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Selective Solubilization of Nitrophenols and Adsorption on Ion Exchange Resins in Nonaqueous Conditions

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Abstract: Separation of nitrophenols (NP) has been studied by selective solubilization in organic solvents of different polarities. *o*-NP dissolves very well in heptane and toluene while intermolecular hydrogen bonding among *p*-NP molecules decreases its solubilization in these solvents. Thus partial separation of *o*-/*p*-nitrophenols is achieved by selective solubilization of *o*-NP in heptane. The trace amounts of *p*-NP from the *o*-NP solutions are removed by its selective sorption on basic ion exchange resins. The sorption of nitrophenols, individually and in mixtures, is experimentally determined from their solutions in heptane, toluene, and methanol by using weakly basic Indion-850 and Duolite A-308 resins and strongly basic Indion-810 resin. The equilibrium adsorption studies show very selective adsorption of *p*-NP from heptane with a high loading capacity on Indion-850.

Keywords: Nitrophenols, solubilization, sorption, ion exchange, separation

INTRODUCTION

Nitration of phenol under mild conditions yields a mixture of *o*- and *p*- nitrophenols in approximately 60:40 proportions. They are reduced to yield aminophenols and also are used as intermediates for dyes and pharmaceuticals. The separation of this isometric mixture is, therefore, of industrial importance. As

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p-nitrophenol is used in the manufacturing of drugs like paracetamol, and obtaining it in an ultra pure form is essential.

Separation of nitrophenols has been reported using a modified solid-liquid dissociation extraction process exploiting the difference in their solubilities and distribution coefficients in organic solvents and in their pKa values (1). The highest value of the separation factor reported by the method was 9. Very few references exist for the adsorption of phenolic compounds from non- aqueous media, while adsorption of organic compounds, especially acids and phenols, from aqueous solutions using anion exchange resins is widely reported in the literature (2–6). Even in the latter case, the recovery of the sorbed compounds is usually achieved by solvent regeneration using polar organic solvents, such as alcohols and ketones. But the adsorption characteristics of these solutes from the organic solvents are rarely reported in these papers.

The deliberate use of basic ion exchange resins for separation of phenolic mixtures under nonaqueous conditions has been reported in our recent work (7, 8). Adsorptive separation of close boiling point mixtures of cresol and xylenol from toluene was carried out by adsorption on basic ion exchange resins (7). Very high recovery and selectivity were obtained by selective solubilization and then by adsorption on weakly basic resin from heptane for the separation of *o*- and *p*-hydroxyacetophenones from each other (8). The mechanism of ion exchange cannot exist in an organic solvent of low dielectric constant which would not allow even the weak phenols to dissociate. The adsorption and separation was found to be dependent on the ability of the phenols to form -OH-NR_2- complexes with the resin.

Although nitrophenols have a considerable difference in their boiling points, normal distillation can not be applied. The distillation is risky particularly when higher boiling point explosive nitro compounds are concentrated in the reboiler at higher temperatures. Conventionally, the separation of nitrophenols is performed using steam distillation where *o*-nitrophenol distills out with steam. The steam is also contaminated with nitrophenols and complete separation is energy inefficient. In the present work, an alternative method is developed for the separation of these isomers with selective solubilization in a suitable organic solvent as the first step followed by adsorptive separation of the trace amounts of *p*-nitrophenol from the *o*-nitrophenol solutions on a suitable ion exchange resins with basic characteristics.

MATERIALS AND REAGENTS

Heptane, methanol, and toluene, used as solvents for the solubility measurements as well as for the adsorption experiments, were obtained from S D Fine Chemicals, Mumbai, India. *o*-Nitrophenol was obtained from Alpha Chemica, Mumbai and *p*-nitrophenol was obtained from Loba Chemie, Mumbai. Both the phenols were purified by solvent crystallization before use. The adsorption studies were carried out on three different basic resins.

All of them were of the macroporous type. Of these, Indion-850 and Indion-810 resins were obtained from Ion Exchange India Ltd., Mumbai, while Auchtel Products Ltd, Mumbai, supplied Duolite A-308. The detailed characteristics of the resins are given in Table 1.

EXPERIMENTAL

Solubility Measurements

A known volume of solvent was taken in a stoppered conical flask in which an excess amount of phenol was added. The solution was kept in a constant temperature bath and was stirred using a magnetic stirrer. The solution was filtered after sufficient time was allowed for equilibration, to remove the undissolved phenol. The filtered saturated solution was analyzed using UV-visible attachment of Jasco Spectrofluorometer-6200 at 256 nm for *o*-nitrophenol and 300 nm for *p*-nitrophenol. The experiments were repeated at different temperatures and for different compositions of the nitrophenol mixtures in *n*-heptane. Each run of the solubility measurements and adsorption

Table 1. Details of ion exchange resins[a]

Properties	Indion-850	Duolite A-308	Indion-810
Type	Weak basic macroporous	Weak basic macroporous	Strong basic macroporous
Matrix structure	Styrene-divinyl benzene copolymer	Styrene-divinyl benzene copolymer	Styrene-divinyl benzene copolymer
Functional group	$-NR_2$	$-NR_2$	$-N^+R_3$
Particle size (m) $\times 10^{-3}$	0.3–1.2	0.3–1.2	0.3–1.2
Ionic form	Free base	Free base	OH^-
Moisture content (Wt %)	47–55	43–49	50–56
Bulk density (dry basis) kg/m^3	610	710	550
Exchange capacity dry basis (meq/kg dry resin)	2250	2400	1650
Internal voidage	0.39	0.32	0.29
Manufacturer	Ion Exchange India Ltd., Mumbai	Auchtel Products Ltd., Mumbai	Ion Exchange India Ltd., Mumbai

$R = CH_3$.

[a]As provided by the manufacturers.

experiments was duplicated under identical experimental conditions with a maximum of 4% error in reproducibility. The experimental solubility values also match with those reported by Jagirdar (1) in literature.

Conditioning of the Resins

The ion exchange resins were kept soaked in 4% NaOH solutions for six hours. The excess alkali was removed by washing with a large volume of distilled water till the washing became alkali free. The alkali free resins were then washed with methanol to remove excess moisture and then dried for six hours at 323 K to 333 K and subsequently cooled to room temperature of 303 K in a dessicator. It was necessary to remove water completely from the mixture because the presence of water in the resin phase affects the adsorption capacity adversely.

Equilibrium Adsorption Studies

A known amount of resin was taken in a stoppered conical flask and a solution of nitrophenol of known concentration was added into the flask. The flask was then kept at a constant temperature water bath to attain equilibrium with occasional shaking. It was determined separately by analyzing the solution after every 15 minutes that nearly six hours of time was needed to attain the final equilibrium. The residual concentration of nitrophenol(s) was obtained by analyzing the solution by UV spectroscopy as mentioned earlier. Several equilibrium studies were done using different resins and solvents and at different temperatures. The experiments were also repeated for the mixtures of nitrophenols in heptane.

