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M. D. Adams[a]
[a] Oretest Pty Ltd., Kewdale, Western Australia, Australia

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Extraction of $MAu(CN)_2$ Ion Pairs into Organic Solvents from Aqueous Solution

M. D. ADAMS*
MINTEK
PRIVATE BAG X3015
RANDBURG 2125, SOUTH AFRICA

ABSTRACT

Factors influencing the extraction and association of $MAu(CN)_2$ ion pairs in organic solvents are elucidated. For extraction of aurocyanide ion pairs with small cations (H^+, Li^+, Na^+, K^+), the most important factor is the solubility of water in the solvent. High extraction efficiencies are related to low association constants for these cations. For extraction of aurocyanide ion pairs with larger, less hydrated cations (Cs^+, NEt_4^+), other solvent-specific parameters, such as dielectric constant and hydrogen-bonding ability, play a role.

INTRODUCTION

This paper provides the results of a detailed study of the extraction of $MAu(CN)_2$ ion pairs by various water-saturated organic solvents, and the extent of ion association in these solvents. Previous studies of the mechanism of extraction of aurocyanide by 1-pentanol (1) and tri-*n*-butyl phosphate (TBP) (2) have resulted in similar conclusions—aurocyanide is extracted in both cases in the form of an $M^{n+}[Au(CN)_2^-]_n$ ion pair. Moreover, the extraction is shown to be selective over base metal cyanide species. Evidence for the association of $HAu(CN)_2$ in alcohols and ketones has also been put forward (3). An ion-pair species has also been invoked in the extraction of aurocyanide by polymeric adsorbents (4–6), ion-exchange resins (7), and activated carbon (8–11). Activated carbon is currently used in the preferred process for the selective extraction of gold and silver from cyanided ores (the carbon-in-pulp process), and ion-exchange resins have been shown to be superior under cer-

*Present Address: Oretest Pty Ltd., 12 Aitken Way, Kewdale, Western Austrailia 6105, Australia.

tain conditions (the resin-in-pulp process). Knowledge of the factors influencing the extraction of aurocyanide by various organic solvents, and the ion association in such solvents, is of prime importance in gaining an understanding of the influence of ion-pairing effects on important commercial extraction processes as diverse as solvent extraction and adsorption on to activated carbon, and this may potentially give rise to superior extractants.

Other applications of aurocyanide ion pairs include ion-selective electrodes (12) for $Au(CN)_2^-$ and ion-pair chromatography (13) for $Au(CN)_2^-$. Selectivity for aurocyanide in both cases could possibly be enhanced by the correct choice of solvent and cation.

EXPERIMENTAL PROCEDURE

Reagents and Chemicals

The $KAu(CN)_2$ salt was supplied by Johnson Matthey (Pty) Ltd. All other salts used were of AR grade, and all solvents were of AR, CP, or spectroscopic grade. All solvents were washed repeatedly with deionized water before use.

Distribution Experiments

In the distribution experiments, 20 mL of water-saturated organic phase was equilibrated with 20 mL of aqueous phase in a 100-mL separating funnel by shaking for 20 minutes on a Voss automatic shaker. Efficient mixing was indicated by the milkiness of the solution. Preliminary experiments showed that equilibrium was attained in 2–3 minutes. The experiments were carried out at 23 ± 1°C. Previous work (1) had shown temperature effects to be small. The aqueous phase in each case contained potassium aurocyanide as well as an excess (0.1 M) of the pertinent chloride salt. The gold concentration in the aqueous phase before and after equilibration was measured by atomic absorption spectrophotometry, with due correction for the effects of the various organics on the absorbance.

Determination of Chloride Concentration in Organic Phases

The chloride concentration in the various organic phases was determined by titrating a 10-mL aliquot dissolved in 50 mL ethanol and 10 mL of 1 M HNO_3 against 0.0255 M $AgNO_3$. A 15-minute preequilibration time was found to be necessary before carrying out the titration. The endpoint was determined potentiometrically with a Labion Model 15 potentiometer, using a platinum electrode in conjunction with a saturated calomel reference electrode.

Determination of Dielectric Constant

An indication of the dielectric constant of several organic mixtures was obtained by measuring the capacitance of the solution using a Wayne–Kerr Autobalance bridge in conjunction with a Radiometer CDC 344 Immersion Conductivity cell comprising three nonplatinized platinum ring electrodes. The temperature was kept at a constant 25.00 ± 0.01°C. A calibration curve was obtained using literature values for the dielectric constant of several pure organic solvents (14, 15).

Determination of Water Content by Automatic Karl-Fischer Titration

The water contents of several water-saturated organic mixtures were determined by automatic Karl-Fischer titration, using a Radiometer TTA 80 automatic titration assembly.

RESULTS

Extraction of Aurocyanide from 0.1 M MCl Solution ($M = H, Li, K, Cs, NEt_4$) by Different Solvents

In this series of experiments, five solvents were selected with a variety of functional groups, dielectric constants (14, 15), water solubilities (16) and other properties: tri-*n*-butyl phosphate (TBP), 1-pentanol (P), methyl isobutyl ketone (MIBK), ethyl acetate (EA), and nitrobenzene (NB). These solvents were contacted with increasing concentrations of aurocyanide, and the background electrolyte (0.1 M MCl) was systematically varied ($M = H, Li, K, Cs, NEt_4$).

When the background electrolyte was 0.1 M HCl (Fig. 1a), about 100% of the gold was extracted into TBP, and over 95% extraction efficiencies were obtained for 1-pentanol. Lower extraction efficiencies were obtained for the other solvents, in the order MIBK $>$ EA $>$ NB, with no drop-off in extraction efficiency occurring over the range studied.

Somewhat lower extraction efficiencies were obtained in the case of 0.1 M LiCl (Fig. 1b), although the order of extraction remained the same, i.e., TBP $>$ P $>$ MIBK $>$ EA $>$ NB. The effect of increasing gold concentration on lowering the extraction efficiency was evident for all five solvents. The effect was most marked for MIBK, and least apparent in the case of TBP.

Even lower extraction efficiencies were obtained in the case of 0.1 M KCl (Fig. 1c), and once again, the order of extraction over the five solvents remained the same. When the background electrolyte was 0.1 M CsCl (Fig. 1d), it was evident that the extraction efficiencies were slightly enhanced, although the order of extraction of aurocyanide by the solvents was again the same as for the other background electrolytes.

