This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Adsorption of Nitroanilines on Ion Exchange Resins in Nonaqueous Conditions

Uttamkumar V. Joshi[a]; Vilas G. Gaikar[a]
[a] Institute of Chemical Technology, University of Mumbai, Mumbai, India

Online publication date: 08 July 2010

To cite this Article Joshi, Uttamkumar V. and Gaikar, Vilas G.(2005) 'Adsorption of Nitroanilines on Ion Exchange Resins in Nonaqueous Conditions', Separation Science and Technology, 39: 5, 1125 — 1147

To link to this Article: DOI: 10.1081/SS-120028575

URL: http://dx.doi.org/10.1081/SS-120028575

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded At: 10:10 25 January 2011

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 5, pp. 1125–1147, 2004

Adsorption of Nitroanilines on Ion Exchange Resins in Nonaqueous Conditions

Uttamkumar V. Joshi and Vilas G. Gaikar*

Institute of Chemical Technology, University of Mumbai, Matunga,
Mumbai, India

ABSTRACT

o-/*p*-Nitroanilines (*o*-/*p*-NAs), which are intermediates for pharmaceutical and dye industries, show widely different solubilization behavior in an organic solvent. For example, *o*-Nitroaniline (*o*-NA) dissolves well in toluene, but *p*-nitroaniline (*p*-NA) does not. The intermolecular hydrogen bonding among the molecules of *p*-NA resists its solubilization in poorly solvating solvents. A selective solubilization of *o*-NA from the mixture thus gives pure *p*-NA as a solid product and an *o*-NA rich solution in toluene with trace amounts of *p*-NA. These traces of *p*-NA could be removed by selective sorption on an acidic resin. The sorption of nitroanilines, individually and in mixture, therefore, was experimentally investigated from their solutions in toluene and methanol, by using a

---

*Correspondence: Professor Vilas G. Gaikar, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India; Fax: 91 22 24145614; E-mails: v.g.gaikar@udct.org/vgg_uict@hotmail.com.

DOI: 10.1081/SS-120028575 0149-6395 (Print); 1520-5754 (Online)
Copyright © 2004 by Marcel Dekker, Inc.
www.dekker.com

ORDER REPRINTS

strongly acidic resin, Indion 190, with sulfonic acid groups. The molecular modeling studies confirmed the Lewis acid–base interactions between the resin's sulfonic acid group and *p*-NA's nitro group. The selective sorption is further aided by poor solvation of *p*-NA in the organic solvents.

Key Words: Nitroanilines; Solubilization; Sorption; Hydrogen bonding; Separation.

INTRODUCTION

Nitroanilines, which are intermediates for dyes, pharmaceuticals, and pesticides, can be manufactured by ammonolysis of nitrochlorobenzenes.[1,2] The resulting product mixture may contain about 35% *o*-nitroaniline (*o*-NA) and 65% *p*-nitroaniline (*p*-NA). Among these isomers, *p*-NA ($pK_a = 1.00$) is more basic, compared to *o*-NA ($pK_a = -0.26$) in aqueous solutions. Because of difference in their basicities, reactive techniques have been suggested for their separation, such as dissociation extraction by using aq. H_2SO_4[3] or by using HCl gas or concentrated H_2SO_4,[4] where the *p*-NA is preferentially neutralized. However, consumption of the acid in the neutralization process and that of an alkali in a subsequent recovery step were the major problems, increasing the overall cost of the separation and also creating a potential waste disposal problem. To reduce the consumption of the neutralizing agent, Jagirdar[5,6] proposed a two-step process; selective solubilization of *o*-NA in a nonaqueous solvent, followed by reactive extraction of *p*-NA in the second step. However, complete removal of the traces of *p*-NA in the second step was not possible because of its very low concentrations. Also, the consumption of the reacting agents could not be avoided, although it was reduced. No temperature effect was investigated by the author, which could be significant, as reported in this paper.

As an alternative to reactive extraction in the second step, we propose the use of acidic ion-exchange resins in nonaqueous conditions as a reactive adsorbent for the separation of these compounds. The resins are sufficiently stable in nonaqueous media at ambient conditions.[7] An acidic resin with sulfonic or carboxylic acid groups can neutralize the amino group of nitroanilines. In the presence of an organic solvent of a low dielectric constant, the resin is expected to reversibly form weak hydrogen bonded complexes with the amines. This interaction is sufficiently strong to take up a large quantity of adsorbate and is weak enough to regenerate the adsorbent by using a polar solvent.[8] Our group has exploited this advantage in the separation of systems such as *o*-/*p*-/*m*-phenylenediamines, *N*-alkyl substituted cyclohexylamines, *o*-/*p*-hydroxyacetophenones, and acetic acid/ethyl acetate/ethanol mixtures.[9–12]

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

Payne's group[13–16] had earlier reported the adsorption of amino compounds such as *N*-alkylanilines, phenols, and alcohols in nonaqueous conditions on a neutral polycarboxylic ester sorbent (XAD-7). In nonaqueous conditions, the H-bonding between the carboxylic ester group and either –OH or –NH groups of the solute was responsible for the adsorption.[17] Payne et al.,[18] by using molecular modeling, showed that the selectivity of para isomer over ortho isomer is because of the poor H-bonding ability of the ortho isomer due to the presence of intramolecular H-bonding in it. However, the use of functional ion-exchange resins instead of neutral adsorbents greatly enhances the separation efficiency because of the ability of the former to differentiate between the acidic–basic strengths of the organic compounds. The pore size of the resins (~100–500 Å) also provides higher rates of uptake as compared with other adsorbents such as molecular sieves for the separation of isomeric compounds.[19] Another advantage of the polymeric resins is the flexibility of modifying the polymeric backbone/or the functional groups for their strength of interaction with the adsorbates. The pore size of the resin also can be manipulated at the manufacturing process to suit the needs of the separation process.

In the present work, we have investigated the sorption of *o*- and *p*-NAs mixtures in a two-step process. The first step involves selective solubilization of *o*-NA. The *o*-NA shows intramolecular hydrogen bonding and can be easily solubilized in organic solvents, whereas, the intermolecular hydrogen bonding in *p*-NA resists its solvation and, in turn, reduces its solubility in organic solvents of nonpolar nature. In the second step, the trace impurities of *p*-NA from the solutions of *o*-NA can be removed by selective sorption on an acidic resin. The resin functions as a functionalized polymer because of the presence of sulfonic acid groups. The sorption is studied in nonaqueous conditions, where the interaction between the acidic group on the resin and both functional groups of nitroanilines can be treated as a Lewis acid–base interaction, unlike the proton exchange in aqueous media. Although our initial guess was of a stronger interaction of the resin with the $-NH_2$ group of nitroanilines, the molecular simulation showed better interaction with the $-NO_2$ group.

