J. Chem. Eng. Data **2004,** *49,* 1279−1284

Ion-Exchange Equilibria for $Au(CN)_2^-/Cl^-$, $Au(CN)_2^-/SCN^-$, and SCN^-/Cl^- in Aqueous Solution at 303 K

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Ion-exchange equilibria are presented for $Au(CN)_2^-/Cl^-$, $Au(CN)_2^-/SCN^-$, and SCN^-/Cl^- in aqueous solution at 303 K using Purolite A500 as the ion exchanger. The effect of the total solution concentration on the ion-exchange isotherm for each binary system is considered. The experimental data are correlated using the law of mass action, modified with activity coefficients, to determine the equilibrium constant for each binary system. It is shown that the isotherm for each binary system is independent of the total solution concentration, within the range of concentration considered. The selectivity of Purolite A500 for a given ion increases in the order $Cl^- < SCN^- < Au(CN)_2^-$. The fitted values of the equilibrium constants are in qualitative agreement with the selectivity of the resin for the various ionic species.

Introduction

Ion-exchange resins have been used extensively in the fields of agriculture, environment, water softening, and wastewater treatment.[1,2] More recently, ion-exchange resins have been considered in the mineral processing industry for the recovery of gold.[3,4] Cyanidation is the principal means by which gold is recovered from ore bodies in commercial mining operations. This process leads to the formation of leach solutions in which the gold is present at very low concentrations (<10 ppm) in the form of the gold cyanide complex $Au(CN)_2^-$. In the carbon-in-pulp process,[5] $Au(CN)_2^-$ is recovered from the leach solution in a more concentrated form by adsorption onto activated carbon.

A variety of ion-exchange resins can also be used to recover $Au(CN)_2^-$ and other metal−cyanide complexes.[6−8] The elution or stripping of $Au(CN)_2^-$ from the resin is typically carried out with an excess concentration of a counterion such as SCN^- (thiocyanate) or $Zn(CN)_4^{2-}$. Although the use of ion-exchange resins has been proposed as an alternative to carbon in gold processing, the technology has yet to be implemented on a large scale in commercial mining operations. This is due to a lack of fundamental data required in the design and scale up of industrial ion-exchange processes for the recovery of gold. The equilibrium distribution of ions between the resin and solution phases forms the basis for the design of such processes.

In this paper, we present binary ion-exchange equilibria for $Au(CN)_2^-/Cl^-$, $Au(CN)_2^-/SCN^-$, and SCN^-/Cl^- in aqueous media at 303 K using commercially available Purolite A500 as the ion exchanger. These systems are relevant to an ion-exchange process in which $Au(CN)_2^-$ is loaded onto the Cl^- form of the ion exchanger, followed by the elution of $Au(CN)_2^-$ using SCN^- as the counterion and the subsequent regeneration of the resin to the Cl^- form. The experimental data are correlated using the law of mass action modified with activity coefficients to determine the equilibrium constant for each binary system.

Table 1. Properties of Purolite A500

property	description
appearance	spherical particles
type of matrix	styrene divinyl benzene
functional structure	$R(CH)_3N^+$
effective size	0.50 mm (average)
moisture content, as supplied	53−58%
pH range	0−14
maximum operating temperature	100 °C
total exchange capacity	1.3 eq/L

Experimental Section

Chemicals. Potassium aurocyanide (99%) and potassium thiocyanate (99%) were supplied by EBS and Associates and Sigma-Aldrich, respectively. The anion-exchange resin, Purolite A500, was supplied by Purolite International. Purolite A500 is a type 1 strong base, divinylbenzene, macroporous resin in the chloride form. The principal properties of the ion-exchange resin are listed in Table 1. Prior to use, the resin was soaked in distilled water for 24 h to stabilize resin swelling. Hydrated ferric nitrate (>98%), used in the determination of SCN^- in solution, was supplied by Asia Pacific Specialty Chemicals. All stock solutions were prepared by volume (1000 ± 0.4 mL) with distilled water. The accuracy of weighing was ±0.0001 g.