The case of 0.1 M NEt_4Cl (Fig. 1e) is interesting, in that the solvent that extracted aurocyanide most poorly in the presence of the previous background

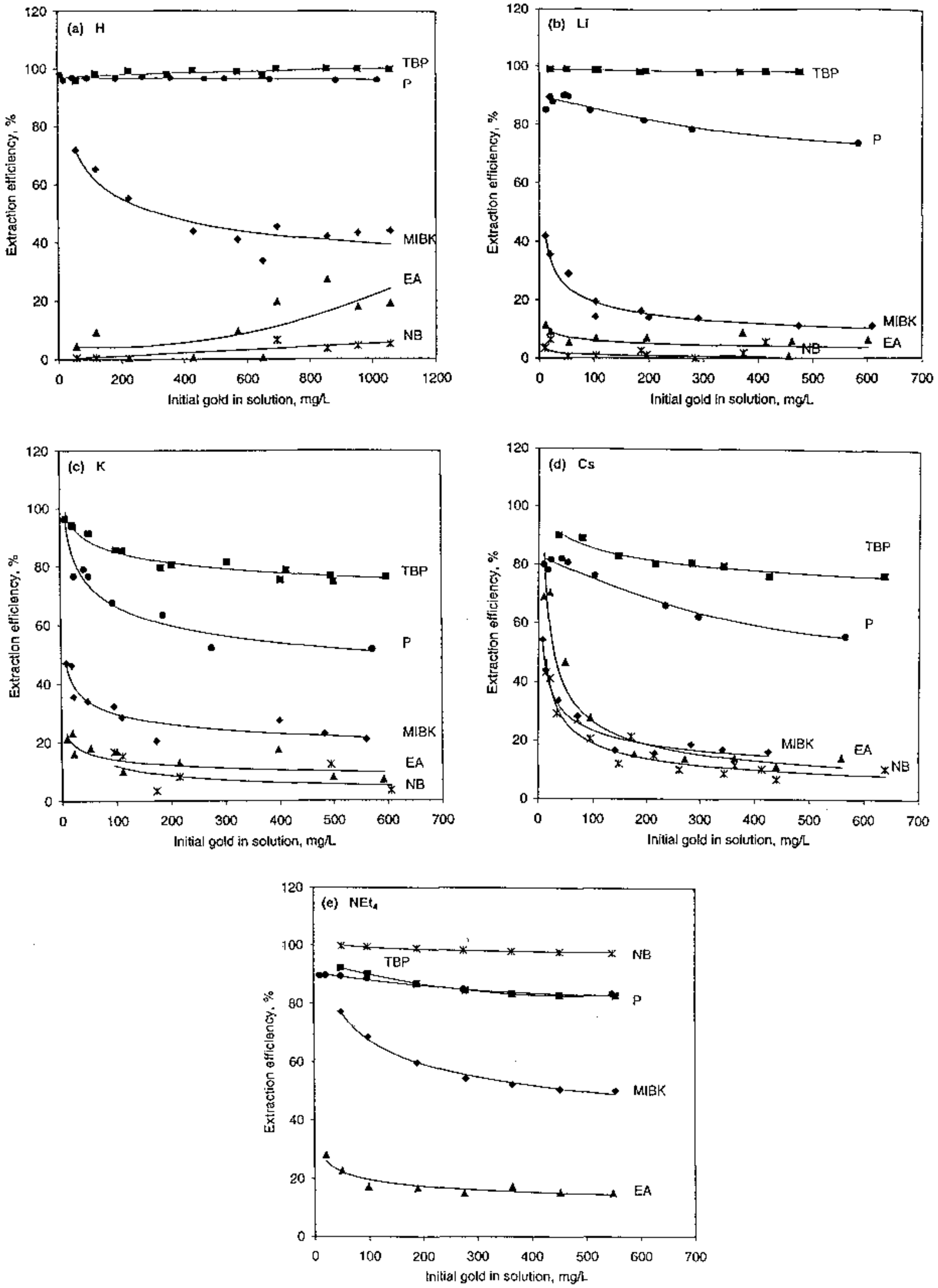

FIG. 1 Effect of solvent (TBP: tri-*n*-butyl phosphate; P: 1-pentanol; MIBK: methyl isobutyl ketone; EA: ethyl acetate; NB: nitrobenzene) on extraction of gold from $MAu(CN)_2$ solution, where M is (a) H, (b) Li, (c) K, (d) Cs, and (e) NEt_4. Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M MCl.

electrolytes now performs the best, with almost 100% extraction efficiencies being obtained. The extraction efficiency curves for 1-pentanol and TBP are both high and almost coincident; those for MIBK and EA follow the same trend as before.

Extraction of Aurocyanide from 0.1 M KCl Solution by Alcohols and Ketones

The extraction of aurocyanide by alcohols occurs in order of the homologous series 1-butanol (B) $>$ 1-pentanol (P) $>$ 1-hexanol (H) $>$ 1-octanol (O), as shown in Fig. 2(a). This trend of increasing extraction efficiencies as the alkane chain decreases in length is further demonstrated for ketones in Fig. 2(b), where the trend methyl ethyl ketone (MEK) $>$ methyl *iso*butyl ketone (MIBK) is evident. Is is also noteworthy that the extraction efficiency decreases as the gold concentration increases.

Effect of Cation on the Extraction of Aurocyanide from 0.1 M MCl Solution ($M = H, Li, K, Cs, NEt_4$) by Different Solvents

Figure 3 demonstrates that the unusual trend previously observed (1) in the effect of cation on the extraction of aurocyanide by 1-pentanol, holds also for other solvents. In the case of both TBP (Fig. 3a) and 1-pentanol (Fig. 3b), minimum extraction was obtained in the presence of 0.1 M KCl:

$$H^+ > Li^+ > NEt_4^+ > Cs^+ > K^+$$

For both MIBK (Fig. 3c) and EA (Fig. 3d), however, it was 0.1 M LiCl that resulted in the lowest extraction efficiencies:

$$H^+ \sim NEt_4^+ > K^+ \sim Cs^+ > Li^+$$

For NB, the anomalously high extraction of aurocyanide (Fig. 3e) in the presence of 0.1 M NEt_4Cl:

$$NEt_4^+ \gg Cs^+ > K^+ \sim H^+ > Li^+$$

is comparable with that obtained for the extraction of M^+ $Au(CN)_2^-$ ion pairs ($M = Li, K, Cs$) into NB in the presence of the linear polyether, Triton X-100 (17).

DISCUSSION

The distribution of $MAu(CN)_2$ into an immiscible solvent can be represented as follows:

$$nM^+ + nAu(CN)_2^- \overset{K}{\rightleftharpoons} \overline{[MAu(CN)_2]_n} \qquad (1)$$

