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Adsorption Isotherms and Thermodynamic Profile of Co(II)–SCN Complex Uptake on Polyurethane Foam

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ABSTRACT

Sorption of cobalt(II)–thiocyanate complex onto polyurethane foam (PUF) has been investigated in detail with respect to the equilibrating time between Co(II)–thiocyanate complex in solution and foam, and concentrations of cobalt(II) and sorbent. The sorption was optimized with respect to the composition of electrolyte. Maximum sorption has been achieved from 0.1 M HCl solution containing 0.5 M SCN after 10 minutes of shaking time. The kinetics and thermodynamics of sorption are studied in detail. The kinetics follow a first-order rate equation with the rate constant, k, equal to 9.57×10^{-2} min.$^{-1}$ The variation of equilibrium constant K_c with temperature (15–50°C) yields values of $\Delta H = -64 \pm 4.6$ kJ·mol^{-1}, $\Delta S = -192.6 \pm 15.6$ J·mol^{-1}·K^{-1}, and $\Delta G = -8.71$ kJ·mol^{-1} at 298 K. The sorption of Co(II)–thiocyanate onto PUF in the presence of common anions and cations has also been measured. The sorption data studied in the concentration range of Co(II) 1.12×10^{-4} to 1.20×10^{-3} M follow Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms. Freundlich parameters $1/n = 0.35 \pm 0.02$ and $A = 0.85 \pm 0.2$ mmol·g^{-1}, Langmuir constants $Q = (5.54 \pm 0.12) \times 10^{-5}$ mol·g^{-1} and $b = (3.55 \pm 0.74) \times 10^{4}$ dm^{3}·mol^{-1} and D–R isotherms $\beta = -0.002999 \pm 0.000189$ kJ^{2}·mol^{-2}, $C_m = 10.66 \pm 0.16 \times 10^{-4}$ mol·g^{-1} and $E = 12.9 \pm 0.4$ kJ·mol^{-1} have been evaluated. The possible sorption mechanism of cobalt–thiocyanate complex onto PUF is also discussed.

INTRODUCTION

Polyurethane foam has been widely used for the extraction of inorganic and organic species from aqueous solutions (1). Bowen (2) has demonstrated the

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potential of solid flexible polyurethane foam as an extractant for a number of substances from aqueous solutions. Considerable efforts have been directed toward the use of polyurethane foam after special treatment with suitable reagents for the separation and preconcentration of metal ions. The application of thiocyanate as a complexing agent has been proved to be a sound basis (3) for the extraction of metal ions including Group VIII elements (4–7). A large number of studies have been carried out to optimize the experimental conditions for the separation and preconcentration of metal ions on polyurethane foam (8–14) and to study the mechanism of the distribution of metal–thiocyanate complexes between polyurethane foam and aqueous solutions (1). The sorption of many divalent metal ions from potassium thiocyanate solutions on polyether-type PUF has been reported (15).

Cobalt, its compounds, and alloys are important from industrial and, technological points of view. They exhibit excellent wear, oxidation, and corrosion resistance and magnetic properties under extreme corrosive conditions and at elevated temperatures. They are used in special alloys in high-speed and high-temperature steels, in making cutting tools and magnets, in jet engines and ordnance products, and as a catalyst for hydrocarbon refining. Cobalt compounds are used in pigments, paints, driers, and ceramic frits. ^{60}Co has applications in radiology, industry, and medicine (16). Cobalt is an important element from fuel processing and waste disposal points of view as well, and ^{60}Co is one of the major radionuclides present in radioactive waste from nuclear installations. Therefore this study was undertaken to demonstrate the potential of polyurethane foam to be used for the separation, preconcentration, and removal of cobalt in the presence of thiocyanate ions.

This paper presents a study of the different parameters which control the sorption of cobalt(II)–thiocyanate complex onto polyurethane and of its kinetic and thermodynamic behaviors. The aim is to acquire better understanding of the mechanism of the processes involved in bringing cobalt–thiocyanate complexes from bulk solution to the surface of the foam.

EXPERIMENTAL

Reagents and Radiotracer

All the reagents used were of analytical or equivalent grade. The solutions were made in doubly distilled deionized water.

^{60}Co radiotracer ($t_{1/2}$ = 5.27 years) was made by irradiating spectroscopic-grade cobalt metal (Johnson & Matthey) in the PARR-1 research reactor of this institute at a flux density of 4×10^{13} n·cm^{-2}·s^{-1}. It was then dissolved in concentrated hydrochloric acid solution, evaporated to dryness, and stored in 0.1 M HCl solution. The concentration of cobalt stock solution was 5.98×10^{-3} M. The radiochemical and radionuclidic purity of the tracer was checked by gamma spectroscopy using a 4k series 85 Canberra multichannel analyzer coupled with a 25 cm^3 Ge(Li) detector.

PUF Plug Preparation

Open pore polyether-type polyurethane foam (PUF) having a density of 22 mg·cm^{-3} was obtained commercially from M/s Diamond Rubber Mills, Karachi, Pakistan and cut into cylindrical plugs of 5 mm diameter and 1 cm length with a borer. The foam plugs were soaked in acetone for 30 minutes to dissolve organic impurities and to open pore cells. The soaked plugs were pressed between filter paper and dried at 80°C. The dried foam plugs were squeezed in 2 M HCl solution to remove inorganic impurities and washed with deionized water several times until washings were acid-free and neutral. The washed foam was then dried at 80°C. The dried foam was squeezed again with acetone for 30 minutes, soaked between filter paper, dried at 80°C, and then stored for further use.

