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Separation of Phenylenediamines by Selective Solubilization and Adsorption on Ion-Exchange Resin

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ABSTRACT

Separation of phenylenediamines (PDAs) was attempted using a combination of selective solubilization in an organic solvent and then adsorption from nonaqueous solutions on commercial acidic ion-exchange resins. Toluene was the best solvent for selective solubilization and also for the subsequent sorption of the amines by an acidic ion-exchange resin having sulfonic acid groups on the styrene-divinylbenzene backbone. The equilibrium sorption studies showed very selective sorption of the amines with a high loading capacity on the resin. The uptake of the amines was reinforced by Lewis acid–base interaction between the lone pair of electrons on the nitrogen of the amine and the sulfonic acid group of the resin. In the sorption studies involving

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mixtures, *p*-PDA was selectively adsorbed. Molecular mechanics calculations confirm the existence of the acid–base interactions.

Key Words: Separation; Selective solubilization; Ion-exchange resin; *o*-/*p*-/*m*-Phenylenediamines; Sorption; Adsorption; Molecular simulation.

INTRODUCTION

Catalytic hydrogenation of mixed dinitrobenzenes gives a mixture of phenylenediamines (PDAs). The separation of these isomers is usually carried out by vacuum distillation.[1–5] But, because of the energy intensive nature of distillation, there is a need to develop other techniques of separation. The separation of organic, acidic/basic, isomeric/nonisomeric compounds by chemical methods has received considerable attention in recent years, when conventional techniques are not practical or are too expensive.[6] The present study deals with the separation of phenylenediamines (PDAs) using a combination of selective solubilization in an organic solvent and adsorption on an acidic ion-exchange resin. The expected interaction is Lewis acid–base type between the hydrogen of sulfonic acid group of the resin and the lone pair of electrons on nitrogen of the amines. In nonaqueous media, the strength of the acid–base interaction depends on the ability of the molecules to form hydrogen-bonded complexes rather than ion exchange.[7]

Sorption on ion-exchange resins in nonaqueous conditions has not received much attention, unlike that of aqueous conditions. Very few references are available regarding the experimental and theoretical studies on the adsorption of aromatic amines from nonaqueous phases on synthetic polymeric resins. Separation of aniline, N-methylaniline, and N,N-dimethylaniline from hexane by adsorption on a commercial polycarboxylic ester sorbent (XAD-7) was reported.[8,9] However, the absence of any specific interaction leads to poor capacity of the resins for anilines. Payne and co-workers also studied the use of nonionic polymeric resins for selective sorption of phenols from organic solvents, both experimentally and by molecular modeling.[10–12] The sorption of nitroanilines on a porous divinyl benzene-styrene copolymer and an acrylonitrile-divinyl benzene copolymer, as studied by Maria and Kolarz,[13] showed that the sorption of nitroaniline isomers increased in the order *meta* < *para* < *ortho* on the surface of the divinyl benzene-styrene copolymer, whereas in the case of acrylonitrile-divinyl benzene copolymer, the sorption increased in the order *para* < *meta* < *ortho*. The sorption behavior of benzoic acid and substituted benzoic acids was also reported with styrene-divinylbenzene copolymer-based sulfonic acid resins.[14] These results indicated that the polymeric backbone of the resin is equally important for sorption of organic compounds.

The ion-exchange resin's stability and sorption behavior in aqueous and mixed solvent media are available in published research along with several other applications and characteristics.[7,15] The strong base ion-exchange resins with sufficient crosslinking are stable in solvents of widely different characteristics to permit their use in analytical separations. The use of ion-exchange resins in bulk separations in nonaqueous conditions, however, received attention recently. The major advantage of ion-exchange resins lies in their availability in different forms, which can be further modified with ease with a number of functional groups. The resin's structure can also be manipulated depending upon the applications. This provides an operational flexibility in the use of functionalized polymers as mass separating agents.

Recently, our group reported adsorption of acetic acid, naphthenic acid, and alkyl phenols from nonaqueous solutions using weakly basic resins.[16–21] These resins showed very high capacity and selectivity for the acidic compounds. Interestingly, the basic resins could distinguish even *o*-/*p*-isomers of hydroxyacetophenone.[20] A two-stage process of selective solubilization followed by adsorption on the resin could give complete separation of the phenol isomers. We expected a similar selective sorption of phenylenediamine isomers by acidic ion-exchange resins under nonaqueous conditions.

MATERIALS AND REAGENTS

All the solvents used for solubilization and adsorption studies were of AR grade. Toluene, 1,2-dichloroethane (DCE), methanol (MeOH), *o*-phenylenediamine (*o*-PDA), and *p*-phenylenediamine (*p*-PDA), were obtained from S. D. Fine Chemicals, Mumbai, India. *m*-Phenylenediamine (*m*-PDA) was procured from Merck India Ltd, Mumbai, and Aarti Industries Ltd, Gujarat. The materials were purified by distillation under reduced pressure before use as they have a strong tendency toward oxidation, if exposed to air. The macroporous, strong cationic exchange resin, Indion 840, in sulfonic acid form was obtained from Ion Exchange India Ltd. (Mumbai, India). The resin has a styrene-divinylbenzene polymeric structure with sulfonic acid groups. The resin beads, each of size nearly 0.5 mm, showed an internal void fraction of 0.39. The exchange capacity was 4.8 $\mathrm{mEq/cm^3}$ on a dry weight basis.