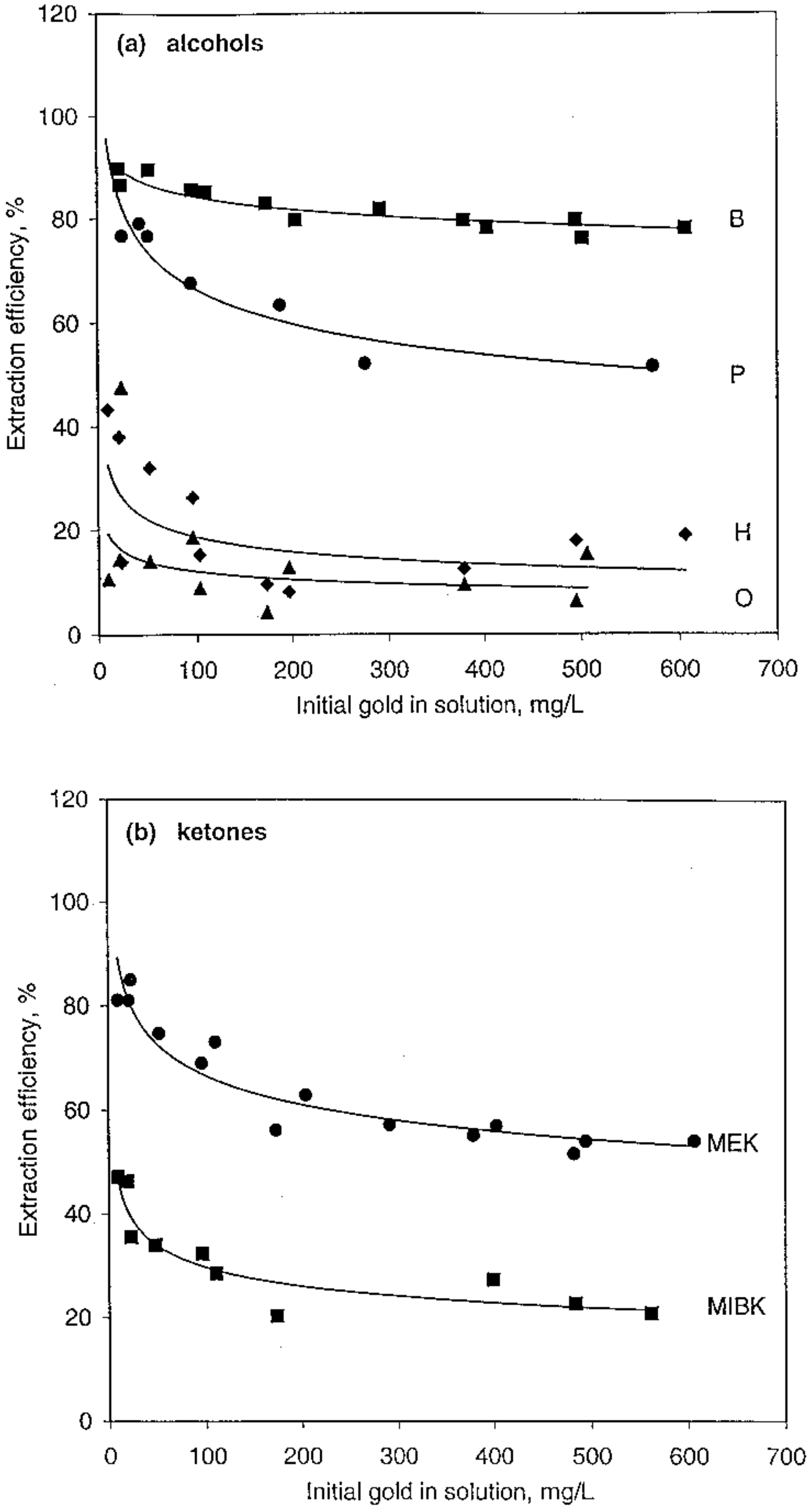

FIG. 2 Extraction of gold from $KAu(CN)_2$ solution by homologous series of (a) alcohols and (b) ketones (B: 1-butanol; P: 1-pentanol; H: 1-hexanol; O: 1-octanol; MEK: methyl ethyl ketone; MIBK: methyl isobutyl ketone). Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

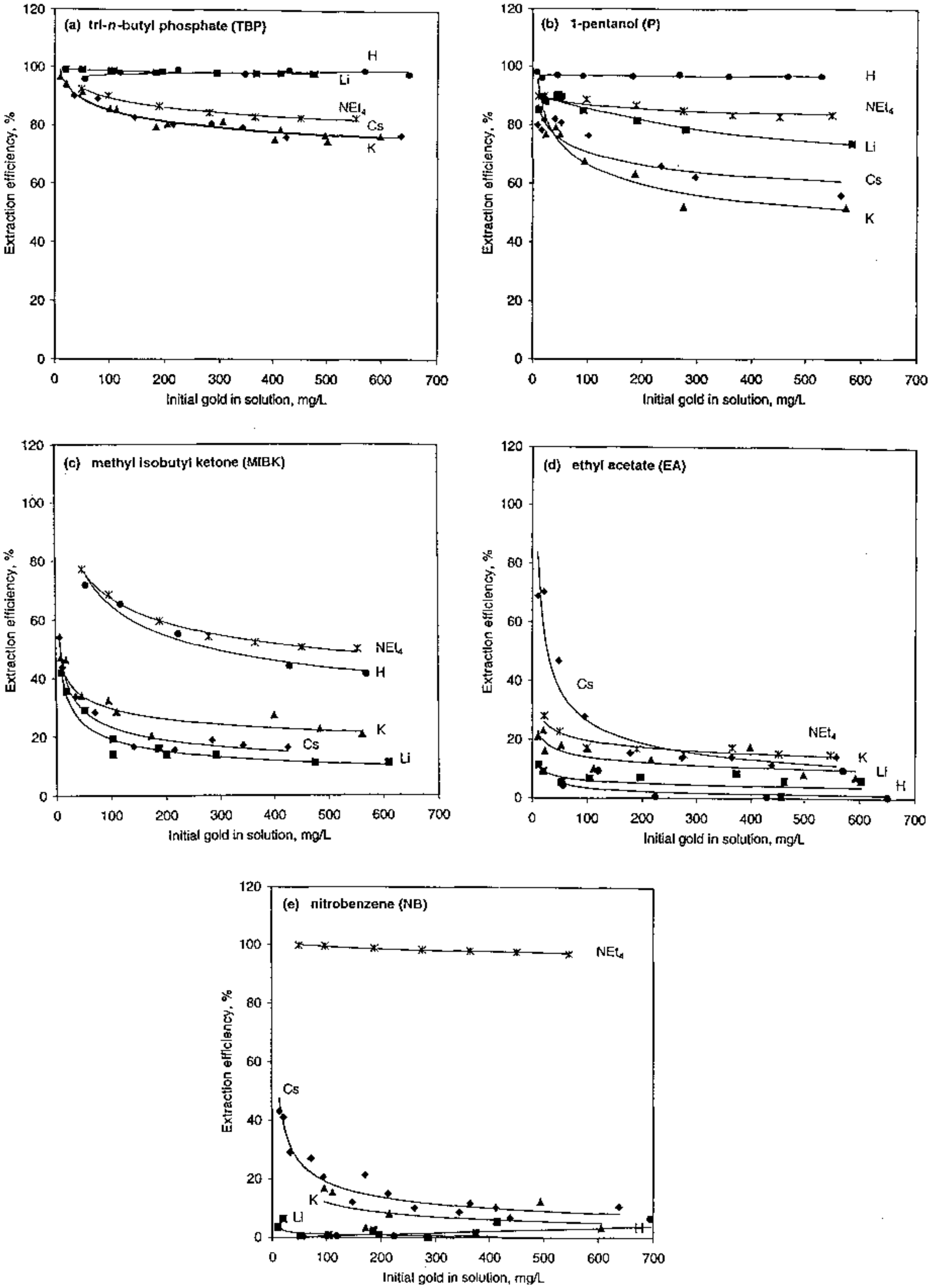

FIG. 3 Effect of cation (M = H, Li, K, Cs, NEt_4) on extraction of gold from $MAu(CN)_2$ solution by various solvents: (a) TBP: tri-*n*-butyl phosphate, (b) P: 1-pentanol, (c) MIBK: methyl isobutyl ketone, (d) EA: ethyl acetate, (e) NB: nitrobenzene. Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M MCl.

where overscoring denotes species in the organic phase. This model assumes there to be one species, $[MAu(CN)_2]_n$, in the organic phase. This assumption has no theoretical basis, but is a useful tool for the interpretation of distribution data.

