

Genesis of Selectivity and Reversibility for Sorption of Synthetic Aromatic Anions onto Polymeric Sorbents

PING LI AND ARUP K. SENGUPTA*

Department of Civil and Environmental Engineering,
13 East Packer Avenue, Lehigh University,
Bethlehem, Pennsylvania 18015

Many environmentally significant synthetic aromatic compounds such as pentachlorophenol, benzene and naphthalene sulfonates, and benzene carboxylates exist as anions in water over a wide range of pH values. Understandably, both ionic charges and nonpolar moieties of these organic compounds govern their sorption characteristics. This study reports the results of very favorable sorption behaviors of these anthropogenic aromatic compounds onto polymeric anion exchangers. Such favorable sorption equilibria are, however, distinctively unique because they are all endothermic processes and accompanied by high positive entropy changes. Solvent dielectric constant, polarity or moisture content of the ion-exchanger matrix, and the nonpolar moiety (NPM) of the aromatic anion are the three fundamental process variables which govern the overall sorption equilibrium. Anomalous enthalpic and entropic changes associated with such sorption processes are explained from a mechanistic viewpoint after taking into consideration appropriate NPM-solvent and NPM-matrix interactions. Experimental observations made in this study are quite analogous to the transfer of hydrophobic methane from self-associated, polar water phase to nonpolar cyclohexane phase.

Introduction

Many synthetic aromatic compounds exhibit acidic characteristics due to the presence of carboxylic, phenolic, and sulfonic acid moieties, and their acidities are often strengthened because of the electron-withdrawing effects of various substituent groups. For example, the pK_a value (i.e., negative logarithm of acid dissociation constants) for phenol is 9.3, while the same for pentachlorophenol or PCP is 4.75. As a result, PCP, which is extensively used in wood preservation industry, exists as an anion in contaminated surface or groundwater at neutral pH. Contrary to other nonionized hydrophobic aromatic compounds, pentachlorophenate or PCP^- is, therefore, more mobile in natural environment and not amenable to efficient removal by conventional hydrophobic sorbents such as activated carbon. Like PCP^- , many other industrially significant aromatic compounds, namely, naphthalene mono- and disulfonates and quaternary ammonium compounds, tend to exist as ions in the aqueous phase and are commonly referred to as hydrophobic ionizable

organic compounds or HIOCs (1, 2). While the aromaticity imparts hydrophobic or nonpolar characteristic, the ionic charge of these compounds enhances hydrophilicity through ion–dipole interaction with water molecules. The solubilities of weak-acid type HIOC compounds, therefore, increase significantly at pH greater than pK_a values. HIOCs should not, however, be confused with surfactants because they are much smaller molecules and do not form micelles or exhibit strong amphiphilic characteristic. Understandably, the sorption behaviors of such aromatic ions will be greatly influenced by the sorbents' hydrophobicity as well as fixed charges.

Nature of Solute–Sorbent and Solute–Solvent Interactions

A polymeric anion exchanger with fixed positive charges will sorb aromatic anions such as PCP^- and naphthalene sulfonates. A typical anion exchange reaction between PCP^- and chloride (Cl^-) can be presented as follows:



where the overbar represents the exchanger phase and R^+ is an anion exchanger with fixed positive charges. Cl^- and PCP^- are identical electrostatically; they both have one negative charge. Strictly from an electrostatic or Coulombic interaction viewpoint, the sorption of PCP^- onto a polymeric anion exchanger in the presence of competing chloride ion is unlikely to be a selective process. Previous studies have, however, shown very favorable sorption behaviors of chlorinated phenols and aromatic anions onto polymeric exchangers in preference to chloride and other inorganic anions (3–5). High ion exchange selectivities have also been reported for aliphatic anions with long alkyl chains (6, 7). Such high sorption affinities have, in general, been attributed to hydrophobic interactions resulting from the nonpolar moiety (NPM) of the aromatic anions. From a phenomenological viewpoint, the NPM-solvent and the NPM-matrix interactions are recognized as the two primary contributors toward high sorption affinity (or lack of it) of aromatic ions in ion-exchange processes. The matrix represents the skeletal organic component in the polymeric ion exchanger besides the charged functional groups. Assuming insignificant change in the hydration of chloride ion between the aqueous and ion exchanger phases, the following ion exchange half reaction is the primary determinant of the overall equilibrium of the reaction eq 1:



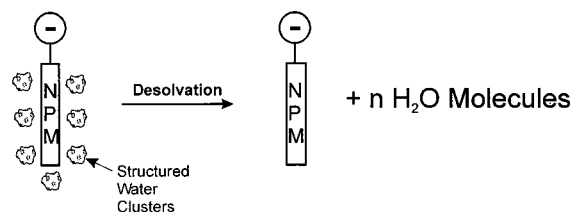
Since PCP^- sorption is favorable, the overall free energy change for eq 2 is negative. The free energy change at the standard state of choice (ΔG°) is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

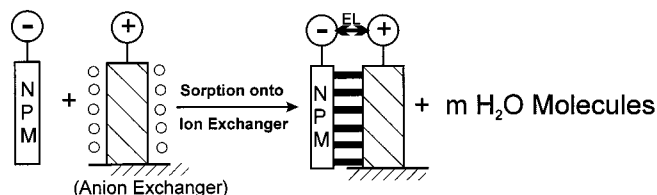
Therefore, both enthalpic (ΔH°) and entropic (ΔS°) changes help decide the overall selectivity of the ion exchange process. Note that the definition of the standard state in the ion exchanger phase may alter the significance of exchanger-phase activity coefficients but in no way alters the relative enthalpic and entropic contributions toward the overall equilibrium. To elucidate interactions associated with PCP^- sorption in accordance with eq 2, the sorption process can

* Corresponding author phone: (610)758-3534; fax: (610)758-6405; e-mail: aks0@lehigh.edu.

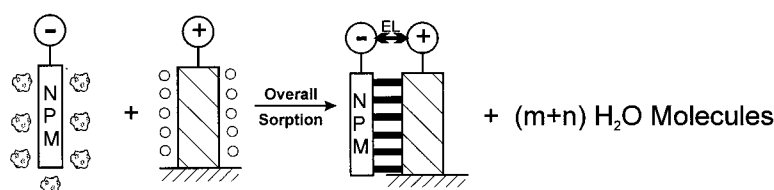
Desolvation: NPM-Solvent Interaction



Sorption: NPM - Matrix Interaction



Overall



- Relatively unstructured water molecules within the ion exchanger phase due to osmotic pressure difference
- ↔ EL Electrostatic or Coulombic interaction
- NPM-matrix interaction
- ⊖ Aromatic anion

FIGURE 1. Schematic illustrating NPM-solvent and NPM-matrix interactions during PCP^- sorption from the aqueous phase.

be broken down into two consecutive steps: first, desolvation or dehydration of PCP^- and second, PCP^- sorption onto the anion exchanger.

Interaction during Desolvation of PCP^- : A hydrophobic or nonpolar moiety (NPM) is not capable of forming hydrogen bonds with polar water molecules. Thus, when an ion with NPM is introduced into water (a polar solvent), the water molecules tend to turn away from NPM and reorganize themselves in clusters through hydrogen bonding. Consequently, there is an overall entropy decrease in the system due to reduced degrees of freedom of these self-associated water molecules. The concept of cluster-like formation of structured water molecules around a hydrophobic solute was first discussed by Frank and Wen (8) and later elaborated by Némethy and Scheraga (9) and others (10–12). As PCP^- leaves the aqueous phase during the course of the ion exchange process, an overall increase in entropy will, therefore, result. Also, the solvent phase needs to absorb heat to break the highly associated cluster-like structure of water molecules, i.e., the process is endothermic.