The resin beads were washed initially with a 5% (w/v) aqueous solution of hydrochloric acid and the excess acid was removed by thorough washing with distilled water. The acid-free resin beads were then washed with methanol and then dried for 6 hours at 330°K in an oven. It was subsequently cooled to ambient temperature of 303°K in a dessicator.

EXPERIMENTAL DETAILS

Solubilization Studies

For the solubility measurements, a suspension of an excess amount of an amine and an organic solvent was stirred for about 2 hours with a magnetic stirrer in a constant temperature bath to saturation. The saturated solution was then filtered to remove undissolved solute and the clear filtrate was analyzed by absorption spectroscopy at $\lambda_{max} = 299$ nm for *o*-PDA, $\lambda_{max} = 300$ nm for *m*-PDA, and $\lambda_{max} = 323$ nm for *p*-PDA, using by a Hitachi U-1100 UV–VIS spectrophotometer by absorption spectroscopy.

Equilibrium Adsorption Studies

The equilibrium sorption studies were carried out in specially designed glass adsorption cells to avoid any loss of solvent during the equilibration process. PDA solutions of known concentrations were added into the cells containing known amounts of the resin. The cells were then kept on a shaker at ambient temperature (303°K) for 8 hours to attain equilibrium. The residual solution concentration of the amines was determined by absorption spectroscopy. The equilibrium sorption studies were repeated at different temperatures (303, 313, and 323°K) and with mixtures of PDAs in different solvents at 303°K. In the mixture studies, the remaining concentration of the amines in the solutions was analyzed by either absorption spectroscopy using a Hitachi U-1100 UV–VIS spectrophotometer, or gas chromatography on a Perkin Elmer 8500 gas chromatograph using a SE-30 column ($l = 2.0$ m and *i. d.* $= 2.2$ mm) equipped with a FID detector.

Kinetic Studies

To estimate the effective diffusivity of three phenylenediamines in the resins, time dependent sorption studies were conducted in a three-necked glass vessel having a capacity of 200 cm^3. The solution of the phenylenediamines in toluene was transferred into the vessel and a known weight of the resin was added to it. The suspension was stirred using a four-blade, pitched turbine impeller with the stirring speed varying between 1200 to 1600 rpm. Within this range, the external film resistance was insignificant as no change in the concentration profile was observed with variation in the speed of agitation. Samples were withdrawn from the vessel at frequent time intervals and analyzed for the concentration of PDAs by UV-spectroscopy.

RESULTS AND DISCUSSION

Selective Solubilization

The solubility data for phenylenediamines in different solvents at 303°K are given in Table 1. The solubilities of *o* and *m*-PDAs are, respectively, 7.65 and 9 times higher than the solubility of *p*-PDA in toluene, while in DCE, the same ratios are 2.38 and 9. *p*-PDA exhibits a typical intermolecular hydrogen bonding that cannot be broken easily by a nonpolar solvent, such as toluene. On the other hand *o*-PDA, because of its intramolecular H-bonding, dissolves into toluene as individual molecules. The solubilities of *m*-PDA in toluene and DCE are the highest. *m*-PDA also has the potential to form an intermolecular hydrogen bond. But different solution behavior of these isomers in toluene and DCE seems to originate from the ability of *p*-PDA to form closely packed, hydrogen-bonded structures because of its symmetrical molecular structure.

Toluene seems to be the best solvent for selective solubilization because of the solubility difference, particularly for *m*/*p*-PDAs. Toluene, when brought in contact with a mixture of *p*-/*m*-PDAs, leaves behind pure *p*-PDA as solid phase while completely dissolving *m*-PDA. The yield of pure *p*-PDA is decided by its solubility in toluene in the presence of *m*-PDA, which is slightly higher, as shown later in this article by the sorption studies of *m*-/*p*-PDAs mixtures from toluene. Although pure *p*-PDA is easy to obtain, removal of its

Table 1. Solubility of *o*/*m*/*p*-PDAs in different solvents.

	Solubility (mol/dm^3)		
Solvent	*o*-PDA	*m*-PDA	*p*-PDA
Toluene	0.153	0.180	0.020
DCE	0.97	3.63	0.408
Methanol	Highly soluble	Highly soluble	Highly soluble

Temperature 303°K.

trace amounts from the solution to get pure *m*-PDA requires its selective sorption by ion-exchange resins.

Swelling of Resins in Organic Solutions

Many cross-linked polymeric networks swell when brought in contact with organic solvents because of the penetration of solvent into the resin phase. Preliminary studies on separation of PDAs by ion-exchange resin (Indion 840) showed that resin swelling by both solvent and the solute, was critical in affecting sorption capacity and selectivity. The swelling of the resins makes more adsorption sites accessible to the solutes. The ability of a solvent, and also that of a solute, to swell the matrix of a polymeric resin is, therefore, important in the determining the resins' sorption capacity for a particular solute.