The equilibrium constant, K, for Reaction (1) can be written as follows:

$$K = \frac{\overline{[MAu(CN)_2]_n}}{[M^+]^n[Au(CN)_2^-]^n} \tag{2}$$

The logarithmic form is:

$$\log[MAu(CN)_2]_n = n\log[M^+] + n\log[Au(CN)_2^-] + \log K \tag{3}$$

In the present series of experiments, $[M^+]$ was kept constant at 0.1 M (as MCl). Thus, $n \log[M^+]$ remains constant. If c_s denotes the total analytical gold concentration in the solvent phase at equilibrium, and c denotes that in the aqueous phase at equilibrium, then a plot of $\ln c_s$ against $\ln c$ would yield n, the aggregation number, which is equal to the slope. An example of such a plot is shown in Fig. 4 for the distribution of $KAu(CN)_2$ between TBP and 0.1 M KCl solution, and the value of $n = 0.69$ obtained indicates that the simple model of Eqs. (1) to (3) above does not hold in this instance. Miller et al. (2)

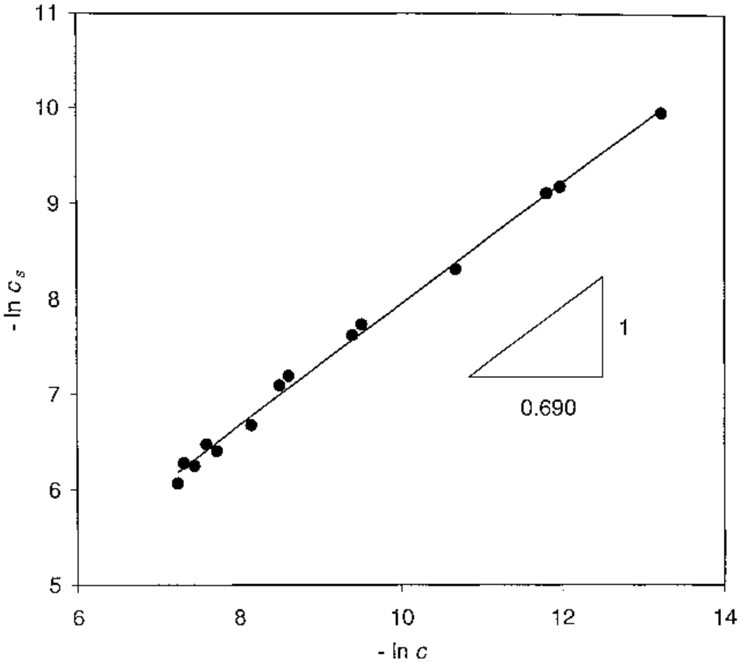

FIG. 4 Distribution of gold between $KAu(CN)_2$ solution and tri-*n*-butyl phosphate (TBP). Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

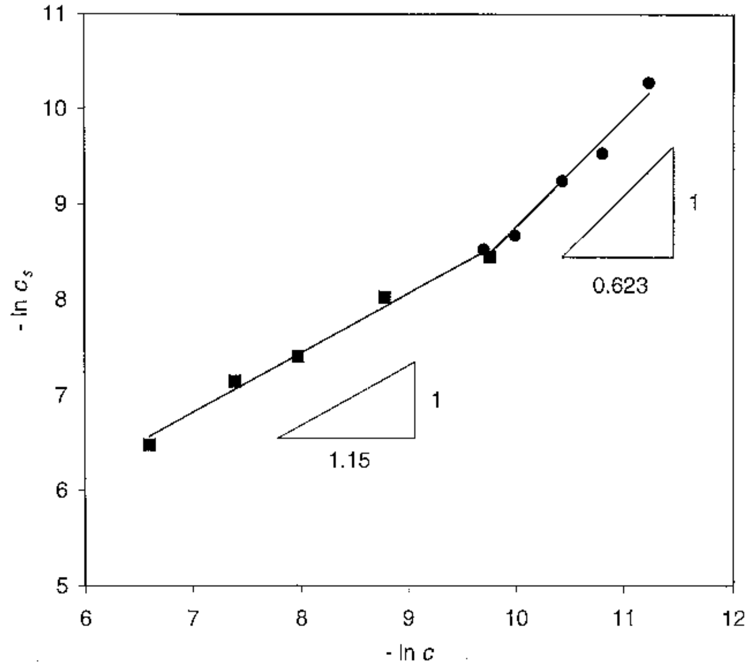

FIG. 5 Distribution of gold between $KAu(CN)_2$ solution and 1-pentanol (P). Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

report a similar effect for $KAu(CN)_2$ extraction into TBP from an aqueous solution containing 0.1 M NaCN/0.1 M NaOH, which they ascribe to "a continual change in the capacity of the organic phase and/or the nature of the mixed solvation structure."

In the light of the present study, an interpretation based simply on dissociation of the $MAu(CN)_2$ species in the organic phase is used. Conductance measurements on the solutions used to generate the data in Fig. 4 have confirmed this premise. Some extent of dissociation of salts in water-saturated organic solvents has been suggested in numerous studies (16), particularly in solvents of higher bulk dielectric constant. Müller and Diamond (18) present similar effects for trilaurylamine. Data on MCl salts in organic solvents (where values of n ranged from less than 1 to greater than 2) were interpreted in terms of dissociation ranging through to aggregation. The interpretation was confirmed by osmometric measurements. Maddock et al. (19) report the dissociation of $HAuCl_4$ in various organic phases, as shown by distribution measurements and confirmed by migration experiments.

A somewhat different situation arises when the solvent is 1-pentanol, as shown in Fig. 5. As well as the behavior discussed above, there is a break in the curve, and at lower concentrations a slope of $n = 1$ is obtained. This is the reverse of the predicted situation, where the degree of association would be expected to increase with increasing concentration. Zvyagintsev et al (3) report similar behavior for the distribution of $HAu(CN)_2$ into 1-pentanol, which they interpret in terms of aqueous phase dimerization, forming nonextractable $[HAu(CN)_2]_2$ species in the aqueous phase. Dimerization is not likely to occur in media of such high dielectric constant, however, and the following interpretation seems more reasonable.

The background electrolyte, in this case KCl, was found to distribute into the 1-pentanol phase to a modest degree. Potentiometric silver nitrate titrations for Cl^- were performed on aliquots of 1-pentanol that had been contacted with aqueous solutions of varying KCl concentrations. The chloride concentration in the 1-pentanol phase that had been contacted with aqueous 0.1 M KCl was found to be about 2×10^{-4} M. This corresponds approximately with the location of the break in the $\ln c_s$–$\ln c$ curve (Fig. 5), at about 1×10^{-4} M.

The behavior at low gold concentrations can therefore most probably be interpreted as simple ion exchange between Cl^- and $Au(CN)_2^-$. The very much higher affinity of the latter ion for the solvent phase ensures the complete exchange of $Au(CN)_2^-$ for Cl^-. Once this point has been reached, no further ion exchange can occur, and the extraction of $K^+Au(CN)_2^-$ takes place, as discussed for the TBP case. In the TBP solutions (Fig. 4), the concentration of chloride was also analyzed, and was found to be about 2×10^{-5} M; therefore the break in the $\ln c_s$–$\ln c$ curve was fortuitously not observed in the concentration region studied.