EXPERIMENTAL

Chemicals

Heptane, methanol, and toluene, used as solvents for the solubility, as well as the sorption studies of nitroanilines, and *p*-NA (all AR grade) were obtained from s. d. Fine Chemicals Ltd., Mumbai, India, and were used as such. The *o*-NA, obtained from E-Merck (India) Ltd., Mumbai, India, was purified by recrystallization. The macroporous strongly acidic resin, Indion-190, in sulfonic

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

acid form with a polystyrene, cross-linked (7–8%) with divinylbenzene backbone, was obtained from Ion Exchange India Ltd., Mumbai, India. The resin beads with an average size of 0.4–0.5 mm, showed an internal void fraction of 0.39 and an exchange capacity of 4.7 meq/g on a dry weight basis.

The resin beads initially were washed with 5% (w/v) aq. HCl solution. The excess acid was removed by thorough washing with distilled water. The acid-free resins were washed with methanol to remove moisture, then dried at 328 K for 10 h, and subsequently cooled to ambient temperature of 303 K in a dessicator.

Solubility Measurements

The solubility studies were conducted by adding excess amounts of nitroanilines in the selected solvent in stoppered test cells. The cells were kept in a constant-temperature water bath with intermittent mixing on a cyclomixer. After giving sufficient time for equilibration, the solutions were analyzed for the dissolved nitroanilines. The experiments were repeated at different temperatures.

Equilibrium Adsorption Studies

The equilibrium adsorption studies were conducted in a special glass adsorption cell to avoid loss of solvent during the equilibration process. A known amount of resin was taken in each of the cells and solutions of known concentrations of nitroanilines were then added into the cells. The stoppered glass cells were then kept in a shaker incubator maintained at constant temperature to attain the equilibrium. The studies were repeated for different solvents.

Both *o*- and *p*-NAs were analyzed by ultraviolet (UV)-visible absorption spectroscopy by using Chemito 2100 UV-VIS spectrophotometer, taking advantage of their characteristic wavelengths. The *o*-NA was analyzed for its concentration in heptane, toluene, and methanol at wavelengths 377, 393, and 404 nm, respectively; while in the same solvents, *p*-NA was analyzed at wavelengths 322, 342, and 372 nm, respectively.

RESULTS AND DISCUSSION

Selective Solubilization Studies

In the search for a selective solvent, solubilities of *o*- and *p*-NAs were determined first in three organic solvents, i.e., heptane, a nonpolar solvent;

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

toluene, an aromatic solvent with a slight polarity; and a polar solvent, methanol. The solubility values, at 303 K, are reported in Table 1, along with a few literature values. The experimentally determined solubility in toluene in this work matches well with that reported in benzene.[5] In all the solvents, the solubility of *p*-NA is lower than that of *o*-NA, the difference being the highest in toluene. Figure 1 shows the difference in hydrogen bonding patterns in *o*- and *p*-NAs. It is easy for a solvent to overcome the weak intermolecular attractive forces among the *o*-NA molecules, which show strong intramolecular hydrogen bonding. On the other hand, *p*-NA molecules are strongly bound to each other by intermolecular hydrogen bonding and resist their solvation by a solvent with poor solvation ability.

The *p*-NA is practically insoluble in heptane, which interacts only through London dispersion forces and is incapable of breaking strong intermolecular attractive forces in *p*-NA molecules. The solubility of *o*-NA, although much higher compared with that of *p*-NA, is also low in heptane, possibly because of poor molecular interaction between the solvent and *o*-NA. Toluene, which is polarizable because of the π electron cloud of its aromatic ring, interacts to a significant extent with *o*-NA, causing its moderate solubility but cannot still overcome the intermolecular hydrogen bonding in *p*-NA molecules resulting in its very low solubility. In methanol, however, both isomers are highly soluble. Methanol, with its own $-OH$ group is a H− bond donor and also an acceptor, and forms strong hydrogen bonds with both $-NO_2$ and $-NH_2$ groups of the nitroaniline. Toluene was selected as a selective solvent for the first step of separation, as it has moderately high

Table 1. Solubilities of nitroanilines in different solvents at 303 K.

	p-NA		*o*-NA	
Solvent	Solubility (mmol/kg solvent)	Activity coefficient (γ)	Solubility (mmol/kg solvent)	Activity coefficient (γ)
Heptane	0.58	8,071	19.50	314.7
Toluene	38.90	138.5	1,820	4.3
Methanol	669	23.6	3,940	5.5
Water[a]	4.11	6,895	8.77	3,727
Chloroform[a]	31.40	176.9	816	5.7
Benzene[a]	41.90	156.4	1,510	5.6

[a] Ref.[5].

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

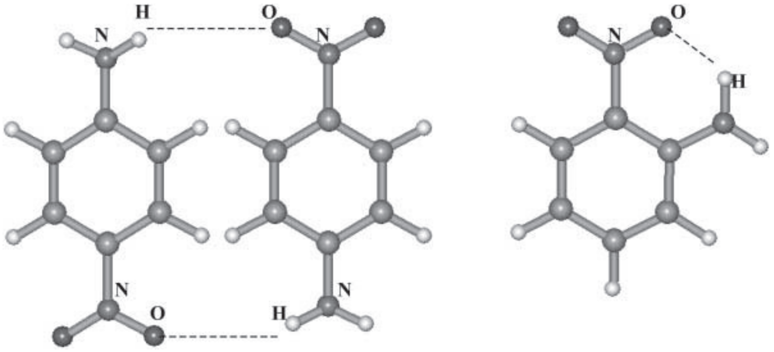


Figure 1. Hydrogen bonding in nitroanilines. (View this art in color at www.dekker.com.)

Downloaded At: 10:10 25 January 2011

solubility of *o*-NA (~16.8 mole%), while keeping the solubility of *p*-NA low (~0.4 mol%) at 303 K.

The activity coefficient (γ) of a solute in the saturated solution is a measure of its interaction with the solvent. Poor solvation means poor interaction between the solvent and the solute, which is indicated by γ values much greater than unity. A large value of γ indicates poor solvation and low solubility of the compound. The activity coefficient of the solute can be related to the fugacity of the standard state f_2^0 to which that activity coefficient refers to and to the fugacity of pure solid ($f_{2,\mathrm{puresolid}}$).