The overall swelling ratio, defined as ratio of the volume of swollen resin to that of dry resin, is shown in Fig. 1 as a function of PDA concentration in the liquid phase. In methanol and dichloroethane, even at low solute concentrations, a significant swelling of the resin was observed. Both these solvents are polar in nature. Methanol can function as both hydrogen bond donor and acceptor, while DCE can work as a weak Lewis acid itself. The swelling of resins in the presence of these solvents seems to be because of the better solvation of the sulfonic acid groups on the resin and/or because of increased repulsive interactions between strongly ionic sulfonic acid groups in polar solvents of moderate dielectric constants.[20] The swelling increased further, in all solvents, in the presence of PDAs. It is obvious that interaction between solutes, solvents, and monomeric segments of the polymer chain should decide the extent of swelling. Even at concentrations as low as 0.5% mole fraction, the solute seems to have a significant interaction with the polymer chains. Particularly with *p*-PDA, at very low concentrations, the resin swelling increased substantially.

Equilibrium Sorption

The uptake of PDA by resins does not take place only because of *ad*sorption of the solutes, but also because a certain amount of solution is *ab*sorbed into the swollen resin. Therefore, it may be necessary to differentiate the *ad*sorbed amount from the *ab*sorbed amount. If it is assumed that the expanded volume of the resin is occupied by the solution having the same composition as the external liquid phase, then the amount of PDA *ab*sorbed in the resin phase can be estimated from material balance. Figure 2 shows moles of PDAs *ad*sorbed and *ab*sorbed per kg of the dry resin from different solvents, respectively, for

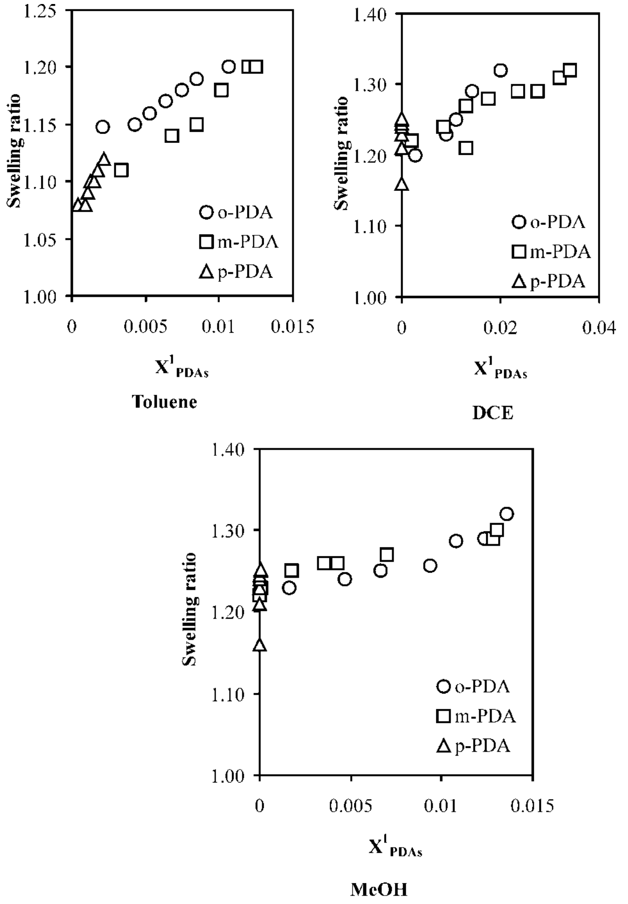
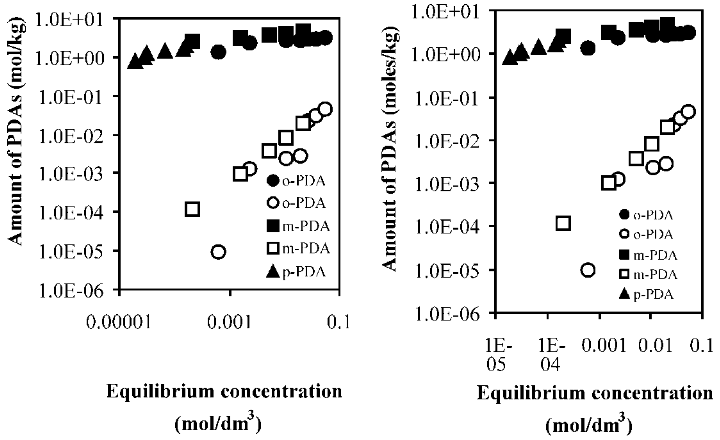


Figure 1. Swelling ratio vs. mole fraction of PDAs in different solvents. Temperature = 303°K; ○ = *o*-PDA; □ = *m*-PDA; and △ = *p*-PDA.

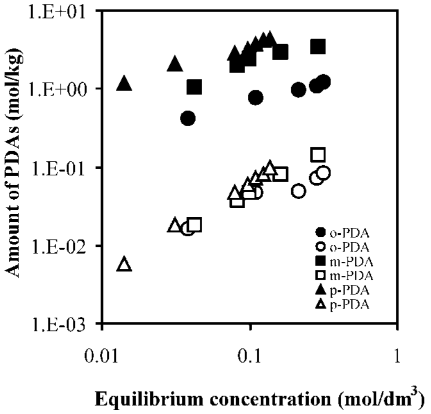
three isomers. The *ad*sorbed amount is much higher than the *ab*sorbed amount in all cases, indicating that adsorption, i.e., interaction with functional sites on the polymeric network, is mainly responsible for the removal of PDAs from various organic solvents. For *p*-PDA, the *ad* from toluene was so selective that at the experimental concentrations of these experiments, the remaining amount of *p*-PDA in the solution was not detectable.