RESULTS AND DISCUSSION

Selective Solubilization Studies

The solubility of both nitrophenols in three organic solvents, i.e. heptane, the most non-polar solvent; toluene, an aromatic solvent with slight polarity, and a polar solvent, methanol, show that the difference in the solubilities of two nitrophenols was the highest in heptane followed by toluene at any temperature. Heptane was the best solvent for selective solubilization of *o*-nitrophenol. *o*-Nitrophenol has an appreciable solubility in heptane (solubility $= 0.81\ \text{mol}/\text{dm}^3$ at 303 K), while *p*-nitrophenol is practically insoluble in heptane (solubility $= 0.4\ \text{mmol}/\text{dm}^3$ at 303 K). Heptane is a saturated linear hydrocarbon with no polarity or very little polarizability. Since *p*-nitrophenol shows strong *inter*molecular hydrogen bonding

because of the strongly polar —NO_2 group which a nonpolar solvent like heptane cannot break down. Any interaction that *p*-nitrophenol has with heptane is due only to nonspecific London's dispersion forces that are not strong enough to overcome the specific cohesive interaction among *p*-nitrophenol molecules. Consequently, *p*-nitrophenol molecules prefer to associate themselves than getting solvated by heptane. *o*-Nitrophenol has on the other hand, strong *intra*molecular bonding and, therefore, prefers to remain individually in the molecular form. The overall charged interactions, therefore, are weakened and *o*-nitrophenol molecules are easily solvated by heptane because of the poor cohesive interaction amongst themselves. Unlike *p*-nitrophenol, *o*-nitrophenol thus shows a considerable solubility in heptane.

Toluene, which is polarizable because of π electron clouds, can interact to a significant extent with both nitrophenols. The difference in the solubilities of two nitrophenols is, therefore, not as high as that in heptane. In methanol, however, both isomers are highly soluble. Methanol, because of its —OH group is a good H— bond donor and acceptor and forms hydrogen bonds with both, —NO_2 and —OH, groups of the phenols. Methanol solubilizes both nitrophenols with similar ease and cannot differentiate between them. Because of the largest difference in the solubilities of *o*-/*p*-nitrophenols, heptane became an obvious choice for the first step of selective solubilization.

The solubilities of nitrophenols at four different temperatures in heptane, alone as well in the presence of other components, are shown in Fig. 1. With the increase in temperature, the solubility of both nitrophenols in heptane increases and the change is more appreciable for *p*-nitrophenol. For example, at 318 K, solubility of *p*-nitrophenol increases from 0.002 gmol/dm^3 to 0.04 gmol/dm^3 in mixture, while for *o*-nitrophenol it shows a slight decrease in the presence of *p*-nitrophenol. The solubility studies of the mixtures of nitrophenols show that in the presence of *o*-nitrophenol the solubility of *p*-nitrophenol in heptane increases, by a factor of 10 to 100 depending upon the *o*-nitrophenol concentration in the solution, in the range of temperature studied. It appears that the presence of *o*-nitrophenol affects the inert structure of the heptane solution phase and because of the molecular interactions with *o*-nitrophenol, a greater amount of *p*-nitrophenol gets dissolved in the heptane solutions. A low temperature solubilization would be a better strategy for selective solubilization of *o*-nitrophenol from the mixtures as maximum separation is possible and handling of the suspension/solution is easier with a minimum energy input at ambient temperatures.

The solutions of polar solutes such as nitrophenols, which show strong intermolecular interactions, are highly non-ideal. Since the solubilities of the nitrophenols are relatively low in heptane, the saturation mole fraction (x) of these phenols can be used to estimate activity coefficients of these phenols in the solution. At saturation, the activity coefficient of the

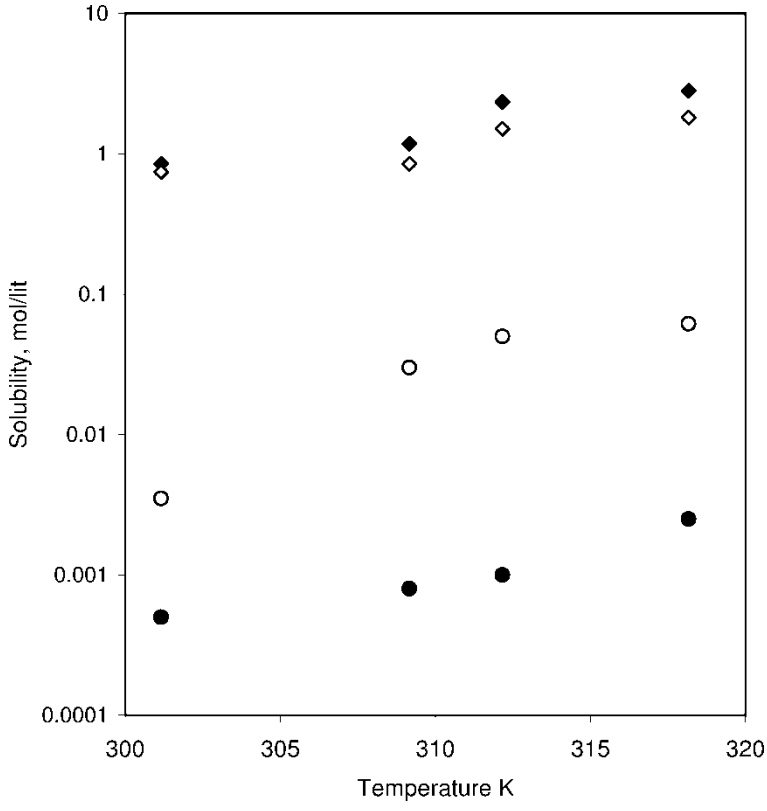


Figure 1. Solubility of nitrophenols in heptane at different temperatures Filled symbols: Solubility as single component; Hollow symbols: Solubility in mixture. ◇: *o*-nitrophenol and ○: *p*-nitrophenol.

solute in a given solvent can be estimated using physicochemical properties of the solute (9).

$$\text{i.e. } \gamma_i = \frac{1}{x_i}\exp\left\{\frac{\Delta h_f}{R}\left[\frac{1}{T_m}-\frac{1}{T}\right] + \frac{1}{RT}\int_T^{T_m}\Delta C_p dT - \frac{1}{R}\int_T^{T_m}\frac{\Delta C_p}{T}dT\right\} \quad (1)$$

The heat of fusion (Δh_f), specific heat capacity (C_p), and melting point (T_m) values for *o*-nitrophenol are 26.8 kJ/mol, 0.43 kJ/mol · K, and 317 K, respectively (10), whereas the corresponding values for *p*-nitrophenol were estimated to be 32.2 kJ/mol, 0.34 kJ/mol · K, and 388 K, respectively (11, 12). These activity coefficients were further utilized to estimate the interaction parameters of UNIQUAC model applied to the nitrophenol solutions,

using a least square technique (13). The interaction parameters of the UNIQUAC model between nitrophenols and solvents are reported in Table 2. Attractive interaction between the components of a pair is indicated by a negative value of the interaction parameter while positive interaction parameters denote the repulsive tendency. The more negative is the interaction parameter, the stronger is the attractive interaction. Heptane dissolves *o*-nitrophenol easily and its preferential solvation is supported by the attractive interaction which increases with increase in temperature.