Procedure

A radiometric method was used to evaluate the distribution of metal complex between the liquid and solid phases. A distribution ratio (K_d) for the sorption of cobalt was calculated from the ratio of the concentration of cobalt in foam to its concentration left in solution with units of cm$^3 \cdot$ g^{-1} although a true equilibrium may not have been reached. The amount sorbed by the foam was measured by comparing radioactivity of equal aliquots of solution before (A_0) and after sorption (A_F). Four cm^3 electrolyte containing a known concentration of cobalt was agitated with PUF (~38.5 mg), usually for 5 minutes, using a wrist-action Griffin and George shaker. The solid concentration of PUF was kept constant except when specified otherwise. After shaking, a 0.5-cm^3 aliquot was withdrawn and assayed radiometrically on a gross gamma Tennelec counter with a well-type NaI(Tl) crystal. The percent sorbed activity of ^{60}Co on PUF and distribution ratio (K_d) were calculated using the equations

$$\%\ \text{Sorption} = \frac{A_0 - A_F}{A_0} \times 100 \tag{1}$$

$$K_d = \frac{A_0 - A_F}{A_F} \times \frac{V}{W} \tag{2}$$

where V is the volume of electrolyte agitated with W grams of PUF. Sufficient ^{60}Co tracer was added to yield a count rate of at least 81,500 cpm/cm^3 for a 4.5-cm^3 sample contained in a shaking vial of 15 mm internal diameter. The sorption measurements were carried out at 23 ± 2°C unless another temperature is specified. The results of K_d and percent sorption are the averages of at least three independent measurements. The precision in most cases is ±3%.

RESULTS AND DISCUSSION

Studies were initially carried out using dilute solutions of HCl, HNO_3, and $HClO_4$ to select the most suitable electrolyte for cobalt sorption onto polyurethane foam. The concentration of cobalt was kept at 3.75×10^{-5} M except where specified otherwise. The solid concentration of foam was the same as mentioned earlier, and 5 minutes shaking time was selected arbitrarily. The results are given in Table 1. It is evident from this table that all three acids give almost the same order of magnitude of sorption. In the case of nitric and perchloric acids, the concentration does not change the K_d values. However, in general the sorption increases with an increase in the concentration of hydrochloric acid used. For subsequent experiments, 0.1 M hydrochloric acid medium was chosen because maximum sorption was obtained from this electrolyte. The sorption of cobalt–thiocyanate was also investigated from varied concentrations of hydrochloric acid in the range of 0.001 to 0.5 M in the presence of a fixed concentration of thiocyanate (0.5 M). The results are shown in Table 1. In the presence of a fixed amount of thiocyanate the sorption of cobalt–thiocyanate complex increases with increasing concentration of hydrochloric acid and attains a maximum value at 0.1 M, thereafter it decreases with any further increase in the acid concentration. A decrease in the absorbance of the thiocyanate complex of ruthenium is observed while varying the hydrochloric acid concentration from 0.1 to 0.5 M and monitoring it spectrophotometrically (7). This decrease in the degree of extraction of Ru with increasing HCl concentration up to 0.2 M is probably due to the forma-

TABLE 1
Uptake of Cobalt–Thiocyanate Complex onto PUF from Acidic Solutions of Different Concentrations

Acid	Concentration (M)	K_d ($cm^3 \cdot g^{-1}$)	Percent adsorption
HNO_3	0.001	2035	95.0
	0.01	2559	96.0
	0.1	2526	96.0
$HClO_4$	0.001	1938	94.8
	0.01	2008	95.0
	0.1	2062	95.1
HCl	0.001	1861	94.6
	0.01	1721	94.2
	0.05	2066	95.2
	0.07	2009	95.5
	0.1	3108	96.7
	0.2	1664	94.0
	0.5	1510	93.5

tion and subsequent extraction of thiocyanic acid (7). A decrease in the extraction of ruthenium–thiocyanate was observed when the HCl concentration was varied from 0.1 to 0.5 M. A similar trend was also witnessed in the case of cobalt–thiocyanate sorption on PUF. The concentrated mineral acid may decompose thiocyanate solution (4), therefore, a maximum 0.1 M HCl solution was used because it was found to be optimum for cobalt–thiocyanate sorption onto the PUF surface.

The effect of the concentration of thiocyanate was examined in the 0.1 to 0.5 M range from 0.1 M hydrochloric acid solution using 5 minutes shaking time and keeping the same concentration of cobalt and PUF constant as mentioned before. The results are depicted in Fig. 1. The sorption increased steeply with an increase in thiocyanate concentration up to 0.4 M from $K_d = {\sim}55$ to ${\sim}842\ \mathrm{cm}^3 \cdot \mathrm{g}^{-1}$, corresponding to a sorption of 35 to 89%. However, in the presence of 0.5 M thiocyanate a substantial rise in the distribution ratio was observed. Therefore, 0.5 M thiocyanate concentration was used for further measurements; solubility problems started to occur beyond this value, so the thiocyanate concentration was not increased above the 0.5 M level. To prevent the decomposition (17) and trimerization (18) of thiocyanic acid resulting in the formation of 5-amino-1,2,4-dithiazole-3-thione, low