Similar behavior was observed in the $HAu(CN)_2$/1-pentanol system (Fig. 6). An analytical value of $[Cl^-]_s$ of 0.0034 M can be compared with the location of the break in the curve, which occurs at about $c_s = 0.0025$ M.

The slope of $n = 1$ found for concentrations of gold less than that for Cl^- in the organic phase is to be expected from the ion-exchange mechanism discussed above, and can easily be derived mathematically (20, 21).

The association constant for $MAu(CN)_2$ in the organic phase can be calculated from distribution data at varying total concentrations of gold, from which Figs. 4 to 6 were derived. Association behavior in these water-saturated solvents will be discussed in terms of the extraction of $MAu(CN)_2$ salts from aqueous solution by various extractants.

The extraction constant for an ion-pair species QX between two phases is given (22) as

$$K_{ex}^{IP} = \frac{a_s(QX)}{a_w(Q^+)a_w(X^-)} \tag{4}$$

where a_s and a_w refer to the activities of the species in the organic and aqueous phases, respectively. In dilute solutions of QX containing only Q^+, X^- ions, and QX ion pairs, the association constant in the organic phase is given as

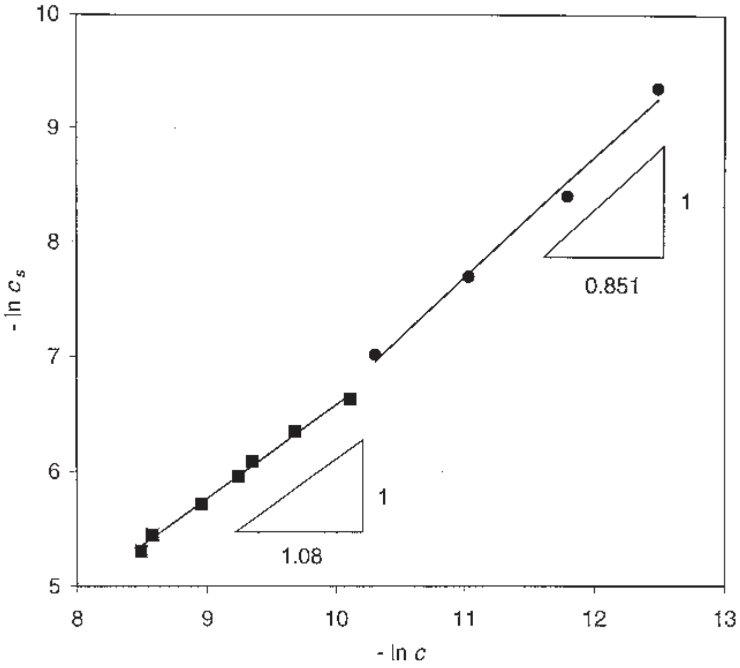

FIG. 6 Distribution of gold between HAu(CN)$_2$ solution and 1-pentanol (P). Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M HCl.

$$K_A = \frac{a_s(QX)}{a_s(Q^+)a_s(X^-)} \tag{5}$$

From Eqs. (4) and (5), a relationship between the apparent distribution ratio D^* and the aqueous concentrations can be deduced (22):

$$D^* + D_{corr} = [a_w(Q^+)a_w(X^-)]^{\frac{1}{2}}K_{ex}^{IP} + (K_{ex}^{IP}/K_A)^{\frac{1}{2}} \tag{6}$$

where D^* is defined as

$$D^* = c_s/[a_w(Q^+)a_w(X^-)]^{\frac{1}{2}} \tag{7}$$

and D_{corr} is a correction term:

$$D_{corr} = [1 - (1/f_s)](K_{ex}^{IP}/K_A)^{\frac{1}{2}} \tag{8}$$

In Eq. (8), f_s is the mean activity coefficient in the organic layer. The D_{corr} term was found to be small and rather unimportant for the calculation, except in the cases cited later.

Equation (4) assumes that the aqueous ions distribute into the organic phase in the form of the ion pair alone. The possibility of the free ions distributing into the organic phase as such necessitates the definition of an ionic extraction constant:

$$K_{\mathrm{ex}}^{\mathrm{ION}} = \frac{a_{\mathrm{s}}(\mathrm{Q}^{+})a_{\mathrm{s}}(\mathrm{X}^{-})}{a_{\mathrm{w}}(\mathrm{Q}^{+})a_{\mathrm{w}}(\mathrm{X}^{-})} \tag{9}$$

If this is combined with Eq. (5), Eq. (10) is obtained:

$$K_{\mathrm{ex}}^{\mathrm{ION}} = K_{\mathrm{ex}}^{\mathrm{IP}}/K_{\mathrm{A}} \tag{10}$$

The total extraction constant, which includes the extraction of both ions and ion pairs, will be defined in a similar manner to that of Iwamoto et al. (23):

$$K_{\mathrm{ex}}^{\mathrm{TOT}} = K_{\mathrm{ex}}^{\mathrm{ION}}K_{\mathrm{ex}}^{\mathrm{IP}} \tag{11}$$

Equation (6) was solved using a linear least-squares algorithm, enabling the calculation of K_{A}, $K_{\mathrm{ex}}^{\mathrm{TOT}}$, $K_{\mathrm{ex}}^{\mathrm{IP}}$, and $K_{\mathrm{ex}}^{\mathrm{ION}}$.

Effect of Solvent

Water Content

Values of K_{A} and $K_{\mathrm{ex}}^{\mathrm{IP}}$ were obtained for $\mathrm{KAu(CN)_2}$ in various solvents from the distribution data in Figs. 1 to 3. There is a correlation between these parameters and the water content of the organic phase expressed in terms of x_{w}, the mole fraction of water, as shown in Fig. 7. The association constant decreases exponentially as the water content of the organic phase increases, while the extraction constants increase with water content. This suggests that the species in the organic phase are preferentially hydrated. Abundant evidence exists (16, 18, 23–26) regarding the preferential hydration of salts in organic solvents originating from distribution experiments. The low values obtained for the hexanol and octanol extraction constants can possibly be ascribed to the high viscosities of these solvents, resulting in entrainment. The distribution data obtained for these two solvents were more scattered than for any other solvent studied.

The K_{A} effect shown in Fig. 7 is simply a manifestation of decreasing hydration forcing the ions to associate in order to fulfill their coordination requirements. The trend of increasing extraction of the species as the water content increases is also a manifestation of this effect. In general, solvents with a high water content are more able to solvate, and therefore extract, the ions and ion pairs effectively.