Figure 2 shows that in all solvents, the uptake of *p*-PDA by the resins is the highest followed by that for *m*-PDA and the lowest for *o*-PDA. The difference in



(a)Toluene

(b)DCE



(c) MeOH

Figure 2. Adsorbed amount (full symbols)/absorbed amounts (empty symbols) vs. equilibrium concentration of PDAs [solvent: (a) toluene, (b) DCE, (c) MeOH]. ○ = *o*-PDA; □ = *m*-PDA; and △ = *p*-PDA.

adsorption behavior is probably due to difference in solvation, as the sorption has to compete with solvation and/or relative interactions between the solvent and amines. If the solute is preferentially solvated, its adsorption tendency becomes weaker, while in poorly solvated conditions, the tendency to get adsorbed becomes stronger. In most organic solvents, *p*-PDA has low solubility; hence its adsorption should be higher in comparison with that of *o*/*m*-PDAs.

Single-Component Adsorption Isotherms

The equilibrium studies showed a significant amount of adsorption for all the amines. The difference between their sorption behaviors in different solvents is probably due to their differential solvation in the respective solutions. These factors complicate the sorption behavior because of mutual attractions between the molecules and between the solute and solvent. To quantify such interactions, the activity coefficient of solute can be useful. Knowing the saturation solubilities, the activity coefficient of PDAs can be approximated as $1/x_s$ for a sparingly soluble solute or the same can be predicated using a liquid phase model or a group contribution method, such as UNIQUAC or UNIFAC.[22–25] For isomeric substances, the group contribution methods, however, fail in the absence of specific data for individual isomers.

Table 2 shows the activity coefficients of the amines in toluene and DCE solutions obtained approximately as the reciprocal of their mole fractions (x_s) at saturation in the respective solvents. The activity coefficient of *p*-PDA in toluene is higher than those of *m*/*o*-PDAs, indicating that *p*-PDA should have an higher affinity for the adsorbent phase. Since the values for *p*-isomer are far from unity, the sorption of the amine is significant. On the other hand, having lower activity coefficients in DCE, *o*/*m*-PDAs exhibit weaker affinity for the resin phase. Table 2 also gives modified equilibrium constants (K_m), which were estimated by incorporating the activity coefficients in the modified Langmuir equation to account for the solute–solvent interactions Eq. (1).

$$\frac{\Gamma}{\Gamma_\infty} = \left(\frac{K_m \gamma_i C}{1 + K_m \gamma_i C_i}\right) \tag{1}$$

If the solute–solvent interaction is solely responsible for the differential sorption behavior, the modified K_m should be the same in all three solvents for a given amine and may be even for all amines. Indeed, the K_m, for three amines

Table 2. Modified Langmuir isotherm constants of PDAs for sorption from different solvents.

Solvent	Toluene			DCE			MeOH		
Solute	γ_i^∞	K_m dm^3/mol	Γ mol/kg	γ_i^∞	K_m dm^3/mol	Γ mol/kg	γ_i^∞	K_m dm^3/mol	Γ mol/kg
o-PDA	62.23	4.4	3.20	4.05	5.6	2.95	~1	13.1	1.39
m-PDA	53.21	9.4	4.90	4.48	13.4	3.31	~1	13.7	4.24
p-PDA	471.0	34.8	2.67	76.2	16.9	2.10	~1	12.1	6.32

are very close in methanol, where all three amines are well solvated. However, *m*-/*p*-PDAs show specific interactions with the resin, as indicated by different K_m values in other solvents and probably with other adsorbed molecules in the adsorbed state too. The equilibrium constant (K_m) is a measure of the strength of the interaction between the solute and the resin. In terms of the availability of the lone pair of electrons, *p*-PDA is the stronger base and thus shows the highest affinity for the acidic group of the resin. The *p*-isomer does not interact very favorably with nonpolar solvents like toluene. Hence, its affinity for adsorption sites is significantly higher than other isomers.

The loading capacity of the resin for the adsorption of amines from different solvents is given in Table 2. The adsorption capacity followed the order *m*-PDA > *o*-PDA > *p*-PDA in toluene and DCE, but was reversed in the case of methanol. We suspect vertical orientation of *o*/*m*-PDAs molecules, which probably does not hinder adsorption of other molecules on the neighboring sites, thus enabling a higher capacity in nonpolar solvents. *p*-PDA probably lies flat on the surface and occupies two sites by the two amino groups and, therefore, shows lower capacity. In methanol, the adsorption capacity of the resin is reversed in the order, *p*-PDA > *m*-PDA > *o*-PDA. The hydrogen bonding between the methanolic oxygen and the protons of the amino nitrogen becomes easier and *p*-PDA also may show a vertical orientation at the interface. A better packing of *p*-PDA than *o*/*m*-PDAs on the surface, therefore, results in its much increased sorption capacity.

The thermodynamic parameters ΔH, ΔG^o and ΔS associated with the sorption process are reported in Table 3. The values of ΔH indicate specific interactions between the resin and PDAs; the ΔH being the highest for *p*-PDA and the lowest for *o*/*m*-PDAs. The favorable values of ΔH as compared to $T\Delta S$

Table 3. Heat of adsorption of PDAs from toluene.