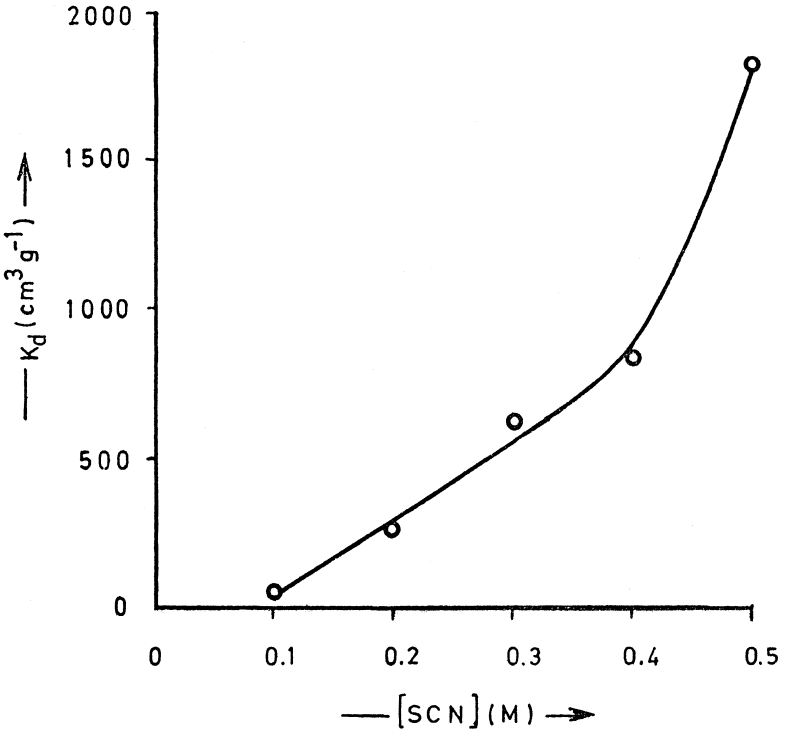

FIG. 1 The influence of sodium thiocyanate on the distribution ratio (K_d) of cobalt (3.66×10^{-5} M) from 0.1 M hydrochloric acid solution.

concentrations of up to 0.5 M of thiocyanic acid were used. A sharp increase in the extraction of iridium was also noticed when the concentration of thiocyanate ions was increased (4).

The influence of polyurethane foam concentration (solid) on the sorption of the cobalt–thiocyanate complex was also investigated with 0.1 M hydrochloric acid using 5 minutes of agitation time in the 9.63 to 77 mg/cm^3 range. The results are presented graphically in Fig. 2. Cobalt–thiocyanate sorption around $\geq$96% was noticed while using 38.5 mg of PUF. Therefore, in further experiments the same amount of PUF was used.

The kinetics of cobalt sorption in the presence of thiocyanate ions (0.5 M) from 0.1 M HCl sorption was studied in the range of 1 to 60 minutes shaking time. The results were subjected to the Morris–Weber equation

$$q_\mathrm{t} = k_\mathrm{d}\sqrt{t} \tag{3}$$

where q_t (mol·g^{-1}) is the amount of cobalt–thiocyanate complex sorbed at times t (minutes) and k_d is the rate constant of intraparticle transport (mol·g^{-1}·min$^{-1/2}$ Moreover, the kinetic data were also evaluated using the

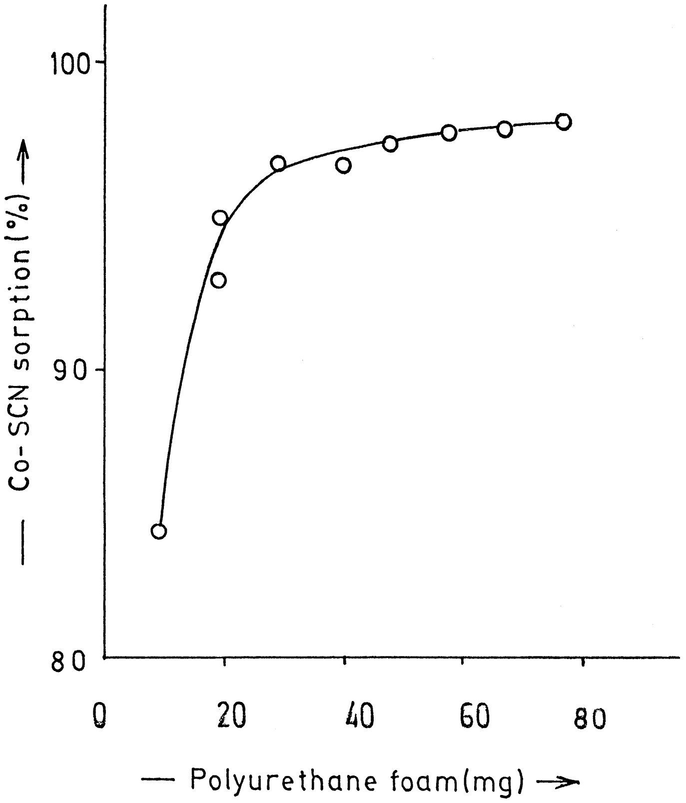

FIG. 2 Percent sorption of cobalt (3.66 × 10^{-5} M) onto PUF from 0.1 M hydrochloric acid containing 0.5 M sodium thiocyanate as a function of solid foam concentration.