Single Component Adsorption Studies

A significant adsorption of both nitrophenols on basic ion exchange resins was observed from all three solvents, the highest was from the heptane and the least was from methanol. The weak base resin consists of a polystyrene divinylbenzene matrix with tertiary amine groups (—NR_2) as the active sites in the case of the weakly basic resins (Indion-650 and Duolite A-308) and quaternary ammonium (—NR_3^+) group with a conjugate ion (OH^-) for the strongly basic resin Indion-810. The nitrogen of the —NR_2 group carries a lone pair of electrons which interacts with the hydrogen of the phenolic -OH group. In the case of the strongly basic resin, charged interactions are expected between the positively charged nitrogen of the resin and the oxygen of phenolic —OH group which has two pairs of electrons, and the oxygen of the NO_2 group. Acid-base interaction between the resin's positively charged cationic site and phenate ion is expected in the presence of the —OH^-.

The sorption capacity was determined from the solute mass balance, knowing the initial feed (C_f) and final bulk (C) concentrations. The total sorbed amount of a nitrophenol can be considered to consist of two parts; the amount associated with the functional sites as *adsorbed* nitrophenol and the remaining nitrophenol in the solution present in the swollen resin bead as the *absorbed* amount. From the swelling of the resin, which was determined

Table 2. Interaction parameters of UNIQUAC method for nitrophenols

Temperature (K)	u_{13} (cal/mol)	u_{31} (cal/mol)	u_{23} (cal/mol)	u_{32} (cal/mol)
301	2.34	1.14	1.80	−0.14
309	2.54	1.06	1.98	−0.19
312	2.64	1.00	2.17	−0.26
318	4.43	0.92	2.48	−0.44

1: *p*-Nitrophenol.
2: *o*-Nitrophenol.
3: Heptane.

separately, the *ab*sorbed quantity can be distinguished from the *ad*sorbed quantity, Γ(mol/kg dry resins). For the estimation of the *ab*sorbed solute in the swollen resin beads, it was assumed that the increased volume due to the swelling of the resins along with the pore volume is occupied by the solution having the same concentration as that in the external liquid phase. The absorbed amount is much smaller than the adsorbed amount and the uptake of the phenols is due to interaction with the functional sites on the resin. The uptake of the nitrophenols on the resin increases with the increase in concentration of phenols in the liquid solutions and on a log-log scale, for *p*-nitrophenol, the uptake appears linear. The total uptake of *p*- and *o*-nitrophenols on Indion-850 resins from different solvents is shown is Figs. 2 and 3, respectively. The experimental data for batch adsorption on

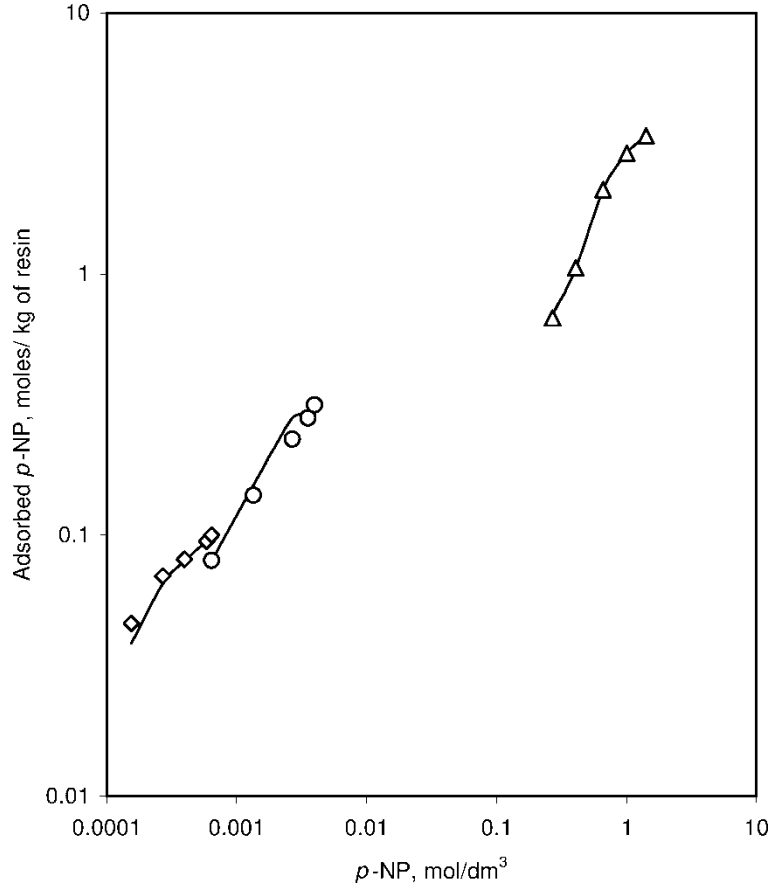


Figure 2. Sorption of *p*-nitrophenol on Indion-850 from different solvents ◇: Heptane, △: Methanol, and ○: Toluene.

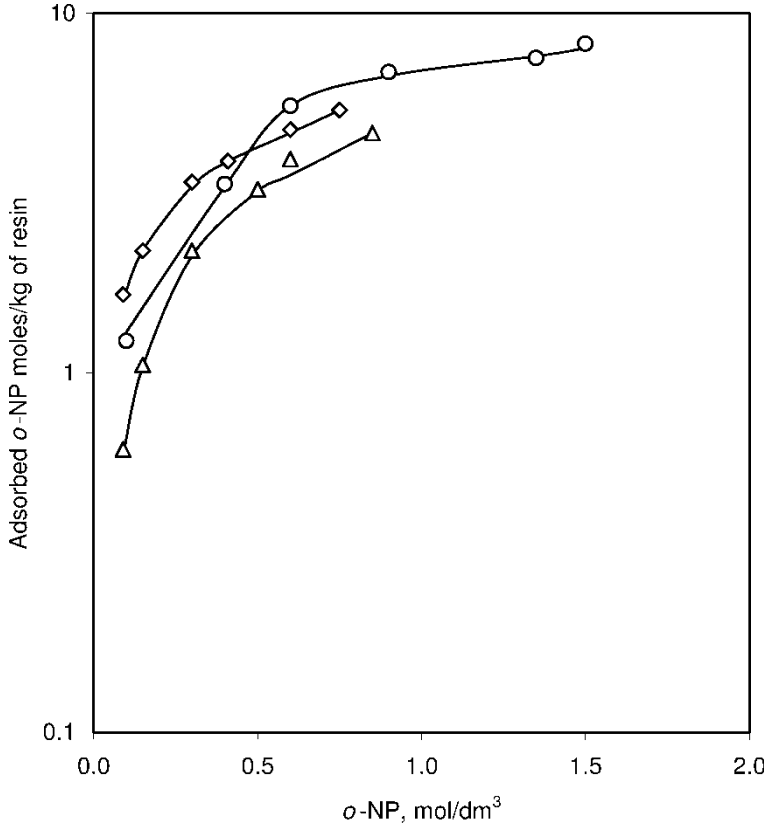


Figure 3. Sorption of *o*-nitrophenol on Indion-850 from different solvents ◇: Heptane, △: Methanol, and ○: Toluene.