Procedure. Ion-exchange equilibria for the $Au(CN)_2^-/Cl^-$ and SCN^-/Cl^- binary systems were determined by contacting the Cl^- form of the resin with a stock solution containing a fixed concentration of $Au(CN)_2^-$ or SCN^-. A 5 ± 0.2 mL (wet and settled volume) sample of the resin was measured and filtered under vacuum to remove excess moisture. The resin was placed in a 250-mL glass container followed by the addition of 100 ± 1 mL of the relevant stock solution. The glass container was sealed and placed in a temperature-controlled orbital shaker (Paton Scientific, 01-2116) for which the temperature was maintained to ±0.5 K. The rotation speed of the orbital shaker was set at 200 orbits/min in all experiments. A duration of 8 h was found to be sufficient for the attainment of equilibrium between the resin and solution phases for all of the binary systems considered in this study.

After equilibrium was established, the solution phase was separated from the resin phase and analyzed for

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10.1021/je034247y CCC: $27.50

$Au(CN)_2^-$ or SCN^-. From a knowledge of the change in concentration of the anion in the solution phase, it was possible to calculate the composition of $Au(CN)_2^-$ or SCN^- on the resin phase at equilibrium. A mass balance was used to determine the equilibrium compositions of the resin and solution phases with respect to Cl^-. The concentration of $Au(CN)_2^-$ in solution was determined by analysis for Au using inductively coupled plasma−atomic emission spectroscopy. The standard uncertainty of the analysis was ±1%. The analysis for SCN^- in solution was carried out in accordance with ASTM D 4193-95. This standard method is based on the reaction of SCN^- with the ferric ion at pH < 2 to form a colored complex. The intensity of the solution is determined by measuring its absorbance at 460 nm using a UV−vis spectrophotometer. The uncertainty of the analysis for SCN^- was ±5%.

The partially loaded resin was then contacted with a fresh 100-mL quantity of the stock solution and allowed to reach equilibrium. The process of draining the solution phase at equilibrium, followed by the addition of a fresh quantity of stock solution to the same sample of resin, was repeated until no further loading of $Au(CN)_2^-$ or SCN^- occurred on the resin. This condition was confirmed when the change in the concentration of the anion in the solution phase was found to be negligible.

Ion-exchange equilibria for the $Au(CN)_2^-/SCN^-$ binary system were determined using resin that had been fully loaded with SCN^-. For this binary system, a 5-mL sample of the SCN^- form of the resin was repeatedly contacted, in the manner described above, with 100 mL of a stock solution containing a fixed concentration of $Au(CN)_2^-$.

By gradually loading the resin to capacity in the manner described, it was possible to construct an ion-exchange isotherm encompassing a wide range of composition for each phase. Ion-exchange equilibria are expressed in terms of equivalent ionic fractions for the solution and resin phases. (See eqs 3 and 4.) The experimental ionic fraction data that are reported represent the average of duplicate runs, with an uncertainty of ±5%.

The effect of the total solution concentration on the ion-exchange isotherms was determined by contacting the resin with stock solutions containing different total concentrations of the loading anion. For the $Au(CN)_2^-/Cl^-$ and $Au(CN)_2^-/SCN^-$ binary systems, ion-exchange equilibria were obtained with stock solutions containing $Au(CN)_2^-$ at concentrations of (0.0025, 0.0051, and 0.0066) M. In the case of the SCN^-/Cl^- binary system, stock solutions containing SCN^- at concentrations of (0.0086, 0.0172, and 0.0224) M were used.

Data Correlation

The replacement of ion A on the resin phase (r) with ion B from the solution phase (s) is governed by a reversible ion-exchange equation as follows:

$$\beta A_r^{\alpha-} + \alpha B_s^{\beta-} \leftrightarrow \beta A_s^{\alpha-} + \alpha B_r^{\beta-} \tag{1}$$

At equilibrium, the solution and resin phases are composed of both ions in proportions that reflect the selectivity of the resin. An equilibrium constant for the ion-exchange process in eq 1 can be defined in accordance with the law of mass action modified with activity coefficients:[9,10]

$$K_{AB} = \frac{(\gamma_A c_A)^\beta (\bar{\gamma}_B q_B)^\alpha}{(\bar{\gamma}_A q_A)^\beta (\gamma_B c_B)^\alpha} \tag{2}$$

where c_i is the molar concentration of ion i in the solution phase, q_i is the molar concentration of ion i in the resin phase, and K_{AB} refers to the equilibrium constant for B entering the resin phase and displacing A. The use of eq 2 to describe the equilibrium constant assumes that swelling-pressure effects are negligible.[11]