Lagergren equation

$$\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \tag{4}$$

where q_e is the concentration of cobalt–thiocyanate complex sorbed at equilibrium and k is the overall rate constant. Plots for the Morris–Weber and Lagergren equations are shown in Fig. 3. The diffusion rate is rapid in the initial stages, and slows down with the passage of time. The value of k_d in the initial stage up to 5 minutes is 42 μmol·g^{-1}·min$^{-1/2}$, which becomes 3.5 μmol·g^{-1}·min$^{-1/2}$ beyond 1.1 minutes of agitation time. These values of k_d were computed from the two distinct slopes of the Morris–Weber plot shown in Fig. 3. The change in the slope may be due to the existence of different sized pores.

The sorption of the cobalt–thiocyanate complex follows the Lagergren equation over the entire range of agitation time explored. From the slope of this plot shown in Fig. 3, the value of first-order rate constant, k, was evaluated to be 9.57×10^{-2} min^{-1}. The use of nonequilibrium conditions makes this method more practical since only a small amount of the test element is left in the liquid phase and the time needed (5 minutes) is far less than the minimum of 1 hour required to establish equilibrium for the sorption of thiocyanate complexes of zinc onto PUF (19).

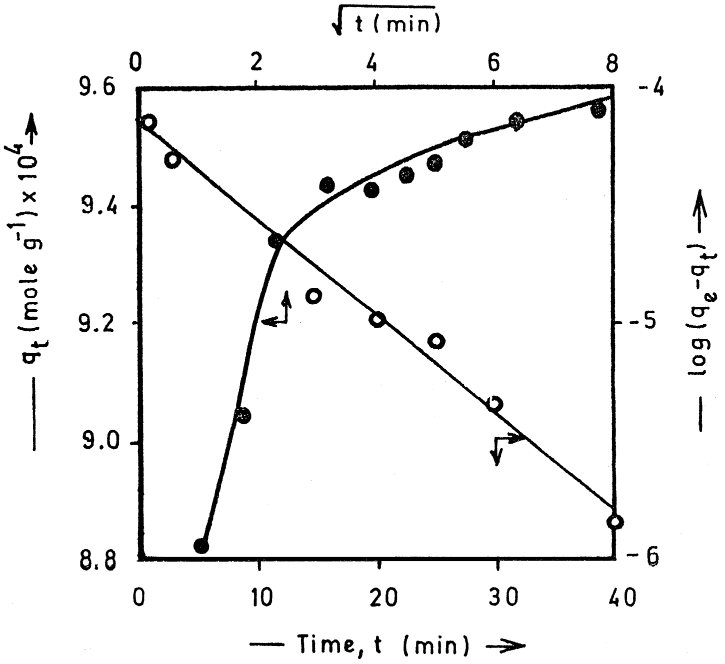

FIG. 3 The sorption of cobalt (3.66×10^{-5} M) onto PUF from 0.1 M hydrochloric acid in the presence of 0.5 M sodium thiocyanate as a function of agitation time.

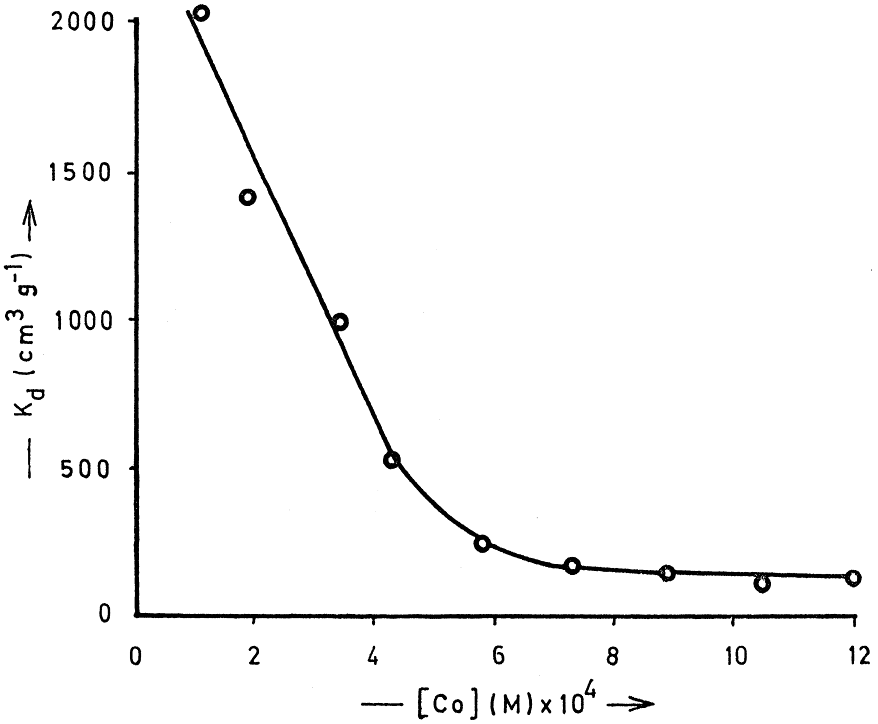

FIG. 4 The relationship between the distribution ratio (K_d) of cobalt (3.66×10^{-5} M) onto PUF from 0.1 M HCl + 0.5 M sodium thiocyanate solution and its own concentration.