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

The following equation gives the activity coefficient of a solute in terms of heat of fusion (Δh^{f}), specific heat of the compound (C_p), and normal melting point, (T_{m}):[20]

$$\gamma_2 = \frac{1}{x_{2,\mathrm{sat}}} \exp\left\{ \frac{\Delta h^{\mathrm{f}}}{R}\left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T}\right) + \frac{1}{RT}\int_T^{T_{\mathrm{m}}} \Delta C_p \, dT - \frac{1}{R}\int_T^{T_{\mathrm{m}}} \frac{\Delta C_p}{T}\, dT \right\} \tag{2}$$

The following values of the parameters in Eq. (2), obtained from the literature,[21] were used to estimate the activity coefficients of nitroanilines (Table 1).

$$\Delta h^{\mathrm{f}}_{p-\mathrm{NA}} = 5.035\,\mathrm{kcal/mol}, \qquad \Delta h^{\mathrm{f}}_{o-\mathrm{NA}} = 3.85\,\mathrm{kcal/mol}$$
$$T_{\mathrm{m},p-\mathrm{NA}} = 420\,\mathrm{K}, \qquad T_{\mathrm{m},o-\mathrm{NA}} = 344\,\mathrm{K}$$

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

and, $C_{p,p\text{-NA}} = 0.414 + 0.138T\,\text{cal/mol K}$, $C_{p,o\text{-NA}} = 2.464 + 0.127T\,\text{cal/mol K}$ For *p*-NA, γ decreases for the solvents selected for solubility measurements in the order, heptane > toluene > methanol. The solvation as expected, is the best in methanol and is indicated by the lowest activity coefficients in the selected solvents for selective solubilization.

The solubilities of nitroanilines were further determined at four different temperatures in three solvents. Figure 2 shows that with the increase in temperature the solubility of both nitroanilines increases, the effect being more for *o*-NA. The activity coefficients from the solubility data were fitted in (UNIQUAC) model of the liquid phase[22] by using the least-square technique to evaluate values of the interaction parameters (a_{ij}) for different pairs (Table 2). For both nitroanilines, these values increase as the polarity of the solvent decreases. The lower a_{ij} values indicate the stronger attraction of the solvent toward a solute. Also, a_{12} values are lower than a_{13} values in the respective solvents, indicating a stronger interaction of solvents with *o*-NA than *p*-NA, i.e., higher solubility of *o*-NA than *p*-NA.

The mixture solubility studies of nitroanilines in toluene, however, show that in the presence of *o*-NA, the solubility of *p*-NA increases three to seven times its solubility when present alone, in the range of temperatures studied. This increase in the solubility of *p*-NA shows that there is an attractive molecular interaction between *o*-NA and *p*-NA molecules in the solution. The attractive interaction may be due to partially positive H of amino group of *o*-NA and partial negative O of the nitro group of *p*-NA and vice versa. Nevertheless, the increase in the solubility of *p*-NA is not high enough to solubilize it to the significant extent in toluene as seen from its concentration values in the mixture studies described further in this paper. It is, therefore, possible to get pure *p*-NA from its mixtures with *o*-NA by selective solubilization of the latter in toluene. It was, therefore, of interest to selectively remove the trace amounts of *p*-NA from the *o*-NA rich solutions by sorption, using the polymeric acidic resins.

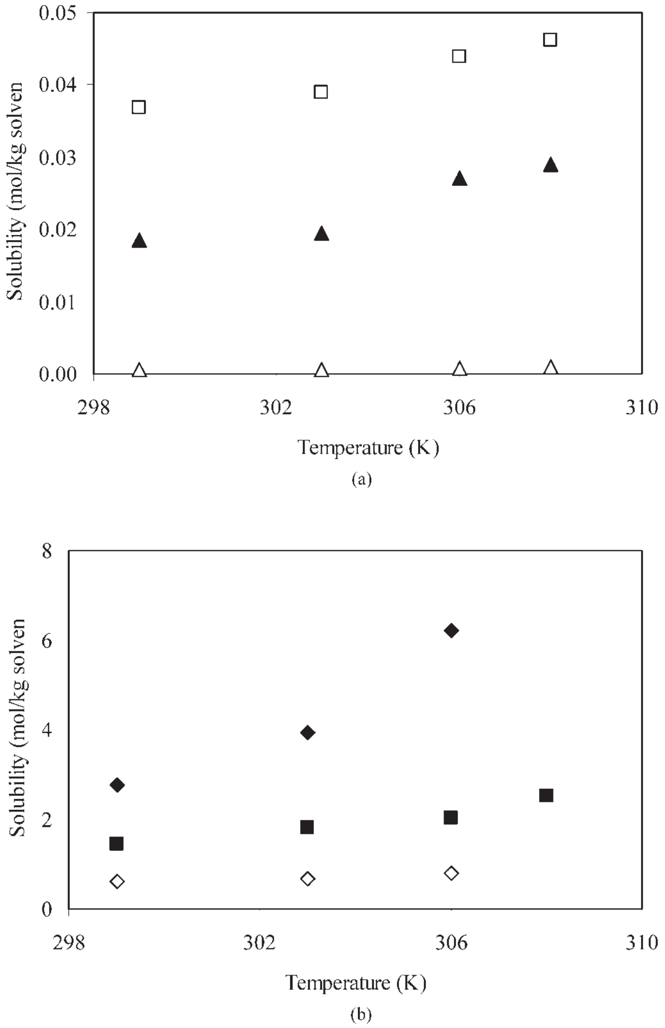
Swelling of Resins in Organic Solutions

The polymeric structure of a resin swells when brought in contact with organic solvents, because of the penetration of solvent into polymeric network of the resin phase. This swelling is because of several factors, such as the tendency of fixed and mobile ions to form solvation shells, the tendency of the interior of ion-exchange resins (which is like a highly concentrated solution) to dilute itself by taking up additional solvent and stretching of the chains of the matrix due to the repulsive electrostatic interactions between the fixed

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS



(a)

(b)

Figure 2. Solubilities of *o*-/*p*-NAs in various solvents. *Key:* ◇, methanol; □, toluene; △, heptane; Filled symbols, *o*-NA; Hollow symbols, *p*-NA.

ionic groups. The extent of swelling depends on the nature of solvent, solute, and polymeric structure, and on the degree of cross-linking in the resin polymer.[8]

The overall swelling ratio R_s is defined as the ratio of the resin volumes in the swollen and dry states. There is a considerable swelling in the case of

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

Table 2. Interaction parameters of UNIQUAC model.

	Solvent		
	Methanol	Toluene	Heptane
a_{12}	87.8	355.6	929.1
a_{21}	1008	36.9	29.055
a_{13}	696.6	846	1500
a_{31}	84.2	0.155	−10

Note: 1, Solvent; 2, *o*-NA; 3, *p*-NA.

nitroaniline solutions in methanol ($R_{s,p\text{-NA}} = 1.24$, $R_{s,o\text{-NA}} = 1.26$), whereas, in toluene, the swelling is negligible ($R_{s,p\text{-NA}} = 1.03$, $R_{s,o\text{-NA}} = 1.05$). Methanol, being a highly polar solvent, swells the polymeric chains of the resins more compared with toluene. Also, through its own −OH group, which is a good H-bond acceptor and donor, it competes with nitroanilines to interact with the functional sites on the matrix. The interaction of methanol with resin is much greater than that of toluene. In both the cases, however, the swelling is independent of the nitroaniline concentration. The resin–solute interaction, in this case, therefore, has no significant effect on the swelling, which is solely due to the interaction between the solvent and the resin.

