alone. This increase in the solubility of *p*-AAP indicates an increased polarity of the toluene phase in the presence of *o*-AAP and also the attractive molecular interactions between the AAP isomers in the solution.

Table 2. Interaction parameters of UNIQUAC model

Interaction energy parameters (K)	*p*-AAP/hexane	Error (%)
a_{12}	339	0.02
a_{21}	284.3	5.2
	p-AAP/toluene	
a_{12}	492	0.4
a_{21}	−149	3.4
	p-AAP/methanol	
a_{12}	−3.8	4.7
a_{21}	410.4	1.1
	o-AAP/hexane	
a_{12}	116.5	1.3
a_{21}	213.5	0.4

Subscript 1: Solvent.
Subscript 2: AAP.

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Batch Equilibrium Adsorption Studies

Many of the cross-linked polymeric networks swell when they come in contact with organic solvents. The preliminary studies on the separation of AAPs by ion exchange resins showed that the swelling of the resin by the solution is a critical phenomenon which affects the resin's capacity and selectivity. The forces responsible for the swelling of the resins are: the tendency of fixed and mobile ions to form solvation shells, the tendency of the interior of ion exchange resins (which is a highly concentrated solution of ions) to dilute itself by taking up additional solvent, and the stretching of the chains of the matrix due to the repulsive electrostatic interactions between the fixed ionic groups. The latter could be significant only in the presence of ionic charges, if any. The swelling of the resin facilitates penetration of the solute molecules into the resin phase and makes the functional sites on the polymer matrix more easily accessible to the solute(s). The swelling ratio (R_s) is the ratio of volume of a swollen resin to that of the dry resin. Hexane, which is a non-polar solvent, causes almost no swelling of Indion-652 resin. Toluene causes a moderate swelling of the resin in the presence of the AAPs ($R_{s,p\text{-AAP}} = 1.2$; $R_{s,o\text{-AAP}} = 1.33$). Methanol, being a highly polar solvent, functions as both a hydrogen bond donor as well as a H-bond acceptor. Indion-190 resin swells more in methanol solutions of AAPs ($R_{s,p\text{-AAP}} = 1.38$; $R_{s,o\text{-AAP}} = 1.4$). The swelling ratios of the resin in pure toluene and methanol were 1.05 and 1.35, respectively. The additional swelling of the resin in the AAPs solutions must be because of the presence of the solutes. Also, methanol competes with AAPs to interact with the functional sites on the matrix through its own hydrogen bonding ability.

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Thus, with the increased polarity of the solvent the resin's swelling also increases. The resin's swelling, however, was independent of the AAP concentration, within the selected concentration range of AAPs.

Sorption Phenomenon

The batch equilibrium adsorption studies showed that some amount of the amines was absorbed into the resin phase along with the solvent because of the swelling of the resin beads while the rest gets adsorbed on the functional sites of the ion exchange resins. The absorbed and adsorbed quantities together constitute the "sorbed" amount of the amines within the resin beads. Assuming that the increased volume of the swollen beads is occupied by the absorbed solution having the same composition as the external bulk phase, the absorbed and adsorbed amounts of an AAP can be estimated. The presence of a large amount of polar aminoacetophenones in the resin matrix may lead to a preferential partitioning of free AAP molecules into the resin matrix. However, due to unavailability of precise data of free AAP

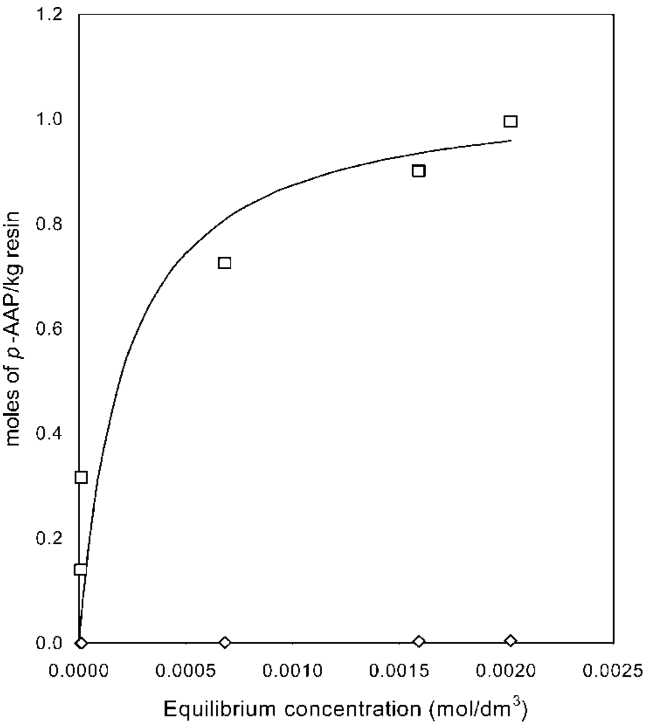

Figure 2. Absorbed and adsorbed concentrations of p-AAP from toluene; temperature: 303 K; resin: Indion-190; ◇: absorbed; □: adsorbed.

