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

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To cite this Article Hasany, S. Moosa , Saeed, M. Mufazzal and Ahmed, M.(2001) 'SORPTION OF PALLADIUM-THIOCYANATE COMPLEXES ONTO POLYURETHANE FOAM FROM AQUEOUS SOLUTION USING RADIOTRACER TECHNIQUE', Separation Science and Technology, 36: 4, 555 — 570
To link to this Article: DOI: 10.1081/SS-100102946
URL: http://dx.doi.org/10.1081/SS-100102946

SEPARATION SCIENCE AND TECHNOLOGY, 36(4), 555–570 (2001)

SORPTION OF PALLADIUM-THIOCYANATE COMPLEXES ONTO POLYURETHANE FOAM FROM AQUEOUS SOLUTION USING RADIOTRACER TECHNIQUE

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SUMMARY

The sorption of palladium-thiocyanate complex onto polyurethane foam (PUF) has been investigated and optimized from aqueous solution of different pHs (1–10) and of acids of varied concentration (0.01–0.5 M). Maximum sorption (~ 99%) of palladium (9.4×10^{-5} M) in the presence of thiocyanate (1.25×10^{-2} M) ions has been achieved from 0.1 M hydrochloric acid solution within 5 min equilibrating time. The variation of palladium concentration ($1.03 \times 10^{-4} - 1.16 \times 10^{-3}$ M) data were subjected to different sorption isotherms.

The data followed both Freundlich and Dubinin-Radushkevich (D-R) isotherms very well, but Langmuir isotherm is not obeyed at very low concentration. The Freundlich parameters $1/n = 0.54 \pm 0.02$ and of $C_m = 35 \pm 7$ mmol g^{-1} have been evaluated, whereas D-R isotherm yields $\beta = -0.003277 \pm 0.000193$ kJ^2 mol^{-2}, $X_m = 1.01 \pm 0.16$ mmol g^{-1}, and of $E = 12.3 \pm 0.35$ kJ mol^{-1}. The Langmuir isotherm gives the value of $Q = 0.27 \pm 0.08$ mmol g^{-1}

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*Corresponding author.

and of $b = (2.83 \pm 0.06) \times 10^4$ L mol^{-1}. The temperature variation (15–55°C) studies have given values of $\Delta H = -48.9 \pm 2.5$ kJ mol^{-1}, $\Delta S = -127.3 \pm 8.2$ J mol^{-1} K^{-1}, and of $\Delta G = -25.2$ kJ mol^{-1} at 298 K. Among the ions tested, thiourea, cyanide, thiosulphate, molybdate, nitrite, and Fe(II) reduce the sorption significantly (31–70%).

Key Words: Palladium-thiocyanate; Polyurethane foam; Aqueous solution; Sorption; Radiotracer technique.

INTRODUCTION

Because of its elastomeric, hydrophobic, inert, and stable nature; low cost; simple apparatus; and specificity polyurethane foam (PUF) has received considerable attention over the last two decades for its use in the separation and preconcentration of a wide variety of organic and inorganic compounds including metal ions from aqueous solutions (1, 2). Since their introduction in 1970 (3) as an adsorbent, PUF has been employed in many analytical techniques before actual analytical measurement for the separation and preconcentration of industrial and environmental samples. PUF has a number of applications in different sciences and technologies as well (4–6). The feasibility of polyether type PUF as a sorbent has been investigated for a number of metal ions from aqueous solutions in the presence of thiocyanate ions in this laboratory (7, 8). In continuation of our earlier studies, present communication describes the results of an investigation undertaken to optimize the sorption of thiocyanate complexes of palladium from aqueous solution in terms of metal, thiocyanate, and acid concentration and time of agitation of solid and liquid phases. The use of thiocyanate as a complexing agent (9) has provided the basis of this investigation. The purpose of this work is to establish the optimal conditions for the formation and sorption of palladium-thiocyanate complex and to study the kinetics and thermodynamics of the processes involved and have better understanding of its mechanism.

Palladium has been chosen for this study because of its applications in electrical and electronic, dental and medical, automobile, and chemical industries. Palladium is also used as a catalyst, in jewelry and in brazing alloys (10).