Downloaded At: 10:10 25 January 2011

Equilibrium Sorption

Adsorption of a solute on the functional site of the resin also is accompanied by absorption of solution, particularly in the swollen resin. After sorption, nitroaniline is present in the resin phase as an adsorbed solute (solute immobilized by attachment to functional site) and also as an absorbed solute (mobile solute present in the absorbed solvent). Assuming that the increased volume of the swollen resin is being occupied by absorbed solution having the same composition as the external bulk phase, the adsorbed amount of nitroaniline can be estimated.

The absorbed and adsorbed amounts of both nitroanilines in toluene and methanol are shown in Figs. 3 and 4, respectively. In the case of toluene, the adsorbed amounts of nitroanilines are much higher than their absorbed amounts in the resin phase. This is due to the stronger interaction of the nitroanilines with the resin than the interaction between nitroaniline and toluene. In the case of methanol, however, the trend is the reverse; the

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

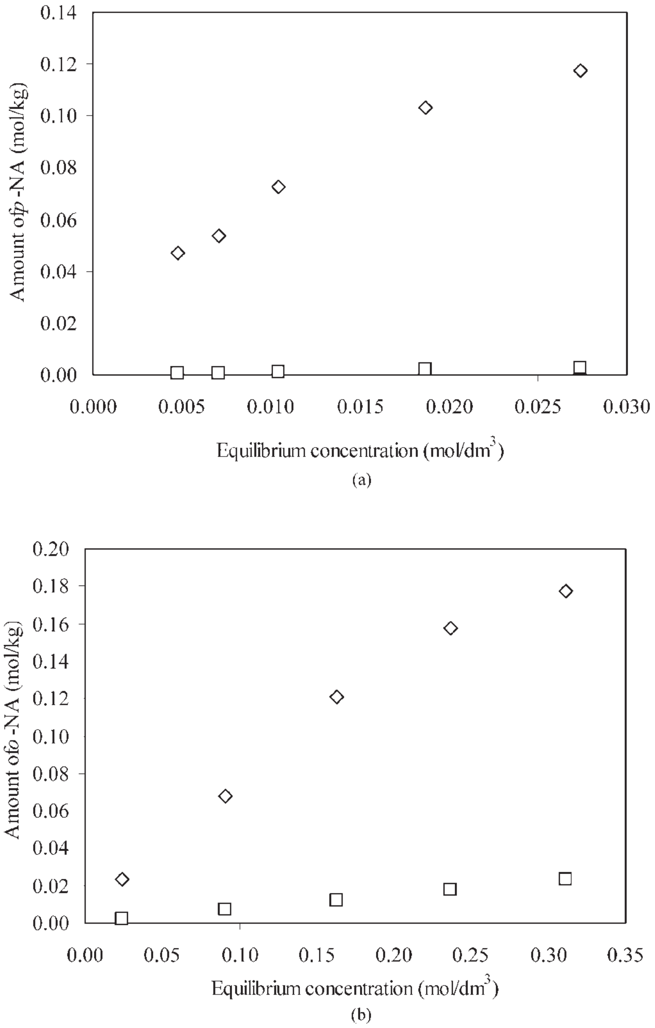


Figure 3. Absorbed vs. adsorbed amounts of (a) *p*-NA and (b) *o*-NA from toluene. *Key:* ◇, adsorbed; □, absorbed.

absorbed amount is more than the adsorbed amount. This is probably due to the following two factors:

a. Nitroanilines interact strongly with methanol, as indicated by their high solubilities in methanol. Their interaction with the –OH group of

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

Downloaded At: 10:10 25 January 2011

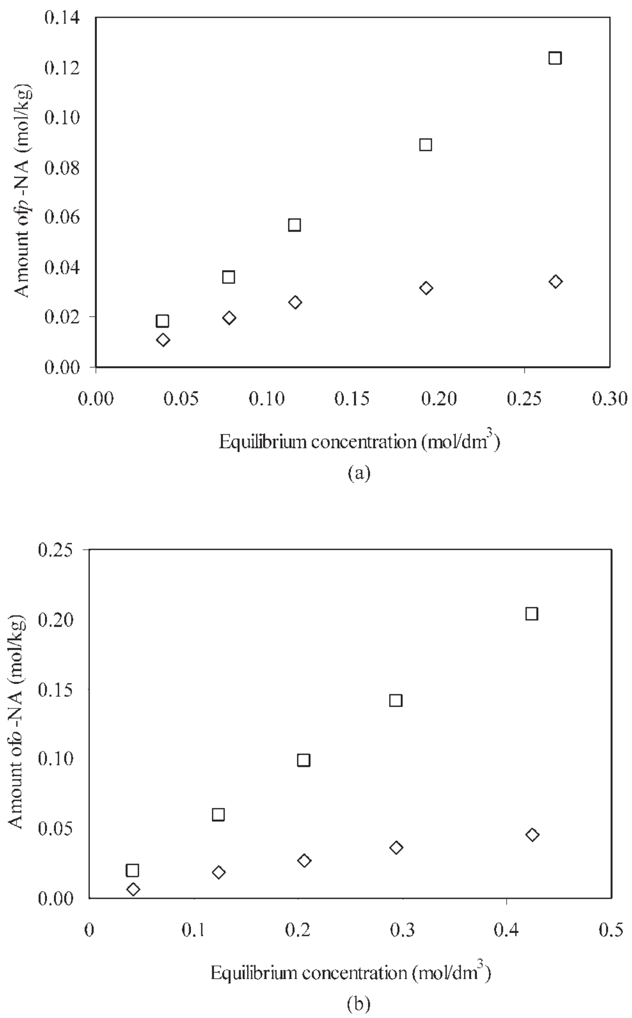


Figure 4. Absorbed and adsorbed amounts of (a) *p*-NA and (b) *o*-NA from methanol. *Key:* ◇, adsorbed; □, absorbed.

methanol should be of the same strength as that of the $-SO_3H$ group of resin, both being H-bondings. However, being immobile, only one sulfonic acid group interacts with a nitroaniline molecule as compared with several methanol molecules that solvate a single nitroaniline molecule (methanol can interact with both amino and nitro groups of nitroaniline).

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

b. Methanol, with its own –OH group, is a good H-bond donor and acceptor, and competes with the nitroaniline molecule to interact with the adsorption site.