Solute	Temperature (°K)	ΔH kcal/mol	ΔG kcal/mol	$T\Delta S$ kcal/mol
o-PDA	303	− 5.87	− 3.23	− 2.63
	313	—	− 3.22	− 2.54
	323	—	− 3.06	− 2.79
m-PDA	303	− 6.64	− 3.57	− 3.07
	313	—	− 3.56	− 3.08
	323	—	− 3.37	− 3.25
p-PDA	303	− 7.38	− 5.58	− 1.80
	313	—	− 5.57	− 1.82
	323	—	− 5.48	− 1.89

Solvent:Toluene; Resin:Indion 840.

indicate that the adsorption of amines is governed mainly by enthalpic interactions between the amines and resin's acidic group.

The separation efficiency of the sorption process is further quantified by calculating the separation factor between the amine and solvent, in a manner analogous to relative volatility in distillation, using the following relation.

$$\alpha = \frac{x^s_{PDA} \times x^l_{solvent}}{x^s_{solvent} \times x^l_{PDA}} \tag{2}$$

where the superscripts s and l indicate the sorbed and liquid phases, respectively. Figure 3 shows that the separation factor is a strong function of PDA concentration. The separation factor decreases with the increase in solute

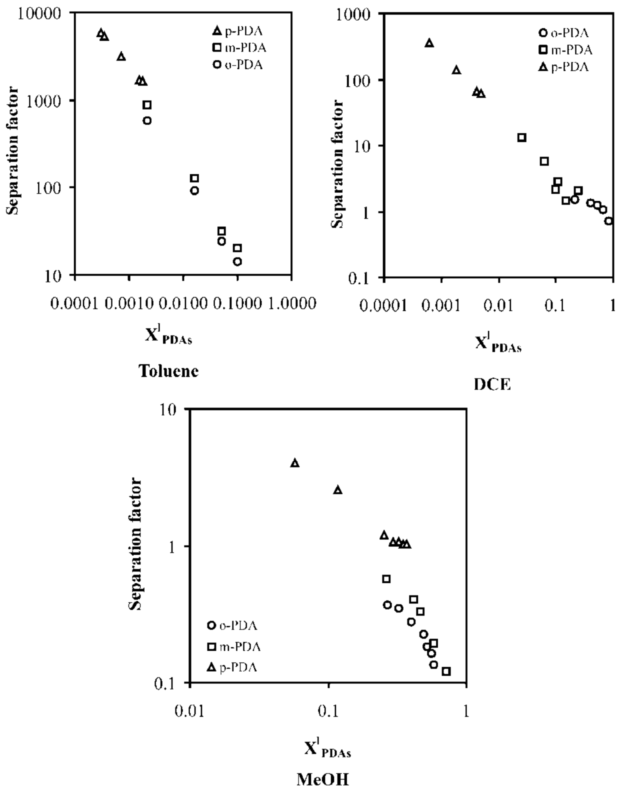
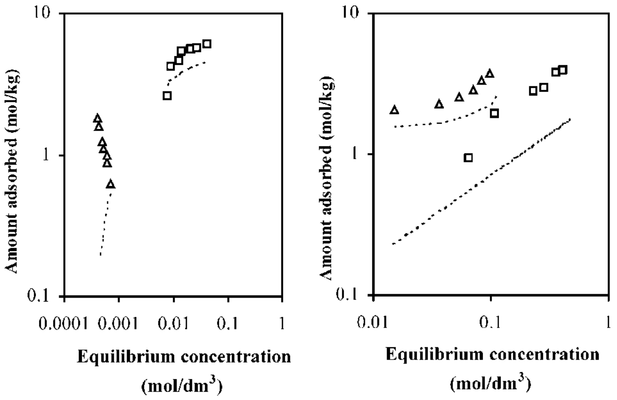


Figure 3. Separation factor vs. mole fraction plots of PDAs in different solvents. ○ = *o*-PDA; □ = *m*-PDA; and △ = *p*-PDA.

concentration. It is the highest in toluene as compared to methanol and DCE. The decrease of separation factor in polar solvents may be due to excessive swelling of the resins and preferential solvation in the solution phase.

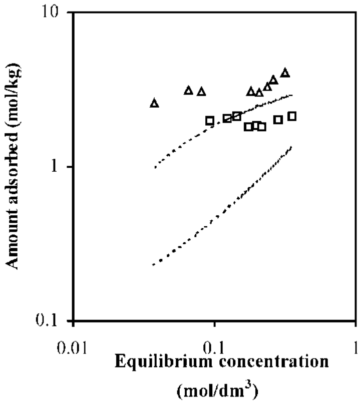
Adsorption of Mixed Amines

The separation of *m*/*p*-PDAs mixtures is more difficult than the separation of *o*/*p*-PDAs. The *m*-/*p*-PDAs separation, predicted by using the K_m of



(a) Toluene

(b) DCE



(c) Methanol

Figure 4. Adsorption of *m*/*p*-PDAs from solvents on the Indion 840 resin, experimental data (points), predicted data(- - -) [solvent: (a) toluene, (b) DCE, (c) MeOH]. ○ = *o*-PDA; □ = *m*-PDA; and △ = *p*-PDA.

the corresponding components obtained from single component sorption studies, is shown in Fig. 4 along with experimental points in three solvents. The experimental adsorption of mixed PDAs from solution shows a considerable positive deviation for both components from their predicted values. For the strongly adsorbing *p*-PDA, the deviation is much larger than the experimental error and also more than that for the weakly adsorbing *m*-PDA. This is an indication of interaction among the adsorbed molecules and thus of a highly nonideal adsorbed phase behavior.