EXPERIMENTAL

Reagents and Radiotracer

All the reagents used were of analytical or equivalent grade. The solutions were made in doubly distilled deionized water. ^{109}Pd ($t_{1/2} = 13.43$ h) was made by irradiating spectroscopic grade palladium sponge (Johnson Matthey) in PARR-1 research reactor of this institute at a neutron flux density of 4×10^{13} n cm^{-2} s^{-1} for 10 min and then dissolved in concentrated hydrochloric acid solution, evaporated to dryness and finally stored in 0.1 M HCl solution. The concentration of palladium in stock solution was 7.52×10^{-3} M. The radiochemical and radionuclidic purity of the tracer was checked by gamma spectroscopy using 4K series 85 Canberra multichannel analyzer coupled with a 25 cm^3 Ge(Li) detector. Buffers of pH 1–4 were made by mixing of 0.1 M solution of KCl + HCl, pH 5–7 of acetic acid and sodium acetate, and pH 8–10 of boric acid and sodium hydroxide. The procedure to prepare PUF plugs (1 cm × 0.5 cm ϕ) of 22 mg cm^{-3} density was described earlier in detail, which were used as a sorbent (7).

Procedure

Radiometric and batch techniques were used to determine the distribution ratio (K_d) and percent sorption. The amount of palladium-thiocyanate complex sorbed onto PUF was measured by comparing the radioactivity of ^{109}Pd of same aliquot before and after the sorption (7). Sufficient ^{109}Pd tracer was added to yield a count rate of at least 815 cpm/cm^3. The sorption measurements were made at 23 ± 2°C unless temperature was specified otherwise. The results of K_d and percent sorption are the average of at least triplicate independent measurements. The precision in most cases is ±3%.

RESULTS AND DISCUSSION

To select a suitable electrolyte for maximum sorption of palladium-thiocyanate complex onto PUF, buffer solutions of different pHs in the range of 1–10 were tested. The concentration of Pd was kept at 5.17×10^{-5} M and sorbent was equilibrated with sorbate for 5 min in the presence of 1.25×10^{-2} M potassium thiocyanate. The results are shown in Fig. 1. The distribution ratio (K_d) decreases drastically with an increase in the pH of the solution. The distribution ratio decreases from around 13470 cm^3 g^{-1} at pH 1 to about 337 cm^3 g^{-1} at pH 5, whereas percent sorption registers a decrease from $\geq$99 to ~76% and further to 136 cm^3 g^{-1} corresponding to $\geq$56% at pH 10. In other words, almost quantitative sorption is achieved at low pH values of <3. Therefore, three acids, namely hydrochloric, perchloric, and nitric acid solutions, were investigated as sorptive medium in the concentration range of 0.01 to 0.5 M. The results are given in Table 1. In all acids used the distribution ratio is low at very dilute acid solutions (0.01 M) and is maximum at 0.1 M acid solution, which corresponds to pH 1. The distribution ratio decreases further with an increase in acid concentration. The de-

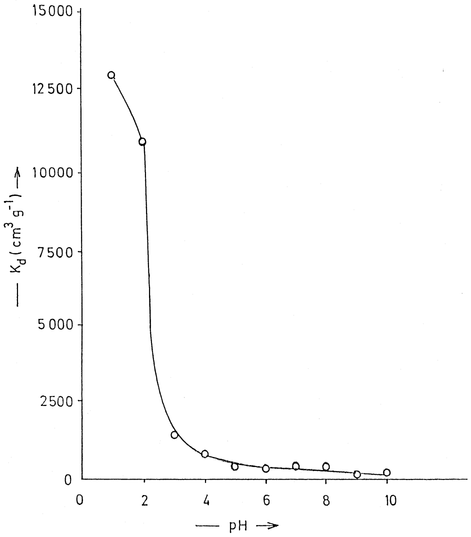


Figure 1. Sorption of Pd onto PUF as a function of pH of aqueous solution in the presence of (1.25×10^{-2} M) thiocyanate ions.

cline in the degree of sorption with an increase in HCl concentration upto 0.1 M is probably due to the formation and subsequent sorption of thiocyanic acid (4). Hydrochloric acid solution of 0.1 M has been selected for further studies. In 0.1 M concentration of all three acids the percent sorption (≥98.5) is almost independent of the nature of the acid employed. At low HCl concentration of 0.1 M in the presence of sodium thiocyanate, the high sorption efficiency in the presence of

Table 1. Sorption of Pd-SCN Complex Onto Polyurethane Foam from Acidic Solutions
$[\mathrm{Pd}] = 9.4 \times 10^{-5}$ M $[\mathrm{SCN}] = 1.25 \times 10^{-2}$ M
PUF = 29 mg/4 ml Shaking Time = 5 min.