Indion-850 resin from different solvents were fitted into the Langmuir adsorption isotherm (14).

$$\Gamma = \frac{\Gamma^{\infty} KC}{1 + KC} \tag{2}$$

The solid lines in Figs. 2 and 3 are the fitted curves and the points denote experimental values. The maximum adsorption capacity (Γ^{∞}) and equilibrium constant (K) obtained for the best fit are given in Table 3. The uptake of the nitrophenol(s) is more from heptane and toluene as compared to that from methanol. The adsorption equilibrium constant (K), which is a measure of interaction between the resin and solute, is much higher for *p*-nitrophenol than *o*-nitrophenol in heptane and toluene. *p*-Nitrophenol has, therefore, stronger interaction with the resin's basic

Table 3. Langmuir adsorption isotherm parameters for sorption on Indion-850

		Indion-850			
		Equilibrium constant, K (dm^3/mol)		Maximum loading capacity, Γ^{∞} (mol/kg of resin)	
Solvent	Temperature (K)	*o*-Nitrophenol	*p*-Nitrophenol	*o*-Nitrophenol	*p*-Nitrophenol
Heptane	303	6.5	106	4.9	6.7
	313	4.6	86	3.6	5.4
	323	3.8	60	2.3	4.9
Toluene	303	0.97	61	4.7	4.0
Methanol	303	1.04	0.41	3.5	4.2

group than its interaction with the organic solvents. Because of the strong intermolecular H-bonding, *p*-nitrophenol is less solvated in both hydrocarbons as compared to *o*-nitrophenol. Toluene is slightly polar than heptane so *p*-nitrophenol is relatively better solvated in toluene than heptane. The total uptake of the phenols on the resins depends on the affinity of the solute towards the resin as well as towards the solvent. Since, *p*-nitrophenol has no specific affinity towards heptane, its adsorption tendency, i.e. to escape from the heptane phase is enhanced. Consequently, *p*-nitrophenol shows higher adsorption equilibrium constant for the adsorption from heptane.

In methanol, however, the situation is completely reversed. *p*-Nitrophenol, being more polar than *o*-nitrophenol, gets solvated better in polar solvents. In methanol, therefore, *p*-nitrophenol has a higher affinity for the methanol phase than for the resin. On the other hand, *o*-nitrophenol has a higher equilibrium constant for adsorption on all resins from methanol. Because of the intramolecular hydrogen bonding, *o*-nitrophenol is less polar than *p*-nitrophenol as confirmed by their dipole moments. Dipole moment of *p*-nitrophenol is 5.67 and that of *o*-nitrophenol is 4.06.

From both heptane and toluene phases, *p*-nitrophenol show the maximum adsorption capacity than *o*-nitrophenol for all the resins. The difference in the adsorption capacities is the highest in the heptane and the difference decreases from heptane to toluene whereas, in methanol, the adsorption capacity values are reversed. Better solvation of *p*-nitrophenol in methanol reduces its ability to concentrate on the surface of resin's internal structure while *o*-nitrophenol does not show such a drastic change as its intramolecular bond is not affected to the same extent.

p-Nitrophenol shows higher adsorption equilibrium constants on all resins from heptane. But the maximum equilibrium constants and the

highest loading capacity were found with Indion-850, followed by Duolite A-308 and then Indion-810. Both, Indion-850 and Duolite A-308, resins are weakly basic resins having the same functional groups with a similar polymeric backbone. The difference in their adsorption behavior should be, therefore, due to the relative inaccessibility of adsorption sites. The accessibility of the functional group depends upon the structure of the resin and the structure of resin matrix. The bulk density of Duolite A-308 resin is higher than that of Indion-850, so the sites could be less accessible. On Indion-810, the K and Γ^{∞} values are the least which can be interpreted in terms of inaccessibility of the adsorption sites to the solute due to the steric hindrance offered by the of three bulky methyl groups on nitrogen. Also in Indion-810, the percent cross-linking is also very high, so resin matrix does not permit easy access to all the sites because of poorer swelling. The values of K and Γ^{∞} for adsorption phenols on different resins from heptane and methanol are reported in Table 4 and the uptake from heptane phase are shown in Figs. 4 and 5.

The difference in the adsorption behaviors, in inert and polar solvents, can be attributed to the differential degree of solvation of the nitrophenols in those solvents. Further, mutual interaction between the adsorbed molecules, interaction between the solute and the solvent and ionization character of the solute complicate the adsorption behavior of the nitrophenols. The non-ideality in the solution phase can be characterized by the activity coefficient (γ). The activity coefficients of corresponding nitrophenols for adsorption on Indion-850 were estimated using UNIQUAC model at relevant concentrations and reported in Table 5. The adsorption equilibrium constants were re-evaluated by incorporating the activity coefficients in the modified Langmuir equation in semi-empirical manner,

Table 4. Langmuir adsorption isotherm parameters for adsorption on different resins

	Equilibrium constant, K (dm^3/mol)		Maximum loading capacity, Γ^{∞} (mol/kg of resin)	
Resin	*o*-Nitrophenol	*p*-Nitrophenol	*o*-Nitrophenol	*p*-Nitrophenol
		Heptane		
Indion-850	6.5	106	4.9	6.7
Duolite	4.9	76	2.1	5.2
Indion-810	0.84	6.5	3.1	3.6
		Methanol		
Indion-850	1.0	0.4	3.5	3.2
Duolite	1.4	0.3	5.9	4.2
Indion-810	11.5	1.5	1.8	0.84

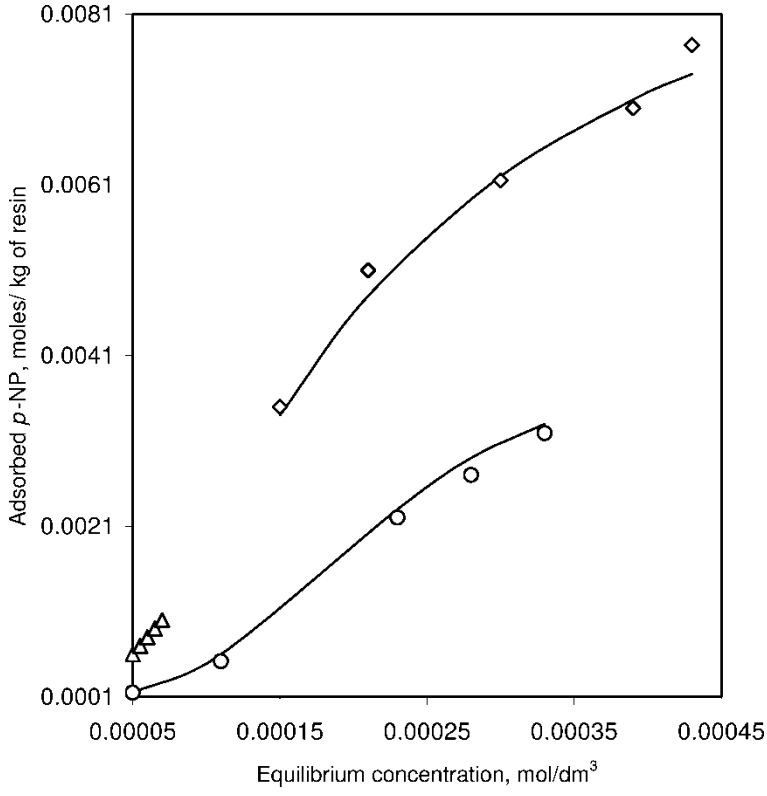


Figure 4. Sorption of *p*-nitrophenol on different resins from heptane ◇: Indion-850, △: Duolite, and ○: Indion-810.

