Ion-Exchange Equilibria for $[Au(CN)_2]^-/Cl^-$, $[Au(CN)_2]^-/SCN^-$, and SCN^-/Cl^- in Acetone + Water Mixtures 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 acetone + water mixtures at 303 K using Purolite A500 as the ion exchanger. The effect of the composition of acetone in the external solution 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 selectivity of Purolite A500 is highly dependent on the composition of the external solution. The selectivity of the resin for $[Au(CN)_2]^-$, in particular, decreases markedly with an increase in the composition of acetone. The fitted values of the equilibrium constants are consistent with the trends observed in the corresponding ion-exchange isotherms.

Introduction

Ion-exchange is increasingly being considered as an alternative to carbon adsorption in the gold industry for the extraction of the gold cyanide complex, $[Au(CN)_2]^-$, from leach solutions.[1,2] Ion-exchange resins have a much higher capacity than carbon for loading gold and other base-metal cyanide complexes and also offer the possibility of recycling free cyanide. Although the loading of $[Au(CN)_2]^-$ onto ion-exchange resin presents relatively few difficulties, the elution (stripping) of this species and the subsequent regeneration of the resin are key issues that need to be resolved before this technology can be adopted widely by industry.

The elution of $[Au(CN)_2]^-$ from the resin is typically carried out with an aqueous solution containing an excess concentration of another cyanide complex such as $[Zn(CN)_4]^{2-}$. This method is not particularly selective for $[Au(CN)_2]^-$ and leads to the formation of HCN during the regeneration of the resin. The formation of this species necessitates further processing to eliminate its presence in waste streams. However, simple counterions such as Cl^- and NO_3^- have been shown to be effective in the selective elution of base-metal cyanide complexes.[3,4]

Nonaqueous solvents have been investigated for many years as a way of altering selectivities in both cation- and anion-exchange processes.[5−9] It has been demonstrated that mixtures of water and organic solvents are more effective than aqueous solutions for the separation of $[Au(CN)_2]^-$ from ion-exchange resin.[10,11] Dipolar polar aprotic solvents such as dimethylformamide, *N*-methyl-2-pyrrolidone, and acetone are particularly well suited for this purpose. Furthermore, the elution can be carried out with simple counterions such as Cl^- and SCN^-.

Although the use of mixed solvents in the elution of $[Au(CN)_2]^-$ from ion-exchange resin has been investigated, there is currently an absence of ion-exchange equilibrium data covering the $[Au(CN)_2]^-$ species in mixed solvents. Previously, we have reported binary ion-exchange equilibria for $[Au(CN)_2]^-/Cl^-$, $[Au(CN)_2]^-/SCN^-$, and SCN^-/Cl^- in aqueous solution using Purolite A500 as the ion exchanger.[12] In this work, we present ion-exchange equilibria for the same binary systems in acetone + water mixtures. The experimental data are correlated using the law of mass action modified with activity coefficients to determine the equilibrium constant for each binary system.

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. Hydrated ferric nitrate (>98%), used in the determination of SCN^- in solution, was supplied by Asia Pacific Specialty Chemicals. Purolite A500 is a type 1 strong base, divinylbenzene, macroporous resin in chloride form. Prior to use, the resin was soaked in distilled water for 24 h to stabilize resin swelling. Acetone (>99%) was supplied by Asia Pacific Specialty Chemicals.

Loading Procedure. The basic loading procedure for determining ion-exchange equilibria in mixed solvent media is identical to that described in previous work.[12] A (5 ± 0.2) mL sample of the resin (wet and settled volume in water) was repeatedly contacted with (100 ± 1) mL of an acetone + water stock solution containing a fixed concentration of the loading anion. For the $[Au(CN)_2]^-/Cl^-$ and SCN^-/Cl^- binary systems, the Cl^- form of the resin was contacted with a stock solution containing $[Au(CN)_2]^-$ and SCN^-, respectively. For the $[Au(CN)_2]^-/SCN^-$ binary system, the SCN^- form of the resin was contacted with a stock solution containing $[Au(CN)_2]^-$.