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concentration in the resin matrix, it was taken as that existing in the external bulk phase. The absorbed and adsorbed amounts of both the AAPs in hexane, toluene and methanol on Indion-190 and Indion-652 resins are shown in Figs. 2 to 7. With the Indion-190 resin, both the isomers were completely adsorbed from hexane. With the Indion-652 resin, no significant adsorption of any of the isomers took place from toluene and methanol solutions. Thus, their isotherms are not shown. With the Indion-190 resin, the adsorbed amounts from toluene solutions are much higher than the absorbed amounts (Figs. 2 and 3). Since the solubility of *p*-AAP in toluene is very low, a sufficient amount of *p*-AAP is not available in the solution to saturate the resin. The sorption is so strong and preferential that, even in the absence of any appreciable resin swelling, almost no *p*-AAP was detectable in the residual solution. Even for *o*-AAP, the adsorbed amount is much higher than the absorbed amount due to swelling of the resin. This is due to a much stronger interaction of AAPs with the resin than that between AAPs and toluene. However, in the case of methanol solutions, the absorbed amounts are significant (Figs. 4 and 5). The increased swelling of the resin in methanol is due to the absorption of a substantial amount of the solvent itself. With the increased concentration of AAP in the solution as

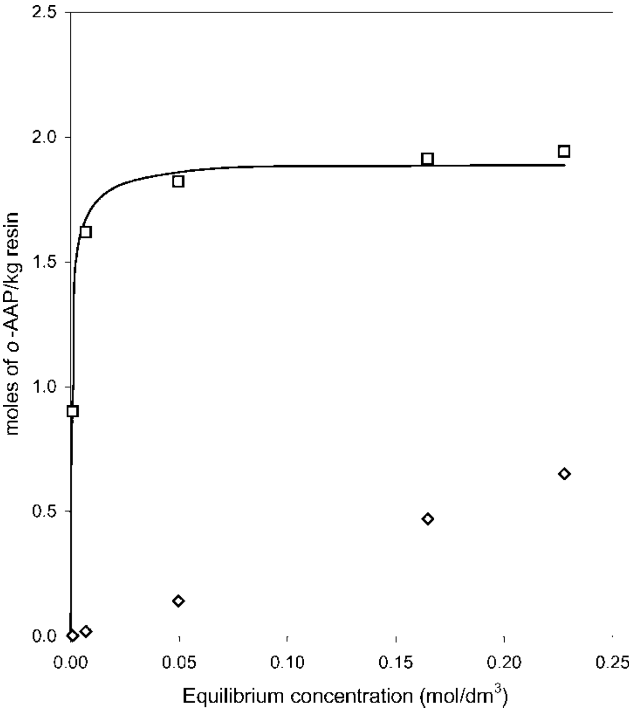

Figure 3. Absorbed and adsorbed concentrations of *o*-AAP from toluene; temperature: 303 K; resin: Indion-190; ◇: absorbed; □: adsorbed.

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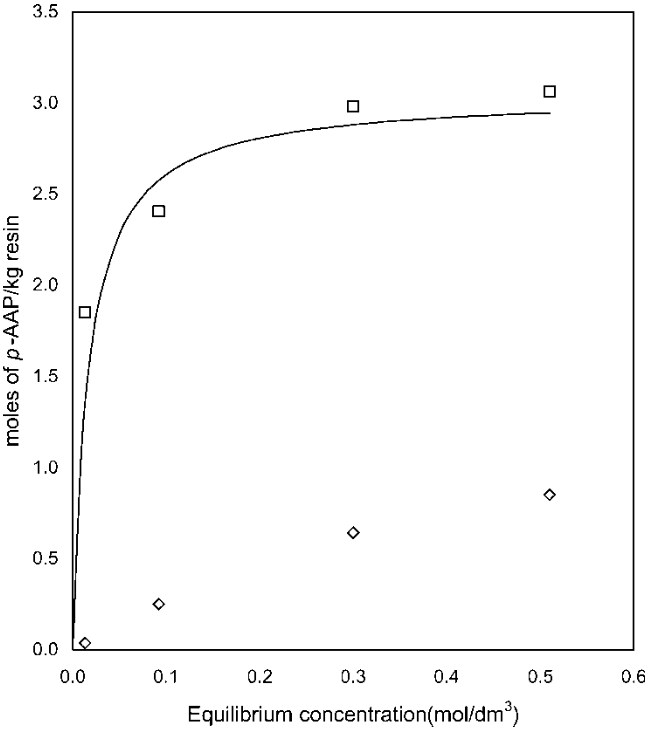

Figure 4. Absorbed and adsorbed concentrations of *p*-AAP from methanol; temperature: 303 K; resin: Indion-190; ◇: absorbed; □: adsorbed.

well as in the resin matrix, the absorbed AAP amount also shows an increasing trend. The presence of a large amount of adsorbed AAP in the resin matrix modifies the resin polarity experienced by AAP molecules and increases the partitioning of AAP towards the resin phase. These results also indicate strong interaction in the admolecules in the resin as well as that between the adsorbed and the absorbed AAP molecules.