	HCl		$HClO_4$		HNO_3	
Acid (M)	K_d ($cm^3\ g^{-1}$)	% Sorption	K_d ($cm^3\ g^{-1}$)	% Sorption	K_d ($cm^3\ g^{-1}$)	% Sorption
0.01	7909	98.3	7085	98.2	3849	96.4
0.1	10883	98.7	11796	98.5	9686	98.5
0.2	4120	96.7	11211	98.7	7468	98.2
0.3	2968	95.5	2731	95.2	3557	96.2
0.5	864	86.2	517	78.9	1120	89.0

sodium ions shows that this ion contributes to distribution of palladium-thiocyanate complex between PUF and aqueous phase most likely through cation-chelation mechanism (11). Five min equilibration time has been used in these investigations because equilibrium has been achieved within three min, as shown later in another experiment.

The effect of equilibration time on the sorption of Pd-SCN complexes from 0.1 M HCl solution has been examined from 1 to 120 minutes. The results of this kinetic investigation are depicted in Fig. 2 where *B*t is plotted against time(t), which is a mathematical function of the ratio of fraction sorbed q_t in mol g^{-1} at time, *t,* and at equilibrium (q_e) in mol g^{-1}.

$$\begin{aligned} F &= q_t/q_e \\ Bt &= -0.4977 - \ln(1 - F) \end{aligned} \tag{1}$$

and of $\log(q_e - q_t)$ vs. time, the Lagergren equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{2}$$

The plot of Bt against time is not a straight line. Moreover, the plot of $\log(q_e - q_t)$ vs. time gives two distinct slopes. In the initial stage up to 20 min the value of $k_1 = 0.1689\ \mathrm{min}^{-1}$, which has been deduced from the initial slope, almost 10 times higher than computed from the slope in the later stage beyond 20 min shaking time, that is, $0.0184\ \mathrm{min}^{-1}$. The sorption is almost complete within three min (~98.5%). For further experiments five min equilibration time between sorbent and sorbate has been selected. The use of short equilibrium time conditions makes this method more practical as only a very small amount of the test element is left in liquid phase and the time needed (5 min) is far less than minimum

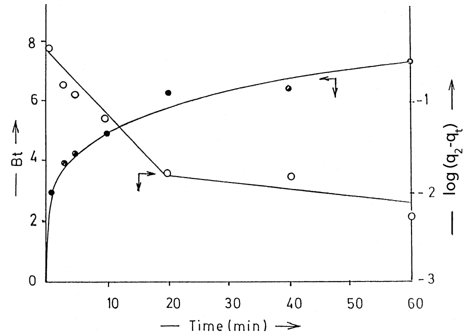


Figure 2. Lagergren and Reichenburg plot of the kinetics of Pd-SCN complexes onto PUF from 0.1 M HCl in the presence of 1.25×10^{-2} M thiocyanate ions.

of 1 h required to establish the equilibrium for the sorption of zinc thiocyanate-complex on PUF (12).

The influence of sodium thiocyanate concentration on the sorption of Pd (5.29×10^{-5} M) onto 38.5 mg of PUF from 4 cm^3 of 0.1 M HCl solution has been investigated. The results are shown in Fig. 3, which indicates a decrease in palladium sorption while increasing the concentration of thiocyanate ions ($6.25 \times 10^{-3} - 5 \times 10^{-2}$ M). The distribution ratio registers a decrease from 73,900 to 14,300 $cm^3\ g^{-1}$ whereas percent sorption remains almost constant ($>99\%$). For further investigations 1.25×10^{-2} M sodium thiocyanate concentration was selected.

The sorption of palladium as a function of its own concentration in the range of 1.03×10^{-4} to 1.16×10^{-3} M has been examined from 0.1 M HCl solution containing 1.25×10^{-2} M sodium thiocyanate. The results are given in Fig. 4. The distribution ratio decreases sharply with an increase in palladium concentration. The foam becomes almost saturated with sorbate rapidly so that distribution ratio (K_d) fell off as the saturation was approached. In this case most favorable distribution ratios were found for more dilute solutions.

