

Precipitation of potassium aurocyanide from dipolar aprotic solvents using a supercritical antisolvent

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Abstract

Gas antisolvent (GAS) precipitation is considered for the quantitative recovery of potassium aurocyanide ($\text{KAu}(\text{CN})_2$) from dipolar aprotic solvents including acetone, dimethylsulfoxide and *N*-methyl-2-pyrrolidone. Experimental data are reported on the solubility of $\text{KAu}(\text{CN})_2$ in the various solvents expanded with carbon dioxide at 308 K. It is shown that carbon dioxide is an effective antisolvent for reducing the solubility of $\text{KAu}(\text{CN})_2$ in acetone and *N*-methyl-2-pyrrolidone. The effect of several process parameters on the GAS process are also discussed in the context of solvent-assisted elution, a process which utilises dipolar aprotic solvents for the desorption of metal-cyanide complexes from activated carbon. The process parameters investigated are the initial solute concentration, the dielectric constant of the solvent and the presence of water in the solvent. It is proposed that the use of mixtures of dipolar aprotic solvents may provide a means of tuning the dielectric constant to satisfy the individual requirements of both processes.

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1. Introduction

Cyanidation is the principal means by which gold and silver are recovered from ore bodies in commercial mining operations. The cyanidation process leads to the formation of large volumes of aqueous cyanide leach solutions in which the precious metals are present at low concentrations in the form of cyanide complexes: $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$. In the carbon-in-pulp process [1], the complexes are recovered from the leach solution in a more concentrated form by adsorption onto activated carbon. The adsorption step is reversed by contacting the carbon with a hot aqueous cyanide solution. Mixtures of water and organic solvents have also been shown to be highly effective for the elution (stripping) of the complexes from activated carbon [2–4]. The principle advantages of solvent-assisted elution (SAE) over other elution techniques are that the process can be completed more rapidly and at lower temperatures.

The main requirement of the organic solvent in SAE is that it must be miscible with water at the given mixture composition. The combined solution must also contain a sufficient concentration of a counter-ion, such as CN^- , for the elution process to proceed [5]. For very polar organic solvents, such as dimethylsulfoxide (DMSO), it is actually possible to dissolve sufficient quantities of CN^- , derived from a salt such as KCN, without the use of water. One of the disadvantages of SAE is that there is a potential fire hazard in the downstream recovery of the metals from the aqueous/organic solution using electrochemical methods. Evaporation of the solvent also represents an energy-intensive option for eliminating this hazard. The recovery of each complex as a precipitated salt is generally more desirable.

A variety of precipitation techniques based on supercritical antisolvents has been investigated in recent years as a means of producing submicronic particles in a number of applications [6–8]. For the most part, these applications are concerned with the precipitation of organic and macromolecular compounds, such as pharmaceuticals and polymers, from polar organic solvents using CO_2 as the antisolvent. There are,

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however, reports on the precipitation of organometallic compounds [9,10] made up of metal cations and large polarisable anions, and even some inorganic compounds [11].

It is worth noting that some dipolar aprotic solvents, DMSO in particular, are stronger cation solvators than water [12,13]. Large polarisable anions are also better solvated in dipolar aprotic solvents in comparison to water [14]. Furthermore, such solvents exhibit a high degree of volumetric expansion with CO₂ at elevated pressure [15]. These features highlight the potential utility of supercritical antisolvents in the recovery of certain organometallic compounds from dipolar aprotic solvents.

In this work, supercritical antisolvent precipitation, also known as gas antisolvent (GAS) precipitation, is considered for the recovery of potassium aurocyanide (KAu(CN)₂) from the following dipolar aprotic solvents: acetone, DMSO and *N*-methyl-2-pyrrolidone (NMP). Carbon dioxide is used as the antisolvent. Experimental data are reported on the solubility of KAu(CN)₂ in the various solvents expanded with CO₂. The various factors that affect the feasibility of the GAS process for the quantitative recovery of KAu(CN)₂ are discussed in the context of the SAE process. These factors include the initial solute concentration in the solvent, the dielectric constant of the solvent and the presence of water in the solvent.

2. Experimental section

2.1. Materials

Liquid CO₂ (99.5%) was purchased from Linde Gases. DMSO (99%) and NMP (99.5%) were obtained from Sigma–Aldrich. Acetone (99.5%) was supplied by Asia Pacific Specialty Chemicals. Due to the hygroscopic nature of DMSO and NMP, and the presence of a small amount of water in the purchased solvents, these solvents were dried prior to use with a type 4A molecular sieve. The molecular sieves were purchased from Labchem in the form of beads 2.5–5 mm in diameter. KAu(CN)₂ (99.9%) was purchased

from EBS and Associates and NaCN (99%) was purchased from BDH chemicals.