A much longer time duration was required to establish equilibrium in the acetone + water mixtures, in comparison with ion-exchange equilibria determined in aqueous media. Kinetic studies were performed to test the effect of resin loading, acetone composition, and type of counterion on the time taken to reach equilibrium. A duration of 4 days was found to be sufficient for the attainment of equilibrium for all of the binary systems considered in this study.

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From a knowledge of the change in concentration of the loading anion in the solution phase, it was possible to calculate the composition of $[Au(CN)_2]^-$ or SCN^- on the resin phase at equilibrium. Mass balance was used to determine the equilibrium compositions of the resin and solution phases with respect to Cl^-. Ion-exchange equilibria are expressed in terms of equivalent ionic fractions for the solution and resin phases (eqs 3 and 4). The experimental ionic fraction data that are reported represent the average of duplicate runs, with an uncertainty of ±5%.

The concentration of $[Au(CN)_2]^-$ in solution was determined by analysis for Au using inductively coupled plasma−atomic emission spectroscopy (ICP−AES). The standard uncertainty of the analysis was ±1%. The concentration of SCN^- in solution was determined using UV−vis spectrophotometry, in accordance with ASTM D 4193-95. The uncertainty of the analysis for SCN^- was ±5%. In both the ICP−AES and UV−vis analyses, calibration curves were established by preparing standards representative of the acetone composition in the samples.

Preparation of Acetone + Water Stock Solutions. The effect of acetone on the ion-exchange isotherm for a given binary system was examined by varying the amount of acetone in the stock solution. To simplify the preparation process, stock solutions were initially prepared on the basis of an unmixed volume of water and acetone. The nominal volume of all stock solutions was (1000 ± 0.4) mL. For example, a stock solution containing a volume fraction of 20% acetone was prepared by combining 200 mL of acetone with 800 mL of water. The compositions in the stock solutions were subsequently converted to mole fractions of acetone.

The loading anion was incorporated into the stock solution as follows. A known mass of $KAu(CN)_2$ or KSCN was weighed (± 0.0001 g) into a volumetric flask. The salt was initially dissolved in distilled water. Once the salt had completely dissolved, the required amount of acetone was added to the flask. During the addition of acetone, some heat was released from the mixture, followed by a contraction in the volume of the solution. The reduction in volume of the solution was taken into account in the calculation of the concentration of the loading anion in each stock solution.

In our previous work, it was established that the ion-exchange isotherms for the given binary systems in aqueous solution were independent of the total solution concentration, within the range of concentration considered (0.002 to 0.02 mol/L). Only a single value of the total solution concentration was therefore employed in the determination of ion-exchange isotherms in acetone + water mixtures. 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 a nominal concentration of 0.005 mol/L. Similarly, a nominal concentration of 0.01 mol/L SCN^- was used in the stock solutions for the SCN^-/Cl^- binary system.

Data Correlation

Ion-exchange equilibrium is established when an ion exchanger (r) of the form A is placed in a solution(s) of ion B, resulting in the displacement of ion A for ion B. The reversible ion-exchange process can be described by

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

The distribution of ions A and B between the two phases is governed by 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[13,14]

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

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 activity coefficients of ion i in the solution phase and resin phase are denoted by γ_i and $\bar{\gamma}_i$, respectively. Molar concentrations in the resin phase are here calculated with respect to the wet and settled volume of the ion-exchange resin. The use of eq 2 to describe the equilibrium constant assumes that swelling-pressure effects are negligible.[15]

As a rule, the equilibrium concentrations of ions in the resin and solution phases are expressed in terms of equivalent ionic fractions. Equivalent concentrations take into account the charges of the exchanging species and therefore better represent an ion-exchange system. For competing ions of equal charge, the equivalent ionic fraction is equal in value to the mole fraction. 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:

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

The calculation of y_i in eq 4 requires the capacity of the resin. In our earlier study, the apparent capacity of the resin was determined experimentally by repeatedly contacting the same sample of resin with a fresh quantity of stock solution until no further loading of counterion occurred. The apparent capacity of the resin was in close agreement with the manufacturer's specification of 1.3 equiv/L.

In this work, however, we were unable to satisfactorily determine the apparent capacity of the resin in acetone + water mixtures containing in excess of a mole fraction of 25% acetone. In these systems, the total loading of the anion on the resin increased relatively slowly in response to the repeated exposure of the resin to the stock solution. This suggested that an exceedingly large number of contacts was required to achieve the theoretical capacity. In view of this uncertainty, the capacity of the resin was set to 1.3 equiv/L for the construction of ion-exchange isotherms in all of the acetone + water mixtures.