The effect of different solid concentrations of PUF on the sorption of palladium was investigated from 0.1 M hydrochloric acid solution containing $1.25 \times$

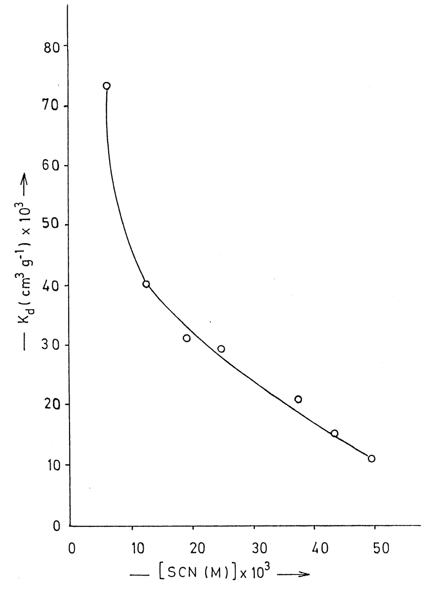


Figure 3. The distribution ratio (K_d) of palladium (5.29×10^{-5}) as a function of thiocyanate ions concentration onto PUF from 0.1 M hydrochloric acid solution.

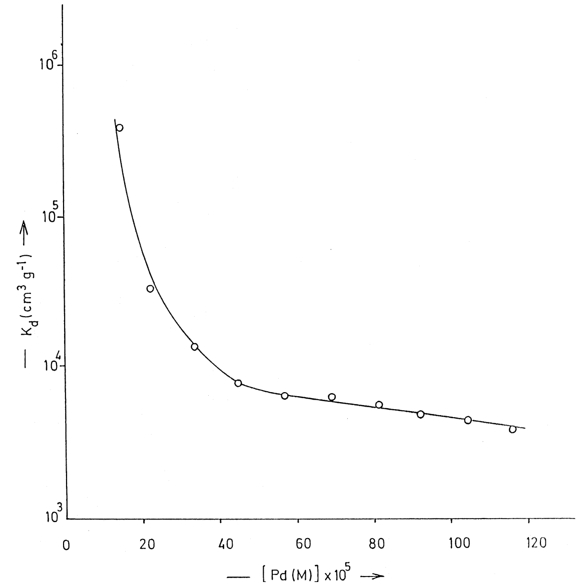


Figure 4. Variation of distribution ratio (K_d) of palladium from 0.1 M HCl solution containing 1.25×10^{-2} M thiocyanate ions as a function of its own concentration.

10^{-2} M sodium thiocyanate and fixed concentration of palladium (9.4×10^{-5} M) using 5 min equilibration time from 7.25 to 58 mg/4 cm^3 solution. The result are shown in Fig. 5. The percent sorption starts increasing with an increase in the solid concentration of PUF and attains an almost constant value (≥99) at 29 mg. Therefore, for further studies this amount of solid sorbent (i.e. PUF) was used in all subsequent measurements.

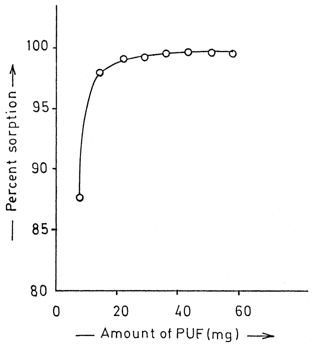


Figure 5. Percent sorption of palladium-thiocyanate complex onto PUF from 0.1 M hydrochloric acid solution as a function of amount of PUF.

The variation of sorption with palladium concentration was subjected to different sorption isotherms. The Langmuir sorption isotherm was tested in the following form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{3}$$

where C_{ads} is the sorbed concentration of palladium-thiocyanate, C_e is the concentration of same entity at equilibrium, and Q and b are Langmuir constants related to sorption capacity and intensity, respectively. In Fig. 6 C_e/C_{ads} is plotted against C_e. It gives a straight line except at very low palladium concentration. Ignoring these values the slope and intercept of the straight line shown in Fig. 6 gives the value of $Q = 0.27 \pm 0.08$ mmol g^{-1} and of $b = (2.83 \pm 0.06) \times 10^4$ dm^3 mol^{-1}. The sorption data were also subjected to Freundlich sorption isotherm in the following form:

$$\log C_{ads} = \log C_m + \frac{1}{n} \log C_e \tag{4}$$

where C_m and $1/n$ are Freundlich parameters related to sorption capacity and intensity. The plot of log C_{ads} vs. log C_e is drawn in Fig. 7, which is a straight line over the entire concentration of palladium studied. The slope and intercept of this plot give the value of $1/n = 0.54 \pm 0.02$ and of $C_m = 35 \pm 7$ mmol g^{-1}. Another isotherm, Dubinin-Radushkevich (D-R), is examined by plotting the value of ln C_{ads} vs. ε^2