A notable exception to these trends occurs when the solvent is TBP. Evidence (16) suggests that a 1:1 TBP:$\mathrm{H_2O}$ adduct is formed in this system, accounting for the high water content. Moreover, Marcus and Kertes (16) assign TBP to a Group II class of solvents, whereas all the oxygen-containing hydrocarbon-type solvents are assigned to Group I. In Group II solvents, the solvent itself is involved in solvating the dissolved species, which is not the case

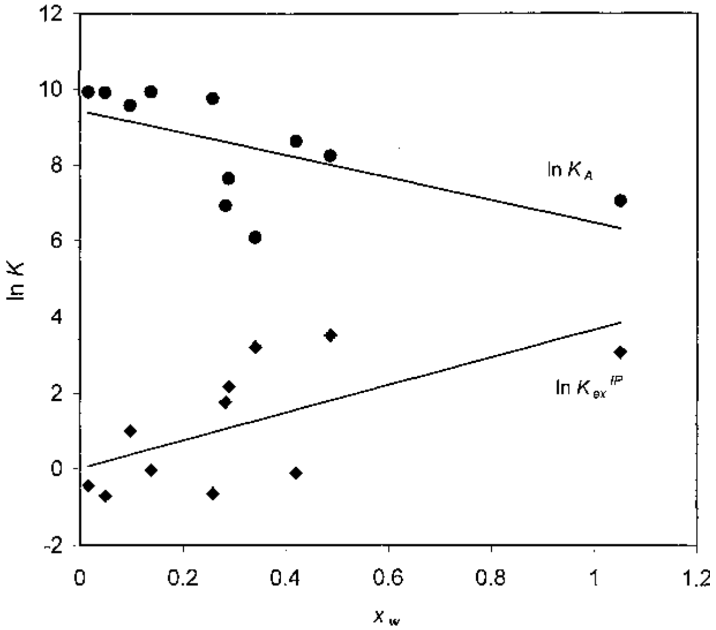

FIG. 7 Effect of organic water content (mole fraction, x_w) on extraction and association constants in the organic phase for $KAu(CN)_2$ in various solvents (listed in Tables 1, 2, and 4). Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

for Group I solvents. The anomalous behavior of TBP may thus be due to a somewhat different extractive mechanism, in which a mixed TBP–H_2O solvate exists. Such a species has been previously postulated (2) to occur in the TBP–H_2O–$KAu(CN)_2$ system.

Dielectric Constant

Table 1 shows the constants obtained for several isodielectric solvents. A comparison of association and extraction constants within each group confirms that a simple inverse cubed Bjerrum-type dependence (27) on dielectric constant does not hold for these systems, described by the Bjerrum equation:

$$K_A = (4\pi L/1000)[z_+ z_- e_0^2/\varepsilon k_B T] \int_2^b e^y y^{-4}\, dy \tag{12}$$

where L is Avogadro's number, z_+ and z_- are the charges on the ions, e_0 is the electronic charge, ε the dielectric constant of the solvent, k_B is Boltzmann's constant, and T is the temperature. The constant b is

$$b = z_+ z_- e_0^2/\varepsilon a k_B T \tag{13}$$

where a is the interionic distance.

TABLE 1

Association and Extraction Constants for $KAu(CN)_2$ in Several Isodielectric Solvents[a]

Solvent	ε^b	n^c	K_A	$10^4K_{ex}^{TOT}$	$10^4K_{ex}^{ION}$	K_{ex}^{IP}	DN^d	δ^e
1-Butanol (B)	17.5	0.82	3,739	2,976	89.22	33.36	19.5	13.6
Methyl ethyl ketone (MEK)	18.0	0.68	2,052	365	42.14	8.65	17.4	
Cyclohexanone (CX)	18.3	0.60	437	13,878	563.4	24.63	17.8	9.9
1-Pentanol (P)	13.9	0.60	1,004	331	57.39	5.76		11.6
Methyl isobutyl ketone (MIBK)	13.1	0.81	14,186	5.25	1.920	2.73		
Ethyl acetate (EA)	6.0	0.92	20,165	0.459	0.477	0.962	17.1	
Tri-*n*-butyl phosphate (TBP)	6.8	0.63	1,160	4134	188.8	21.90	23.7	

[a] Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

[b] Dieletric constant (14, 15).

[c] Aggregation number (slope of ln c_s–ln c plot).

[d] Gutmann's donor number (28–30).

[e] Solubility parameter (31).

TABLE 2

Association and Extraction Constants for KAu(CN)$_2$ in Diethyl Ether and Nitrobenzene[a]

Solvent	ε[b]	n[c]	K_A	$10^4K_{ex}^{TOT}$	$10^4K_{ex}^{ION}$	K_{ex}^{IP}	$[Cl^-]_s$ (mol/L)[d]	DN[e]	δ[f]
Diethyl ether (DE)	4.2	0.91	20 103	0.121	0.245	0.493	N.D.[g]	19.2	7.4
Nitrobenzene (NB)	34.8	0.99	20 403	0.203	0.315	0.643	6×10^{-6}	4.4	10.0

[a] Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

[b] Dielectric constant (14, 15).

[c] Aggregation number (slope of ln c_s–ln c plot).

[d] Determined by potentiometric titration with AgNO$_3$ solution.

[e] Gutmann's donor number (28–30).

[f] Solubility parameter (31).

[g] Not detectable.

A comparison of the values obtained from n, the slope of ln c_s–ln c plot, confirms that lower n values correspond to a higher degree of dissociation. In fact, for both diethyl ether and nitrobenzene, two solvents of very different dielectric constant (Table 2), values of approximately $n = 1$ were obtained, and the association constants proved to be large, indicating that for these solvents, the ion pair is the predominant species. It should be noted that the ion-exchange mechanism discussed earlier does not account for these results, since effectively no chloride could be detected in the organic phases by potentiometric silver nitrate titration.

Donor Number (DN) and Solubility Parameter (δ)

Tables 1 and 2 show that neither the solvent *DN* (28–30) nor δ (31) are the most important parameters influencing the association and extraction constants, once again confirming the importance of water content on the association and distribution behavior of the system. Empirical relationships have been established (27) between association constants and other parameters, such as solubility products. It is likely that these, as well as other parameters not discussed, also have some effect on the association constants in different solvents.

Effect of Diluent

Benzene and cyclohexane were found to extract no measurable quantity of gold from a 0.003 M KAu(CN)$_2$ aqueous solution in the presence of 0.1 M KCl, and are thus effectively inert diluents. The effect of these diluents (1:1 mole ratios with 1-pentanol) on the distribution of KAu(CN)$_2$ was investi-