Two methods are available for the calculation of individual ionic activity coefficients appearing in eq 5. Shallcross et al.[14] have used the Pitzer method[16] to estimate solution-phase activity coefficients. However, the required param-

Table 1. Debye−Hückel Parameters for Acetone (1) + Water (2) Mixtures at 303 K[a]

$100x_1$	ϵ^b	$A/(\mathrm{mol/L})^{-1/2}$	$10^{-7}B/(\mathrm{mol/L})^{-1/2}\,\mathrm{cm}^{-1}$
5.73	68.66	0.61	3.487
13.9	59.81	0.75	3.736
26.7	47.78	1.05	4.180
68.6	24.16	2.91	5.878

[a] Parameters were calculated according to Robinson and Stokes.[19] [b] Data are from Marcus.[23]

eters for the pure and mixed electrolytes relevant to this study are not available in the literature. Furthermore, Hovath[17] highlights that the Pitzer equation is incapable of dealing with electrolytes in mixed solvent systems. Alternatively, Kielland[18] suggests 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 for estimating mean ionic activity coefficients that are measurable. The values of a_i pertinent to this study are given elsewhere.[12] The Debye−Hückel parameters appearing in eq 6 are equivalent to those in the corresponding equation for the mean ionic activity coefficient and depend on temperature and the dielectric constant (ϵ) of the solvent.[19] The dielectric constants and Debye−Hückel parameters for the acetone + water mixtures are listed in Table 1.

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. This method has been applied successfully in the correlation of binary ion-exchange equilibria for cationic systems in nonaqueous and mixed solvents.[5] The relevant equations for the exchange of ions A and B are

$$\ln \bar{\gamma}_\mathrm{A} = 1 - \ln(y_\mathrm{A} + y_\mathrm{B}\Lambda_\mathrm{AB}) - \frac{y_\mathrm{A}}{y_\mathrm{A} + y_\mathrm{B}\Lambda_\mathrm{AB}} - \frac{y_\mathrm{B}\Lambda_\mathrm{BA}}{y_\mathrm{B} + y_\mathrm{A}\Lambda_\mathrm{BA}} \tag{8}$$

$$\ln \bar{\gamma}_\mathrm{B} = 1 - \ln(y_\mathrm{B} + y_\mathrm{A}\Lambda_\mathrm{BA}) - \frac{y_\mathrm{B}}{y_\mathrm{B} + y_\mathrm{A}\Lambda_\mathrm{BA}} - \frac{y_\mathrm{A}\Lambda_\mathrm{AB}}{y_\mathrm{A} + y_\mathrm{B}\Lambda_\mathrm{AB}} \tag{9}$$

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. The working equation for this calculation procedure is obtained by rearranging eq 5 as follows:

$$y_\mathrm{B} = \frac{K_\mathrm{AB}\bar{\gamma}_\mathrm{A} x_\mathrm{B} \gamma_\mathrm{B}}{K_\mathrm{AB}\bar{\gamma}_\mathrm{A} x_\mathrm{B} \gamma_\mathrm{B} + (1 - x_\mathrm{B})\gamma_\mathrm{A}\bar{\gamma}_\mathrm{B}} \tag{10}$$

Equation 10 was used to generate calculated values of y_B from the experimental values of x_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

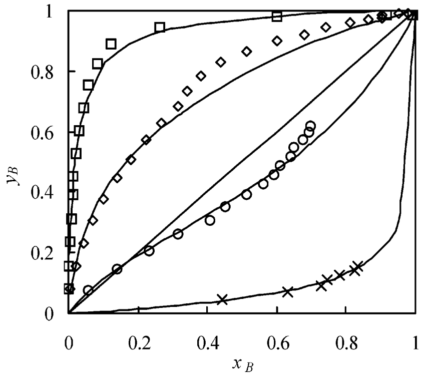

Figure 1. Ion-exchange isotherms for $[\mathrm{Au(CN)_2}]^-$(B)/$\mathrm{Cl^-}$(A) in various acetone (1) + water (2) mixtures at 303 K: □, $x_1 = 0.0573$; ◇, $x_1 = 0.139$; ○, $x_1 = 0.267$; ×, $x_1 = 0.686$. The solid curve represents the correlation of the data with eq 10.