Another feature evident from Figs. 2 to 7 is the amount of the AAPs adsorbed per kg of the resin from toluene and methanol. The adsorbed amounts of *o*-AAP, particularly from methanol are very high, even higher than the exchange sites available in the resin. For a dry resin, sites equivalent to 4.7 moles/kg of resin are available for the adsorption. For the Langmuir type of adsorption, that should be the maximum adsorption capacity. Although for *p*-AAP, the adsorption is well below this saturation capacity, for *o*-AAP from methanol the saturation amount is almost twice that of the exchange capacity. The intermolecular interaction among the *o*-AAP molecules in the resin matrix seems to have increased, either giving rise to multilayer adsorption or providing a resin matrix medium with a higher polarity than methanol itself. There was no swelling of Indion-652 resin in

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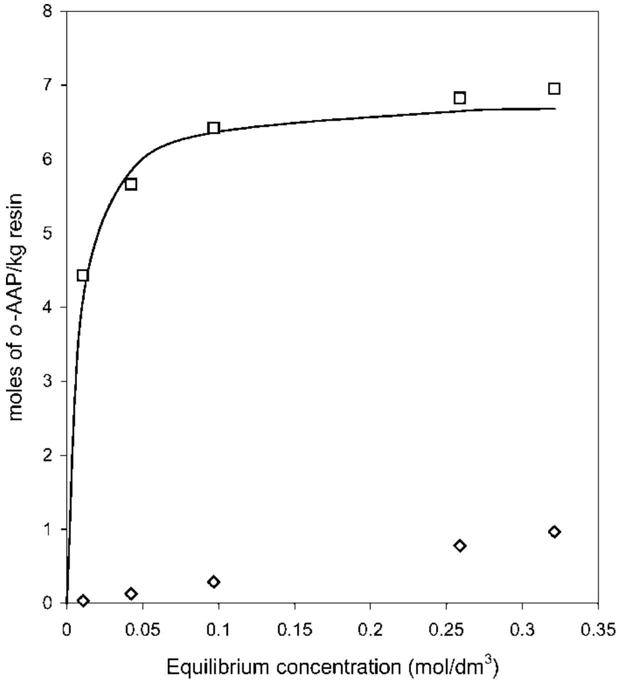

Figure 5. Absorbed and adsorbed concentrations of *o*-AAP from methanol; temperature: 303 K; resin: Indion-190; ◇: absorbed; □: adsorbed.

the hexane solutions of both the isomers with hexane. Thus, the absorbed quantities were negligible in these cases (Figs. 6 and 7).

The nitrogen of the amine group of AAPs possesses a lone pair of electrons and thus carries a partial negative charge and is expected to form a hydrogen bond with the acidic proton of the sulphonic acid group of Indion-190 resin or the carboxylic group of Indion-652 resin. This Lewis acid-base interaction is expected to be responsible for the adsorption of AAP isomers on the resin. Moreover, *p*-AAP is more basic than *o*-AAP. Therefore, its interaction with the resin is supposed to be stronger than that of *o*-AAP with the resin. So, the uptake of *p*-AAP by the resin was expected to be greater than that of *o*-AAP. In a non-aqueous phase the concept of pK$_a$, unlike that in an aqueous phase, may not be strictly in terms of proton exchange. The non-polar nature of the organic hydrocarbon solvent does not permit dissociation of a proton from the resin's functional group because of strong electrostatic attraction. It would rather permit the interaction in the form of hydrogen bonding between the two interacting centers. *p*-AAP with no hindrance to both the functional groups on the aromatic ring can interact with the resin's acidic group more easily as compared to *o*-AAP.