by replacing the concentration by its product with the activity coefficient which is applicable at low concentrations of the phenols.

$$\Gamma = \frac{\Gamma^{\infty} K' \gamma_i C}{1 + K' \gamma_i C} \tag{3}$$

The modified equilibrium constants (K') are also reported in Table 5. This approach has isolated the solvent effect from the true interaction between the adsorbent and the nitrophenols. Even the modified equilibrium constant, K' indicates a more selective adsorption of *p*-nitrophenol. The adsorption equilibrium constants for a given resin and a nitrophenol, in apparently different solvents are now very close. It should be, therefore, possible to predict the adsorption behavior of nitrophenols in other solvents, provided the non-ideality in the solution phase can be taken into account using the corresponding activity coefficients.

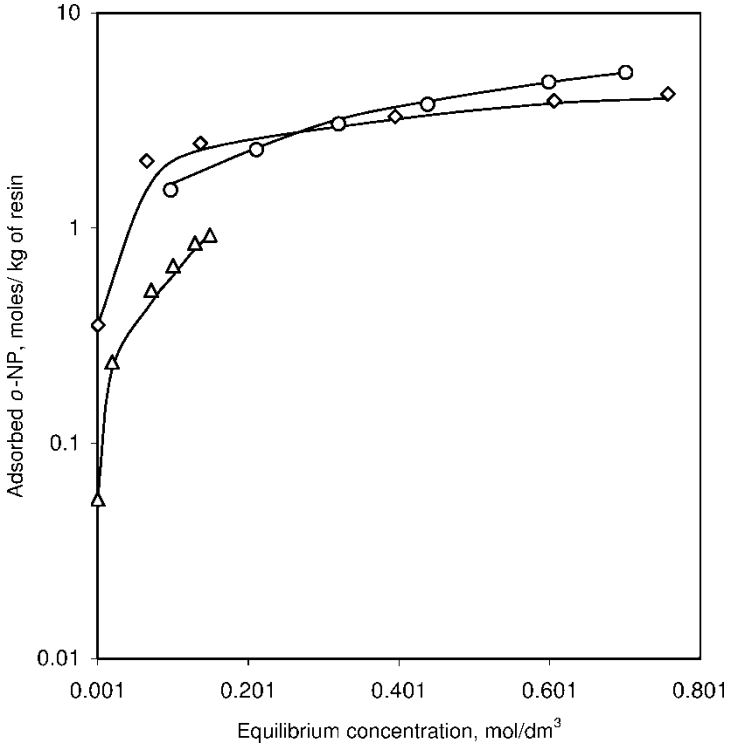


Figure 5. Sorption of *o*-nitrophenol on different resins from heptane ◇: Indion-850, △: Duolite, and ○: Indion-810.

Temperature Effects

Since heptane gave the best sorption values, further temperature studies were carried out for adsorption of nitrophenols from heptane on Indion 850 resin. Figures 6 and 7 show the uptake of nitrophenols at 303 K,

Table 5. Activity coefficients and modified equilibrium constants of nitrophenols for adsorption on Indion-850

	p-Nitrophenol		*o*-Nitrophenol	
Solvent	γ Range	Modified equilibrium constant, K' (dm^3/mol)	γ Range	Modified equilibrium constant, K' (dm^3/mol)
Toluene	190–290	120	0.19–0.29	4.52
Heptane	341–340	118	196–30	4.50

313 K and 323 K. The values of K and Γ^{∞} for these temperatures are also reported in Table 3. With the increase in temperature, the total uptake capacities of the resins to adsorb nitrophenols decreases, so are also the equilibrium constants. The heat of adsorption of *p*-nitrophenol evaluated by the Vant Hoff's equation is -2.08 kcal/mole while that for *o*-nitrophenol is -1.35 kcal/mole. These values are very low indicating very weak interaction between the sorbent and the solute and apparently the adsorption is strongly influenced by the apathy of the solvent towards the phenols. The low adsorption heat also points to easy regenerability of the resins.

Multi-component Adsorption Studies

The main objective of the present work was preferential sorption of *p*-nitrophenol from the nitrophenols mixtures. Batch equilibrium studies were carried out to investigate adsorption behavior of nitrophenols mixture.

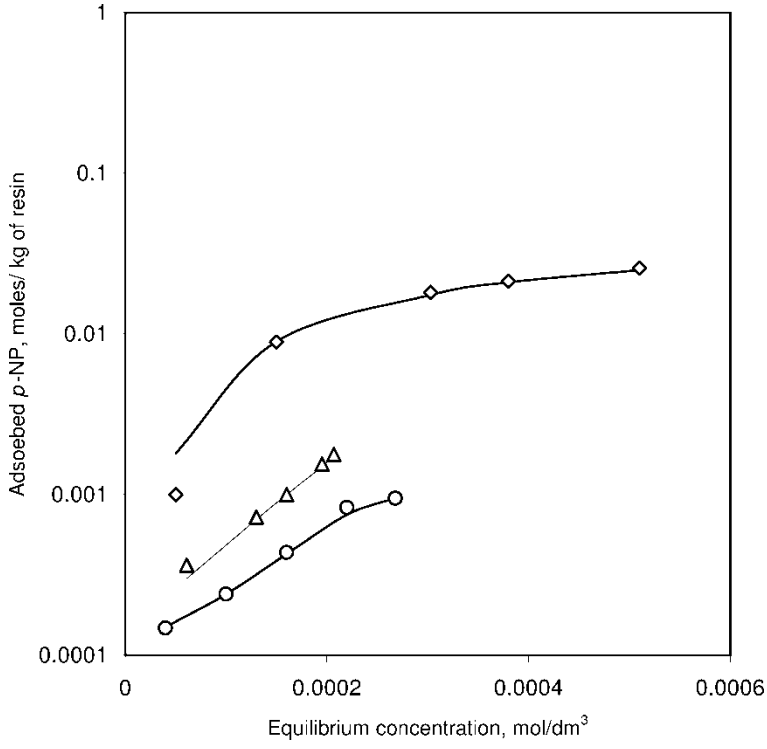


Figure 6. Sorption of *p*-nitrophenol on Indion-850 from heptane at different temperatures ◇: 303 K, △: 313 K, and ○: 323 K.