Interaction during PCP^- Sorption onto the Polymeric Exchanger: Once a PCP^- molecule enters the exchanger phase and binds to the fixed positive charge, its nonpolar moiety (NPM) tends to be in direct contact with the nonpolar matrix of the ion exchanger. This results in expulsion of polar water molecules from the exchanger phase, which are present primarily due to the osmotic pressure difference

between the exchanger phase and the solvent. Although thermal energy is required for such localized dehydration within the exchanger, the resulting increase in overall entropy due to the direct contact between these two nonpolar substances (matrix and NPM of PCP^-) makes such a binding energetically advantageous (13).

Figure 1 illustrates a mechanistic interpretation of the foregoing two steps of the sorption process. Note that hydrophobic interactions energetically comprise both NPM-solvent and NPM-matrix interactions. Although not explicit, the effect of solvent-matrix interaction is also included in Figure 1. The weaker the solvent-matrix interaction, the smaller will be the energy required to expel the solvent molecules from the matrix and hence, more favorable will be the sorption process and vice versa. For negligible swelling/shrinking of the polymeric exchanger, the overall free energy change for an ion exchange reaction involving a counterion with nonpolar moiety (NPM) is thus contributed by electrostatic (el), NPM-solvent and NPM-matrix interactions.

$$\Delta G_{\text{overall}}^{\circ} = \Delta G_{\text{el}}^{\circ} + \Delta G_{\text{NPM-solvent}}^{\circ} + \Delta G_{\text{NPM-matrix}}^{\circ} \quad (4)$$

When eq 4 is applied to homovalent PCP^- - Cl^- exchange in eq 1, the free energy change due to electrostatic interaction cancel out, and we get the following:

$$\begin{aligned}\Delta G_{\text{overall}}^{\circ} &= \Delta G_{\text{NPM-solvent}}^{\circ} + \Delta G_{\text{NPM-matrix}}^{\circ} \\ &= (\Delta H_{\text{NPM-solvent}}^{\circ} + \Delta H_{\text{NPM-matrix}}^{\circ}) - \\ &\quad (T\Delta S_{\text{NPM-solvent}}^{\circ} + T\Delta S_{\text{NPM-matrix}}^{\circ}) \\ &= \Delta H_{\text{overall}}^{\circ} - T\Delta S_{\text{overall}}^{\circ}\end{aligned}\quad (5)$$

Note that only overall enthalpic and entropic changes during the sorption process can be determined experimentally. However, by changing the nonpolar moiety of the solute, dielectric constant of the solvent, and polarity of the matrix, one can assess the relative contributions of NPM-solvent and NPM-matrix interaction toward the overall free energy change. The overall free energy change is again related to the equilibrium constant, K , of the reaction in eq 1 as follows

$$\Delta G_{\text{overall}}^{\circ} = -RT \ln K \quad (6)$$

where R is the universal gas constant and T is the temperature in degree Kelvin. For homovalent $\text{PCP}^- - \text{Cl}^-$ exchange, the equilibrium constant, K , is given by

$$K_{\text{PCP/Cl}} = \frac{y_{\text{PCP}} f_{\text{PCP}}}{y_{\text{Cl}} f_{\text{Cl}}} \frac{x_{\text{Cl}} \gamma_{\text{Cl}}}{x_{\text{PCP}} \gamma_{\text{PCP}}} \quad (7)$$

where y_i and x_i represent equivalent fractions of counterion i in the exchanger phase and in the aqueous phase, respectively, while f_i and γ_i represent activity coefficients in the corresponding two phases. For ions with identical charges, the activity coefficients in dilute aqueous solutions tend to be equal, i.e., $\gamma_{\text{PCP}}/\gamma_{\text{Cl}}$ is unity (14). The separation factor for PCP^-/Cl^- exchange can be determined experimentally at a particular resin loading and is given by

$$\alpha_{\text{PCP/Cl}} = \frac{y_{\text{PCP}} x_{\text{Cl}}}{y_{\text{Cl}} x_{\text{PCP}}} \quad (8)$$

The variation in exchanger-phase loading for $\text{PCP}^- - \text{Cl}^-$ exchange is, however, contained between $y_{\text{PCP}} = 0$ and $y_{\text{PCP}} = 1.0$. For homovalent ion exchange, the equilibrium constant can then be approximated as the average separation factor value, integrated over the entire exchanger-phase composition i.e.,

$$\begin{aligned}\ln K_{\text{PCP/Cl}} &= \frac{\int_{y_{\text{PCP}}=0}^{y_{\text{PCP}}=1} \ln \alpha_{\text{PCP/Cl}} dy_{\text{PCP}}}{\int_{y_{\text{PCP}}=0}^{y_{\text{PCP}}=1} dy_{\text{PCP}}} = \frac{\int_{y_{\text{PCP}}=0}^{y_{\text{PCP}}=1} \ln \alpha_{\text{PCP/Cl}} dy_{\text{PCP}}}{1} = \\ &\quad \int_{y_{\text{PCP}}=0}^{y_{\text{PCP}}=1} \ln \alpha_{\text{PCP/Cl}} dy_{\text{PCP}}\end{aligned}\quad (9)$$

The overall free energy change for $\text{PCP}^- - \text{Cl}^-$ exchange is now

$$\begin{aligned}\Delta G_{\text{overall}}^{\circ} &= -RT \ln K = RT \int_0^1 \ln \alpha_{\text{PCP/Cl}} dy_{\text{PCP}} \\ &= -RT \int_0^1 \ln \frac{y_{\text{PCP}}(1 - x_{\text{PCP}})}{(1 - y_{\text{PCP}})x_{\text{PCP}}} dy_{\text{PCP}}\end{aligned}\quad (10)$$

The above integral can now be computed from the binary sorption isotherm data.

If the equilibrium constant values are determined at different temperatures around 298 K where standard enthalpy change (ΔH°) may be assumed to be considered constant, the van't Hoff equation gives

$$\frac{d(\log K)}{d(1/T)} = -\frac{\Delta H^{\circ}}{2.3R} \quad (11)$$

where T is the absolute temperature in K. The standard enthalpy change can be computed from the slope of $\log K$ vs $1/T$ plot. Similar approaches have been successfully used earlier to determine ΔH° values during sorption processes at ambient temperature (6, 15). Enthalpic changes thus determined agreed well with the values obtained independently using microcalorimetric technique (15). The standard entropic contribution at 298 K ($T\Delta S^{\circ}$) can subsequently be determined from the following relationship

$$T\Delta S^{\circ} = \Delta H^{\circ} - \Delta G^{\circ} \quad (12)$$

Premises of the Study. Ion exchange processes are characterized by equivalent exchange of solutes or counterions but the relative selectivities among exchanging counterions are often derived from concurrent interactions other than electrostatic ones. For environmental separation of target contaminants, high selectivity is desirable for favorable sorption, while reversibility, i.e., reduced selectivity, enhances the efficiency of the regeneration process. High selectivities of counterions with nonpolar moieties result from hydrophobic interactions, which are again manifested in enthalpic and entropic changes. Altogether, there are three independent process variables, namely, hydrophobicity of the solute, polarity of the ion exchanger matrix, and the dielectric constant of the solvent influencing the selectivity of a specific aromatic anion. Table 1 provides the salient properties of PCP and other chlorinated phenols, while Table 2 gives the compositions and other details of two anion exchangers used in the study. Specific objectives of the study are to provide sufficient experimental evidences pertaining to high selectivities of aromatic anions toward polymeric exchangers compared to competing inorganic counterions;

present enthalpic and entropic changes associated with sorption of aromatic anions and their relationships with ion-exchanger matrix composition, solvent dielectric constant, and solute hydrophobicity;

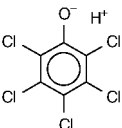
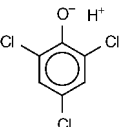
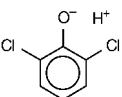
elucidate the synergistic role of counterion and the solvent dielectric constant in attaining sorption reversibility or high efficiency of regeneration.