$$\mathrm{SSRD} = \sum_{i=1}^{M}\left(\frac{y_\mathrm{B}^\mathrm{calcd} - y_\mathrm{B}^\mathrm{exptl}}{y_\mathrm{B}^\mathrm{exptl}}\right)_i^2 \tag{11}$$

where M is the number of data points and $y_\mathrm{B}^\mathrm{calcd}$ and $y_\mathrm{B}^\mathrm{exptl}$ 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

$$\mathrm{AARD}/\% = \frac{100}{M}\sum_{i=1}^{M}\left|\frac{y_\mathrm{B}^\mathrm{calcd} - y_\mathrm{B}^\mathrm{exptl}}{y_\mathrm{B}^\mathrm{exptl}}\right|_i \tag{12}$$

Results and Discussion

Ion-exchange equilibria for $[\mathrm{Au(CN)_2}]^-/\mathrm{Cl^-}$, $[\mathrm{Au(CN)_2}]^-/\mathrm{SCN^-}$, and $\mathrm{SCN^-/Cl^-}$ in acetone + water mixtures at 303 K are presented in Figures 1 to 3. The numerical data pertaining to these Figures are presented in Tables 2 to 4. The equivalent ionic fractions are plotted with respect to ion B, the loading anion, in accordance with the ion-exchange process presented in eq 1. The resin is considered to be selective toward ion B if the isotherm lies above the diagonal.

For the $[\mathrm{Au(CN)_2}]^-/\mathrm{Cl^-}$ binary system (Figure 1), it can be seen that the resin is generally selective toward $[\mathrm{Au(CN)_2}]^-$ (ion B) in acetone + water mixtures containing less than a mole fraction of 25% acetone. The selectivity for this species decreases as the composition of acetone in the external solution increases. For acetone + water mixtures containing greater than a mole fraction of 60% acetone, the selectivity of the resin changes dramatically in favor of $\mathrm{Cl^-}$. The qualitative features of the ion-exchange isotherms for $[\mathrm{Au(CN)_2}]^-/\mathrm{Cl^-}$ are also evident in the other binary systems. In particular, a reversal in the selectivity of the resin occurs in acetone + water mixtures containing relatively high levels of acetone. Thus, for mixtures containing greater than a mole fraction of 60% acetone, the selectivity of the resin for a given anion increases in the following order: $[\mathrm{Au(CN)_2}]^- < \mathrm{SCN^-} < \mathrm{Cl^-}$. Note that this is opposite to the selectivity sequence obtained in purely aqueous solutions.

Table 2. Ion-Exchange Equilibria for $[Au(CN)_2]^-$(B)/Cl^-(A) in Acetone (1) + Water (2) Mixtures at 303 K

x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]
$100x_1 = 5.73\%$											
0.0008	0.0784	−0.0016	0.0121	0.3900	0.0215	0.0429	0.6795	−0.0212	0.2642	0.9467	−0.0174
0.0021	0.1566	−0.0021	0.0149	0.4518	−0.0065	0.0574	0.7534	−0.0402	0.6004	0.9777	0.0041
0.0041	0.2347	−0.0026	0.0226	0.5284	0.0022	0.0834	0.8246	−0.0441	0.9183	0.9841	0.0134
0.0080	0.3125	0.0276	0.0307	0.6044	−0.0133	0.1249	0.8895	−0.0463	0.9925	0.9847	0.0151
$100x_1 = 13.9\%$											
0.0064	0.0787	−0.0086	0.1395	0.4451	0.0166	0.3407	0.7347	−0.0607	0.6808	0.9221	−0.0385
0.0202	0.1563	0.0027	0.1799	0.5100	0.0078	0.3804	0.7833	−0.0797	0.7404	0.9425	−0.0331
0.0434	0.2321	0.0236	0.2227	0.5716	−0.0035	0.4383	0.8274	−0.0817	0.8107	0.9574	−0.0200
0.0705	0.3058	0.0258	0.2687	0.6290	−0.0137	0.5138	0.8656	−0.0705	0.8619	0.9682	−0.0123
0.1019	0.3769	0.0206	0.3136	0.6829	−0.0276	0.5994	0.8971	−0.0534	0.9023	0.9758	−0.0062
$100x_1 = 26.7\%$											
0.0574	0.0755	−0.0052	0.4069	0.3082	0.0296	0.5943	0.4580	0.0143	0.6736	0.5713	−0.0414
0.1406	0.1442	−0.0006	0.4530	0.3520	0.0140	0.6097	0.4889	−0.0089	0.6939	0.5956	−0.0475
0.2316	0.2058	0.0063	0.5146	0.3906	0.0215	0.6402	0.5175	−0.0121	0.6974	0.6196	−0.0724
0.3137	0.2607	0.0081	0.5632	0.4258	0.0239	0.6475	0.5454	−0.0387			
$100x_1 = 68.6\%$											
0.4413	0.0438	−0.0034	0.7284	0.0898	0.0143	0.7816	0.1270	−0.0081	0.8325	0.1537	−0.0075
0.6303	0.0728	0.0008	0.7449	0.1098	−0.0050	0.8248	0.1407	0.0040			