Table 2. Apparent Capacities of the Ion-Exchange Resin

system	apparent capacity/equiv L^{-1} [a]
$Au(CN)_2^-/Cl^-$	1.23
SCN^-/Cl^-	1.32
$Au(CN)_2^-/SCN^-$	1.34

[a] The capacity is measured with respect to the wet and settled volume of the resin.

Molar concentrations in the resin phase are here calculated with respect to the wet and settled volume of the ion-exchange resin. The activity coefficients of ion i in the solution phase and resin phase are denoted by γ_i and $\bar{\gamma}_i$, respectively. The molar concentration terms in eq 2 can be replaced by equivalent ionic fractions by employing the following relations:

$$x_i = \frac{z_i c_i}{N} \tag{3}$$

$$y_i = \frac{z_i q_i}{Q} \tag{4}$$

where x_i and y_i are the equivalent ionic fractions in the solution phase and resin phase, respectively, z_i is the valence of ion i, N is the total normality of exchanging ions in the solution phase, and Q is the capacity of the resin (equiv/L). Substituting eqs 3 and 4 into eq 2 and noting that $\alpha = \beta = 1$ for all species in this study leads to the following expression for the equilibrium constant:

$$K_{AB} = \frac{(\gamma_A x_A)(\bar{\gamma}_B y_B)}{(\bar{\gamma}_A y_A)(\gamma_B x_B)} \tag{5}$$

In the calculation of values of y_i using eq 4, the capacity of the resin was set at a value corresponding to the maximum amount of anion loaded onto a given form of the resin, as determined experimentally using the procedure described previously. The experimental values of the resin capacity obtained in this way are presented in Table 2. As such, these values represent the apparent capacity of the resin and agree closely with the manufacturer's specification of 1.3 equiv/L.

Strictly speaking, the individual ionic activity coefficients appearing in eq 5 cannot be determined experimentally. Kielland[12] has pointed out, however, that individual ionic activity coefficients in sufficiently dilute solutions may be calculated from an extended form of the Debye−Hückel limiting law as follows:

$$\log \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + B a_i \sqrt{I}} \tag{6}$$

$$I = \frac{1}{2}\sum_i z_i^2 c_i \tag{7}$$

where A and B are the Debye−Hückel parameters, a_i is the effective diameter of the hydrated ion, and I is the ionic strength of the solution phase in molar units. This semiempirical approach is often used to estimate mean ionic activity coefficients that are measurable. The Debye−Hückel parameters appearing in eq 6 are equivalent to

Table 3. Debye–Hückel Parameters for Aqueous Solutions at 303 K and Effective Hydrated Diameters of $Au(CN)_2^-$, SCN^-, and Cl^-

		$10^8 a_i$/cm		
A/(mol/L)$^{-1/2}$	10^{-7}B/(mol/L)$^{-1/2}$ cm^{-1}	$Au(CN)_2^-$	SCN^-	Cl^-
0.5161[a]	3.301[a]	4.5[b]	3.5[b]	3.0[b]

[a] Data are from Robinson and Stokes.[13] [b] Data are from Kielland.[12] The value for $Au(CN)_2^-$ is the lower limit of the range (4.5 to 7) suggested for organic ions.

those in the corresponding equation for the mean ionic activity coefficient and depend on temperature and the dielectric constant of the solvent.[13] The values of A, B, and a_i required in this study are listed in Table 3. Note that cations are also included in the summation in eq 7.