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2 \tag{5}$$

where ε is Polanyi potential, which is equal to $\varepsilon = RT \ln(1/C_e + 1)$. This plot is given in Fig. 8. The slope of this curve yields the value of $\beta = -0.003277 \pm$

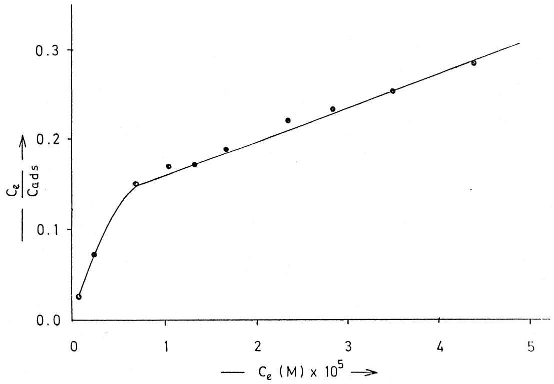


Figure 6. Langmuir sorption isotherm of palladium-thiocyanate complex onto PUF.

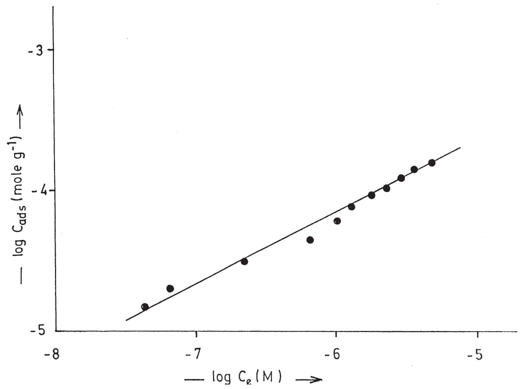


Figure 7. Freundlich sorption isotherm of palladium-thiocyanate complex onto PUF.

0.000193 kJ^2 mol^{-2} and maximum sorption, $X_m = 1.01 \pm 0.16$ mmol g^{-1} and sorption energy E, which is related to β through the following equation:

$$E = 1/\sqrt{-2\beta} \tag{6}$$

Equation (6) gives the value of $E = 12.3 \pm 0.35$ kJ mol^{-1}, which is close to $E =$ 12.9 ± 0.4 kJ mol^{-1} and of $E = 12.4 \pm 0.3$ estimated for the sorption of mercury (7) and cobalt (8) thiocyanate complexes onto PUF from acidic solution. The

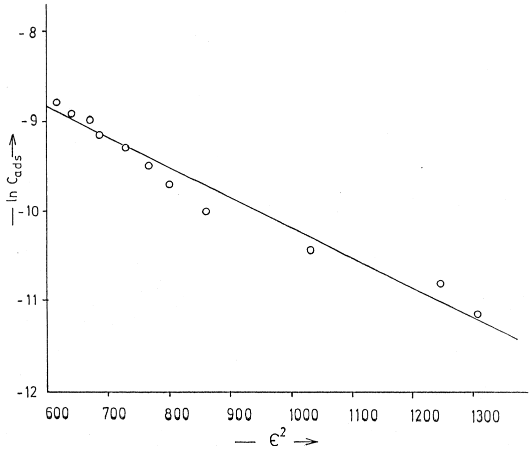


Figure 8. Dubinin-Radushkevich (D-R) isotherm of palladium-thiocyanate complex onto PUF.

correlation factor (γ) for the three isotherms using linear regression analysis is in the range of 0.9847–0.9971, close to unity.