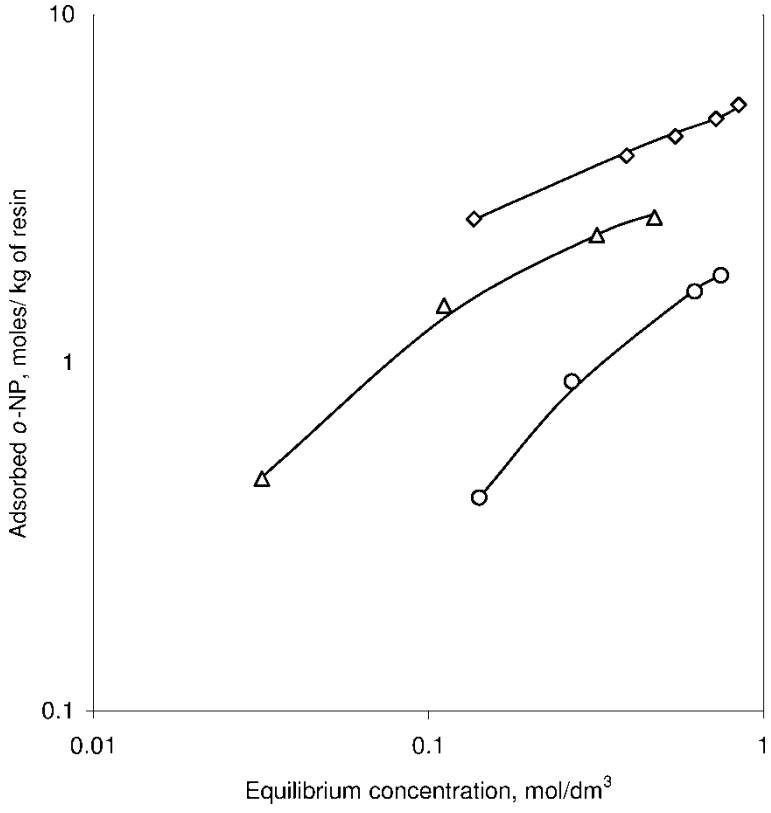


Figure 7. Sorption of *o*-nitrophenol on Indion-850 from heptane at different temperatures ◇: 303 K, △: 313 K, and ○: 323 K.

Figures 8 to 10 show the equilibrium adsorption of the nitrophenols mixtures on different resins in heptane. In the mixtures, the adsorption capacity of both the phenols decreased indicating competitive access to the basic sites. The presence of nitrophenols in the heptane solution increases the overall polarity of the solvent phase. This increase also increases solvation of the phenols in the hydrocarbon phase and reduces their adsorption tendencies.

Langmuir adsorption isotherm can be extended to two components adsorption as given below

$$\frac{\Gamma_1}{\Gamma_1^{\infty}} = \frac{K_1 C_1}{1 + K_1 C_1 + K_2 C_2} \tag{4}$$

$$\frac{\Gamma_2}{\Gamma_2^{\infty}} = \frac{K_2 C_2}{1 + K_1 C_1 + K_2 C_2} \tag{5}$$

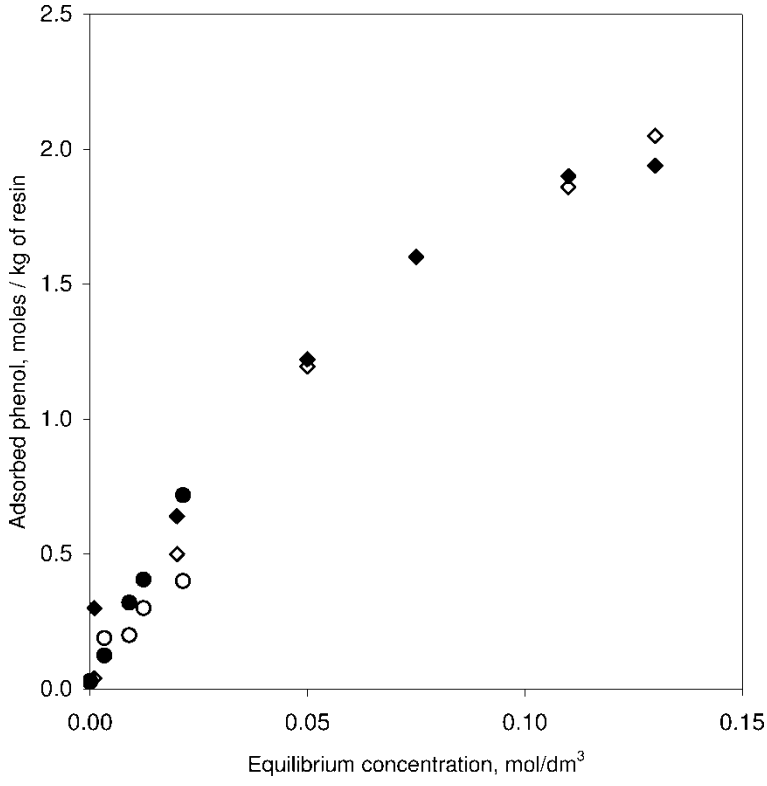


Figure 8. Adsorption behavior of nitrophenol mixtures on Indion-850 from heptane Filled symbols: Predicted values Hollow symbols: Experimental values ◇: *o*-nitrophenol and ○: *p*-nitrophenol.

K_1 & K_2 are the equilibrium constants of components 1 & 2 for adsorption from single component data and Γ_1^∞ & Γ_2^∞ are the single component loading capacities of components 1 & 2, respectively. The experimental single component data when extended to predict the adsorbed amounts of the phenols show somewhat higher predicted values than experimental adsorbed amounts of both nitrophenols. This decrease in the sorption has been ascribed to the intermolecular interactions among the nitrophenols in the heptane phase. It is still evident that at low nitrophenol concentrations the Indion-850 resin shows very selective sorption of *p*-nitrophenol from heptane.

MOLECULAR MODELING

The usefulness of ion exchange resins in the separation of organic mixtures in non-aqueous media has already been established by experimental studies. The

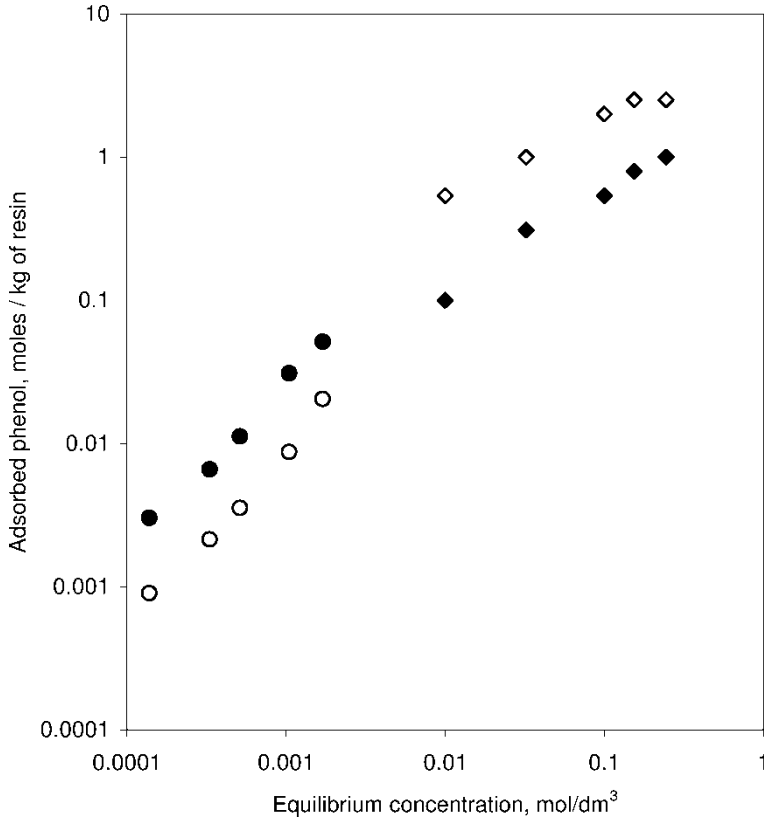


Figure 9. Adsorption behavior of mixture of nitrophenols on Duolite from heptane Filled symbols: Predicted values Hollow symbols: Experimental values ◇: *o*-nitrophenol and ○: *p*-nitrophenol.