The individual ionic activity coefficients in the resin phase were also calculated using a semiempirical approach involving the Wilson equations formulated for vapor–liquid equilibria.[14] This method has been applied successfully in the correlation of binary ion-exchange equilibria for cationic systems.[15–17] The relevant equations for the exchange of ions A and B are

$$\ln \bar{\gamma}_A = 1 - \ln(y_A + y_B\Lambda_{AB}) - \frac{y_A}{y_A + y_B\Lambda_{AB}} - \frac{y_B\Lambda_{BA}}{y_B + y_A\Lambda_{BA}} \tag{8}$$

$$\ln \bar{\gamma}_B = 1 - \ln(y_B + y_A\Lambda_{BA}) - \frac{y_B}{y_B + y_A\Lambda_{BA}} - \frac{y_A\Lambda_{AB}}{y_A + y_B\Lambda_{AB}} \tag{9}$$

where Λ_{AB} and Λ_{BA} are the Wilson parameters.

In view of the fact that Λ_{AB} and Λ_{BA} are adjustable parameters, it was not possible to calculate the equilibrium constant directly from eq 5. Instead, K_{AB}, Λ_{AB}, and Λ_{BA} for each binary system were regressed from the experimental data (three-parameter regression). The working equation for this calculation procedure is obtained by rearranging eq 5 as follows:

$$y_B = \frac{K_{AB}\bar{\gamma}_A x_B \gamma_B}{K_{AB}\bar{\gamma}_A x_B \gamma_B + (1 - x_B)\gamma_A \bar{\gamma}_B} \tag{10}$$

Equation 10 was used to generate calculated values of y_B from the experimental values of x_B and y_B and for given values of K_{AB}, Λ_{AB}, and Λ_{BA}. The optimum values of K_{AB}, Λ_{AB}, and Λ_{BA} for a given isotherm were obtained by minimizing the sum of the squared relative deviations (ssrd) with respect to the resin-phase composition:

$$\text{ssrd} = \sum_{i=1}^{M} \left(\frac{y_B^{\text{calc}} - y_B^{\text{exp}}}{y_B^{\text{exp}}} \right)_i^2 \tag{11}$$

where M is the number of data points and y_B^{calc} and y_B^{exp} are the calculated and experimental values of the equivalent ionic fraction of ion B in the resin phase, respectively. In the discussion that follows, the average absolute relative deviation (aard) is defined as

$$\text{aard}(\%) = \frac{100}{M} \sum_{i=1}^{M} \left| \frac{y_B^{\text{calc}} - y_B^{\text{exp}}}{y_B^{\text{exp}}} \right|^i \tag{12}$$

Alternatively, Mehablia et al.[18] have described a method in which the equilibrium constant is first calculated independently and then used in the regression of Λ_{AB} and Λ_{BA} from the experimental data (two-parameter regression). The equilibrium constant is calculated using

Table 4. Ion-Exchange Equilibria for $Au(CN)_2^-$(B)/Cl^-(A) in Aqueous Solution at 303 K and for Various Total Solution Concentrations

x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]
Total Solution Concentration = 0.0025 M					
0.0007	0.0375	0.0219	0.0072	0.6166	0.0365
0.0005	0.0761	−0.0056	0.0083	0.6553	0.0276
0.0003	0.1147	−0.0600	0.0104	0.6939	0.0344
0.0008	0.1533	−0.0034	0.0120	0.7324	0.0219
0.0009	0.1919	−0.0149	0.0148	0.7708	0.0192
0.0009	0.2306	−0.0462	0.0196	0.8091	0.0231
0.0011	0.2692	−0.0474	0.0240	0.8471	0.0110
0.0016	0.3078	−0.0108	0.0335	0.8848	0.0094
0.0026	0.3463	0.0634	0.0518	0.9181	0.0115
0.0031	0.3848	0.0692	0.0927	0.9535	0.0073
0.0042	0.4233	0.1067	0.3636	0.9783	0.0144
0.0038	0.4618	0.0425	0.6470	0.9921	0.0056
0.0043	0.5007	0.0333	0.9193	0.9952	0.0044
0.0051	0.5395	0.0353	0.9229	0.9982	0.0015
0.0060	0.5779	0.0345	0.9113	1.0000	−0.0004
Total Solution Concentration = 0.0051 M					
0.0002	0.0776	−0.0477	0.0099	0.6966	0.0219
0.0005	0.1553	−0.0555	0.0129	0.7656	0.0008
0.0011	0.2328	−0.0157	0.0201	0.8379	−0.0029
0.0015	0.3104	−0.0263	0.0423	0.9123	0.0023
0.0023	0.3879	−0.0063	0.2280	0.9722	0.0138
0.0034	0.4653	0.0113	0.6633	0.9984	−0.0005
0.0047	0.5426	0.0121	0.9592	1.0000	−0.0002
0.0067	0.6197	0.0169			
Total Solution Concentration = 0.0066 M					
0.0003	0.1029	−0.0510	0.0201	0.8183	0.0175
0.0009	0.2057	−0.0254	0.0441	0.9167	0.0012
0.0016	0.3084	−0.0110	0.3376	0.9848	0.0071
0.0027	0.4111	0.0094	0.8978	0.9947	0.0048
0.0044	0.5135	0.0262	0.9587	0.9973	0.0025
0.0071	0.6157	0.0347	0.9652	1.0000	−0.0001
0.0115	0.7174	0.0298			