[a] $\delta y_B = y_B^{calcd} - y_B^{exptl}$.

Table 3. Ion-Exchange Equilibria for $[Au(CN)_2]^-$(B)/SCN^-(A) in Acetone (1) + Water (2) Mixtures at 303 K

x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]	x_B	y_B	δy_B[a]
$100x_1 = 5.73\%$											
0.0096	0.0777	−0.0040	0.0696	0.3771	0.0040	0.1636	0.6514	−0.0103	0.3150	0.8828	−0.0054
0.0218	0.1544	−0.0007	0.0918	0.4484	0.0087	0.1991	0.7137	−0.0059	0.3774	0.9316	0.0016
0.0371	0.2299	0.0092	0.1133	0.5179	0.0024	0.2378	0.7729	−0.0032	0.4318	0.9762	0.0013
0.0524	0.3042	0.0072	0.1333	0.5859	−0.0124	0.2781	0.8290	−0.0026	0.5167	1.0000	0.0000
$100x_1 = 13.9\%$											
0.0441	0.0757	0.0101	0.2624	0.4655	−0.0081	0.4474	0.7084	0.0077	0.6282	0.9165	0.0003
0.0733	0.1491	−0.0083	0.3159	0.5197	0.0129	0.4869	0.7490	0.0133	0.6683	0.9428	−0.0010
0.1070	0.2199	−0.0178	0.3469	0.5710	0.0077	0.5138	0.7876	0.0095	0.6969	0.9668	−0.0073
0.1497	0.2873	−0.0115	0.3797	0.6197	0.0059	0.5556	0.8228	0.0153	0.7181	0.9892	−0.0162
0.1819	0.3456	−0.0155	0.4284	0.6645	0.0203	0.5849	0.8558	0.0129	0.7597	1.0000	−0.0181
0.2239	0.4070	−0.0097				0.6064	0.8870	0.0066			
$100x_1 = 26.7\%$											
0.1187	0.0705	0.0020	0.3698	0.3043	0.0204	0.4942	0.4364	0.0155	0.5909	0.5766	−0.0275
0.1750	0.1366	−0.0084	0.4059	0.3519	0.0107	0.5408	0.4729	0.0261	0.6053	0.6082	−0.0450
0.2317	0.1981	−0.0118	0.4493	0.3959	0.0107	0.5437	0.5091	−0.0072			
0.3033	0.2539	0.0038				0.5622	0.5438	−0.0235			
$100x_1 = 68.6\%$											
0.2876	0.0559	0.0001	0.5324	0.1810	−0.0030	0.6381	0.2416	0.0097	0.6934	0.3170	−0.0219
0.3945	0.1033	−0.0010	0.5891	0.2132	0.0018	0.6642	0.2677	0.0044	0.7509	0.3364	0.0196
0.4771	0.1443	0.0008				0.6750	0.2930	−0.0130			

[a] $\delta y_B = y_B^{calcd} - y_B^{exptl}$.