Another parameter which influences the sorption of cobalt on PUF is its own concentration. The concentration of cobalt was varied over tenfold from 1.1×10^{-4} to 1.2×10^{-3} M from a 0.1 M HCl solution containing 0.5 M thiocyanate ions using 5 minutes of shaking time and 38.5 mg of PUF. The results are recorded in Fig. 4. The distribution ratio (K_d) decreases with an increase in the concentration of cobalt. A similar trend was noticed when the sorption of palladium–thiocyanate complex on PUF was studied while varying the concentration of palladium (20). The sorption data were evaluated by different sorption isotherms, namely Langmuir, Freundlich, and Dubinin–Radushkevich (D–R). The Langmuir equation was tested in the following form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{5}$$

where C_e is the cobalt–thiocyanate concentration at equilibrium in solution (M), C_{ads} is the sorbed concentration ($mol \cdot g^{-1}$), and Q and b are constants related to the sorption capacity and energy. A plot of C_e/C_{ads} vs C_e, shown in Fig. 5, is linear throughout the entire concentration range of cobalt investigated. From the slope and intercept the values of Q and b for this sorption system on PUF have been evaluated to be $(5.54 \pm 0.12) \times 10^{-3}$ $mol \cdot g^{-1}$ and $(3.55 \pm 0.74) \times 10^4$ $dm^3 \cdot mol^{-1}$. The sorption capacity can be compared with the value of 0.06 $mmol \cdot g^{-1}$ for Hg(II) (2) from 0.2 M HCl solution on PUF.

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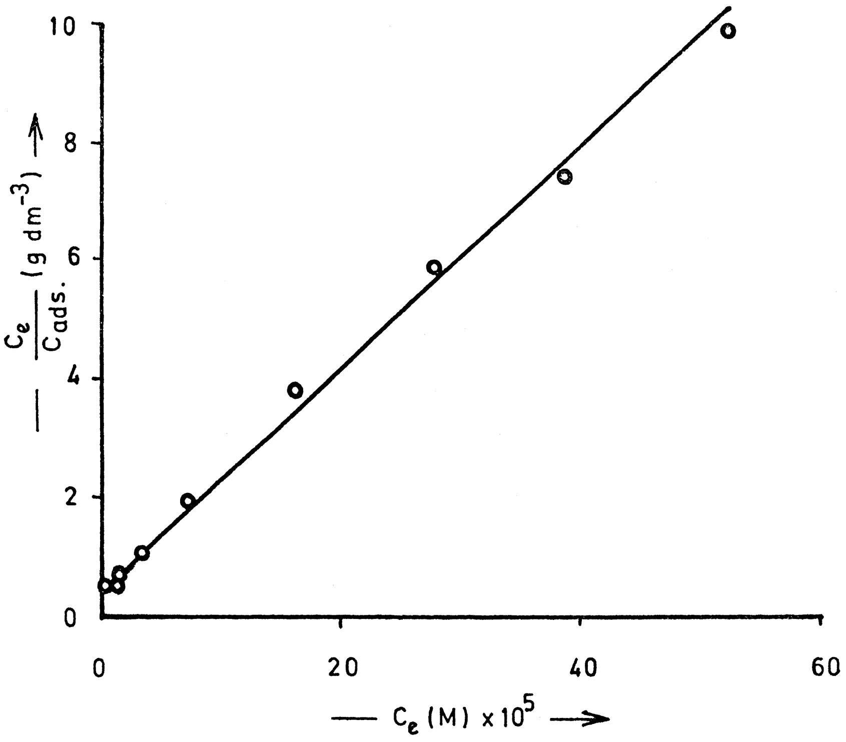

FIG. 5 The Langmuir sorption isotherm of cobalt–thiocyanate complex onto PUF.

The sorption data were also compared by Freundlich equation in the following form:

$$\log C_{\mathrm{ads}} = \log A + \frac{1}{n} \log C_{\mathrm{e}} \qquad (6)$$

where A and $1/n$ are Freundlich parameters. The plot of $\log C_{\mathrm{ads}}$ vs $\log C_{\mathrm{e}}$, shown in Fig. 6, is a straight line. The sorption data follow the Freundlich

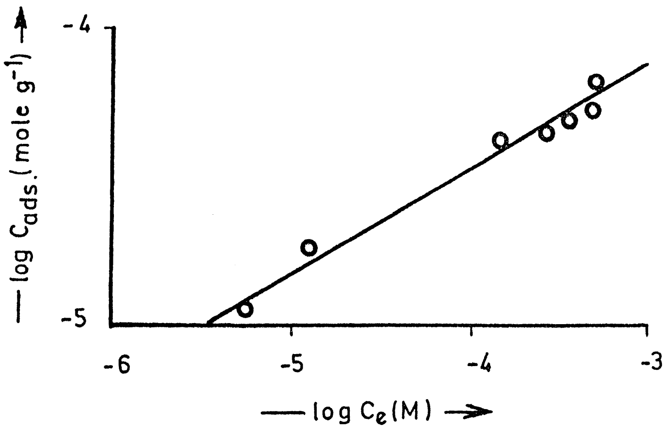

FIG. 6 The Freundlich sorption isotherm of cobalt–thiocyanate complex onto PUF.

sorption isotherm as well. The values of A and $1/n$ were computed from the intercept and slope of the plot shown in Fig. 6. They are $A = 0.85 \pm 0.2\ \text{mmol}\cdot\text{g}^{-1}$ and of $1/n = 0.35 \pm 0.02$. These values of A and $1/n$ can be compared with the corresponding values evaluated for the Hg–SCN complex sorbed onto PUF; i.e., $A = 3.86 \pm 0.9\ \text{mmol}\cdot\text{g}^{-1}$ and $1/n = 0.44 \pm 0.02$ (21).