Figure 5 shows that the separation factor of the strong adsorbate, i. e., *p*-PDA in the mixtures is strongly dependent on the composition of the mixture. The nonideal concentration-dependent adsorption selectivity for the liquid–solid interface was analyzed by following the statistical thermodynamics treatment of Lee and Ihm.[26] The main assumptions of this approach are that the potential

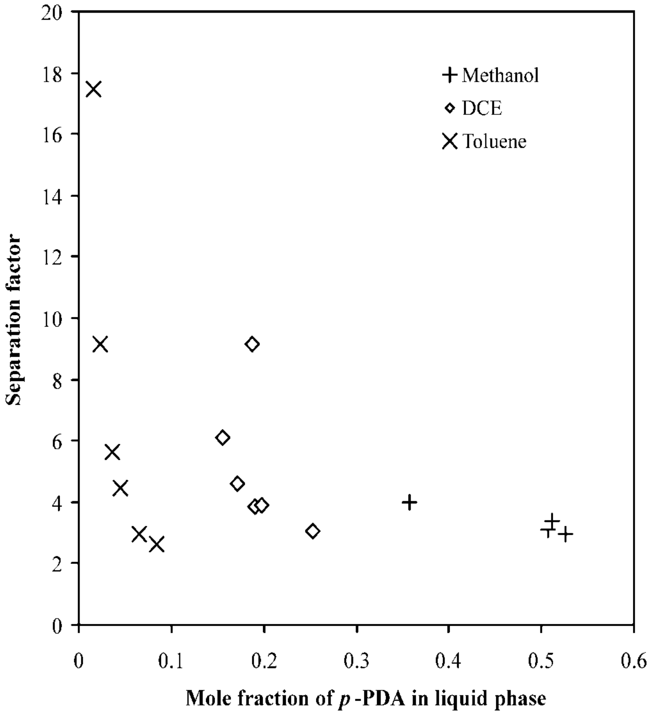


Figure 5. Separation factor ($\alpha_{m/p}$) vs. mole fraction of *p*-PDA in different solvents. Solvent: ×, Toluene; ◇, DCE; and +, MeOH.

energy for the adsorbate–surface interaction has a constant value and the potential energy for the intermolecular interactions in the adsorbed phase is also constant.

A measure of interaction energy ($cW/2kT$) between two different adsorbed molecules is obtained by plotting $\ln \alpha$ vs $(1 - x_1^s)$, where x_1^s is the surface excess of the solute and slope of the line ($\sim cW/2kT$) is a measure of the interaction between the adsorbed species. Surface excess is the extent by which the surface concentration of a given component exceeds its concentration in the bulk liquid and can be taken as a measure of the specific affinity of a solute toward the sorbent. In terms of experimentally measurable quantities, the surface excess (n^e) is expressed in terms of n^t, i. e., the total moles of the solution at the beginning and x^0 and x^l, which are the mole fractions of the solute initially and at equilibrium, respectively, as:

$$n^e = n^t(x^0 - x^l) \tag{3}$$

In the absence of any interaction among the adsorbed solutes, the plot of $\ln(\alpha)$ vs $(1 - 2x_1^s)$ should show a zero slope.

The interaction energy plots for *m*/*p*-PDAs in different solvents are shown in Fig. 6. The nonzero slopes of the plots indicate strong interaction among the adsorbed molecules. The interaction energy estimated from the slope of the linear plots of $\ln(\alpha)$ vs $(1 - 2x_1^s)$ are reported in Table 4. The negative interaction energy values indicate a significant attractive interaction between the adsorbed molecules. This adsorbed phase interaction is responsible for the increased sorption of the two components in the presence of each other.

Kinetic Studies

The concentrations of the PDAs in toluene are shown as dimensionless concentration (C/C_0) vs time in Fig. 7. The experimental kinetic data were fitted in a mathematical model described in our previous communication,[17,21] to evaluate the effective diffusivity of phenylenediamines within the resin phase.

The expected diffusivity can also be estimated from the molecular diffusivity, porosity, and the tortuosity of resin ($D_e = D_m\varepsilon/\tau$). The dependence of the diffusivity on the solute concentration needs to be estimated from the experimental kinetic data. It was assumed that the effective diffusivity is a function of the adsorbed solute concentration in the following manner:

$$D_e = D_0 \exp(-K_a\phi) \tag{4}$$

where ϕ is the fractional saturation of the resin by the adsorbed phase. The values of the adjustment factors (K_a), effective diffusivities (D_0 at zero