Single Component Adsorption Isotherms

The equilibrium adsorption data were fitted into Langmuir adsorption isotherm. Table 3 shows the Langmuir equilibrium constants and maximum loading capacities for different runs. The adsorption equilibrium constant (K), which is a measure of interaction between the resin and solute, was higher for p-NA than that of o-NA in toluene. A solute molecule gets adsorbed if the interaction between the solute and adsorbent is stronger than the interaction between the solute and the solvent. The p-NA has a very low solubility in toluene, which indicates its poor interaction with toluene. On the other hand, as explained later in this paper, the interaction between weakly basic p-NA and the sulfonic group of the resin is of a Lewis acid–base type and, hence, stronger. Consequently, p-NA has a higher adsorption constant, whereas, o-NA, with its higher solubility and weaker basicity, has a lower adsorption equilibrium constant for adsorption from toluene.

With methanol as a solvent, the solute–solvent interactions are much stronger. The oxygen in –OH group of methanol has two lone pairs of electrons and forms a stronger H-bond with the partially positive hydrogen atoms of the

Table 3. Langmuir model parameters and activity coefficients for adsorption of nitroanilines at 297 K.

	Solvent	
	Toluene	Methanol
Maximum loading capacity (Γ^{∞}) (mol/kg)		
p-NA	0.20	0.06
o-NA	0.28	0.18
Equilibrium constant (K) (dm^3/mol)		
p-NA	52.41	5.42
o-NA	4.45	0.89
Activity coefficients (γ_i)		
p-NA	149–160	39–65
o-NA	9–11	15–19
Modified equilibrium constant (K') (dm^3/mol)		
p-NA	0.33	0.09
o-NA	0.42	0.05

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

amino group of the nitroaniline molecules. These interactions are comparable with the interactions between nitroanilines and the sulfonic group of resin, resulting in the much lower adsorption equilibrium constants as compared with the values in toluene. The lower values of the adsorption equilibrium constant in methanol should permit its use as a solvent for regeneration of the resin.

The maximum loading capacities are lower for *p*-NA than *o*-NA in both the solvents. The loading capacity should be dependent upon the number of sites, such as acidic sites, under the premise of the Langmuir adsorption that one molecule adsorbs on one site. However, considering that there is a strong cohesive interaction between the nitro-substituted molecules and if both nitro as well as amino groups are involved in the adsorption process by dipole–dipole interactions with the acidic groups of resin, then the orientation of adsorbed species becomes important, e.g., two neighboring sites may interact with a single molecule of *p*-NA, giving a lower adsorption capacity than the adsorption capacity expected from the number of exchange sites available and lower than the capacity of the resin to adsorb *o*-NA.

The uptake of nitroaniline isomers was substantially different from different solvents. This difference in the adsorption behaviors in toluene and in methanol, is mainly due to different degrees of solvation of nitroanilines in these solvents, i.e., differences in the interaction between the solute and solvent, and the nature of solvent. These solvent effects, or nonidealities, in the solution, because of intermolecular interaction in the solution phase, can be accounted for, to some extent, by incorporating activity coefficients of solutes in the Langmuir adsorption equation. The modified Langmuir equation can be written as

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

where K' is the modified adsorption equilibrium constant, which should represent the true interaction between the solute and the resin.

The activity coefficients of corresponding nitroanilines were estimated by using the UNIQUAC model of the group contribution method and the parameters obtained from solubility data, and they are reported, along with the modified adsorption equilibrium constants, in Table 3.

The modified adsorption equilibrium constants of *p*-NA in both the solvents are closer ($K'_{\text{toluene}}/K'_{\text{methanol}} = 3.5$), compared with unmodified values ($K'_{\text{toluene}}/K'_{\text{methanol}} = 9.7$). The differences in the extent of adsorption in different solvents, therefore, seem to be mainly due to the nonidealities in the solutions. However, in the case of weakly adsorbing *o*-NA, the K' value in toluene is approximately eight times higher than that in methanol. This model does not take into account the interaction of the solvent with the resin, and,

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

where the solvent–resin interaction is predominant, compared with a solute–resin interaction, as in case of *o*-NA in methanol, it fails to account for the solvent effect, if any.

In both the cases, the adsorption of *o*-NA and *p*-NA has shown a very low adsorption saturation capacity, which is much lower than the exchange capacity of the resins used in the studies. The adsorption constant, which one can estimate even from the linear part of Langmuir isotherm, is an indication of the solute–resin interaction, which is not significantly higher when compared with the experimental data reported with other aniline isomers.[9] Thus, apart from the solvent effect, molecular interaction does seem to be affected by substituents on the aniline ring. It appears that weaker bases, like nitroanilines, could not be significantly interacting with acidic functional group on the resin matrix. The solvent polarity, particularly, seems to be more important in methanol, as the adsorption from methanol is extremely weak for both solutes (i.e., a low value of *K*).

Downloaded At: 10:10 25 January 2011

Mixture Batch Adsorption Studies

The experimental data for adsorption of nitroaniline mixtures are shown in Fig. 5, along with the predicted curves. The estimated values were obtained by using single component adsorption data and extending the Langmuir model to the binary system. Although the single component adsorption data was well fitted in the Langmuir adsorption model, the adsorbed concentration of *o*-NA was much higher than the predicted values in the mixture batch studies. The presence of *p*-NA in the adsorbed state seems to be attracting more of *o*-NA into the resin phase. The mixture solubility studies in toluene show that the solvent is not capable of solvating the individual molecules in competition with the interaction among themselves. Then the similar interaction among the adsorbed molecules cannot be overlooked and also is reflected in the increased solubility of isomers in the presence of other isomers in toluene.

The interaction energy of the adsorbed molecules in the adsorbed phase was estimated following a statistical mechanics approach developed by Ihm and Lee.[23] The interaction energy, W between the adsorbed molecule, is obtained by plotting ln α vs. $(1 - x_1^s)$ for Eq. (4) where W represents the interaction energy for admolecules and x_1^s 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:

$$K^0 - \ln\alpha + (1 - 2x_1^s)\left(\frac{cW}{2kT}\right) = 0 \qquad (4)$$

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

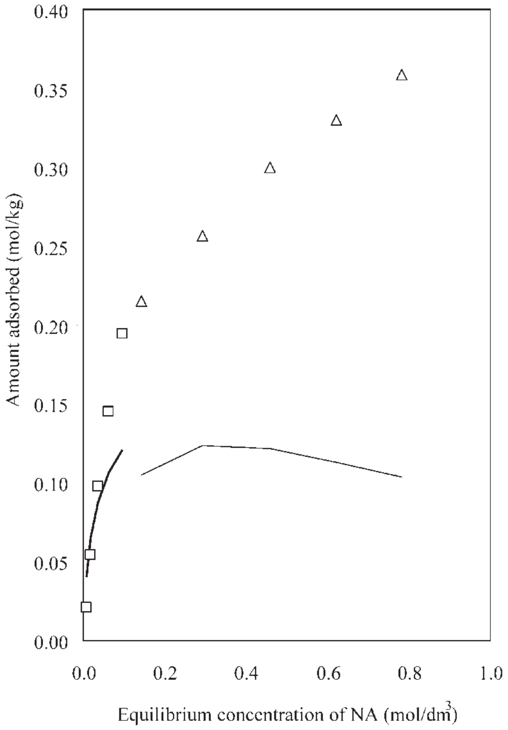


Figure 5. Adsorption of nitroanilines from their mixtures in toluene (the lines indicate the expected competitive adsorption from the single component adsorption data and Langmuir adsorption isotherm). *Key:* □, *p*-NA experimental; ▬, *p*-NA predicted; △, *o*-NA experimental; —, *o*-NA predicted.

The value of K^0 and $cW/2kT$ can be estimated from the intercept and slope of the linear plot, as shown in Fig. 6. The nonzero negative slope confirms an attractive interaction between *p*-NA and *o*-NA molecules in the adsorbed phase. In the absence of any interaction between adsorbed molecules, the zero slope of the line was expected.

Separation factor for the mixture studies in toluene was calculated on a solvent-free basis as

$$\alpha_{12} = \frac{(x_1^{\mathrm{s}}/x_2^{\mathrm{s}})}{(x_1^{\mathrm{l}}/x_2^{\mathrm{l}})} \tag{5}$$

The α values are plotted in Fig. 7 against the mole fraction of *p*-NA on a solvent-free basis. A separation factor in excess of 4 could be achieved with a

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

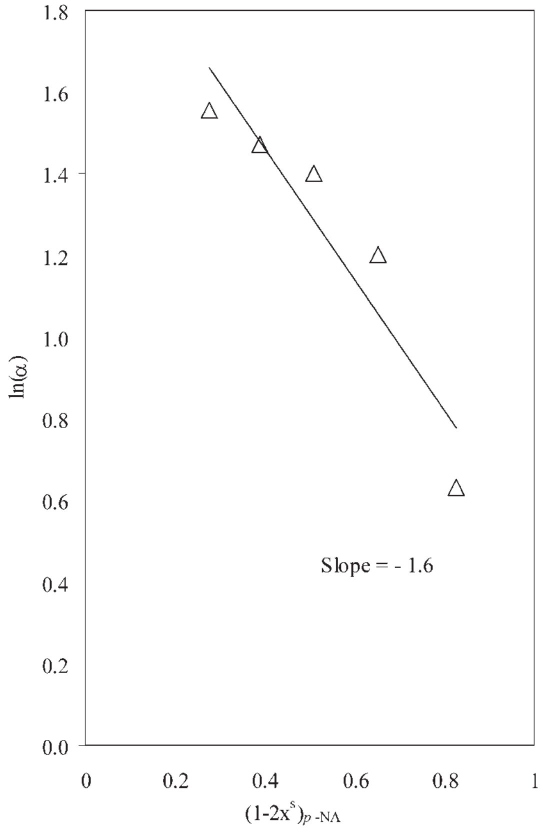


Figure 6. Interaction energy of adsorbed molecules in toluene.

para to ortho ratio of 9 : 100. For the concentration range studied, the separation factor increased with the mole fraction of *p*-NA but approached a constant value at the *p*-NA mole fraction of 0.09. But even at a low concentration of *p*-NA and in the presence of a large amount of *o*-NA, the selectivity in the specific adsorption of *p*-NA is noticeable.

UNDERSTANDING SORPTION OF NITROANILINES BY ION EXCHANGE RESINS

The resin, which is based on a polystyrene–divinylbenzene matrix has sulfonic acid group ($-SO_3H$) as the functional group. The oxygens of the

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

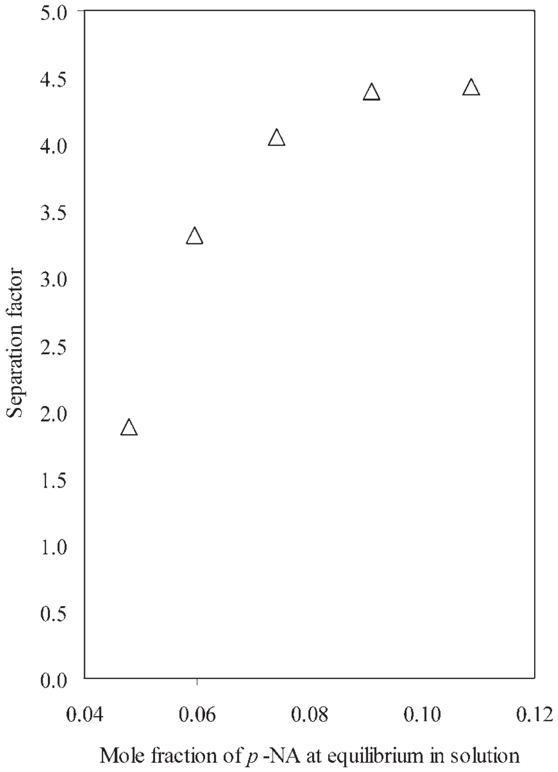


Figure 7. Separation factor of *p*-NA/*o*-NA mixtures in toluene.