2.2. Equipment

A schematic of the experimental apparatus used for the precipitation experiments is shown in Fig. 1. The precipitation chamber consisted of stainless steel sample cylinder with an internal volume of approximately 150 mL. A 0.5 μm frit was fitted at the bottom of the precipitation chamber. The whole assembly was immersed in a water bath for which the temperature was maintained at ±0.2 K with a heater/circulator (Thermoline, Unistat 130). The pressure inside the chamber was measured with a pressure transducer with an uncertainty of ±0.035 MPa (Druck, PDCR 911). Carbon dioxide was introduced into the precipitation chamber with a syringe pump (ISCO, Model 260D).

2.3. Procedure

In a typical SAE process, the final concentration of KAu(CN)₂ in the stripping solution varies between 10 and 20 g/L. In the determination of the solubility of KAu(CN)₂ in each of the expanded solvents, we employed solutions initially containing marginally higher concentrations of the solute. This was done in an attempt to construct a more expanded view of the effect of pressure on solubility, while avoiding the possibility of phase separation in the liquid phase during the expansion of the solvent. The initial concentrations of KAu(CN)₂ were 20, 43 and 50 g/L for acetone, NMP and DMSO, respectively. The solubility of KAu(CN)₂ in these solvents increases in the following order: acetone < NMP < DMSO (see Table 1). The initial concentrations of KAu(CN)₂ selected for the three solvents also reflect this trend.

An amount of 10 ml of solution, containing the dissolved KAu(CN)₂, was placed in the precipitation chamber. The precipitation chamber was pressurised slowly with CO₂ up to the desired value. The CO₂ was passed through the 0.5 μm frit via valves V1 and V2 to facilitate the saturation of the liquid

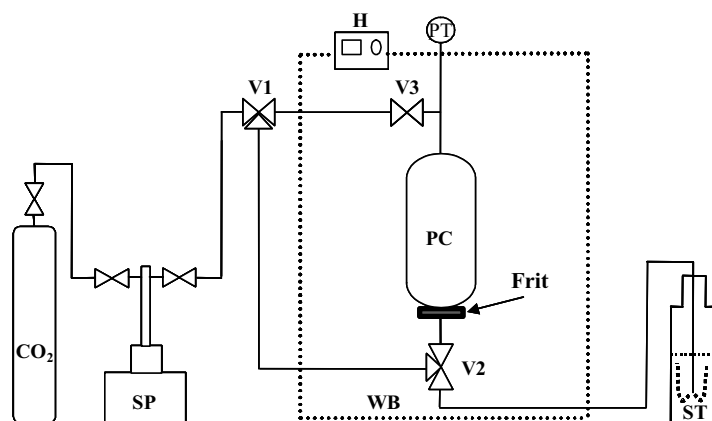


Fig. 1. Schematic diagram of the GAS precipitation apparatus. CO₂, carbon dioxide cylinder; H, heater; PC, precipitation chamber; PT, pressure transducer; SP, syringe pump; ST, solvent trap; V, valve; WB, water bath.

Table 1
The normal solubilities (S_N) of $\text{KAu}(\text{CN})_2$ and KCN in selected dipolar aprotic solvents and water

Solvent	Dielectric constant ^a	S_N (g/L)	
		$\text{KAu}(\text{CN})_2$	KCN
Acetone	21.0	82 ^b	0.03 ^c
NMP	32.6	510 ^b	0.26 ^b
DMSO	47.2	740 ^b	7.8 ^c
Water	80.1	143 ^d	500 ^d

^a Dielectric constant at 20 °C [23].

^b Solubility at 30 °C. Data determined experimentally by dissolving an excess amount of salt into 20 ml of each solvent with continuous stirring for 2 days. The solutions were then analysed for Au and K using atomic absorption spectroscopy.

^c Solubility at 25 °C [24].

^d Solubility in cold water [23].

phase with CO_2 . The system was assumed to be at equilibrium once the pressure inside the chamber had stabilized. The duration of time required for equilibrium varied between 30 and 60 min. A duration of time approaching 1 h was only evident at the highest values of pressure and was attributed to the large increase in the solubility of CO_2 in the liquid phase [16].