[a] $\delta y_B = y_B^{\text{calcd}} - y_B^{\text{exptl}}$. The y_B^{calcd} values are those calculated in the three-parameter regression.

$$\ln K_{AB} = (z_A - z_B) + \int_0^1 \ln(\lambda_{AB})\, dy_B \tag{13}$$

$$\lambda_{AB} = \left(\frac{\gamma_A c_A}{y_A}\right)^{\beta} \left(\frac{y_B}{\gamma_B c_B}\right)^{\alpha} \tag{14}$$

where λ_{AB} is the equilibrium quotient defined in relation to eq 1. Thus, the equilibrium constant can be estimated by integrating the area under a plot of $\ln(\lambda_{AB})$ versus y_B. The Wilson parameters are then regressed using the procedure described above in which eq 10 is used to generate calculated values of y_B, followed by the minimization of the objective function in eq 11. The advantage of this method is that it decouples the intercorrelation between the equilibrium constant and the pair of Wilson parameters.

Results and Discussion

Ion-exchange equilibria for $Au(CN)_2^-/Cl^-$, $Au(CN)_2^-/SCN^-$, and SCN^-/Cl^- in aqueous solution at 303 K are listed in Tables 4 to 6 and presented graphically in Figures 1 to 4. The equivalent ionic fractions in Figures 1 to 4 are plotted with respect to ion B, the loading anion, in accordance with the ion-exchange process shown in eq 1. The selectivity of the resin can be ascertained from the shape of the isotherm. The resin is considered to be selective toward ion B if the isotherm lies above the diagonal.

Table 5. Ion-Exchange Equilibria for $Au(CN)_2^-$(B)/SCN^-(A) in Aqueous Solution at 303 K and for Various Total Solution Concentrations

x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]
Total Solution Concentration = 0.0025 M					
0.0020	0.0349	−0.0070	0.1460	0.7250	−0.0062
0.0051	0.0725	−0.0042	0.1778	0.7538	0.0126
0.0077	0.1086	−0.0089	0.1974	0.7804	0.0109
0.0122	0.1446	0.0049	0.2249	0.8075	0.0126
0.0147	0.1804	−0.0056	0.2569	0.8335	0.0138
0.0179	0.2162	−0.0109	0.2835	0.8585	0.0083
0.0228	0.2517	−0.0035	0.3024	0.8829	−0.0029
0.0246	0.2759	−0.0130	0.3465	0.9058	−0.0034
0.0339	0.3097	0.0217	0.4405	0.9244	0.0095
0.0375	0.3414	0.0134	0.5232	0.9411	0.0119
0.0408	0.3750	0.0001	0.6321	0.9540	0.0162
0.0477	0.4083	0.0060	0.6832	0.9650	0.0116
0.0545	0.4413	0.0076	0.8016	0.9720	0.0156
0.0586	0.4742	−0.0058	0.7626	0.9803	0.0044
0.0643	0.5069	−0.0131	0.7916	0.9876	−0.0003
0.0673	0.5395	−0.0327	0.8327	0.9934	−0.0030
0.0780	0.5718	−0.0242	0.9279	0.9959	0.0004
0.0871	0.6037	−0.0251	0.9546	0.9975	0.0002
0.0966	0.6352	−0.0274	0.9399	0.9996	−0.0026
0.1059	0.6649	−0.0311	0.9888	1.0000	−0.0005
0.1343	0.6952	0.0009			
Total Solution Concentration = 0.0051 M					
0.0056	0.0716	0.0030	0.1503	0.7382	−0.0112
0.0137	0.1426	0.0226	0.2021	0.7957	0.0022
0.0196	0.2132	0.0078	0.2677	0.8484	0.0078
0.0279	0.2832	0.0056	0.3486	0.8953	0.0067
0.0424	0.3521	0.0327	0.4692	0.9327	0.0088
0.0519	0.4204	0.0158	0.5924	0.9615	0.0040
0.0621	0.4879	−0.0036	0.7499	0.9791	0.0045
0.0756	0.5544	−0.0157	0.8422	0.9903	0.0007
0.0944	0.6196	−0.0186	0.9147	0.9963	−0.0007
0.1158	0.6801	−0.0220	0.9429	1.0000	−0.0029
Total Solution Concentration = 0.0066 M					
0.0068	0.0897	−0.0005	0.1712	0.7577	0.0010
0.0158	0.1785	0.0074	0.2409	0.8262	0.0090
0.0250	0.2666	−0.0002	0.3468	0.8818	0.0180
0.0364	0.3536	−0.0055	0.4765	0.9291	0.0137
0.0590	0.4385	0.0316	0.6269	0.9628	0.0073
0.0750	0.5220	0.0137	0.7759	0.9830	0.0029
0.0958	0.6037	0.0005	0.8904	0.9929	0.0012
0.1230	0.6829	−0.0092	0.9128	1.0000	−0.0045