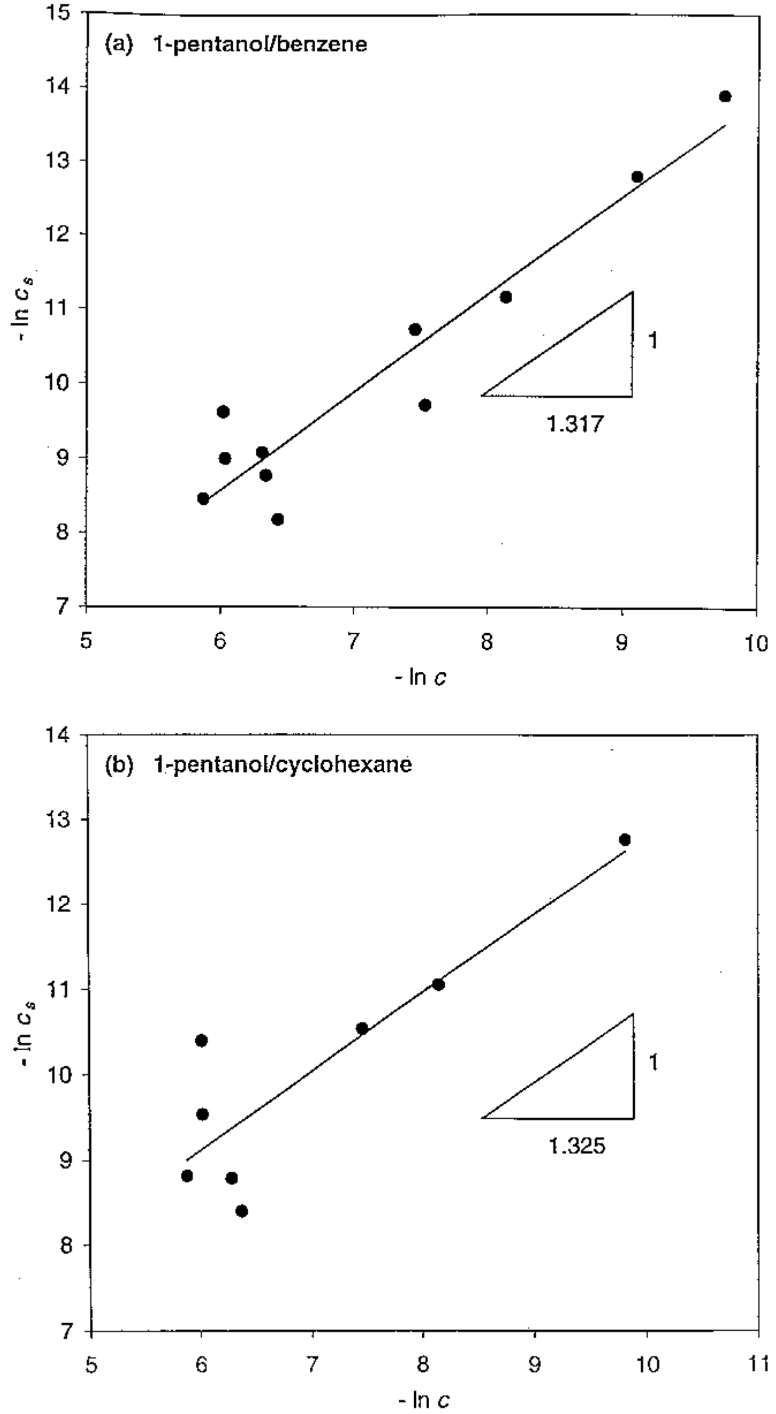

FIG. 8 Distribution of gold between $KAu(CN)_2$ solution and 1:1 mole ratio mixtures of 1-pentanol (P) with (a) benzene, and (b) cyclohexane. Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M KCl.

gated. Figure 8 shows ln c_s–ln c plots for benzene and cyclohexane as diluents. Table 3 summarizes the relevant properties of these mixtures.

Aggregation numbers exceeding $n = 1.0$ indicate that aggregation beyond the ion pair is occurring, e.g.,

$$2\mathrm{K}^+\mathrm{Au(CN)}_2^- \overset{K_q}{\rightleftharpoons} [\mathrm{K}^+\mathrm{Au(CN)}_2^-]_2 \tag{14}$$

The fact that the aggregation number lies between 1 and 2 indicates that a mixture of ion pairs and dimers is probably present. The species are presumably all hydrated, forming solvent-separated ion pairs and dimers.

The interpretation of these results in terms of triple ion formation, i.e.:

$$\mathrm{K}^+ + \mathrm{K}^+\mathrm{Au(CN)}_2^- \overset{K_t}{\rightleftharpoons} \mathrm{K}^+\mathrm{Au(CN)}_2^-\ \mathrm{K}^+ \tag{16}$$

$$\mathrm{Au(CN)}_2^- + \mathrm{K}^+\mathrm{Au(CN)}_2^- \overset{K_t}{\rightleftharpoons} \mathrm{Au(CN)}_2^-\ \mathrm{K}^+\mathrm{Au(CN)}_2^- \tag{17}$$

cannot be discounted. However, the very existence of triple ions has been questioned (32, 33) because the conductivity effects which led initially to triple ions being postulated can in several instances be explained in terms of the effects of concentration on permittivity. Moreover, the presence of any ionic species in media of such low dielectric constant and water content is doubtful.

Table 3 shows that the dielectric constant of the solution is about half that of pure 1-pentanol; however, the water content has been reduced by a factor of about 6. Water content is once again the most important factor that influences the ion-pair formation and aggregation in this system.

The presence of species such as dimers in mixtures of solvents and diluents also serves to explain certain anomalous behavior reported previously. In an attempt to assign a solvation number to the extracted species, Mooiman (34) reports an upward curvature to a plot of log D against log[TBP] for the distri-

TABLE 3
Aggregation Numbers and Relevant Properties of Solvent Mixtures

Solvent mixture (1:1 molar ratio)	n[a]	ε[b]	$100x_w$[c]	wt%w[d]	ρ (g/mL)[e]
Pentanol/benzene	1.317	9.5	5.4	1.17	0.841
Pentanol/cyclohexane	1.325	5.5	4.0	0.82	0.794
Pentanol	0.60	13.9	28.3	7.5	0.814
Benzene	—[e]	2.28	0.31	0.072	0.879
Cyclohexane	—[e]	2.03	0.48	0.072	0.779

[a] Aggregation number (slope of ln c_s–ln c plot).
[b] Dielectric constant (14, 15; mixtures—this work).
[c] x_w refers to the mole fraction of water in the water-saturated mixtures (this work).
[d] Weight % water in the organic phase.
[e] Densities of the water-saturated mixtures are reported, and they compare well with theoretical values for the pure mixture (31).

bution of $KAu(CN)_2$ between an aqueous solution and a TBP solution with *o*-xylene as diluent ($\varepsilon = 2.568$). Under these conditions, dimerization would be expected to occur to some extent. Thus, analysis based on an assumption that the only species in the organic phases is the ion pair, may be invalid under these conditions.

Effect of Cation

The effect of cation on the distribution and association parameters for $KAu(CN)_2$ in five different solvents is shown in Table 4.

The effect of cationic radius on the total extraction constant, $K_{\mathrm{ex}}^{\mathrm{TOT}}$, is similar for several different solvents. The total extraction constant goes through a minimum at K^+, with $K_{\mathrm{ex}}^{\mathrm{TOT}}$ increasing toward both lower cationic radius (Li^+, H^+), as well as higher cationic radius (Cs^+, NEt_4^+). (It should be pointed out that the use of the crystallographic radius merely represents a convenient scale for comparison. No cognizance has been taken in Table 4 of hydrated or solvated radii, these being somewhat difficult to quantify.) This confirms the similar trend that has been established in previous work (3) on the distribution of aurocyanide ion-pairs into 1-pentanol.

The fact that a similar trend is evident in solvents of such varying dielectric constant and water content suggests that a similar mechanism is prevalent for the extraction of $MAu(CN)_2$ by each of these solvents.

The trend to greater $K_{\mathrm{ex}}^{\mathrm{TOT}}$ as one ascends the series K^+, Li^+, H^+ is probably a manifestation of the structure of the hydrated species in each case. Diamond (35) discusses a related effect observed in the extraction of $HInCl_4$ into organic solvent. Water molecules are much smaller than solvent molecules, and hence more water molecules can pack around a cation to form a primary hydration shell. This fact, coupled with the greater solvation energy associated with ion–water interactions as compared to ion–organic solvent interactions, means that to extract into the solvent without great loss in solvation energy, the cation must retain its primary hydration shell and undergo further solvation of this hydrated species in the organic phase.