The optimized values of K_{AB}, Λ_{AB}, and Λ_{BA} for the binary systems in acetone + water mixtures are presented in Table 5. The solid lines in Figures 1 to 3 represent the values of y_B calculated using the optimized parameters and the experimental values of x_B. The AARD with respect to y_B ranges from (1 to 10)%, and this is similar to the level of accuracy obtained for the ion-exchange equilibria of the same species in aqueous solution. It should be noted, however, that the highest AARDs are observed for the acetone + water mixtures containing in excess of a mole fraction of 60% acetone.

According to the triangle rule,[20] the equilibrium constants of two of the three constituent binary systems of a 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

$$K_{AC} = K_{AB}K_{BC} \tag{13}$$

The equilibrium constants derived from eq 13 for $[Au(CN)_2]^-/Cl^-$ in acetone + water mixtures are plotted in Figure 4. The equilibrium constants predicted from the triangle rule are qualitatively in agreement with the optimized values, although the former are consistently overestimated relative to the latter. The relative deviation between the two sets of data is more significant for acetone + water mixtures containing less than a mole fraction of 25% acetone.

The values for Λ_{AB} and Λ_{BA} in the mixed solvent systems fall generally within the range of 0 to 5. This range of values for Λ_{AB} and Λ_{BA} is consistent, although slightly larger, than that observed for the ion-exchange equilibria in aqueous solution (0 to 3). The products of the Wilson parameters are presented in Table 6 to assess the validity of the reciprocity relation proposed by Allen et al.[21]

The reciprocity relation is most consistently observed for the $[Au(CN)_2]^-/Cl^-$ binary system. In many cases, one of the Wilson parameters is significantly less than 0.2, which indicates that only a single Wilson parameter is required to correlate the ion-exchange equilibria accurately. In this

Table 4. Ion-Exchange Equilibria for SCN^-(B)/Cl^-(A) in Acetone (1) + Water (2) Mixtures at 303 K

x_B	y_B	$\delta y_B{}^a$	x_B	y_B	$\delta y_B{}^a$	x_B	y_B	$\delta y_B{}^a$	x_B	y_B	$\delta y_B{}^a$
					$100x_1 = 5.73\%$						
0.0148	0.1545	−0.0004	0.1967	0.6996	−0.0009	0.5840	0.9477	−0.0256	0.9754	1.0000	−0.0031
0.0378	0.3054	0.0028	0.3509	0.8014	−0.0287	0.7781	0.9825	−0.0157	0.9842	1.0000	−0.0020
0.0710	0.4512	−0.0032	0.4830	0.8825	0.0080	0.8550	1.0000	−0.0202			
0.1228	0.5888	−0.0062				0.9137	1.0000	−0.0113			
					$100x_1 = 13.9\%$						
0.0331	0.1532	−0.0060	0.4590	0.7329	−0.0103	0.7943	0.9378	−0.0222	0.9539	1.0000	−0.0173
0.0962	0.2964	0.0137	0.5441	0.8051	−0.0253	0.8647	0.9592	−0.0124	0.9600	1.0000	−0.0150
0.1788	0.4265	0.0223	0.6382	0.8624	−0.0263	0.8857	0.9773	−0.0219	0.9732	1.0000	−0.0099
0.2621	0.5434	0.0056	0.6988	0.9052	−0.0368	0.8987	0.9934	−0.0328			
0.3453	0.6472	−0.0181				0.9457	1.0000	−0.0205			
					$100x_1 = 26.7\%$						
0.1005	0.1440	−0.0114	0.5028	0.5272	0.0151	0.7360	0.7558	0.0003	0.8534	0.8911	−0.0042
0.2267	0.2678	0.0092	0.5461	0.5999	−0.0217	0.7608	0.7849	−0.0035	0.8611	0.9087	−0.0083
0.3557	0.3710	0.0379	0.6292	0.6593	−0.0044	0.8343	0.8114	0.0407	0.8945	0.9256	0.0067
0.4056	0.4661	−0.0153	0.6609	0.7136	−0.0300	0.8380	0.8676	−0.0014			
					$100x_1 = 68.6\%$						
0.3612	0.1002	−0.0175	0.6807	0.2176	0.0190	0.7692	0.2903	0.0215	0.7918	0.3558	−0.0304
0.5703	0.1676	−0.0001	0.7467	0.2574	0.0352	0.7906	0.3232	0.0085	0.8075	0.3860	−0.0467

[a] $\delta y_B = y_B^{\text{calcd}} - y_B^{\text{exptl}}$.