[a] $\delta y_B = y_B^{calcd} - y_B^{exptl}$. The y_B^{calcd} values are those calculated in the three-parameter regression.

Table 6. Ion-Exchange Equilibria for SCN^-(B)/Cl^-(A) in Aqueous Solution at 303 K and for Various Total Solution Concentrations

x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]
Total Solution Concentration = 0.0086 M					
0.0175	0.1352	0.0134	0.1454	0.7747	0.0173
0.0254	0.2694	0.0155	0.2517	0.8777	0.0070
0.0351	0.4022	0.0002	0.4872	0.9483	0.0080
0.0571	0.5320	0.0213	0.7149	0.9876	−0.0046
0.0910	0.6571	0.0272	0.9050	1.0000	−0.0045
Total Solution Concentration = 0.0172 M					
0.0195	0.2570	−0.0282	0.7414	0.9648	0.0203
0.0516	0.5057	0.0173	0.9157	0.9869	0.0091
0.1321	0.7332	0.0383	0.9714	0.9944	0.0043
0.3750	0.8970	0.0352	0.9786	1.0000	−0.0009
Total Solution Concentration = 0.0224 M					
0.0186	0.3397	−0.0936	0.9520	0.9890	0.0088
0.0914	0.6542	0.0313	0.9769	0.9970	0.0020
0.3441	0.8813	0.0418	0.9937	1.0000	−0.0003
0.7368	0.9724	0.0124			

[a] $\delta y_B = y_B^{calcd} - y_B^{exptl}$. The y_B^{calcd} values are those calculated in the three-parameter regression.

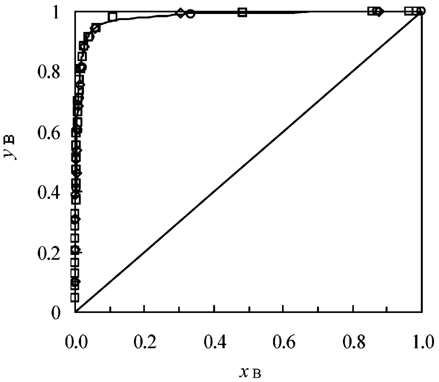

Figure 1. Ion-exchange isotherms for $Au(CN)_2^-$(B)/Cl^-(A) in aqueous solution at 303 K and for various total solution concentrations: □, 0.0025 M; ◇, 0.0051 M; ○, 0.0066 M. The solid curve represents the correlation of the data with eq 10 (three-parameter regression).