major advantage is the flexibility with which the resins can be tailored for a desired application. It may not be possible to predict *a priori* the adsorption capacity and/or the absolute values of interaction constants, but relative adsorption characteristics can be compared to either select a resin for a required process or design a new resin for the same (15).

Molecular mechanics is a mathematical formalism which attempts to reproduce molecular geometries and energies by adjusting bond lengths, bond angles, and torsion angles to equilibrium values that are dependent on its bonding scheme. The molecular modeling software package Sybyl 6.91 (TRIPOS) was used for the molecular modeling. The solute, solvent, and repeating unit of resin were created separately and then were optimized for their intrinsic energies individually. The interaction studies were then carried out by bringing together the optimized structures of the resin unit and the solute in the different solvent media, which was approximated by a

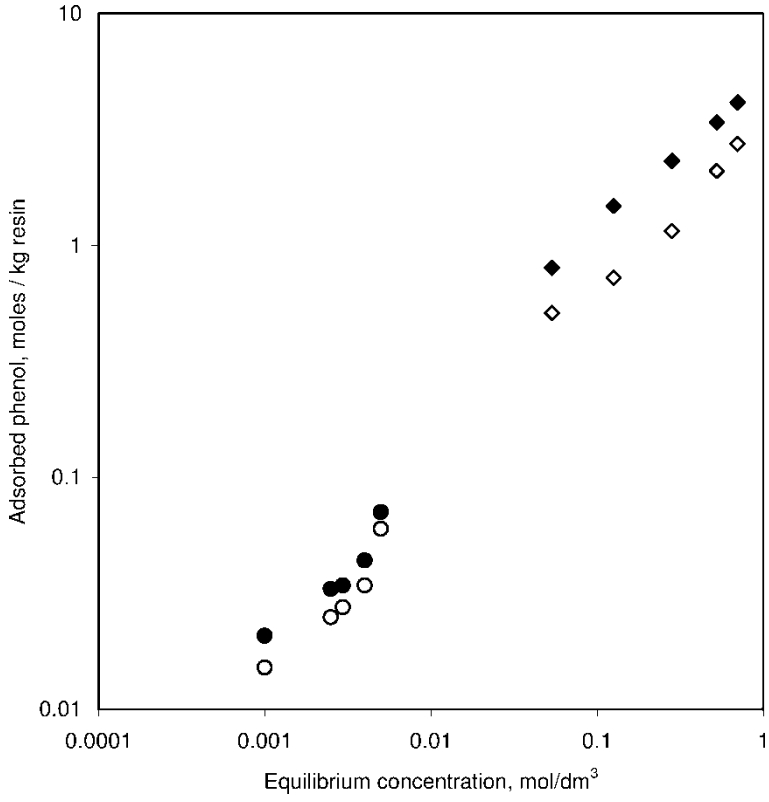


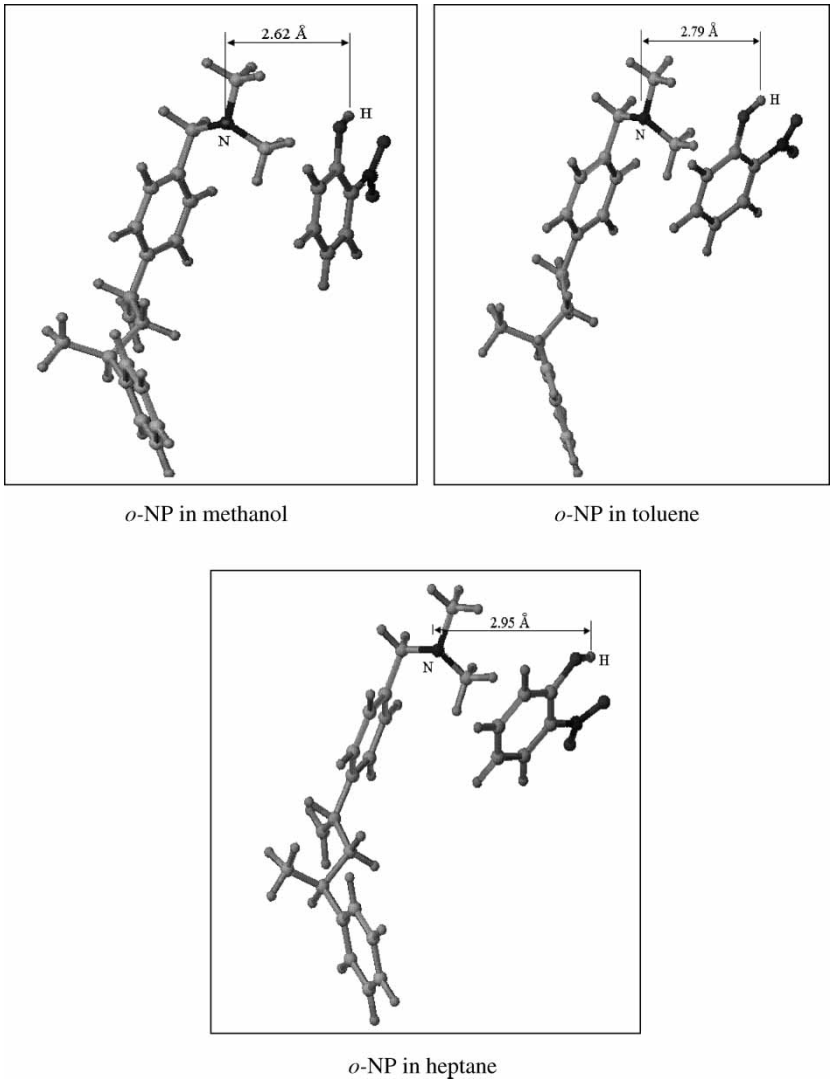
Figure 10. Prediction of adsorption behavior of nitrophenol mixtures on Indion-810 from heptane Filled symbols: Predicted values Hollow symbols: Experimental values ◇: *o*-nitrophenol and ○: *p*-nitrophenol.

solvent box of fixed dielectric constant containing discrete solvent molecules. Quasi-Newton procedure (BFGS) was used for the energy minimization calculations in MM2 force field starting with different orientations of interacting species. The lowest energy configuration of the system was selected as the optimized configuration of the stabilized complex of solute with the resin. The interaction energies were estimated by subtracting the individual MM energies of the ion exchange resin and the solute from the energy of the optimized structure of solute with resin in various solvent conditions. Though MM ignores the electronic motions and calculates the energy of the system as a function of the nuclear position only, it can perform calculations on systems containing a significant number of atoms (16).