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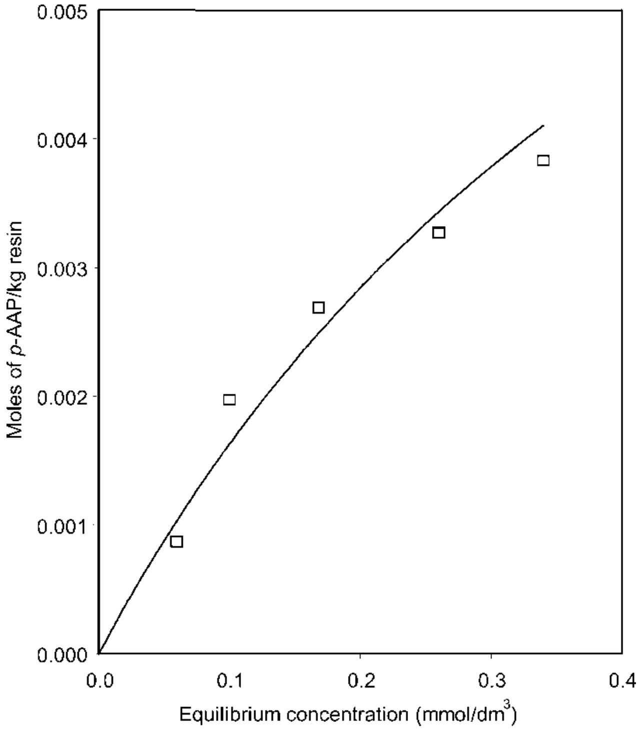

Figure 6. Adsorption of *p*-AAP from hexane. Resin: Indion-652; temperature: 303 K; □: adsorbed amount.

The experimental data for single component adsorption were fitted into Langmuir adsorption isotherm. The adsorption equilibrium constants (K) along with saturation loading capacities (Γ^{∞}) are reported in Table 3. The fitted curves of adsorption isotherms also are shown in Figs. 3 to 7. *p*-AAP shows stronger adsorption and a higher adsorption equilibrium constant on the strongly acidic Indion-190 resin from toluene which implies that the resin-solute interactions are stronger than the solute-solvent interactions. With reference to Table 3, the adsorption of *p*- and *o*-AAPs on Indion-190 and Indion-652 resins are treated separately as follows:

Adsorption on Indion-190 Resin

In hexane, the solubility of both the isomers is very low. Therefore, the solute-solvent interaction in hexane is so weak compared to the solute-resin interactions that both the isomers are strongly adsorbed on the Indion-190 resin. In the toluene phase, the solubility of both the isomers increased but the solubility of *p*-AAP is still very low. There is significant adsorption of

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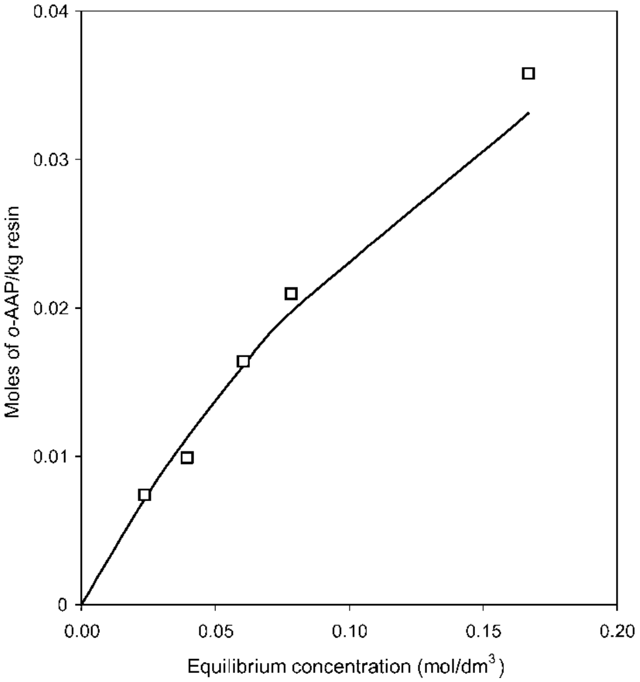

Figure 7. Adsorption of *o*-AAP from hexane. Resin: Indion-652; temperature: 303 K; □: adsorbed amount.

both the isomers from the toluene solutions. Also, as expected from the adsorption from hexane solutions, *p*-AAP shows a higher adsorption constant than that of *o*-AAP. This difference in the adsorption behaviors of AAPs can be exploited for their separation. In the methanol phase, the solute-solvent interactions are stronger as both the isomers are highly soluble. These interactions are comparable with the interactions between AAPs and the sulphonic acid group of these resins as the adsorption equilibrium constants are much reduced from those in the toluene phase. The lower values of the adsorption constant in the methanol solutions should facilitate the use of methanol as a regenerating solvent for the recovery of amines from the resin.