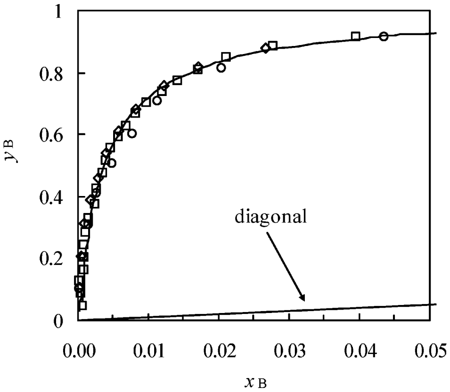

Figure 2. Expanded view of the ion-exchange isotherm shown in Figure 1.

For the $Au(CN)_2^-/Cl^-$ system (Figure 1), it can be seen that the resin is highly selective for $Au(CN)_2^-$ (ion B). An expanded view of the data in Figure 1 is provided in Figure 2. The suitability of this type of ion-exchange resin for the recovery of $Au(CN)_2^-$ from leach solutions is particularly evident from the relatively high loading that is attained when the resin is in contact with a dilute solution of $Au(CN)_2^-$. For the $Au(CN)_2^-/SCN^-$ system (Figure 3), the resin is again more selective toward $Au(CN)_2^-$ (ion B), whereas in the SCN^-/Cl^- system (Figure 4), the resin exhibits a preference for SCN^- (ion B). Overall, it can be generalized that the selectivity of the resin for a given ion increases in the order $Cl^- < SCN^- < Au(CN)_2^-$.

For sufficiently dilute solutions and where the various chemical species are stable under the given conditions of pH, ion-exchange isotherms for ions of the same valence are generally independent of the total solution concentration. This is clearly evident in Figures 1 to 4 and suggests that a single equilibrium constant can be used to describe the ion-exchange equilibria within the ranges of concentration considered. A comparison of the two methods used for determining K_{AB}, Λ_{AB}, and Λ_{BA} is presented in Table 7. It can be seen that the independently calculated values of K_{AB} are comparable to those derived from the three-parameter regression. Also, the correlation of the data with the three-parameter regression is slightly more accurate than that obtained with the two-parameter regression. The aard with respect to y_B, using either method, ranges from 2 to 10%, and this highlights the fact that the calculated values of y_B agree well with the experimental values for all three systems.

According to the triangle rule,[18] the equilibrium constants of two of the three constituent binary systems of a

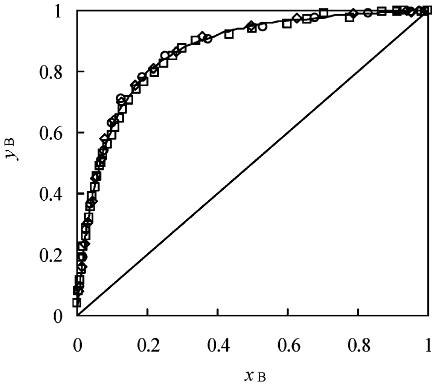

Figure 3. Ion-exchange isotherms for $Au(CN)_2^-$(B)/SCN^-(A) in aqueous solution at 303 K and for various total solution concentrations: □, 0.0025 M; ◇, 0.0051 M; ○, 0.0066 M. The solid curve represents the correlation of the data with eq 10 (threeparameter regression).

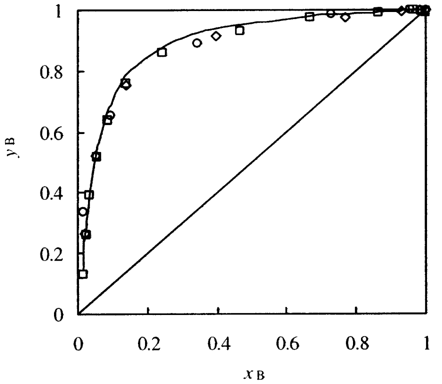

Figure 4. Ion-exchange isotherms for SCN^-(B)/Cl^-(A) in aqueous solution at 303 K and for various total solution concentrations: □, 0.0086 M; ◇, 0.0172 M; ○, 0.0224 M. The solid curve represents the correlation of the data with eq 10 (three-parameter regression).