Materials and Procedures

Materials. Pentachlorophenol (PCP), 2,4,6-trichlorophenol (TCP), and 2,6-dichlorophenol (DCP) were used in this study. PCP and DCP were purchased from Sigma, while TCP (purity >98%) was obtained from Aldrich. In this study, two types of ion-exchange resins, namely, IRA-900 and IRA-958, were used. Tables 1 and 2 include salient information about chlorophenols and ion exchangers used in this study.

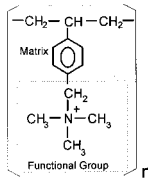
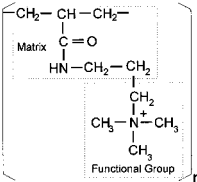
Column Runs. The fixed-bed column runs were carried out using a glass column (11 mm diameter and 250 mm length), a constant-flow pump, and an ISCO fraction collector. All column runs were performed essentially under the same hydrodynamic conditions; the superficial liquid velocity (SLV) and the empty bed contact time (EBCT) were identical and equal to 1.2 m/h and 1.8 min. The effluent samples were collected continuously with the fraction collector, and the concentrations of the different species in effluent samples were analyzed. After the fixed-bed column runs, the ion exchanger materials were divided into three equal portions and used in regeneration tests using different regenerant media. The regeneration tests were performed with the same setup used in the column runs. Blank tests confirmed that pentachlorophenol did not undergo any photocatalytic degradation in the laboratory environment.

TABLE 1. Properties of Chlorophenols^b

chlorophenols	molecular formula	molecular weight	pK _a	log K _{OW} ^a
pentachlorophenol		266.5	4.8	5.2
2,4,6-trichlorophenol		197.5	6.1	3.7
2,6-dichlorophenol		163	6.9	2.6

^a Undissociated phenols. ^b The data are cited from ref 22.

TABLE 2. Salient Properties of Polymeric Anion Exchangers

Resin	IRA-900	IRA-958
Structure (Repeating Unit)		
Functional Group	Quaternary ammonium	Quaternary ammonium
Matrix	Polystyrene, macroporous	Polyacrylic, macroporous
Capacity (meq/g air-dried resin)	3.6	3.4
Manufacturer	Rohm and Haas Co., Philadelphia	Rohm and Haas Co., Philadelphia

Isotherm Tests. Batch isotherm tests at ambient temperature ($22 \pm 1^\circ\text{C}$) under controlled laboratory environment were carried out using 200-mL glass bottles with Teflon lined caps. Varying amounts of ion exchangers (IRA-900 or IRA-958) were placed in solutions containing different initial concentrations of chlorophenols and chloride ions; the bottles were shaken in a gyratory shaker for 5 days to attain equilibrium. Solution pH was at least two units greater than the pK_a values of corresponding chlorophenols during the entire equilibration period. From the initial and final concentrations of chlorophenols and chloride ions, ion exchanger uptakes were determined through mass balance.

Isotherm tests with various chlorophenols were also carried out at other temperatures within the range of 7 – 38°C . For isotherms in the vicinity of $8 \pm 1^\circ\text{C}$ and $37 \pm 1^\circ\text{C}$, the equilibrium batch tests were conducted in a temperature-controlled chamber ($\pm 1^\circ\text{C}$). The procedure was identical to that at ambient temperature excepting that the agitation to attain equilibrium between the solution phase and exchanger phase was achieved through use of magnetic stirrers.

Analyses. The concentrations of chlorophenols were determined spectrophotometrically at the following wavelengths: PCP, 320 nm; 2,4,6-trichlorophenol, 312 nm; 2,6-dichlorophenol, 300 nm; using a UV/vis spectrophotometer (Perkin-Elmer, Lambda 2). The concentrations of chloride

and sulfate were analyzed by using an ion chromatograph (Dionex 120). The concentration of bicarbonate was determined by analyzing the content of inorganic carbon with a TOC analyzer (Shimadzu 5050A).

Results and Discussion

Fixed-Bed Column Runs and Stoichiometry. Figure 2 shows the complete effluent history of a fixed-bed column run using IRA-900 (polystyrene matrix, quaternary ammonium functional group) for an influent containing trace concentration of dissolved PCP⁻ (2.7 mg/L or 0.01 mmol/L) along with much higher concentrations of competing bicarbonate, chloride, and sulfate ions. Note that while the inorganic anions including divalent sulfate broke through fairly early, monovalent PCP⁻ was completely removed well over 10 000 bed volumes, and the column run lasted for several months. The higher preference of monovalent PCP⁻ over divalent sulfate demonstrates that the electrostatic or Coulombic interaction is not the primary determinant of relative selectivity in such an ion exchange process.

Figure 3 shows the comparison of PCP⁻ breakthrough during two separate column runs using IRA-900 and XAD-2, under otherwise identical conditions. The number of bed volumes before PCP⁻ breakthrough from XAD-2 column is practically insignificant (less than 10 bed volumes) compared to that observed for IRA-900 (over 10 000 bed volumes). Note that both IRA-900 and XAD-2 have identical macroporous polystyrene matrix and divinylbenzene cross-linking, but XAD-2 does not have any anion exchanging functional groups. Thus, in the absence of an ion exchange process, the effect of NPM-matrix interaction is inconsequential and PCP⁻ sorption is negligible. From a broader perspective, very early PCP⁻ breakthrough from the XAD-2 column suggests that the migration of aromatic anions such as PCP⁻ will not be retarded by highly hydrophobic subsoil system or river sediment, due to their lack of anion-exchange capacity.

A batch equilibrium test was carried out to confirm the stoichiometry of PCP⁻–Cl⁻ exchange. An anion exchanger presaturated in chloride form was gradually loaded with PCP⁻ by adding PCP⁻ in the solution phase. Figure 4 shows the plot of a stepwise PCP⁻ uptake onto IRA-900 versus the corresponding stepwise release of chloride ions into the aqueous phase in milliequivalent or meq units. Note that for a wide range of ion exchange site coverage, the plot is essentially a perfect straight line passing through the origin with a slope equal to unity. Thus, an uptake of PCP⁻ by the exchanger is always accompanied by the desorption of equivalent amount of chloride ions.