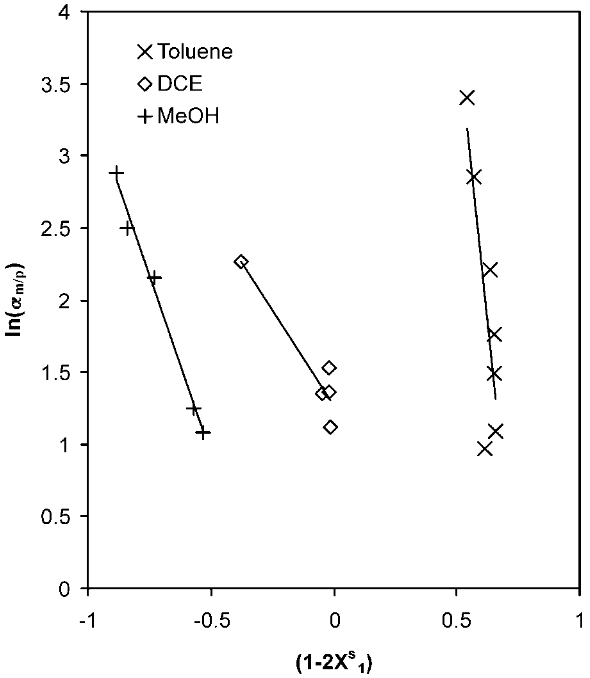


Figure 6. Energy of interaction between the molecules in the mixtures of *m*/*p*-PDAs in adsorbed phase. Solvent: ×, Toluene; ◇, DCE; and +, MeOH.

loading), and the molecular diffusivities as estimated from the correlations are reported in Table 5. The continuous curves in Fig. 7 denote the predicted values from the model, while the points denote the experimental values. Although, the diffusivity of *p*-PDA is somewhat higher than that of other two isomers, there is not much difference in the effective diffusivities of the three amines.

Table 4. Interaction energy and separation factor of *m*/*p*-PDAs in different solvents.

Solvent	Separation factor ($\alpha_{m/p}$)	Interaction energy ($CW/2^okT$)
Toluene	2.64–17	−16.18
DCE	3.8–9.6	−3.82
Methanol	2.9–4.0	−1.48

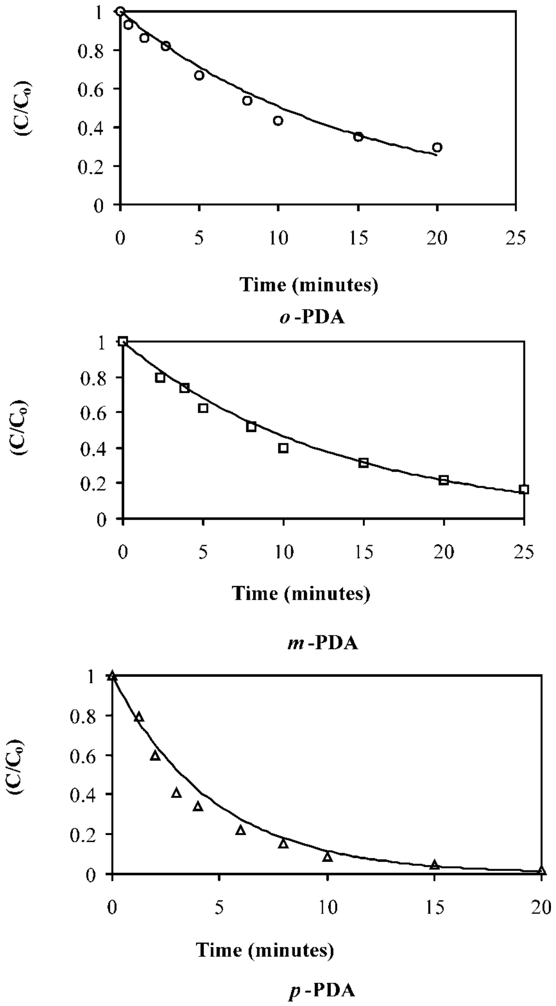


Figure 7. Kinetics of sorption of *o*/*m*/*p*-PDAs from toluene. ○ = *o*-PDA; □ = *m*-PDA; △ = *p*-PDA.

The diffusional selectivity may not play any significant role in the separation of PDAs by adsorption on the ion-exchange resins. Since, the pore size of the resin is significantly larger than the kinetic diameter of the three solutes, all three solutes can diffuse with almost the same ease through the resin. However,

Table 5. Molecular diffusivity (D_m) and effective diffusivity (D_e) of PDAs.

Component	D_m (cm^2/sec)	D_o (cm^2/sec)	K_a
o-PDA	1.732×10^{-5}	8.473×10^{-6}	1.385
m-PDA	1.932×10^{-5}	8.751×10^{-6}	1.254
p-PDA	2.245×10^{-5}	9.016×10^{-6}	1.123

Solvent: Toluene.

substantial dependence of diffusivity on the loading of the resin does exist, as indicated by the value of K_a.

Molecular Modeling

Since the sorption from nonaqueous conditions into ion-exchange resins is relatively an unexplored area, the interaction between ion-exchange resin and the PDAs was investigated by molecular modeling calculations using Chem-X, a molecular modeling software, developed by Molecular Design Ltd, Oxford. Molecular mechanics is a widely used calculation method to predict a priori structures and energies of molecules. The method is based on the idea of bonds between atoms having natural lengths and angles. Van der Waals and other intermolecular interaction forces exist between nonbonded atoms. Molecules adjust their geometries so as to take up optimum values in simple cases. In addition, steric interactions are included using Van der Waals potential functions. The general form of molecular mechanics energy includes bond strain energy (V_b), angle strain energy (V_a), torsion energy (V_{to}), nonbonded or polarization energy (V_{nb}), electrostatic energy (V_{el}), out of plane bending energy (V_{oop}), hydrogen bonding energy (V_{hb}), and restraints energy (V_r).[27]