The sorption of palladium-thiocyanate complex onto PUF has also been measured in the presence of common anions and cations. The anions were added as their sodium or potassium salts, whereas cations were included as their chlorides. The concentration of additional ions was kept at 10 mg/cm^3. The results are listed in Tables 2 and 3. All the ions tested have reduced the sorption significantly especially thiourea, cyanide, thiosulphate, Fe(II), molybdate, and nitrite. In the presence of these ions the percent sorption is reduced to $>31 < 70\%$. These ions need to be removed from the sorptive solution, otherwise low yield of sorption would result. The reduction in sorption of palladium-thiocyanate complex may be interpreted in term of low sorption affinity of palladium complexes of these anions or the displacement of palladium-thiocyanate complex by these ions from the surface of PUF. Stronger complexes of palladium with cyanide (13), thiourea, nitrite (14), and bromide (13) have been reported in the literature. The increase in

Table 2. Influence of Anions on The Sorption of Pd-SCN Complex From 0.1 M HCl Solution on Polyurethane Foam
$[\mathrm{Pd}] = 9.4 \times 10^{-5}$ M $[\mathrm{SCN}] = 1.25 \times 10^{-2}$ M

Anion Added	K_d (cm^3 g^{-1})	% Adsorption
Nil	10883	98.7
Bromide	5455	97.5
Nitrate	3853	96.5
Sulphate	2943	94.6
Ascorbate	2259	94.9
Phosphate	2066	92.7
Chloride	2055	93.7
Iodide	1124	89.0
Fluoride	878	86.4
Oxalate	784	85.0
Citrate	567	80.4
Acetate	528	79.0
EDTA	480	77.7
Tartrate	388	73.8
Nitrite	272	66.4
Molybdate	235	62.9
Thiosulphate	141	50.5
Cyanide*	108	50.2
Thiourea	63	31.4

* Potassium salt used.

Table 3. Effect of Cations on the Sorption of Pd-SCN Complex From 0.1 M HCl Solution of Polyurethane Foam
[Pd] = 9.4×10^{-5} M [SCN] = 1.25×10^{-2} M

Cation Added	K_d ($cm^3\ g^{-1}$)	% Adsorption
Nil	10883	98.7
Pb(II)	5445	97.5
Fe(III)	2983	95.4
Ni(II)	1567	91.9
Mn(II)	1524	91.6
Ba(II)	1467	91.4
Li(I)	1411	91.1
Co(II)	1277	90.5
Ce(III)	1248	90.0
Bi(III)	1182	89.6
Sr(II)	1152	89.3
Tl(I)	1082	88.7
Cr(III)	898	86.7
Zr(IV)	845	86.1
La(III)	539	79.7
Al(III)	449	76.4
Fe(II)	320	69.9

the sorption of palladium in the presence of bromide may also be explained in terms of stronger affinity of bromide complex of palladium on PUF surface.

The sorption of palladium-thiocyanate complex from 0.1 M HCl solution was measured at 15–55°C. The value of equilibrium constant, $K_c = F_e/(1 - F_e)$ where F_e is the fraction sorbed at equilibrium was plotted against $1/T$ and is shown in Fig. 9, where T is temperature in Kelvin. The thermodynamic parameters (i.e., ΔH, ΔS, and ΔG) were computed using the following relationships:

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \tag{7}$$

$$\Delta G = -RT \ln K_c \tag{8}$$

The values of ΔH and ΔS are estimated from the slope and intercept of the curve shown in Fig. 9, whereas ΔG was evaluated using Eq. (8). These values are $\Delta H = -48.9 \pm 2.5$ kJ mol^{-1}, $\Delta S = -127.3 \pm 8.2$ J mol^{-1}K^{-1}, and of $\Delta G = -25.2$ kJ mol^{-1} at 298 K. These values were estimated using a linear regression analysis program (15), which gives a value of 0.9908 for correlation factor (γ).

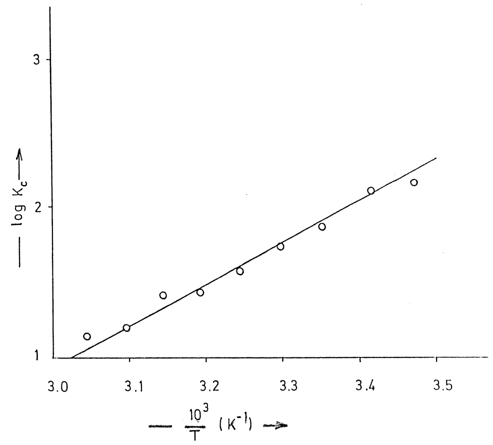


Figure 9. Variation of equilibrium constant (K_c) of Pd-SCN complex uptake onto PUF with temperature.