Adsorption on Indion-652

Indion-652 is a much weaker acidic resin than Indion-190 resin. Therefore, the solute-resin interactions with the Indion-652 resin are expectedly weaker than that with the Indion-190 resin. Consequently, there is much reduced adsorption of both the isomers on the Indion-652 resins

Table 3. Langmuir isotherm parameters, modified adsorption equilibrium constant and activity coefficients for the adsorption of aminoacetophenones on Indion-190 and Indion-652 Resins

	K (dm^3/mol)	K′ (dm^3/mol)	Γ^∞ (mol/kg)	γ
Solvent: Hexane; Resin: Indion-652				
p-AAP	1700	0.4	0.01	1074–1073
o-AAP	3.9	0.08	0.08	35.7–31.3
Solvent: Toluene; Resin: Indion-190				
p-AAP	4708	510.2	1.1	49.6–49.2
o-AAP	1055.4	107.6	1.9	7.6–9.1
Solvent: Methanol; Resin: Indion-190				
p-AAP	60	12.6	3.0	9.8–7.8
o-AAP	138.2	60.7	6.8	2.5–2.7

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(as indicated by the *K* values), as against their complete adsorption on Indion-190. In toluene and methanol solutions the solute-solvent interactions of both the isomers are stronger than the solute-resin interactions. So, there is no appreciable sorption of any of these isomers from the toluene and methanol solutions.

The difference in the adsorption behaviors, in different solvents, is due to many factors like different degrees of solvation of AAPs in these solvents, mutual interaction between the adsorbed molecules and specific interaction between the solute and the resin. The solvent effects can be accounted for by incorporating activity coefficients of solutes (γ_2) into the Langmuir adsorption isotherm to estimate the true interaction between the adsorbent and the adsorbate. The modified Langmuir equation can be written as

$$\Gamma = \frac{\Gamma^\infty K' \gamma_2 C_{\text{eq}}}{1 + K' \gamma_2 C_{\text{eq}}} \tag{3}$$

where K' is modified adsorption equilibrium constant, C_{eq} is the equilibrium concentration.

The activity coefficients of AAPs in different solvents were estimated using the UNIQUAC model (24). and the interaction energy parameters previously determined from the solubility studies (Table 2). The activity coefficients of *o*-AAP, in the toluene and methanol solutions, were estimated by UNIFAC method (25) as it showed very high solubility in these solvents. The range of activity coefficient along with the modified adsorption equilibrium constants is reported in Table 3. By incorporating the activity coefficients in the isotherm, it is expected that the modified equilibrium constant (K') represents the true solute-resin interactions. The K' values for each of the isomers with Indion-190 resin were expected to be closer, irrespective of the solvent used (toluene and methanol in this case). However, the K' values for both the isomers in methanol are lower than the corresponding K' in toluene. This may be due to competition of methanol with AAPs to interact with the resin which has not been taken into account. It is also to be noted that high values of K for the adsorption of aminoacetophenones from hexane on the Indion-652 resin (Table 3) should not be treated as an high adsorption tendency. This is because the adsorption is driven by solution phase non-idealities, as indicated by high values of activity coefficient, especially in case of adsorption of *p*-AAP from the hexane solutions. The lower adsorption capacity of Indion-652 and low solubility of AAPs in hexane lead to poor utilization of the resin. Indion-190 resin was selected for the further batch adsorption studies of the mixture of aminoacetophenones from toluene solutions.

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Mixture Batch Adsorption Studies

The effect of the presence of *o*-AAP on the adsorption of *p*-AAP from their mixtures was investigated using Indion-190 resin and toluene as solvent. The expected adsorbed phase concentrations can be estimated from the single component batch adsorption equilibrium parameters using the Langmuir adsorption equation extended to the binary mixture. The experimental and the predicted values of the adsorbed quantities of the two isomers are shown in Fig. 8. The adsorbed quantities of *o*-AAP are much greater than the predicted values. Even for *p*-AAP the adsorbed amount was higher in the presence of a larger amount of *o*-AAP. This indicates that there is an attractive interaction between the two isomers in the adsorbed phase too. This interaction leads to more amount of *o*-AAP from the solution getting sorbed along with *p*-AAP in the resin matrix.

Separation factor for the adsorption of *o*-/*p*-AAPs was calculated on the solvent-free basis as follows:

$$\alpha_{12} = \frac{x_1^s/x_1^l}{x_2^s/x_2^l} \tag{4}$$

where ‘x’ is the mole fractions of the AAP in the sorbed phase (superscript ‘s’) and in the equilibrium solution phase (superscript ‘l’).