Table 7. Optimized Values of K_{AB}, Λ_{AB}, and Λ_{BA} for Ion-Exchange Equilibria Obtained at 303 K

system (B/A)	K_{AB}[a]	Λ_{AB}	Λ_{BA}	aard(%)
Three-Parameter Regression				
$Au(CN)_2^-/Cl^-$	224.3	2.571	4×10^{-5}	8.7
$Au(CN)_2^-/SCN^-$	14.94	0.254	2.028	2.4
SCN^-/Cl^-	15.56	1.828	4×10^{-4}	3.8
Two-Parameter Regression[b]				
$Au(CN)_2^-/Cl^-$	185.0	2.799	−0.003	10.3
$Au(CN)_2^-/SCN^-$	13.38	1.036	1.036	3.4
SCN^-/Cl^-	11.65	1.906	−0.061	5.3

[a] K_{AB} refers to the equilibrium constant for ion B entering the resin phase and displacing ion A. [b] K_{AB} is calculated independently with eq 13.

ternary system can be used to predict the equilibrium constant of the third binary system. For the $Au(CN)_2^-$(C)/SCN^-(B)/Cl^-(A) ternary system, this rule may be stated as

$$K_{AC} = K_{AB}K_{BC} \qquad (15)$$

In the three-parameter regression, the triangle rule is obeyed to within less than 4% ($K_{AC} = 224.3$ and $K_{AB}K_{BC} = 232.5$). In the two-parameter regression, the product on the right-hand side of eq 15 is 16% lower than the experimental value of K_{AC}. The underestimation of the equilibrium constant in the latter method is partially attributed to the value of the equilibrium constant for the SCN^-/Cl^- system. In using eq 13 to estimate the equilibrium constant, experimental data are required over the whole range of resin composition. However, as can be seen in Table 6, experimental data for the SCN^-/Cl^- system are limited to values of y_B in the range of 0.14 to 1.00. Thus, some underestimation of the equilibrium constant is expected.

The values for Λ_{AB} and Λ_{BA} obtained in this study fall generally within the range of 0 to 3. A similar range of values for the Wilson parameters has been reported for cation-exchange systems.[15−17] In the two-parameter regression, the optimization routine yielded some slightly negative values for the Wilson parameters, even though positive values are required to maintain consistency with the Wilson model. Allen et al.[19] have noted that the product of the two parameters is approximately equal to unity for a range of binary systems. This relation is evident only for the parameters derived for the $Au(CN)_2^-/SCN^-$ system. Significant deviations from unity have also been observed in other studies.[15,18] The Hála constraint,[20] which relates the three pairs of Wilson parameters required in a ternary system, is not obeyed in either the three-parameter or the two-parameter regression.

The large value of K_{AB} for the $Au(CN)_2^-/Cl^-$ system is consistent with the strong preference of the resin for the $Au(CN)_2^-$ species. The value of K_{AB} for the $Au(CN)_2^-/SCN^-$ systems is more than an order of magnitude lower in comparison to that for the $Au(CN)_2^-/Cl^-$ system. This reflects the reduced ability of $Au(CN)_2^-$ to displace SCN^- from the resin in comparison to its ability to displace Cl^-. Alternatively, this can be interpreted to mean that SCN^- is a more effective counterion than Cl^- for the elution of $Au(CN)_2^-$ from the resin. The isotherm in Figure 3 suggests that such an elution process nonetheless requires an excess concentration of SCN^-. Similarly, the regeneration of the resin from the SCN^- form to the Cl^- form requires an excess concentration of Cl^- (Figure 4).

Conclusions

Ion-exchange equilibria obtained for $Au(CN)_2^-/Cl^-$, $Au(CN)_2^-/SCN^-$, and SCN^-/Cl^- in aqueous solution at 303 K confirm the high affinity of Purolite A500 for the $Au(CN)_2^-$ species. The selectivity of the resin for a given ion increases in the order $Cl^- < SCN^- < Au(CN)_2^-$. The ion-exchange isotherm for each binary system is independent of the total solution concentration within the range of concentration considered. The law of mass action modified with activity coefficients provides a satisfactory correlation of the ion-exchange equilibria for all systems. The fitted values of the equilibrium constants are in qualitative agreement with the selectivity of the resin for the various ionic species.

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Received for review November 20, 2003. Accepted June 1, 2004. This work was funded by the Australian Research Council under grant no. C00106549.

JE034247Y