The situation is different for larger cations, such as Cs^+ and NEt_4^+, which have smaller hydration enthalpies and virtually no primary hydration shell. Such ions displace a considerable volume of the hydrogen-bonded water structure in the aqueous phase, and are hydrophobic, being squeezed out into the organic phase. This hydrophobic effect is also evidenced by the decreasing aqueous solubilities of aurocyanide salts as the cationic radius increases (1).

It is significant that the order of decreasing extractability prevalent in Table 4, i.e.,

$$\text{TBP} > \text{1-pentanol} > \text{MIBK} > \text{ethyl acetate}$$

is also the order of decreasing water content of the saturated solvents.

TABLE 4

Distribution and Association Data for $MAu(CN)_2$ in Various Solvents[a]

Solvent	Constant	H	Li	K	Cs	NEt_4
1-Pentanol (P)	K_A	2,418	1,045	1,004	377.1	9,949
	$10^4K_{ex}^{TOT}$	185,347	2,821	330.5	489.0	2,052
	$10^4K_{ex}^{ION}$	875.5	164.3	57.39	113.9	45.11
	K_{ex}^{IP}	211.7	17.17	5.76	4.29	44.88
	n[b]	0.70	0.67	0.60	0.63	0.87
Methyl isobutyl ketone (MIBK)	K_A	2,188	2,364	14,186	4,724	701.1
	$10^4K_{ex}^{TOT}$	156.7	1.04	5.25	2.87	234.8
	$10^4K_{ex}^{ION}$	26.76	2.10	1.92	2.47	57.87
	K_{ex}^{IP}	5.86	0.50	2.73	1.16	4.06
	n[b]	0.79	0.66	0.81	0.63	0.59
Ethyl acetate (EA)	K_A	[c]	856,486	20,165	[c]	34,736
	$10^4K_{ex}^{TOT}$	[c]	0.00892	0.459	[c]	0.658
	$10^4K_{ex}^{ION}$	[c]	0.102	0.477	[c]	0.434
	K_{ex}^{IP}	[c]	0.874	0.962	[c]	1.51
	n[b]	1.0	0.87	0.92	0.88	0.76
Tri-*n*-butyl phosphate (TBP)	K_A	806.9	4,184	1,160	2,053	1,457
	$10^4K_{ex}^{TOT}$	2.80×10^8	497,415	4,134	3,555	6,077
	$10^4K_{ex}^{ION}$	58,850	1,090	188.8	131.6	204.2
	K_{ex}^{IP}	4,749	456.2	21.90	27.01	29.96
	n[b]	0.74	0.68	0.63	0.70	0.67
Nitrobenzene (NB)	K_A	[c]	7,210	20,403	[c]	[c]
	$10^4K_{ex}^{TOT}$	[c]	4.29×10^{-9}	0.203	[c]	[c]
	$10^4K_{ex}^{ION}$	[c]	0.00771	0.315	3.76	10,318
	K_{ex}^{IP}	[c]	0.00556	0.643	[c]	[c]
	n[b]	1.0	0.56	0.99	0.50	0.50

[a] Aqueous and organic volumes: 20 mL; time: 20 minutes; temperature: 23°C; background electrolyte: 0.1 M MCl.

[b] Aggregation number (slope of ln c_s–ln c plot).

[c] Data unobtainable due to insufficient degree of extraction.

The effect of cation on K_{ex}^{ION} is shown in Table 4, and from the similarity to the effect on K_{ex}^{TOT}, it is clear that the ionic component contributes considerably to the total extraction trend.

The data for nitrobenzene in some cases yielded slightly negative values, indicating complete dissociation in the organic phase. Moreover, in these cases the aggregation number, *n*, proved to be very close to 0.5, which is the theoretical value obtained when dissociation is complete. This is a manifestation of the high dielectric constant of nitrobenzene ($\varepsilon = 34.82$), and the inverse dependence of K_A on ε, by the Bjerrum equation (Eq. 12). The data for K_{ex}^{ION}, however, have physical significance. A similar trend to the other solvents is evident, except in the case of NEt_4^+, which displays a markedly higher extraction into nitrobenzene. Nitrobenzene is relatively noncoordinating, being a poor donor solvent, and therefore has a low water content, thus providing a medium more compatible with the nonhydrated tetraethylammonium cation than a solvent with a higher water content. Moreover, large hydrophobic cations such as NEt_4^+ behave as "structure makers" in aqueous solution (36), so a 0.1 M NEt_4Cl background in the aqueous phase would result in a loss of entropy and an increase in enthalpy of water, resulting in an enhanced "squeezing out" of the hydrophobic $NEt_4^+Au(CN)_2^-$ ion pair from the aqueous phase.

The effect of cationic radius on both K_{ex}^{IP} and K_A does not show as clearcut a trend as the effect of K_{ex}^{ION} and K_{ex}^{TOT}. The effect on K_{ex}^{IP} is qualitatively similar, displaying a minimum. However, the difference in solvation of the various ion pairs must be considerable, and could account for the shifting minimum.

A general trend to lower K_A is observed as the cationic radius increases, and this is in agreement with data for the association of tetraalkylammonium halides in various solvents (14), and is consistent with the theoretical dependence of K_A on a, the interionic distance in the Bjerrum equation (14). The anomalous behavior of the $NEt_4^+Au(CN)_2^-$ ion pair in 1-pentanol is probably a manifestation of the hydrogen-bonded structure of the alcohol, making it water-like and therefore subject to the same thermodynamic considerations as discussed above for the aqueous phase.

The effect of solvent water content on the values of extraction and association constants obtained for the H^+, Li^+, Cs^+ and NEt_4^+ systems with $Au(CN)_2^-$ is also shown in Table 4. The behavior observed for the extraction of $HAu(CN)_2$ and $LiAu(CN)_2$ is similar to that for the extraction of $KAu(CN)_2$, with solvent water content being the most important solvent parameter influencing the extraction and association constants, as discussed earlier. For the larger, less hydrated Cs^+ and NEt_4^+ cations, a similar trend does not exist, and other specific solvent properties, such as dielectric constant and hydrogen-bonding ability, play a role.

CONCLUSIONS

Factors influencing the extraction and association of $MAu(CN)_2$ ion pairs in organic solvents were elucidated. For extraction of aurocyanide ion pairs with small cations (H^+, Li^+, Na^+, Ca^{2+}), the most important factor is the solubility of water in the solvent. High extraction efficiencies are related to low association constants for these cations. For extraction of aurocyanide ion pairs with larger, less hydrated cations (Cs^+, NEt_4^+), other specific solvent parameters, such as dielectric constant and hydrogen-bonding ability, play a role.

Selectivity for aurocyanide could possibly be enhanced by the correct choice of solvent and cation in existing applications of aurocyanide ion pairs, including ion-selective electrodes, ion-pair chromatography, as well as liquid and solid extractants for gold.

The present work also sheds further light on the nature of ion-pair species shown to be involved in the extraction of aurocyanide by activated carbon in the commercial carbon-in-pulp process.

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