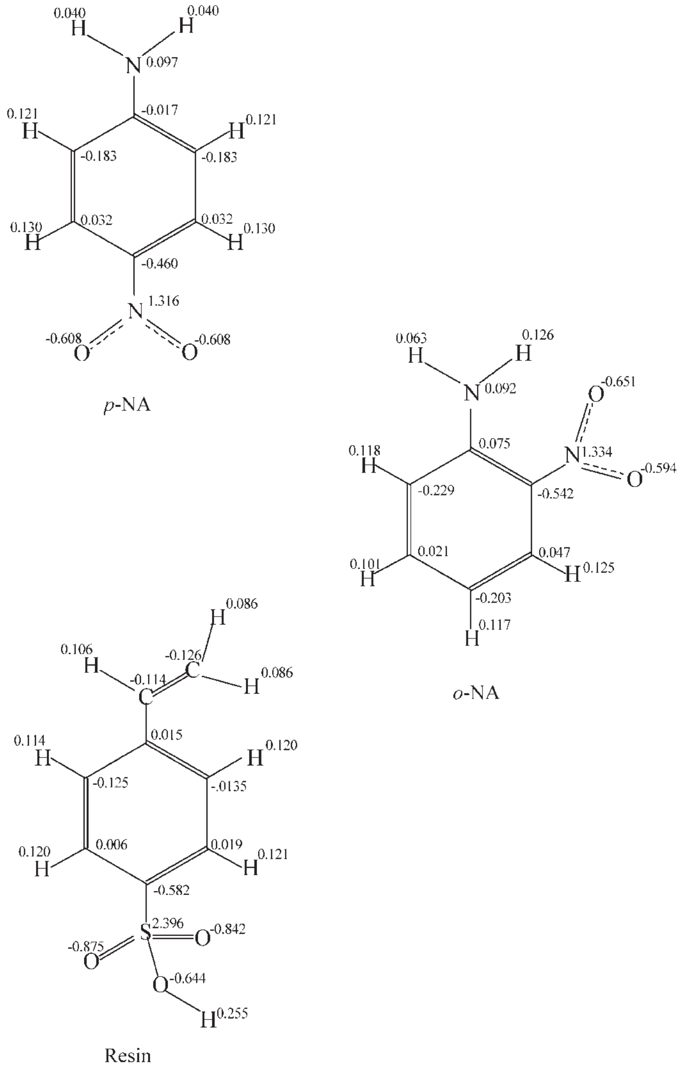
nitro group of a nitroaniline molecule carry the highest negative charge (0.608 and 0.594 for *p*-NA and *o*-NA, respectively) and are expected to form a H-bond with the hydrogen of the sulfonic group on the resin, which carries a positive charge of 0.255 (Fig. 8). The Lewis acid–base type of interaction seems to be responsible for the adsorption of nitroaniline isomers on the resin in nonaqueous conditions, unlike the proton transfer in aqueous conditions.

In the present work, the quantum mechanics (QM) energies of nitroanilines and vinyl benzene sulfonic acid (used as an analogue of the repeating unit of the polymer) were minimized individually and also as of their associated complex, in toluene by using Hyperchem (v7.0) from Hypercube Inc. The QM uses potential energy calculations at electron levels based on ab initio methods or parameter sets (used in various semi-empirical methods)

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS



p-NA

o-NA

Resin

Figure 8. PM3 optimized structures of nitroanilines and sulfonic acidic resin.

developed for a number of atoms, to estimate the interaction energies of different molecules.

The potential energy of a molecule depends on bond lengths, bond angles, torsion angles, and nonbonded interactions (including van der Waals forces, electrostatic interactions, and hydrogen bonds). On this basis, the internal

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

energy of a molecule can be calculated by using a QM semi-empirical method. Energies derived in this way can be used for determining preferred confirmations and intermolecular interactions.

The semi-empirical method "PM3" developed by Stewart[24,25] and the Polak–Ribiere method were used for the energy minimization calculations. The procedure involves geometrical optimization of the molecule in which a systematic altering of coordinates of the atoms is carried out until the minimum energy of the system is reached.

The binding energy of the solute with the resin can be estimated from the difference in energies of the associated complex and the sum of energies of the individual species.

$$\begin{aligned}\text{Interaction energy} &= (\text{QM energy of solvated complex}) \\ &\quad - (\text{QM energy of resin} + \text{solvated molecule}) \qquad (6)\end{aligned}$$

The interaction energies of *p*- and *o*-NAs with the simplified resin unit were estimated to be -8.5 and $-6.0\,\text{kcal/mol}$, respectively. The energy value for *p*-NA shows that it interacts strongly with the resin than with *o*-NA.

Figure 9 shows the optimized structures of *p*- and *o*-NAs with the sulfonic acid resin in toluene. In the optimized state, the oxygen of the nitro group of both isomers forms a hydrogen bond with the hydrogen of the sulfonic acid group. The charges on hydrogen of the amino group and oxygen of the sulfonic acid group, although favorable to interact, their interaction seems to be weaker than the above-mentioned hydrogen bonding. The presence of multiple interaction sites, on one hand, should increase the strength of adsorption but, on the other hand, can facilitate intermolecular interactions, reducing the selectivity. The molecular modeling approach may serve well to identify such interactions and should help in designing more selective adsorbent resins.

CONCLUSION

Toluene is the best solvent for selective solubilization of nitroanilines mixture, as it selectively dissolves *o*-NA. The *p*-NA has very low solubility in toluene. A primary separation, therefore, could be achieved at the first step. The trace amounts of *p*-NA in the solution can be adsorbed from the organic phase on an ion exchange resin functionalized with an acidic group. The bonding of nitroanilines to the functional group of resin is through H-bonding between O of the nitro group and H of the sulfonic group.

The extent of swelling was different for the different solvents. In toluene, there is negligible swelling of resin, whereas, resin swells considerably in

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

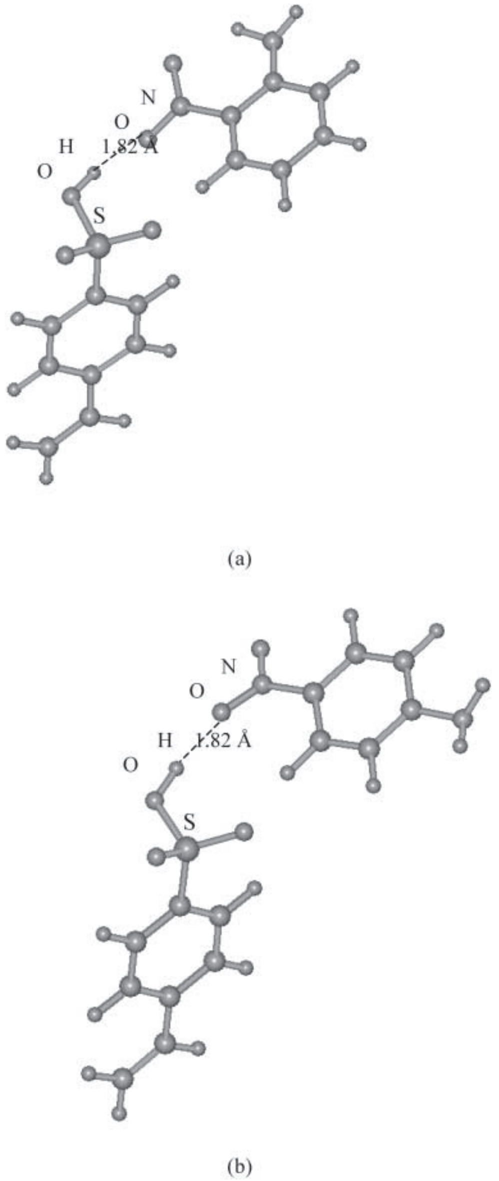


Figure 9. PM3 optimized structures of adsorbed nitroanilines on resin functional group. (a) *o*-NA resin complex, (b) *p*-NA resin complex. (View this art in color at www.dekker.com.)