The Dubinin–Radushkevich (D–R) isotherm was tested in the following linear form:

$$\ln C_{\text{ads}} = \ln X_{\text{m}} - \beta\varepsilon^2 \tag{7}$$

where X_{m} is the maximum sorption, β is a constant related to energy, and ε is the Polanyi potential:

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_{\text{e}}}\right) \tag{8}$$

where R is a gas constant in $\text{kJ}\cdot\text{mol}^{-1}$ and T is the temperature in Kelvin. Ln C_{ads} is plotted against ε^2 in Fig. 7 and yields a straight line. This shows that sorption data can also be tested using the D–R isotherm. The values of X_{m} $[(1.66 \pm 0.16) \times 10^{-4}\ \text{mol}\cdot\text{g}^{-1}]$ and β $[-0.002999 \pm 0.000189\ \text{kJ}^2\cdot\text{mol}^{-2}]$ have been computed from the intercept and slope of the plots shown in Fig. 7.

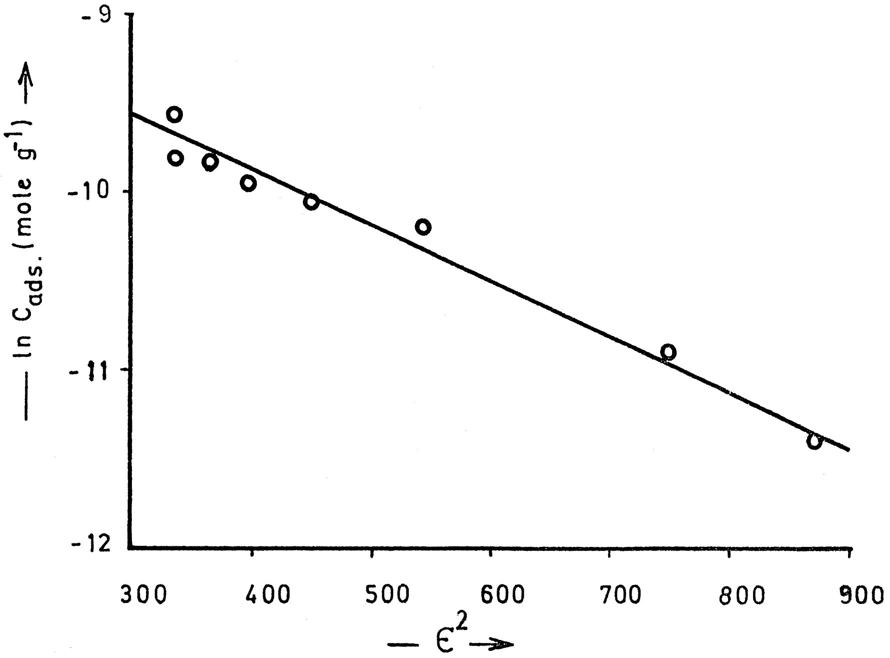

FIG. 7 The Dubinin–Radushkevich (D-R) isotherm of cobalt–thiocyanate complex onto PUF.

The value of sorption energy, E, can be correlated to β by using the following relationship:

$$E = 1/\sqrt{-2\beta} \tag{9}$$

The value of E was found to be 12.9 ± 0.4 $\text{kJ}\cdot\text{mol}^{-1}$; this is close to 13.3 $\text{kJ}\cdot\text{mol}^{-1}$ found for the cobalt (22) sorption system on PUF loaded with thenoyltrifluoroacetone (HTTA). A value of $E = 12.3 \pm 0.26\ \text{kJ}\cdot\text{mol}^{-1}$ has been estimated for the Hg–SCN complex sorbed onto PUF (21). The correlation factor (γ) for all the three sorption isotherms for this system worked out to be $0.988 < \gamma < 0.998$. However, Kinniburg (23) suggested that nonlinear regression allows for a decrease in statistical bias in a linearized procedure.

The thermodynamics of cobalt–thiocyanate complex sorption onto polyurethane foam from 0.1 M hydrochloric acid solution was studied from 15 to 50°C. To plot log K_c vs $1/T$ (K), $K_c = F_e/(1 - F_e)$ at different temperatures was calculated, where F_e is the fraction sorbed at equilibrium. A plot of log K_c vs $1/T$, shown in Fig. 8, is a straight line. Values of ΔH, ΔS, and ΔG were estimated from the following relationships:

$$\begin{aligned} \log K_c &= \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \\ \Delta G &= -RT \ln K_c \end{aligned} \tag{10}$$