Effect of Polymer Matrix. Figure 5 shows the average PCP⁻/Cl⁻ separation factor values ($\alpha_{\text{PCP/Cl}}$) for the two polymeric anion exchangers used in the study, namely, IRA-900 and IRA-958. The high $\alpha_{\text{PCP/Cl}}$ values (well over unity) for both anion exchangers clearly demonstrate their high preference toward PCP⁻ over Cl⁻. However, for IRA-958 with a more polar polyacrylic matrix, $\alpha_{\text{PCP/Cl}}$ is significantly lower compared to IRA-900. This observation corroborates that the solute-matrix, i.e., NPM-matrix interaction, as illustrated in Figure 1, contributes toward the relative selectivity of PCP⁻. For both the exchangers, the fixed positive functional groups reside in the gel phase and that is where PCP⁻ sorption is predominant. Between polyacrylic and polystyrene matrices, the former is more polar (i.e., less hydrophobic) due to its open-chain aliphatic structure containing carbonyl groups. Polyacrylic resins, therefore, tend to imbibe more water molecules within the exchanger phase. A physical examination of air-dried IRA-958 and IRA-900 in chloride forms clearly indicates more moistened and stickier nature of IRA-958. Earlier, SenGupta and Clifford (16) showed that the water content of an air-dried polyacrylic matrix anion exchanger was 158 mL for one equivalent capacity; the corresponding

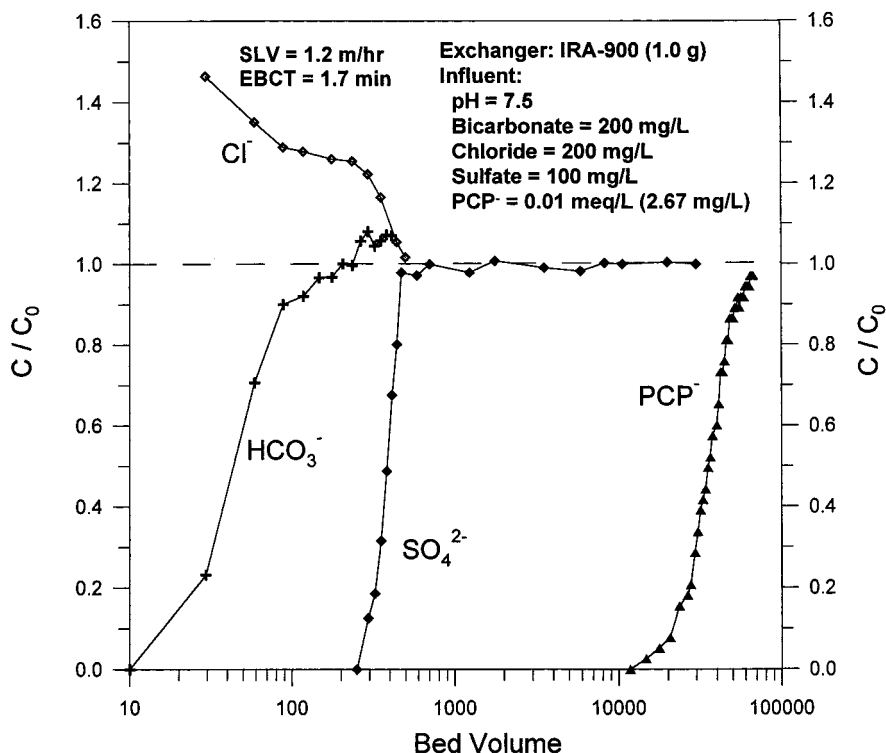


FIGURE 2. Complete effluent history of PCP^- and other competing inorganic anions during a fixed-bed column run with IRA-900 in chloride form.

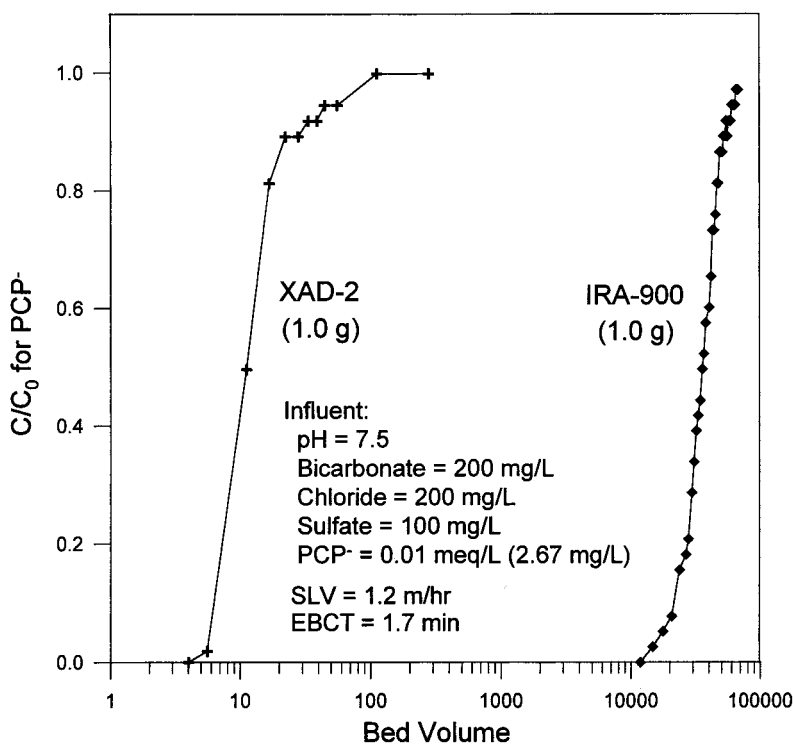


FIGURE 3. Comparison of PCP^- breakthroughs during two separate fixed-bed column runs with IRA-900 and XAD-2 under identical conditions.

number for an air-dried polystyrene matrix anion exchanger was only 56.0 mL. Thus, expelling water molecules imbibed into the more polar matrix of IRA-958 is energetically more difficult. Consequently, the affinity of PCP^- toward IRA-958 is significantly lower compared to IRA-900, which has a relatively nonpolar polystyrene matrix. Experimental results provided in this section and in the previous one, although not quantitative from a theoretical standpoint, clearly suggest

that first, PCP^- has a much greater affinity compared to sulfate, chloride, and other inorganic anions (Figure 2); second, NPM-matrix interaction plays a significant role in influencing sorption affinity (Figure 5); and third, the sorption essentially follows an ion-exchange stoichiometry (Figure 4).

Sorption Isotherms and Enthalpic vs Entropic Contribution. Figure 6A–C provides binary PCP^-/Cl^- isotherms

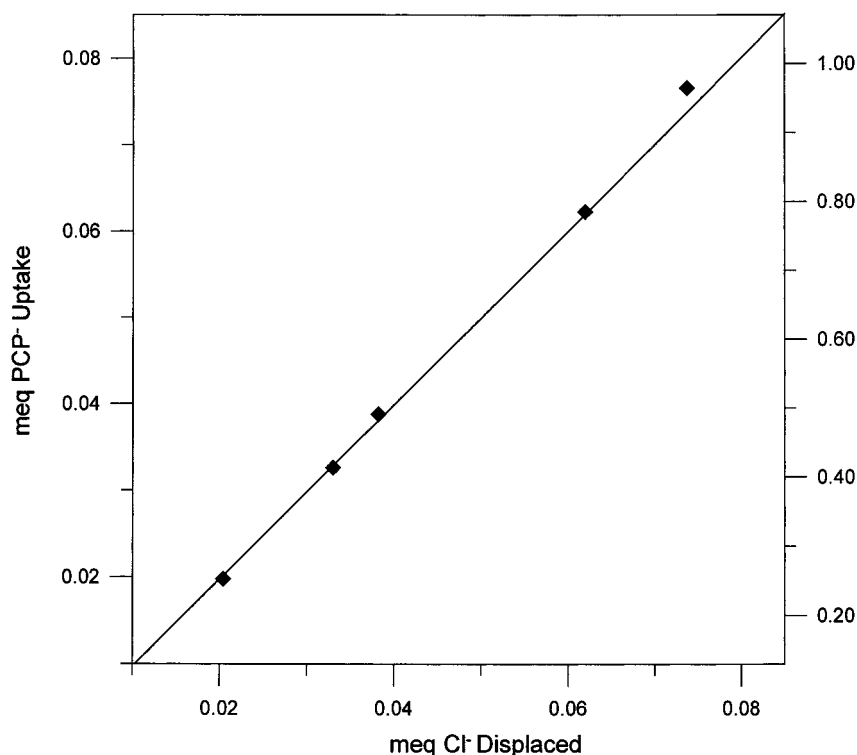


FIGURE 4. Milliequivalents of PCP⁻ uptake onto the anion exchanger versus the corresponding release of Cl⁻ into the aqueous phase.