Sorption Mechanism

Several possible mechanisms have been suggested for the sorption of metal ions from aqueous solutions onto polyether-type polyurethane foam. The predominant one will depend on the conditions of sorption and nature of the species sorbed. The metal ions are sorbed on some sites on the polymer surface. The sorption capacity for the palladium ions estimated using D-R isotherm comes out to be ~ 1 mol/kg, which indicates absorption rather than adsorption process. The surface mechanism has been rejected by several workers (3, 16) because of higher values of sorption capacities of metal ions onto PUF.

Table 1 shows that as hydrochloric acid concentration is increased from 0.01 to 0.5 M, the palladium sorption decreased slowly from 98% (log $K_d = 3.90$) to 86.0% (log $K_d = 2.94$). At higher acidity, the degree of sorption remained almost independent of the nature of the acid. The extent of sorption decreased sharply from 1.35×10^4 $cm^3 g^{-1}$ at pH 1 to 337 cm^3 g^{-1} at pH 5 and further to 136 cm^3 g^{-1} at pH 10 correspondent to $\geq 99\%$ to 76% to 56% sorption. The results suggest that hydrochloric acid influences the distribution of palladium-thiocyanate complex between foam and solution and not the formation of sorbable species. Figure 1 indicates more than 56% of palladium is sorbed from basic solution where neutral protonated species $H_2Pd(SCN)_4$ is very unlikely to form. It is also obvious that 0.1 M HCl solution is sufficient to have a maximum sorption of palladium, a much lower concentration than 3 M reported for the extraction into ethyl acetate (17). These results along with higher K_d values (10^4 cm^3 g^{-1}) obtained show that polyether-type PUF cannot be taken as an analog for diethyl ether. It can be concluded that other factors are responsible for the distribution of $[\mathrm{Pd(SCN)_4}]^{2-}$ between foam and aqueous solutions.

The sorption of the metal ions through a "ligand addition" or exchange has also been suggested (16) and is attributed to the fact that polyurethane foam contains large number of lone electron pairs on its nitrogen and oxygen atoms, which may be involved in coordinate bonding to the metal.

$$MX_n^{m-} + ZL \rightleftharpoons (MX_{n-z}L_Z)^{(m-z)-} + ZX^-$$
$$MX_n^{m-} + ZL \rightleftharpoons (MX_nL_Z)^{m-}$$

where L represents the lone pair and its associated atom in polyurethane. The results given in Table 1 show a decrease in the amount of palladium sorbed on the foam surface with increasing HCl concentration beyond 0.1 M concentration. The high degree of extraction from 0.1 M HCl solution does not indicate greater affinity of polyether foam for palladium through the ligand substitution mechanism, or

$$\mathrm{PdCl}_4^{2-} + 2L \rightleftharpoons \mathrm{PdCl}_2L_2 + 2\mathrm{Cl}^-$$

The results shown in Fig. 3 indicate a decrease in the sorption of Pd(II) with increasing thiocynate concentration up to 5×10^{-2} M. The results depict that at 1×10^{-2} M thiocynate the percent sorption is 99.8% ($\log K_d = 4.86$) to 98.8% ($\log K_d = 4.04$) at 5×10^{-2} M. Because the sorption decreases with increasing thiocyanate concentration very drastically above 1×10^{-2} M, the formation of $\mathrm{Pd(SCN)_4^{2-}}$ is almost complete at this thiocyanate concentration. It seems that $\mathrm{Pd(SCN)_2}$ is the species involved in the sorption rather than $\mathrm{Pd(SCN)_4^{2-}}$.

$$\begin{array}{l}
\mathrm{PdCl_2} + 2\mathrm{SCN}^- \rightleftharpoons \mathrm{Pd(SCN)_2} \overset{\mathrm{SCN}^-}{\rightleftharpoons} \mathrm{Pd(SCN)_4^{2-}} \\
\qquad\qquad\qquad\qquad\ \upharpoonleft\!\downharpoonright \\
\qquad\qquad\qquad\ \overline{\mathrm{Pd(SCN)_2}} + \overline{2L} \rightleftharpoons \overline{\mathrm{Pd(SCN)_2}L_2}
\end{array}$$