Table 5. Optimized Values of K_{AB}, Λ_{AB}, and Λ_{BA} for Ion-Exchange Equilibria in Acetone (1) + Water (2) Mixtures at 303 K

$100x_1$	$K_{AB}{}^a$	Λ_{AB}	Λ_{BA}	aard/%	$100x_1$	$K_{AB}{}^a$	Λ_{AB}	Λ_{BA}	aard/%
				$[Au(CN)_2]^-/Cl^-$					
0^b	224.3	2.571	4×10^{-5}	8.7	26.7	0.642	3.028	0.330	5.3
5.73	55.71	3.073	0.325	2.9	68.6	0.020	3.461	0.289	6.2
13.9	5.573	3.277	0.306	4.6					
				$[Au(CN)_2]^-/SCN^-$					
0^b	14.94	0.254	2.028	2.4	26.7	0.772	2.303	0.138	4.3
5.73	10.50	1×10^{-4}	2.123	0.9	68.6	0.157	3.044	0.063	2.7
13.9	2.932	0.084	1.708	2.5					
				SCN^-/Cl^-					
0^b	15.56	1.828	4×10^{-4}	3.8	26.7	1.339	2×10^{-5}	2.902	2.8
5.73	10.36	1.109	1.127	1.2	68.6	0.091	4×10^{-6}	5.012	8.8
13.9	3.732	2.477	0.404	2.6					

[a] K_{AB} refers to the equilibrium constant for ion B entering the resin phase and displacing ion A. [b] Optimized parameters in aqueous solution are from Jayasinghe et al.[12]

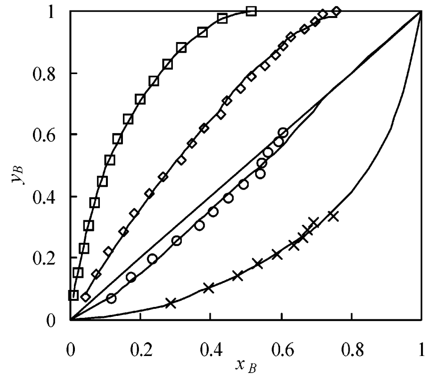

Figure 2. Ion-exchange isotherms for $[Au(CN)_2]^-$(B)/SCN^-(A) in various acetone (1) + water (2) mixtures at 303 K: □, $x_1 = 0.0573$; ◇, $x_1 = 0.139$; ○, $x_1 = 0.267$; ×, $x_1 = 0.686$. The solid curve represents the correlation of the data with eq 10.

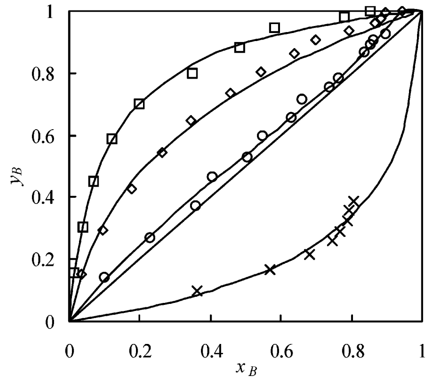

Figure 3. Ion-exchange isotherms for SCN^-(B)/Cl^-(A) in various acetone (1) + water (2) mixtures at 303 K: □, $x_1 = 0.0573$; ◇, $x_1 = 0.139$; ○, $x_1 = 0.267$; ×, $x_1 = 0.686$. The solid curve represents the correlation of the data with eq 10.

situation, it is expected that the reciprocity relation is generally not applicable. This explains why the reciprocity relation is not observed for $[Au(CN)_2]^-/SCN^-$ in acetone + water mixtures. The same explanation can be used for SCN^-/Cl^- in acetone + water mixtures containing greater than a mole fraction of 25% acetone. Furthermore, the Hála constraint,[22] which relates the three pairs of Wilson parameters required in a ternary system, is not obeyed in any of the acetone + water mixtures.