For the concentration range studied, the separation factor increased from about 6 to 10 with increase in the mole fraction of *p*-AAP in the solution. The mixture studies and variable separation factor indicate a non-ideal behavior in the adsorbed phase. There is a strong interaction among the adsorbed molecules as against the simplified assumption of Langmuir isotherm of not having any interaction between the molecules in the adsorbed phase. The non-ideal concentration-dependant adsorption

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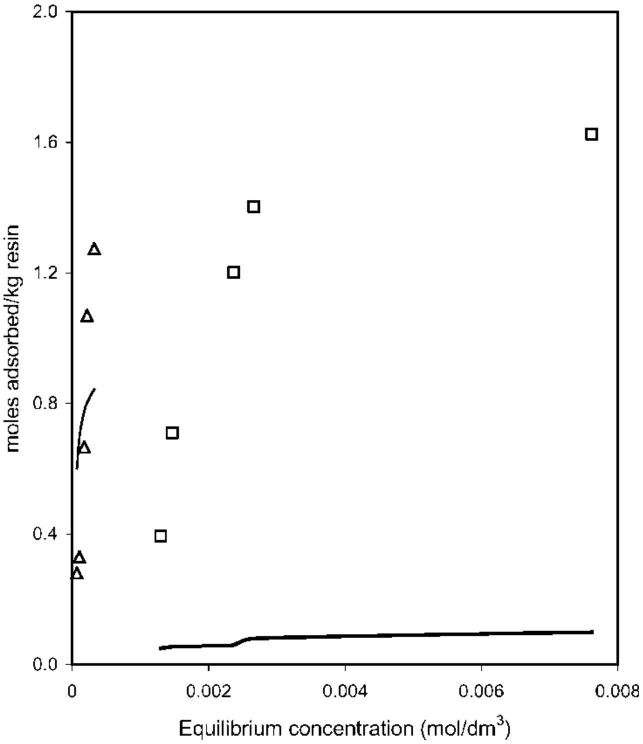

Figure 8. Adsorption of aminoacetophenones mixtures from toluene. Temperature: 303 K; Resin: Indion-190; △: *p*-AAP experimental; □: *o*-AAP experimental; ___ *p*-AAP predicted; ____ *o*-AAP predicted.

selectivity for the liquid-solid interface was analyzed by following the statistical mechanics treatment of adsorption as suggested by Ihm and Lee (26). The interaction energy (W) between two adsorbed molecules is given by the following equation: (26)

$$K^o - \ln \alpha_{12} + (1 - 2x_1^{se}) \cdot \left(\frac{cW}{2kT}\right) = 0 \tag{5}$$

where x_1^{se} is the surface excess of component '*1*', i.e. the amount by which the adsorbed phase concentration of component '*1*' exceeds its equilibrium liquid phase concentration. The values of K^o and $(cW/2kT)$ were estimated to be -0.953 and 2.26, respectively, from the intercept and slope of the linear plot of $\ln(\alpha_{12})$ vs $(1 - 2x_1^{se})$ (Fig. 9). The non-zero negative slope of the line confirms attractive interactions between *p*-AAP and *o*-AAP molecules in the adsorbed phase. In the absence of interaction between the admolecules the plot should be with zero slope. Due to this attractive interaction for *o*-AAP

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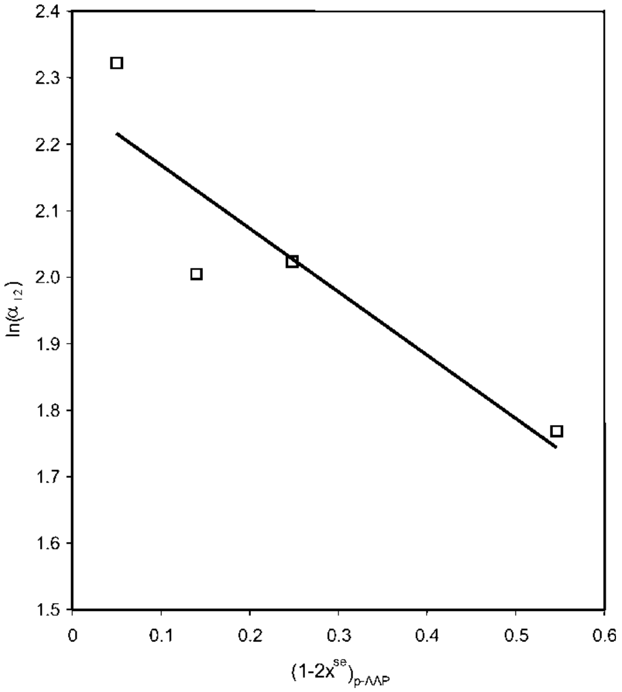

Figure 9. Interaction energy plot Ihm and Lee (26) for the adsorption of aminoacetophenones mixture.

in the presence of *p*-AAP, the experimental values of adsorbed phase concentrations for *o*-AAP were much greater than the predicted values (Fig. 8).