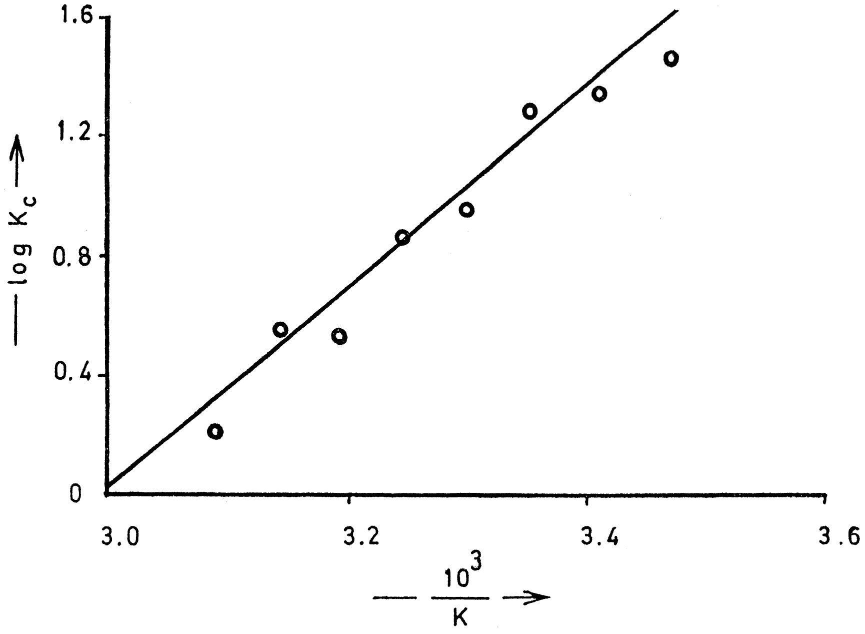

FIG. 8 The variation of equilibrium constant (K_c) of Co–SCN complex uptake onto PUF with temperature.

Their values are $\Delta H = -64 \pm 4.6$ kJ·mol^{-1}, $\Delta S = -192 \pm 15.6$ J·mol^{-1}·K^{-1}, and $\Delta G = -8.71$ kJ·mol^{-1} at 298 K. The correlation factor (γ) for linear regression analysis was found to be 0.9839. The negative values of ΔH and ΔG indicate an exothermic and a spontaneous nature of sorption, respectively.

The influence of common anions and cations on the sorption was also examined. The anions were added as their sodium or potassium salts whereas the cations were included mostly as their chlorides or nitrates. The concentration of these anions and cations was kept at 10 mg/cm^3. The results are listed in Tables 2 and 3. Ba(II), Cl, and Br enhance the sorption whereas EDTA, citrate, Fe(III), Hg(II), Fe(II), cyanide, oxalate, and nitrite reduce the sorption significantly, $\leq 22\%$. These ions cause interference in the sorption of the cobalt–thiocyanate complex on PUF. Ions which tend to reduce the sorption need to be removed from the sorptive solution to avoid low yields. The low sorption in the presence of anions can be visualized in terms of the stronger complexes of these ions with cobalt(II) (24) as compared to their thiocyanate complexes and of cations in the formation of stronger complexes of thiocyanate of metal ions compared to cobalt(II) (25).

TABLE 2
Influence of Anions on the Uptake of Cobalt–Thiocyanate Complex onto PUF from 0.1 M HCl Solution

Anion	K_d (cm^3·g^{-1})	% Adsorption
Nil	3108	96.8
Bromide	7836	98.7
Chloride	7054	98.6
Nitrate	3249	96.9
Phosphate	3246	96.6
Perchlorate	2964	96.6
Iodide	2422	95.9
Thiourea	2248	95.6
Sulfate	2099	95.3
Ascorbate	2073	95.2
Thiosulfate	1942	94.9
Fluoride	1857	94.7
Tartrate	760	87.9
Nitrite	22.1	17.4
Oxalate	11.7	10.1
Cyanide	5.7	5.2
EDTA	<1	<1
Citrate	<1	<1

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TABLE 3
Effect of Cations on the Sorption of Cobalt–Thiocyanate onto PUF from 0.1 M HCl Solution

Cation	K_d ($cm^3 \cdot g^{-1}$)	% Adsorption
Nil	3108	96.8
Ba(II)	9494	99.9
Li(I)	2534	96.0
Mg(II)	2419	95.8
Ce(III)	2117	95.3
Sr(II)	1727	94.3
Cr(III)	1241	92.3
K(I)	1176	91.9
Mn(II)	964	90.3
Mo(VI)	962	90.2
Ni(II)	823	88.8
Al(III)	718	87.4
Zr(IV)	550	84.1
Cd(II)	136	56.7
Fe(II)	13.9	11.6
Hg(II)	8.4	7.5
Fe(III)	5.7	5.3

Sorption Mechanism

Several possible mechanisms have been proposed by different workers for the sorption of metal ions onto polyether-type PUF from aqueous solutions such as ligand addition or exchange (26), cation chelation (27), ion-association (28), and surface sorption (2). The dominant one will depend upon the conditions of sorption and on the nature of the species sorbed. Co(II)–SCN is sorbed on PUF as a blue-colored complex. The foam with the Co–SCN complex was washed with deionized water by squeezing it to remove the free chloride, thiocyanate, and Co(II) ions present in the foam and pressing it between filter paper for drying. This dried foam was shaken with different organic solvents for dissolution of the blue Co–SCN complex sorbed on PUF. It was observed that the complex was not soluble in chloroform, benzene, diethyl ether, dioxane, and carbon tetrachloride, but decomposed in ethanol. However, it was quite soluble in acetone and stable for 2 days. The absorption spectra of the complex in acetone is shown in Fig. 9 with a λ_{max} at 620 nm. The sorption process and absorption spectra reveal that:

1. The color of the aqueous solution before equilibrium is light pink and transparent.

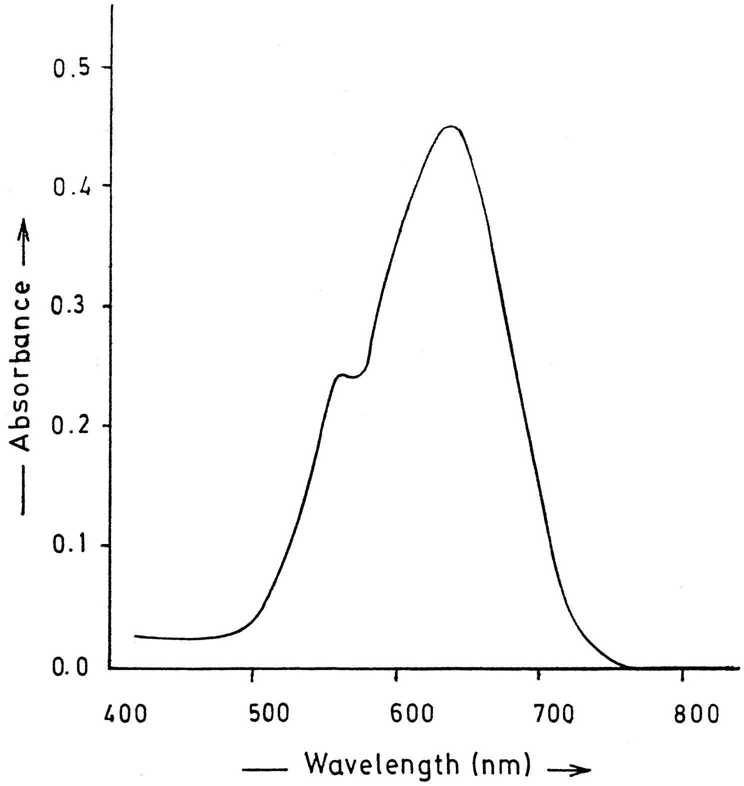
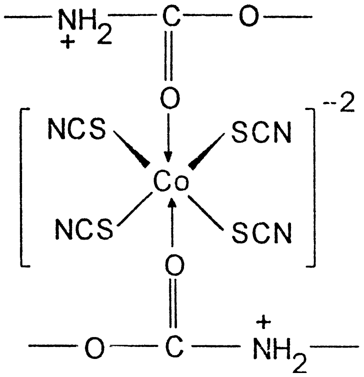


FIG. 9 The absorption spectra of Co–SCN complex after sorption onto PUF in acetone.

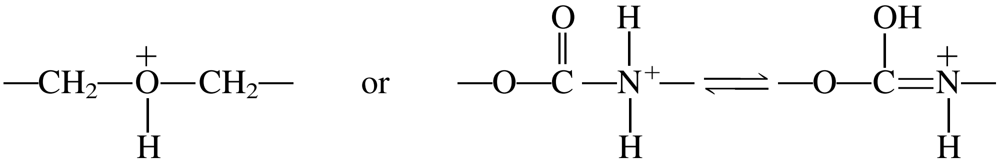
2. The sorbed complex is blue, soluble, and stable in acetone, decomposes in ethanol, and is insoluble in other solvents.
3. The absorption spectra of cobalt in acetone is similar to the octahedral complex but in aqueous solution it is tetrahedral (29).
4. The exothermic nature of the sorption process and a decrease in the entropy indicate that the Co(II)–SCN complex formed in aqueous solution becomes more ordered during accumulation on PUF.

The absorption spectra of the tetrahedral complex of cobalt(II) in the excited state shows a well-defined doublet, but octahedral complexes show a singlet peak. The absorption of the cobalt–thiocyanate complex sorbed on PUF is blue whereas in aqueous solution its color is pink, indicating that the coordinating sites of the PUF are also participating in the adsorption process of the Co–SCN complex and change the geometry of Co(II) metal ions from tetrahedral to octahedral. The solubility in acetone compared to diethyl ether indicates that the carbonyl group of acetone also takes part in the complex formation rather than the oxygen group of the ether.

The main functional groups of PUF are the carbonyl group of urethane and oxygen atoms of the ether group. The solubility indicates that the carbonyl group of the urethane also interacts directly with the Co(II) ions and changes the geometrical configuration from tetrahedral to octahedral. The most probable species to be sorbed is of the $[Co(SCN)_4{\cdot}2D]^{-2}$ type, where D is the carbonyl group of the PUF. This probability is further supported by Mössbauer studies of $Fe(SCN)_3{\cdot}3D$ complexes sorbed on PUF (30). The geometric configuration of the sorbed complex of Co(II)–SCN onto PU foam is given as



Trans addition of the carbonyl group of PUF stabilizes the sorbed complex as compared to cis addition, and hence the absorption is shifted toward lower energy. The existence of anion-exchange sites arises due to the tendency of both the nitrogen atom of the urethane linkage and the oxygen atom of ether to accept protons to give



$$—CH_2—\overset{+}{\underset{H}{\underset{|}{O}}}—CH_2— \quad \text{or} \quad —O—\overset{O}{\overset{\|}{C}}—\overset{H}{\overset{|}{\underset{H}{\underset{|}{N^+}}}}— \rightleftharpoons —O—\overset{OH}{\overset{|}{C}}=\overset{+}{\underset{H}{\underset{|}{N}}}—$$

and hence polyether-type PUF will have anion-exchange sites of various strengths. Charge neutralization is possible due to the interaction of the protonated nitrogen atoms of PUF with the $[Co(SCN)_4{\cdot}2D]^{-2}$ complex. Further studies on measurement of the magnetic susceptibility of the Co(II)–SCN complex are needed to confirm the geometrical configuration of the complex sorbed and the proposed sorption mechanism.

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