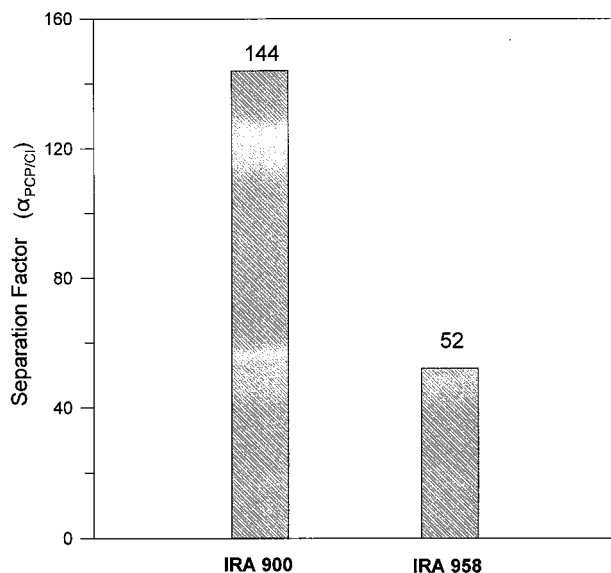


FIGURE 5. PCP⁻/Cl⁻ separation factor values for two anion exchangers, IRA-900 and IRA-958, at 50% PCP⁻ loading, i.e., $y_{PCP} = 0.5$.

(y_{PCP} versus x_{PCP}) at three different temperatures for (i) IRA-900 and water, (ii) IRA-958 and water, and (iii) IRA-900 and methanol–water (50/50 vol %) solvent. Note that when pure water is the solvent, PCP⁻ uptake increases with an increase in temperature strongly for IRA-900 and moderately for IRA-958, i.e., the PCP⁻/Cl⁻ exchange is endothermic. However, as water (dielectric constant, $\epsilon = 78$) is replaced by methanol–water solvent ($\epsilon \approx 55$) for IRA-900, the effect of temperature is reversed, i.e., PCP⁻–Cl⁻ exchange becomes an exothermic process (i.e., ΔH° is negative). Equilibrium constant values were subsequently determined for each individual isotherm using eq 9 for the three systems in Figure 6A–C. Figure 7 shows van't Hoff plots ($\ln K$ vs $1/T$) and includes corresponding ΔH° and $T\Delta S^\circ$ values for the three

above-mentioned isotherms. The following observations are noteworthy:

(a) For all the three systems, PCP⁻ sorption onto the exchanger is preferred over Cl⁻, i.e., $\ln K$ is greater than zero and ΔG° values are negative. In pure water system, IRA-900 gives rise to high positive ΔH° value, while the same for IRA-958 is marginally greater than zero. Favorable ion exchange type sorption behaviors with positive enthalpy changes (endothermic) are very unusual but have previously been reported for long-chain alkanesulfonates and quaternary ammonium compounds (6, 17). Note that the entropy contribution (i.e., $T\Delta S^\circ$) for IRA-900 with nonpolar polystyrene matrix is significantly larger than that for IRA-958 with a relatively polar matrix, all other conditions remaining identical. High endothermicity of the exchange reaction with IRA-900 makes PCP⁻ sorption gradually less favorable as the temperature decreases. The van't Hoff plots of IRA-900 and IRA-958 intersect at 11 °C, as may be seen in Figure 7, i.e., PCP⁻ sorption onto IRA-958 is thermodynamically more favorable than with IRA-900 at temperature lower than 11 °C.

(b) Contrary to the pure water system, the van't Hoff plot for IRA-900 in the presence of a cosolvent (methanol) has a positive slope, i.e., PCP⁻–Cl⁻ exchange is exothermic and accompanied by a negative enthalpy change. In pure water systems, negative ΔG° values result from positive entropic contributions, i.e., favorable PCP⁻ sorption is an entropy-driven process. In contrast, the negative free energy change for methanol–water solvent is an enthalpy-driven process.

To interpret the significance of various experimentally determined ΔH° and $T\Delta S^\circ$ values during the sorption of aromatic anions, we will consider the classical work pertaining to the dissolution of gaseous nonpolar methane between cyclohexane (a nonpolar, nonassociated solvent) and water (a polar, self-associated solvent) (18). ΔH° and $T\Delta S^\circ$ values are provided for the transfer of methane from water to cyclohexane in Figure 8a where subscripts "s" and "w" represent solvent cyclohexane and water, respectively. Note