The energies of interaction between the hydrogen of the phenolic —OH and the nitrogen of the resin's functional group are reported in Table 6. Figures 11 and 12 show the optimized structures of one molecule, each of *o*-nitrophenol and *p*-nitrophenol, respectively, interacting with the IER in

Table 6. MM energies for the interaction on *o*-NP/p-NP with resin

		Solvent		
	Solute	Methanol	Toluene	Heptane
Interaction Energy (kcal/mol)	*o*-NP	−38.32	−43.28	−48.60
	p-NP	−19.31	−69.46	−86.12



o-NP in methanol

o-NP in toluene

o-NP in heptane

Figure 11. Optimized structure of *o*-nitrophenol and resin in different solvents.

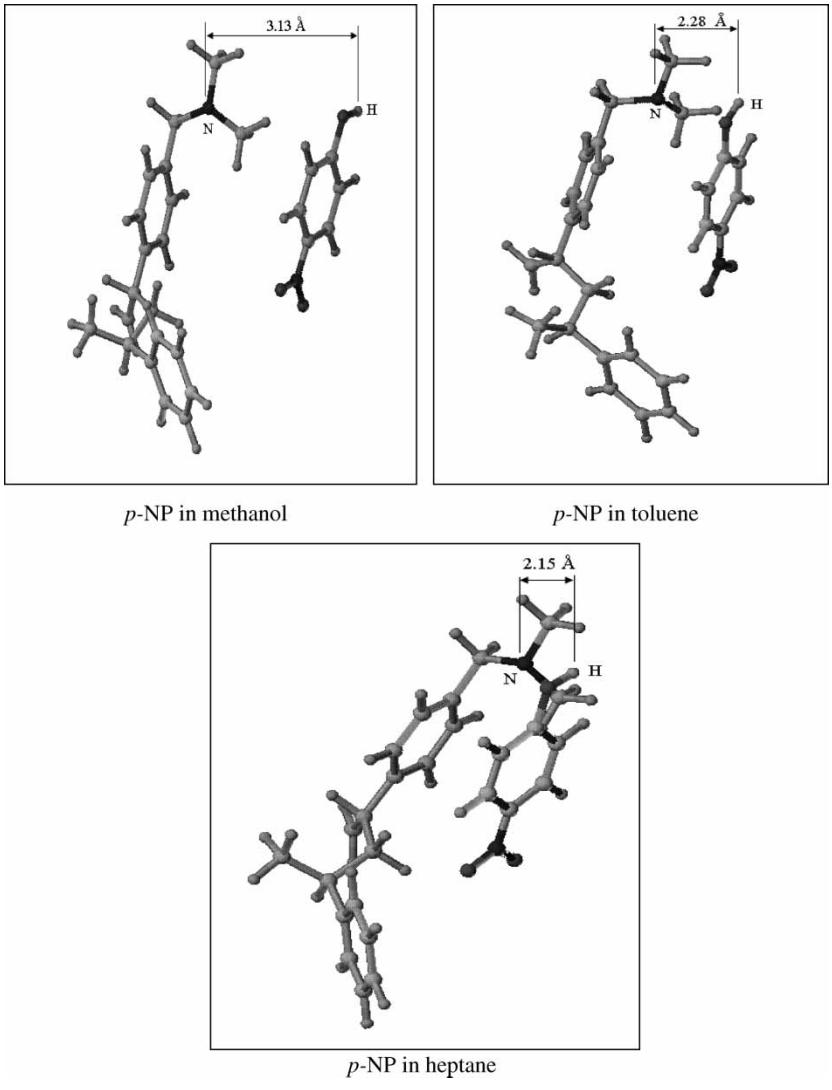


Figure 12. Optimized structure of *p*-nitrophenol and resin in different solvents.

methanol, toluene and heptane. The interaction of *p*-nitrophenol with the resin's functional group is much higher than *o*-nitrophenol in heptane. On the other hand, the interaction energies in methanol depict poorer interaction of *p*-nitrophenol with the resin than *o*-nitrophenol. These simulations are consistent with the experimental results since the equilibrium constant '*K*' is the highest for *p*-nitrophenol in heptane (Table 4). The better solvation of *o*-nitrophenol in heptane than *p*-nitrophenol gives less interaction of *o*-NP with the resin in heptane. The converse is true for *p*-NP, which has the

higher selectivity for getting adsorbed from heptane. In methanol, the simulation shows the breaking of the intramolecular H-bonding in *o*-nitrophenol and *p*-nitrophenol starts interacting more strongly with methanol molecules surrounding it leading to preferential solvation and weaker adsorption.

Molecular modeling thus can be used to identify the possibility of such separations from the estimated interaction energies. Though these energies can not directly quantify the strength of interaction, these predictions are useful in understanding interactions with the resins qualitatively as well as in solvents of various polarities.

CONCLUSION

Heptane is the best solvent for selective solubilization of nitrophenol mixtures, as it selectively dissolves *o*-nitrophenol. *p*-Nitrophenol, due to its intermolecular forces, is less soluble in heptane. Therefore maximum separation could be achieved in the first step of separation by selective solubilization of o-nitrophenol in heptane. The trace amounts of *p*-nitrophenol from the *o*-nitrophenol solutions in heptane can be adsorbed on an ion exchange resin functionalized with the basic group. Since the uptake of *p*-nitrophenol by the resins is selective and significant even at low concentrations, the traces of p-nitrophenol can be effectively removed by selective sorption, particularly by the weak base resin as selectivity as well as capacity are very high with these resins. Even though the single component Langmuir isotherm provides a good fit to the experimental equilibrium data it overpredicts the adsorbed amounts of the phenols, when extended to the two–component Langmuir isotherm. However, it is still evident that at low nitrophenol concentrations the Indion-850 resin shows very selective sorption of *p*-nitrophenol from heptane. The adsorbed nitrophenols can be desorbed using methanol for regeneration of the resins.

NOTATIONS

a_i	activity of component i
C	concentration, mol/lit
C_e	equilibrium concentration, mol/li
C_f	feed concentration, mol/lit
C_p	specific heat capacity, kJ/mol · K
ΔH	heat of adsorption, kcal/mol
Δh_f	heat of fusion, kJ/mol
K	equilibrium constant for Langmuir isotherm, lit/mol
K'	modified equilibrium constant for Langmuir isotherm, lit/mol
R	universal gas constant, kJ/mol · K
T	temperature, K

T_m melting point temperature, K
u_{ij} interaction parameter for interaction of component I with j, cal/mol

Greek Letters

Γ_i equilibrium loading capacity of component *i*, moles of solute/kg resin
Γ^{∞} maximum loading capacity, moles of solute/kg resin
γ_i activity coefficient of component *i*

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