Generally, the values of K_{AB} for $[Au(CN)_2]^-/Cl^-$, $[Au(CN)_2]^-/SCN^-$, and SCN^-/Cl^- decrease with an increase in the composition of acetone in the external solution. A decrease in K_{AB} implies a decrease in the selectivity of the resin for the loading anion (B). The decrease in K_{AB} with the addition of increasing amounts acetone is particularly significant in the $[Au(CN)_2]^-/Cl^-$ binary system. For example, the equilibrium constant for the mixed solvent containing a mole fraction of 5.73% acetone is around 4

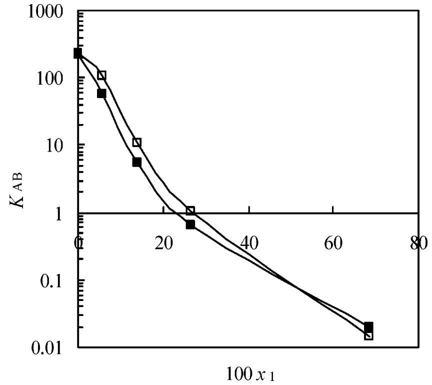

Figure 4. Comparison of the equilibrium constants for the $[Au(CN)_2]^-$(B)/Cl^-(A) binary system in various acetone + water mixtures: ■, optimized values of K_{AB} (eq 10); □, the triangle rule (eq 13).

Table 6. Reciprocity Relation Applied to the Wilson Parameters Derived from Ion-Exchange Equilibria in Various Acetone (1) + Water (2) Mixtures

	$\Lambda_{AB} \times \Lambda_{BA}$		
$100x_1$	$[Au(CN)_2]^-/Cl^-$	$[Au(CN)_2]^-/SCN^-$	SCN^-/Cl^-
5.73	0.999	2×10^{-4}	1.250
13.9	1.003	0.144	1.000
26.7	1.000	0.318	6×10^{-5}
68.6	1.000	0.193	2×10^{-5}

times lower than that in aqueous solution. The equilibrium constant is further reduced by an order of magnitude for a relatively modest increase in the organic solvent mole fraction from (5.73 to 13.9)% acetone.

An equilibrium constant that is less than 1, in particular, indicates a reversal in the selectivity of the resin (i.e., the resin is selective for anion A). In this situation, the ion-exchange isotherm moves from above to below the diagonal when the equivalent ionic fractions are expressed in terms of anion B. The data in Table 5 clearly demonstrate the reversal in the selectivity of the resin as the composition of acetone in the external solution increases. The acetone compositions at which $K_{AB} < 1$ is first observed are in agreement, in all cases, with the corresponding isotherms in Figures 1 to 3.

A comparison of the equilibrium constants for the $[Au(CN)_2]^-/Cl^-$ and $[Au(CN)_2]^-/SCN^-$ binary systems confirms an important distinction between SCN^- and Cl^- as counterions for the elution of $[Au(CN)_2]^-$. In acetone + water mixtures containing less than a mole fraction of 25% acetone, the K_{AB} values are lower for SCN^- as the counterion. The opposite trend is evident in acetone + water mixtures containing more than a mole fraction of 25% acetone. These results suggest that Cl^- is a better counterion than SCN^- for displacing $[Au(CN)_2]^-$ from the resin in acetone + water mixtures containing high levels of acetone. The equilibrium constant for SCN^-/Cl^- in the mixed solvent containing a mole fraction of 68.6% acetone further supports this observation.

Conclusions

The ion-exchange equilibria for $[Au(CN)_2]^-/Cl^-$, $[Au(CN)_2]^-/SCN^-$, and SCN^-/Cl^- in acetone + water mixtures demonstrate that the selectivity of Purolite A500 is highly dependent on the composition of the mixed solvent. The selectivity of the resin for $[Au(CN)_2]^-$ decreases markedly with an increase in the composition of acetone in the mixed solvent. For solutions containing in excess of a mole fraction of 60% acetone, the selectivity of the resin for a given anion increases in the order $[Au(CN)_2]^- < SCN^- < Cl^-$. This is opposite to the selectivity sequence obtained in purely aqueous solutions. The law of mass action modified with activity coefficients provides a satisfactory correlation of the ion-exchange equilibria in the range of mixed-solvent composition considered. The optimized values of K_{AB} are consistent with the trends observed in the corresponding ion-exchange isotherms.

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