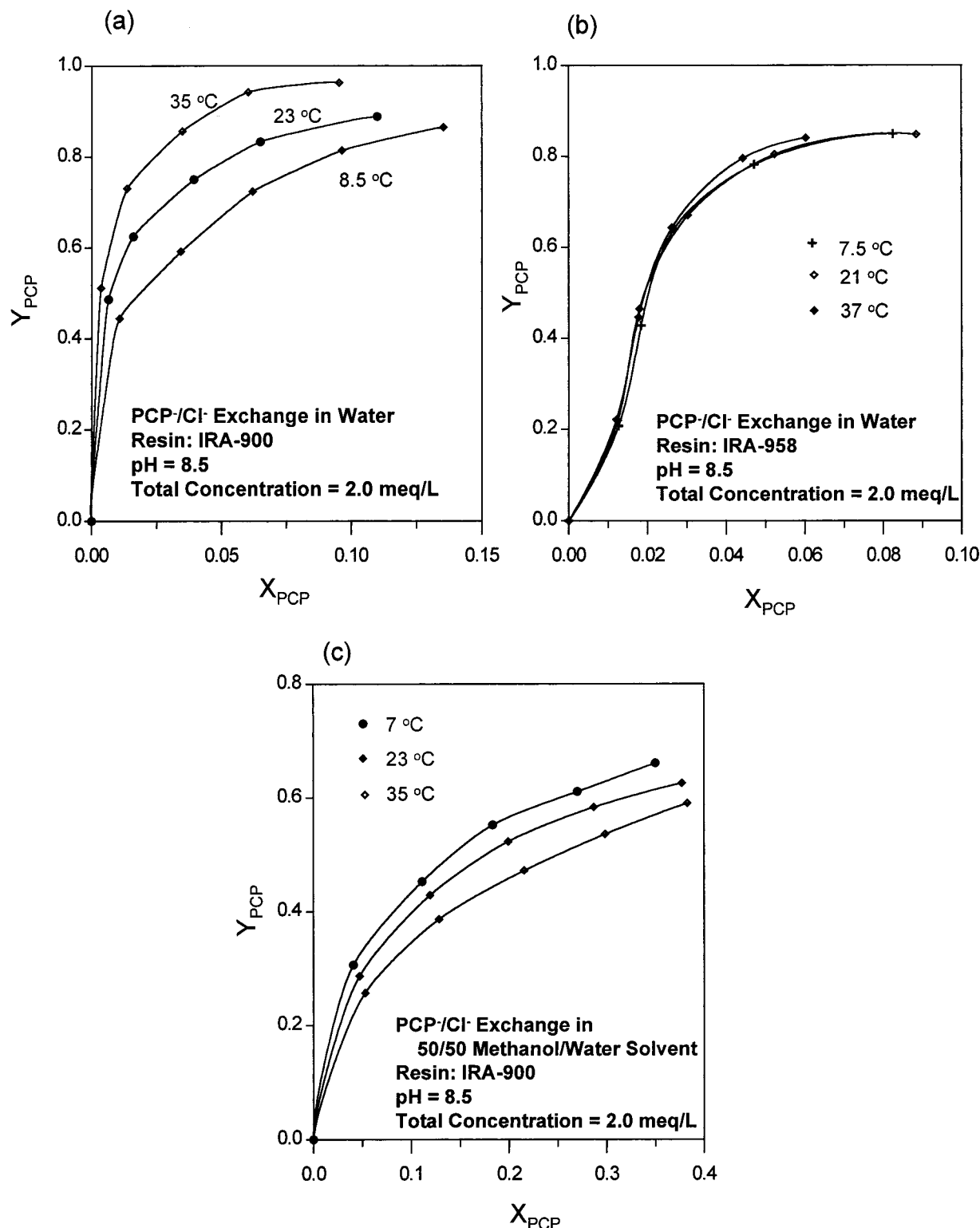


FIGURE 6. PCP-/Cl- isotherms at three different temperatures for (a) IRA-900 and water, (b) IRA-958 and water, and (c) IRA-900 and methanol/water systems.

that the enthalpic and entropic changes for transfer of methane from polar water to nonpolar cyclohexane are positive. Since the overall free energy change (ΔG_{W-S}°) is negative, the methane transfer is a favorable, endothermic, and an entropy-driven process. To draw an analogy and assess the relative magnitude of different interactions, ΔH° and $T\Delta S^\circ$ values of ion exchange processes involving aromatic anions and chloride under different experimental conditions are included in the same figure. The following provides a

generic analysis attempting to unify experimentally determined enthalpic and entropic changes under varying conditions:

(i) In Figure 8b, IRA-900 has a highly hydrophobic polystyrene matrix and is analogous to nonpolar cyclohexane in Figure 8a. Similar to methane transfer in Figure 8a, PCP- sorption onto IRA-900 is thermodynamically favorable (i.e., negative ΔG°) and endothermic and involves positive entropy changes.

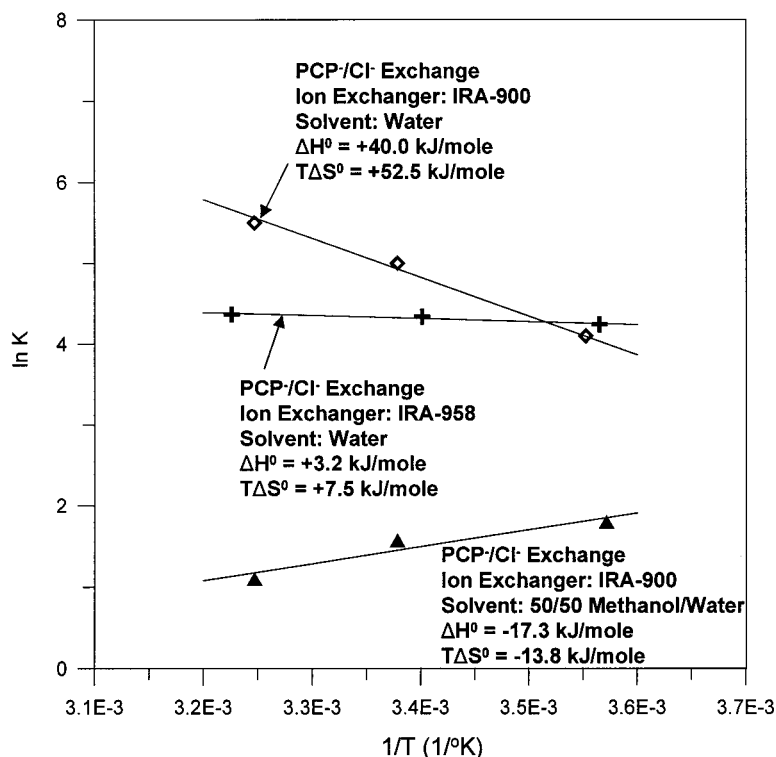


FIGURE 7. van't Hoff plots ($\ln K$ versus $1/T$) for three different types of isotherms reported in Figure 6.

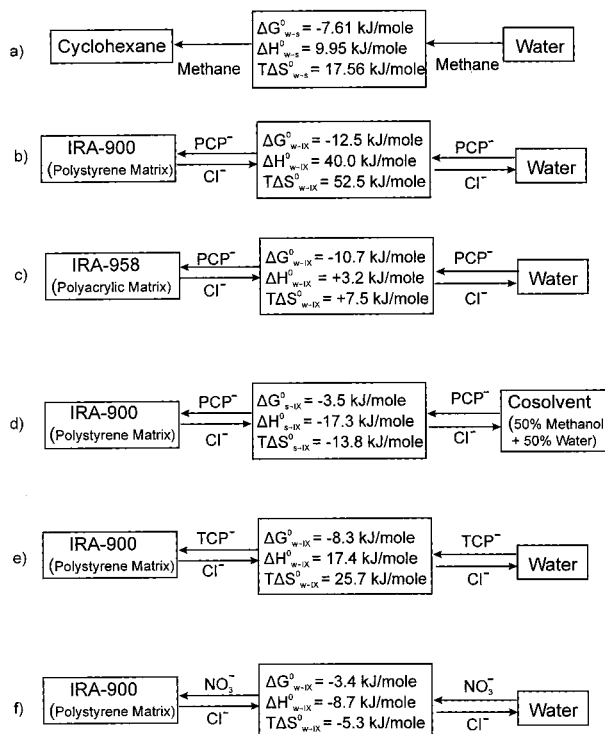


FIGURE 8. Enthalpic and entropic changes during PCP⁻ sorption under varying conditions and their relationships to methane transfer between cyclohexane and water.

(ii) In Figure 8c, IRA-958 has a more polar matrix, i.e., it is equivalent to replacing cyclohexane in Figure 8a with a more polar solvent. As a result, although favorable, PCP⁻ sorption is much less endothermic (ΔH° is near zero), and positive entropic contribution is relatively low.

(iii) In Figure 8d, water is replaced by 50/50 methanol–water solvent with a significantly lower dielectric constant

($\epsilon = 55$). This is analogous to using a high nonpolar solvent in the place of water in the methane transfer process. Understandably, PCP⁻ desorption from such a solvent, as illustrated in Figure 1, no longer involves a significant structure breaking of solvent molecules. Positive entropy change associated with the desorption step, therefore, diminishes sharply. Also, a lesser amount of heat needs to be absorbed because the structure breaking of solvent molecules is unwarranted. All in all, the overall equilibrium becomes much less favorable for PCP⁻ sorption (i.e., lower negative ΔG° value), and the process is exothermic (i.e., negative ΔH°).