The individual structures of the *o*-PDA, *m*-PDA, *p*-PDA and the ion-exchange resin were first optimized by quantum mechanics (QM) calculations. The ion-exchange resin was approximated by its repeating unit, i.e., sulfonated styrene molecule. The nitrogen carries a negative charge of −0.3968, −0.3983, and −0.3984, on *o*/*m*/*p*-PDAs respectively, while the hydrogen of the SO_3H group of the resin shows a partial positive charge of 0.2324. The effect of the medium on the interaction energy between the resin and solute was approximated by considering the medium as having a dielectric constant equal to that of the solvent. This effect of the medium is particularly

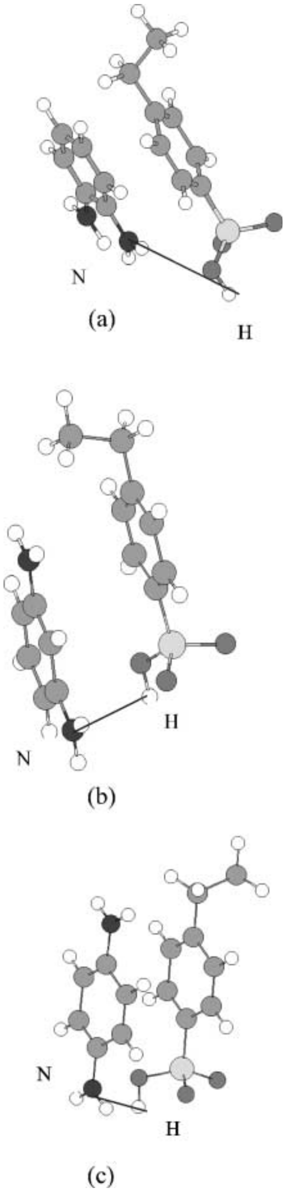


Figure 8. Optimized structures representing molecular interaction between PDAs and ion-exchange resin, Indion 840. (a) *o*-PDA; (b) *m*-PDA; and (c) *p*-PDA.

important for the adsorption studies and hence it would by preferable to simulate the environment of the structure more closely. To investigate the interaction, the solute molecule and the resin structure were brought together followed by MM energy optimization of the overall system. After starting with a large number of different conformations, the final lowest energy conformation was taken to be the stabilized complex. The interaction energies were obtained by subtracting the individual MM energies of the ion-exchange resin and the PDAs from the energy of the optimized structure.

$$\begin{aligned} Interaction\ \ Energy = {} & Energy_{optimized\,structure} \\ & - \{Energy_{IER} + Energy_{solute}\} \end{aligned} \tag{5}$$

There is a large difference in the interaction energies in three solvents. The interaction between PDAs and the resin is maximum in toluene, intermediate in DCE, and minimum in methanol. Apart from the alignments of aromatic rings of the amine and of the resin, the hydrogen of the SO_3H group of the resin and the nitrogen of the PDAs are oriented toward each other in the optimized structures, as shown in Fig. 8. The MM interaction energies of the optimized structures and the distance between the nitrogen of the PDAs and the hydrogen of the SO_3H group of the resin are reported in Table 6. The minimum distance for the formation of a hydrogen bond is 3.2 Å. The distance between the optimized structure of *p*-PDA nitrogen and the resin H is less than 3.2 Å, indicating the existence of a hydrogen bond. For the optimized structures of

Table 6. Interaction energy for optimized structures of PDAs and ion-exchange resins in different solvents.

Solvent	Component	MM energy (kcal/mol)	Distance (Å) between H of resin and N of amine	Interaction energy (kcal/mol)
Toluene	*o*-PDA	5.7295	4.47	− 8.27
	m-PDA	2.7288	3.44	− 8.50
	p-PDA	− 1.6752	2.55	− 8.54
DCE	*o*-PDA	10.3168	4.47	− 3.62
	m-PDA	7.9078	3.49	− 4.39
	p-PDA	6.2047	2.53	− 5.07
MeOH	*o*-PDA	11.3717	4.47	− 2.55
	m-PDA	8.9607	3.49	− 3.55
	p-PDA	7.7074	2.55	− 4.38

m-PDA and *o*-PDA, on the other hand, the distance is more than 3.2 Å. Hence, the adsorption of *m*-PDA and *o*-PDA may not be due to very specific interactions. It is also seen that the interaction is the highest for *p*-PDA, followed by that for *m*-PDA and then for *o*-PDA. The distances between the H of NH_2 group and the double-bonded O of sulfonic acid are 3.4 Å to 5.3 Å. This distance is considerably higher than that required to form a hydrogen bond. So the additional interaction due to their presence can be neglected.

CONCLUSION

Toluene, as compared to DCE and methanol, is the best solvent for the separation of PDAs by selective solubilization, because of the larger solubility difference. Ion-exchange resins can be used for the separation of the PDAs under nonaqueous conditions. The separation is governed by the acid–base interaction in the form of weak hydrogen-bonded complexes between the resin and amines. The swelling of the resin is a critical factor in the adsorption of nonaqueous solution. It is the highest in methanol as compared to toluene. The major factor in the uptake of amines by resins is Lewis acid–base interaction. The adsorption tendency of *p*-PDA is higher than *o*/*m*-PDAs in toluene and DCE, while in the case of methanol, the values are comparable. Molecular modeling can be used to predict a priori the adsorption behavior and interaction between the amines and resin.

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