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

methanol. Separation factor in the excess of 4 could be achieved, and, with the possible high recovery of the solvents, this route seems attractive for industrial application.

NOMENCLATURE

a_{ij}	Interaction parameter for interaction of component i with j, cal/mol
c	Number of neighboring sites
C_{eq}	Equilibrium concentration, mol/dm^3
ΔC_p	Heat capacity difference, cal/mol K
Δh^{f}	Heat of fusion at atmospheric melting point, cal/mol
K	Equilibrium constant for Langmuir equation, dm^3/mol
K'	Modified equilibrium constant for Langmuir equation, dm^3/mol
K^0	Constant in Eq. (4)
k	Boltzmann constant, cal/K
R_{s}	Swelling ratio
R	Gas constant, cal/mol K
T	Temperature, K
T_{m}	Melting point, K
W	Interaction energy, cal/mol
x_i	Mole fraction of component i

Greek Letters

α	Separation factor
Γ	Equilibrium loading capacity, mol solute/kg resin
Γ^{∞}	Maximum loading capacity, mol solute/kg resin
γ_i	Activity coefficient of component i

Superscripts

s	Solid phase
l	Liquid phase

ACKNOWLEDGMENTS

We wish to thank Ion Exchange (I) Ltd. for free samples of ion-exchange resins for these experiments and Department of Science and Technology (GOI.), for support of this work.

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

REFERENCES

1. Booth, G. Nitro compounds aromatic. In *ULLMANN's Encyclopedia of Industrial Chemistry,* 5th Ed.; Elvers, B., Hawkins, S., Schulz, G., Eds.; VCH Publishers: New York, 1991; Vol. A-17, 411.
2. Bryant, J.G. Chlorinated benzenes. In *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th Ed.; How-Grant, M., Ed.; John Wiley & Sons, Inc.; 1993; Vol. 6, 98.
3. Kemula, W.; Buchowski, H.; Pawlowski, W. Separation of *o*- and *p*-nitroanilines by extraction. Roozniki Chem. **1961**, *35*, 703–710c.f. C.A., 55, 23391 (1961).
4. Jagiradar, G.C.; Sharma, M.M. Separation of close boiling substituted anilines: gas–liquid vs conventional liquid–liquid dissociation extraction. J. Separ. Proc. Technol. **1981**, *2* (4), 7–12.
5. Jagirdar, G.C. Separation of nitroanilines. Chem. Ind. **1984**, *16*, 586–587.
6. Jagirdar, G.C. Two-step separation process: alternative to distillation. Ind. Eng. Chem. Process Des. Dev. **1985**, *24*, 886–887.
7. Thomas, J.D.R. Some aspects of ion–exchange in non-aqueous and mixed solvents. J. Chromatography. **1974**, *102*, 209–215.
8. Helfferich, F.G. *Ion-Exchange*; McGraw Hill Co. Inc.: New York, 1962.
9. Gaikar, V.G.; Kamble, S.P. Selective solubilization and adsorptive separation of phenylenediamines using ion exchange resin. Sep. Sci. Technol. **2003**, *38* (14), 3409–3430.
10. Chakrabarti, D.P. *Adsorptive Separations Using Ion-Exchange Resins (Separations of Cyclohexylamines)*; University of Mumbai; 1999M. Chem. Engg. Thesis.
11. Gaikar, V.G.; Anasthas, H.M. Separation of *o*-/*p*-hydroxyacetophenones by selective solubilization and sorption on weak base ion-exchange resins. Ind. Eng. Chem. Res. **2002**, *41*, 1335–1343.
12. Gaikar, V.G.; Anasthas, H.M. Adsorption of acetic acid on ion-exchange resins in non-aqueous conditions. React. Funct. Polym. **2001**, *47*, 23–35.
13. Payne, G.F.; Payne, N.N.; Ninomiya, Y.; Shuler, M.L. Adsorption of nonpolar solutes onto neutral polymeric sorbents. Sep. Sci. Technol. **1989**, *24* (5&6), 457–465.
14. Payne, G.F.; Ninomiya, Y. Selective adsorption of solutes based on hydrogen bonding. Sep. Sci. Technol. **1990**, *25* (11&12), 1117–1129.
15. Payne, G.F.; Maity, N. Adsorption from aqueous solutions based on a combination of hydrogen bonding and hydrophobic interactions. Langmuir **1991**, *7*, 1247–1254.
16. Payne, G.F.; Maity, N.; Chipchosky, J.L. Adsorptive separations based on the differences in solute–sorbent hydrogen bonding strengths. Ind. Eng. Chem. Res. **1991**, *30*, 2456–2463.

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

ORDER REPRINTS

17. Payne, G.F.; Brune, B.J.; Koehler, J.A.; Smith, P.J. Correlation between adsorption and small molecule hydrogen bonding. Langmuir **1999**, *15*, 3987–3992.
18. Payne, G.F.; Glemza, A.J.; Mardis, K.L.; Chaudhary, A.A.; Gilson, M.K. Competition between intra- and intermolecular hydrogen bonding: effect on para/ortho adsorptive selectivity for substituted phenols. Ind. Eng. Chem. Res. **2000**, *39*, 463–472.
19. Gaikar, V.G.; Anasthas, H.M. Adsorptive separations of alkylphenols using ion-exchange resins. React. Funct. Polym. **1999**, *39*, 227–237.
20. Prausnitz, J.M. *Molcular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall, Inc.; 1969; 385–406.
21. Perry, R.H.; Green, D.W.; Maloney, J.D. *Perry's Chemical Engineers' Handbook,* 7th Ed.; McGraw-Hill; 1997.
22. Anderson, T.F.; Prausnitz, J.M. Application of UNIQUAC equation to calculation of multicomponent phase equilibria. 1. Vapor-liquid equilibria. Ind. Eng. Chem. Process Des. Dev. **1978**, *17* (4), 552–560.
23. Ihm, S.; Lee, H. Effect of the interaction between admolecules on the sorption equilibrium at the liquid–solid interface for the Y zeolites. In *New Developments in Zeolite Science and Technology*; Murakami, Y., Iijima, J., Ward, J.W., Eds.; Elsevier Science Publishers: Amsterdam, 1986; 571.
24. Stewart, J.J.P. Optimization of parameters for semi-empirical methods I. Method. J. Comput. Chem. **1989**, *10*, 209–220.
25. Stewart, J.J.P. Optimization of parameters for semi-empirical methods II. Applications. J. Comput. Chem. **1989**, *10*, 221–264.

Received May 2003
Revised September 2003

Downloaded At: 10:10 25 January 2011

Copyright © Marcel Dekker, Inc. All rights reserved.

Downloaded At: 10:10 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SS120028575