(iv) Figure 8e shows the results of a sorption process very similar to Figure 8b except that the solute PCP⁻ has been replaced with trichlorophenol or TCP⁻. The nonpolar moiety of TCP⁻ is less hydrophobic than that of PCP⁻, as reflected in their K_{OW} values. As a result, TCP⁻ sorption is favorable and the sign of ΔH° and $T\Delta S^\circ$ remain unchanged, i.e., both are positive, but their absolute values are lower compared to those obtained with PCP⁻.

(v) To distinguish the difference between strictly inorganic ion exchange and the exchange involving aromatic anions, results of nitrate–chloride ($\text{NO}_3^-/\text{Cl}^-$) exchange are included in Figure 8f. Other conditions, namely, the ion exchanger and solvent, are essentially the same as those shown in Figure 8b. Nitrate sorption is favorable, i.e., free energy changes are negative. But contrary to sorption of PCP⁻ or TCP⁻, the favorable equilibrium in this case is driven by negative enthalpy changes, i.e., nitrate–chloride exchange is essentially an exothermic process accompanied by an overall decrease in entropy. The foregoing observation is true for typical inorganic ion exchange processes, both cationic and anionic, where the energy of solvation is the primary determinant of the relative selectivity of exchanging counterions (19, 20).

Effect of Hydrophobicity of the Solute. As already indicated, the NPM–solvent and the NPM–matrix interactions are postulated to be the underlying reasons for the high affinity of a polymeric anion exchanger toward PCP⁻ over chloride. Therefore, for a given solvent (say water) and a

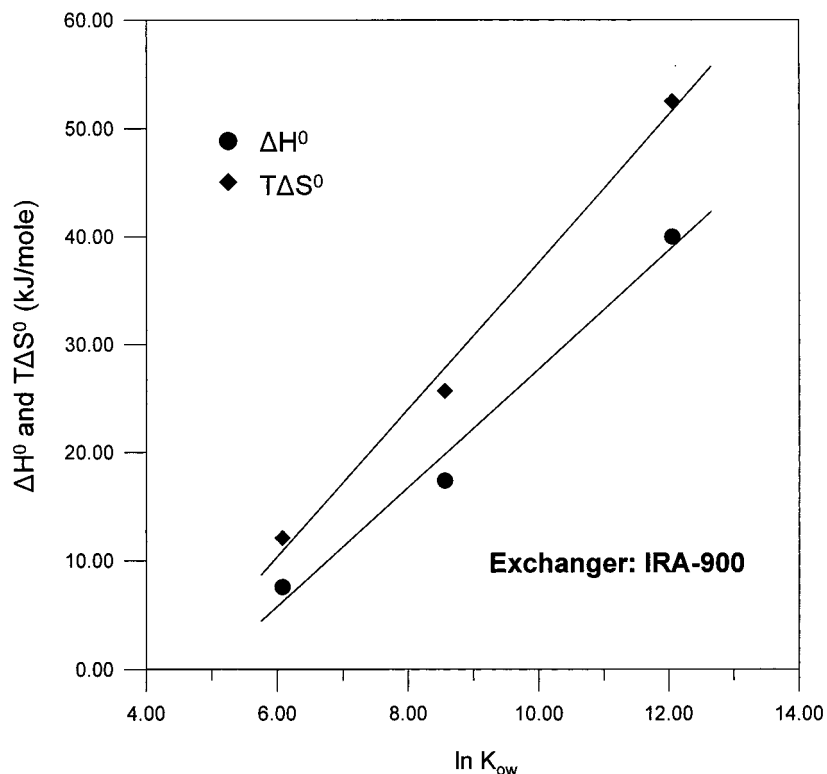


FIGURE 9. Plots of experimentally determined ΔH° and $T\Delta S^\circ$ values versus $\ln K_{ow}$ for three different chlorophenols.

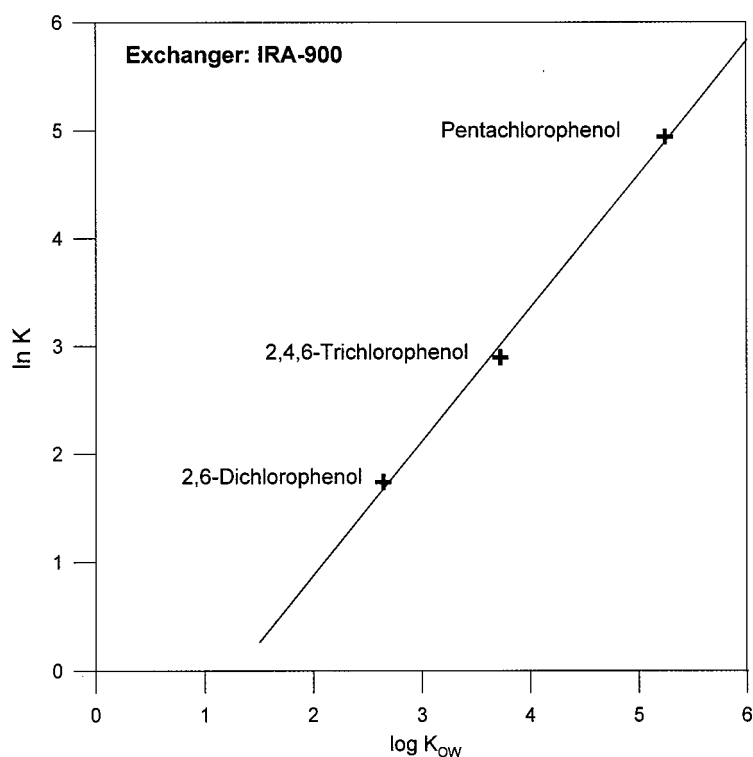


FIGURE 10. Plot of experimentally determined $\ln K$ values versus $\log K_{ow}$ for three chlorophenols.

given polymeric anion exchanger (say IRA-900), the solute affinity should be strongly correlated to the hydrophobicity of its NPM. The octanol–water partition coefficient (K_{ow}) of an undissociated chlorophenol may be a representative measure of the NPMs hydrophobicity. The derivative of the free energy change with respect to $\ln K_{ow}$ for a monovalent hydrophobic anion during exchange with chloride should then be a constant, i.e.

$$\frac{d\Delta G^\circ}{d \ln K_{ow}} = \text{constant} \quad (13)$$

$$\frac{d\Delta H^\circ}{d \ln K_{ow}} - \frac{dT\Delta S^\circ}{d \ln K_{ow}} = \text{constant} \quad (14)$$

Assuming both enthalpic and entropic changes are governed independently by the hydrophobicity of the NPM, the individual derivatives corresponding to the first and