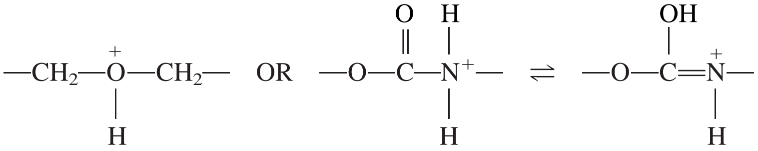
where bars indicate foam phase. The extraction of a neutral thiocyanate of iron (i.e., $\mathrm{Fe(SCN)_3L_3}$ by polyether foam) is reported (16). The decrease in the sorption at thiocyanate concentration $>1 \times 10^{-2}$ M suggests that sorption does not take place by ligand addition or exchange mechanism.

$$\mathrm{Pd(SCN)_4^{2-}} + ZL \rightleftharpoons [\mathrm{Pd(SCN)_4}L_Z]^{2-} \qquad (Z = 1 \textit{ or } 2)$$
$$\mathrm{Pd(SCN)_4^{2-}} + 2L \rightleftharpoons [\mathrm{Pd(SCN)_2}L_2] + 2\mathrm{SCN}^-$$

The first possibility is ruled out on the basis that Pd(II) coordination number is very unlikely to be five or six, which is rare in its solvent extraction (18).

In the ligand substitution mechanism replacement of strongly bound sulfur atom by the nitrogen or oxygen atoms on the foam is unlikely and has not been reported even for strongly donating solvents (19). Therefore, in the presence of excess of thiocyanate, palladium is sorbed as $Pd(SCN)_4^{2-}$. Bowen (3) has suggested that sorption of anionic metal complex could be due to the weaker or stronger anionic exchange polyurethane foam.

The existance of anion-exchange sites arising from the tendency of both nitrogen and oxygen atoms accepting protons of polyurethane to give



$$-CH_2-\underset{H}{\overset{+}{O}}-CH_2- \quad \text{OR} \quad -O-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{H}{N^+}}- \;\rightleftharpoons\; -O-\overset{OH}{C}=\underset{H}{\overset{+}{N}}-$$

and hence polyether type polyurethane foam will have anion exchange sites of various strengths. More than 56% was sorbed from pH 10 basic solution and more than 99% was sorbed at pH 1, which is unlikely to be acidic enough for protonation of the foam. Therefore, the sorption of $Pd(SCN)_4^{2-}$ via anion-exchange seems to be improbable (20).

Cation-chelation has been mentioned as the major means of extraction of $[Pd(SCN)_4]^{2-}$ complex by polyether-type polyurethane foam (11). According to this mechanism polyether-type polyurethane can chelate metal ion similar to their chelation of cyclic or linear polyethers probably due to the helical configuration around the cations. The extent of sorption will depend on the chelation affinity of cation as well as on the nature and hydrophobicity of anionic metal complex. The sorption of $[Pd(SCN)_4]^{2-}$ from acidic solutions by cation-chelation mechanism is also possible because the acid concentration needed for palladium extraction is less than that reported for its extraction into ethyl acetate (21). Fig. 4 indicating the distribution ratio as a function of palladium concentration supports that $[Pd(SCN)_4]^{2-}$ is sorbed through cation-chelation mechanism from acidic solution.

The spectra of 0.1 M HCl solution containing Pd(II) (9.4×10^{-5} M) and 0.0125 M thiocyanate ions in ultraviolet region were recorded before and after the sorption onto PUF. The spectra showed characteristic maxima at 220, 278, and 308 nm before sorption and 234, 278, and 308 nm after sorption. The absorbance at 234 nm has been assigned to $PdCl_2$ and at 220 and 278 nm to $PdCl_4$ (22) and at 308 nm to $[Pd(SCN)_4]^{-2}$ (20).

The value of $E = 12.3 \pm 0.35$ kJ mol^{-1} computed from D-R isotherm indicates chemical sorption based on ion exchange. The negative value of ΔH and ΔG also confirm exothermic and spontaneous nature of chemisorption. The exothermic nature of sorption may be explained in terms of solvation type bond formation between metal ion and solid surface based on hydrogen and or ionic bonding comprising ion-exchange or ion-association interactions (23–24).

CONCLUSIONS

PUF is an economical and effective sorbent for palladium-thiocyanate complex. Its accumulation onto PUF is obeyed by Freundlich and D-R isotherms. The negative values of ΔH and ΔG indicate exothermic and spontaneous nature of Pd-SCN sorption respectively. Thiourea, cyanide, thiosulphate, molybdate, nitrite, and Fe(II) reduce the sorption significantly.

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Received December 30, 1999
Revised May 2000

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