Column Studies

The breakthrough curve was obtained by plotting the dimensionless concentration of the solute in the effluent versus the number of bed volumes of the solution passed through the column. Figure 10 shows the break-through curves for the adsorption of an *o*-/*p*-AAPs mixture from toluene solutions. At the experimental conditions, the break point of *o*-AAP occurred after about 12 bed volumes of the feed solution were passed through the bed, whereas for *p*-AAP it occurred after about 25 bed volumes. Even at 40 bed volumes the concentration of *p*-AAP in the effluent was negligible. Only after 80 bed volumes of the solution was passed through the column the concentration of *p*-AAP in the effluent became appreciable. Also, the breakthrough fronts are well separated. This shows that a nearly complete separation of the isomers using Indion-190 ion exchange resin is possible. During the column studies at some time the exit concentration of *o*-AAP

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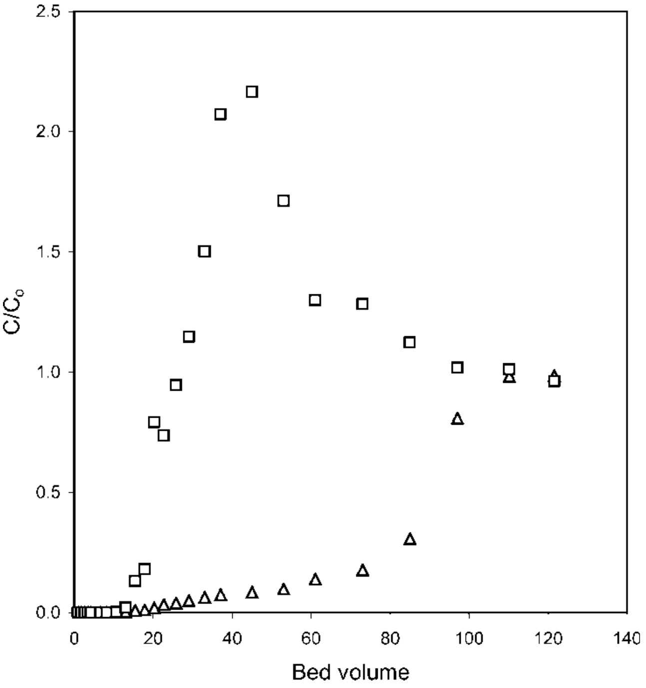

Figure 10. Breakthrough curves for adsorption of *o*- and *p*-AAPs from toluene; △: *p*-AAP; □: *o*-AAP.

exceeded its feed concentration. For the short adsorption time *p*-AAP is predominantly adsorbed at the inlet region of the bed, since its interaction with the resin is stronger than that of *o*-AAP while *o*-AAP flows ahead and is weakly adsorbed on the subsequent portions of the column. After longer operating times as more *p*-AAP enters into the column and it starts replacing the already weakly adsorbed *o*-AAP. This desorbed *o*-AAP gets added to the incoming solution and at some time its outlet concentration becomes greater than the inlet concentration. Figure 11 shows the desorption curve using methanol as a regenerant. The initial rate of desorption was very fast due to a large driving force (concentration difference). More than 90% of the adsorbed aminoacetophenones were recovered by passing just about 10 bed volumes of methanol. A complete regeneration of the bed, if necessary, is possible by an acid wash of the resin.

MOLECULAR MODELING

Molecular modeling simulation was conducted to check the plausible mechanism by which the adsorption on the resin takes place. It gives a

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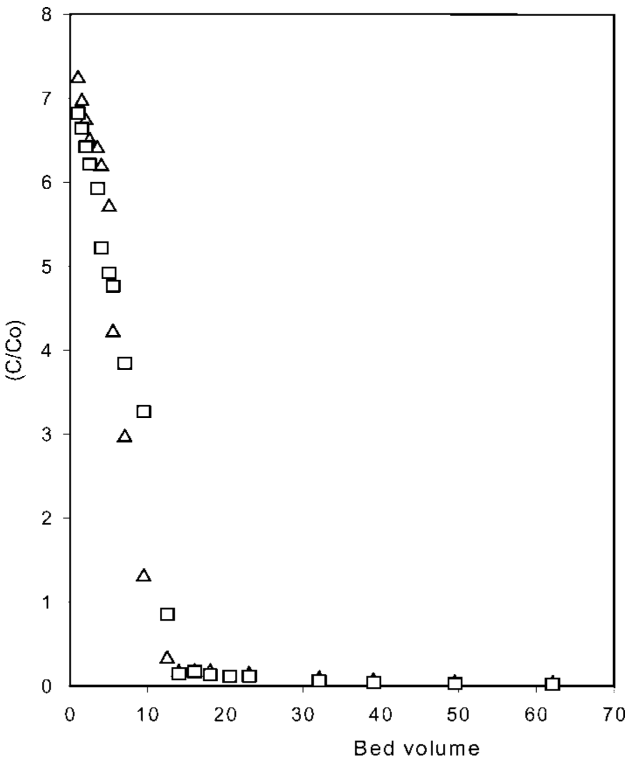

Figure 11. Desorption of *o*- and *p*-AAPs with methanol. △: *p*-AAP; □: *o*-AAP.

theoretical background to the experimental work done, by estimating the interactions between the resin and different solutes using molecular mechanics. In molecular mechanics, a molecule is represented by a Newtonian ball and spring model with the atoms as Newtonian particles interacting through a potential energy function. The potential energy of a molecule depends on bond lengths, bond angles, torsion angles, and non-bonded interactions (including van der Waals forces, electrostatic interactions and hydrogen bonds). On this basis, the internal energy of a molecule can be calculated using a force field. Energies derived in this way can be used for determining preferred conformations and intermolecular interactions.