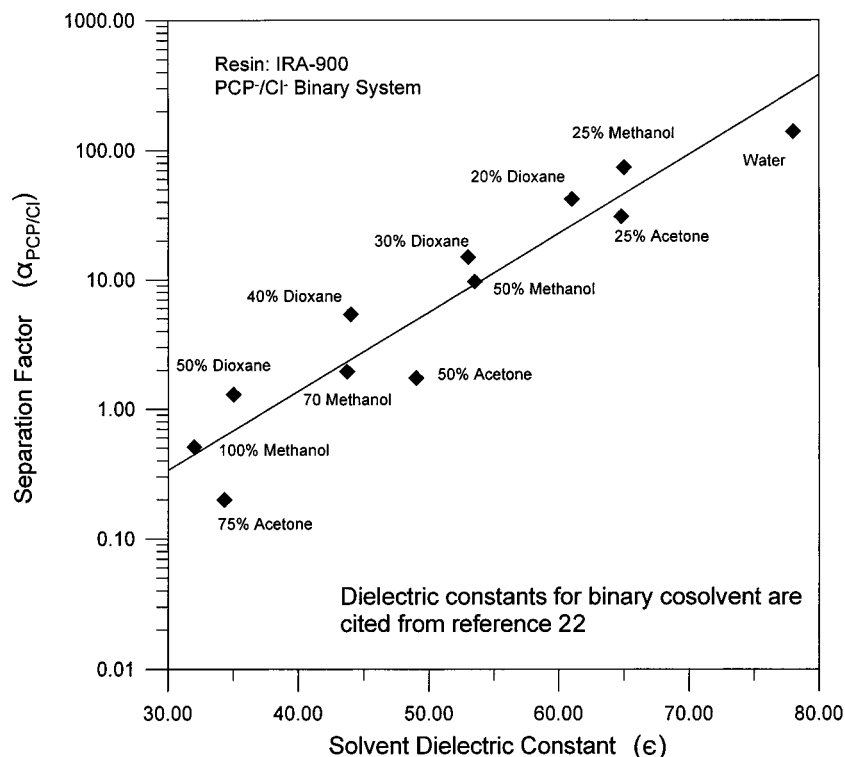


FIGURE 11. PCP^-/Cl^- separation factor values versus the dielectric constant of the solvent medium.

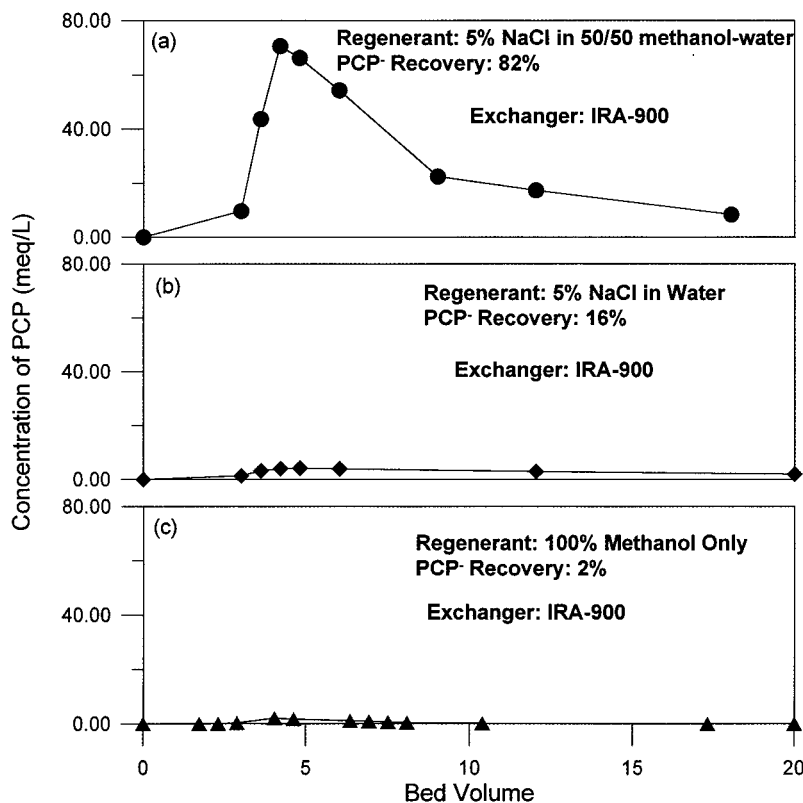


FIGURE 12. Concentration profile of desorbed PCP^- during separate regenerations with (a) 5% NaCl in methanol/water, (b) 5% NaCl in water, and (c) 100% methanol only.

second terms in eq 14 will also be constants, i.e., the plot of ΔH° vs $\ln K_{\text{OW}}$ and $T\Delta S^\circ$ vs $\ln K_{\text{OW}}$ will be straight lines. Using binary isotherm data at different temperatures and the van't Hoff relationship as per eq 11, ΔH° and $T\Delta S^\circ$ values were determined for two other chlorophenates, namely, 2,4,6-trichlorophenate and 2,6-dichlorophenate, for exchange with

chloride. Figure 9 shows plots of ΔH° vs $\ln K_{\text{OW}}$ and $T\Delta S^\circ$ vs $\ln K_{\text{OW}}$; fairly good linear relationships are observed. Also

$$\Delta G^\circ = -RT \ln K \quad (15)$$

Thus, from eqs 13 and 15

$$-RT \frac{d \ln K}{d \ln K_{OW}} = \text{constant}$$

or

$$\frac{d \ln K}{d \ln K_{OW}} = \text{constant} \quad (16)$$

Therefore, a linear relationship exists between $\ln K$ and $\ln K_{OW}$. Figure 10 shows a plot of experimentally determined K values of three different chlorophenols for IRA-900 and their corresponding K_{OW} values. The plot, in general, recognizes the strong correlation between eq 16 and the experimental data. It is noteworthy that as the $\log K_{OW}$ value drops near 2.0, the hydrophobic interaction is no longer predominant over electrostatic interaction and $\ln K$ tends to be zero or K is close to unity. Under such conditions, the basic premises of eqs 5 and 13 are no longer valid.

Sorption Reversibility and Efficiency of Regeneration. To be viable, an ion-exchange process needs to be amenable to efficient regeneration, i.e., sorption of aromatic anions should be reversible. To this effect, the solvent dielectric constant is the single most important variable influencing the sorption affinity through ion-solvent interaction. Figure 11 shows the plot of PCP^-/Cl^- separation factor values for IRA-900 versus the dielectric constant (ϵ) of the solvent medium. A meaningful correlation is observed and note that the separation factor value drops from 145 with pure water ($\epsilon = 78$) to less than unity with pure methanol ($\epsilon = 32$).

To investigate the regenerability of the PCP^- loaded anion exchanger, the exhausted IRA-900 from the column run in Figure 2 was divided in three portions. They were separately regenerated using first, 50/50 methanol-water and 5% NaCl; second, 5% NaCl in water; and third, 100% methanol only. Figure 12a-c shows concentration profiles of desorbed PCP^- during the three regeneration processes. Note that while the combination of methanol and sodium chloride provides very efficient regeneration (82% recovery of PCP^- in 15 bed volumes), aqueous solution of sodium chloride and methanol alone is practically unable to desorb PCP^- . From a mechanistic viewpoint, the experimental observations clearly suggest that both ion exchange (caused by the presence of chloride anions) and an enhanced NPM-solvent interaction (due to reduced solvent dielectric constant) are simultaneously operative toward achieving efficient regeneration. The results of the three regeneration processes in Figure 12 can be explained as follows:

Regenerant: Cl^- in water

Remark: unfavorable equilibrium



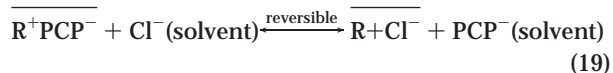
Regenerant: Methanol alone, no counter-ion

Remark: Absence of ion exchange



Regenerant: Cl^- in solvent with
reduced dielectric constant

Remark: Enhanced NPM-solvent interaction
coupled with ion exchange



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