Molecular modeling can be used to predict behavior of different systems for the selection/development of adsorbents and catalysts (27). Brune et. al. (28) have investigated interaction between different phenolic solutes and an acrylic ester polymeric sorbent in hexane medium using molecular modeling. Hydrogen bonding between the phenolic hydrogen and the carbonyl oxygen of the acrylic ester was shown to be responsible for the adsorption.

In the present work, HYPERCHEM 7 (Version 7) from Hypercube Inc. was used to minimize the molecular mechanics energy of aminoacetophenones and vinyl benzene sulphonic acid (used as an analogue of the repeating unit of the polymer), individually and as an associated complex in toluene. The Polak-Ribiere method was used for the energy minimization and 'MM^+' force field was selected for carrying out the simulation. The interaction energy of the system was estimated by substracting the molecular mechanics energies of the individual resin and the solvated molecule of AAP in toluene. The interaction energy for the adsorption of *p*-AAP and *o*-AAP molecules in toluene on the resin was estimated to be -47.6 and $-32.8\,\mathrm{kJ/mol}$. This supports that *p*-AAP shows stronger interactions with the resin than *o*-AAP.

Figures 12 and 13 show the optimized structures of *p*- and *o*- AAPs with the strongly acidic resin, Indion-190, in toluene. The partial charges on different atoms were calculated by quantitative structure activity relationship (Q.S.A.R.) module. In the optimized states, the distance between the nitrogen of amino group of *p*-AAP, carrying the highest negative partial charge (-0.32) and the hydrogen of the sulphonic group (0.226) on the resin is 2.49 Å. Thus, hydrogen bonding is possible between N of $-NH_2$ group and H of $-SO_3H$ group of the resin. Whereas, in the case of *o*-AAP, the intramolecular hydrogen bonding is prevalent between H of $-NH_2$ and O of $-COCH_3$, as the distance between them is 2.6 Å. This interaction competes with the interaction between N of $-NH_2$ and H of $-SO_3H$ of the resin. This leads to lower interaction of *o*-AAP with the resin compared to that of *p*-AAP, as indicated by the interaction energy values.

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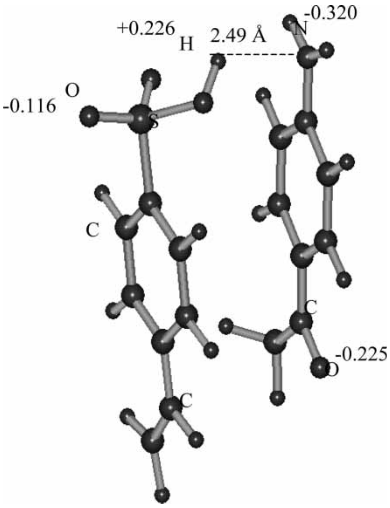

Figure 12. Optimised structure of *p*-AAP adsorbed on Indion-190.

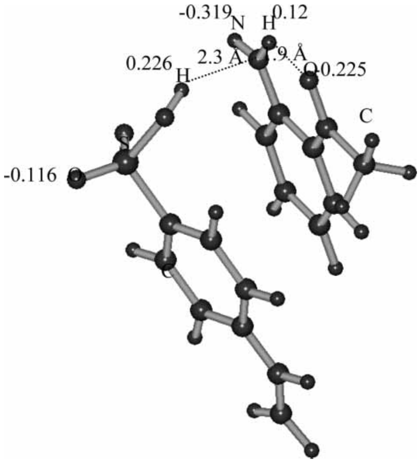

Figure 13. Optimised structure of *o*-AAP adsorbed on Indion-190.

CONCLUSIONS

Toluene was found to be the most selective solvent which solubilizes *o*-AAP preferentially giving primary separation of the aminoacetophenone isomers. From solutions of mixture of *p*- and *o*-AAPs in toluene, *p*-AAP was selectively adsorbed on the strongly acidic Indion-190 ion exchange resin. Indion-652, however, being a weak acidic resin, showed a poor adsorption of the isomers. A polar solvent, like methanol, can be used for regenerating the resin and recovering the solutes. The solution phase non-idealities of the isomers were accounted for by modifying the Langmuir adsorption equation. The isomers showed attractive interaction in solution and also in the adsorbed phase.

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