The solution was then removed from the chamber via valve V2 and collected in a solvent trap filled with water. During this step, the pressure was held constant by introducing fresh CO_2 via valves V1 and V3. Fresh CO_2 was introduced into the chamber for at least 45 min to ensure that all of the solution was removed. The chamber was then depressurised and washed with water to recover the $\text{KAu}(\text{CN})_2$ precipitated on the frit. The mass of $\text{KAu}(\text{CN})_2$ recovered in the solvent trap and the mass of precipitated $\text{KAu}(\text{CN})_2$ were determined using atomic absorption spectroscopy. The maximum deviation between the mass of $\text{KAu}(\text{CN})_2$ in the initial solution and the combined mass of $\text{KAu}(\text{CN})_2$ collected from the frit and the solvent trap was found to be less than 10%. All experiments were carried out at 308 K.

To calculate the solubility of $\text{KAu}(\text{CN})_2$ in a given solvent, the total volume of the expanded solution is required. This information was obtained from volumetric expansion data for the various pure solvents with CO_2 . The actual volumetric expansion data used for calculation purposes in this study are presented in Fig. 2. The following equation was used to calculate the solubility (S) of the solute at a given temperature (T) and pressure (P):

$$S(T, P) = \frac{m(T, P)}{V_i(T, P^*)[1 + E(T, P)/100]} \quad (1)$$

where m is the non-precipitated mass of solute collected in the solvent trap, V_i is the initial volume of solution at the reference pressure ($P^* = 0.1$ MPa) and E is the volumetric expansion of the pure solvent expressed as a percentage. The definition used for E is described in [16]. The solubility at a given set of conditions was calculated from the mean of duplicate runs, where the maximum deviation between runs was less than 10%. Solubility is expressed in units of mass of solute per unit volume of expanded solution (g/L).

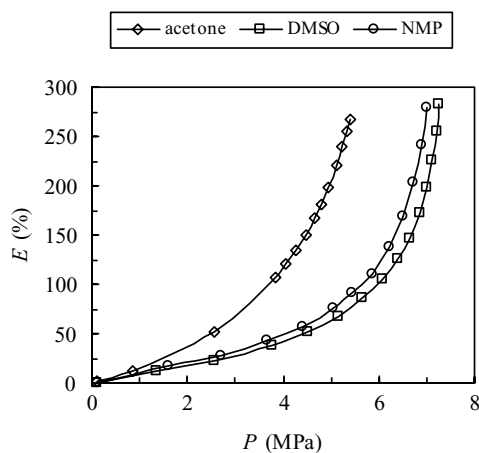


Fig. 2. Volumetric expansion of acetone, DMSO and NMP with CO_2 at 308 K. Data are from [16].

In the calculation of the solubility data, two main assumptions were made. Firstly, it was assumed that the presence of the solute, at the initial concentrations described above, did not affect the expansion behaviour of the solvents significantly. Secondly, it was assumed that the mixtures of CO_2 /DMSO and CO_2 /NMP formed a single phase at pressures above 8 MPa (excluding the precipitated solute) and which, therefore, occupied the entire volume of the precipitation chamber. In this situation, the volume occupied by the solution was around 150 mL and this value was used as the denominator in Eq. (1).

Vega Gonzalez et al. [17] have reported vapour–liquid equilibrium data for the CO_2 /DMSO system at four temperatures from 309 to 329 K. Their study confirms that the mixture critical point for this binary system at 308 K occurs below 8 MPa. Rajasingam et al. [16] have presented experimental data on the solubility of CO_2 in DMSO and NMP at three temperatures from 298 to 318 K and pressures approaching the mixture critical point for each binary system. At each temperature, the P - x curve for NMP lies below that for DMSO over the whole range of pressure considered (1–7 MPa). This suggests that the mixture critical point for CO_2 /NMP at 308 K also occurs below 8 MPa.

To assess the validity of the first assumption, some volumetric expansion measurements were carried out using a modified form of the apparatus shown in Fig. 1. The precipitation chamber was replaced with a sight gauge (Jerguson, 13-R-32) and a scale with 1 mm graduations was fitted along the visible length of the gauge. In order to facilitate some degree of mixing, the CO_2 was passed through the 0.5 μm frit and sparged through the liquid solvent. Note the volumetric expansion measured with this technique tends to be underestimated due to leakage of the liquid phase through the frit. Nonetheless, the volumetric expansions of the pure solvents were measured and compared with those for the corresponding solutions containing $\text{KAu}(\text{CN})_2$ at the initial concentrations specified above.

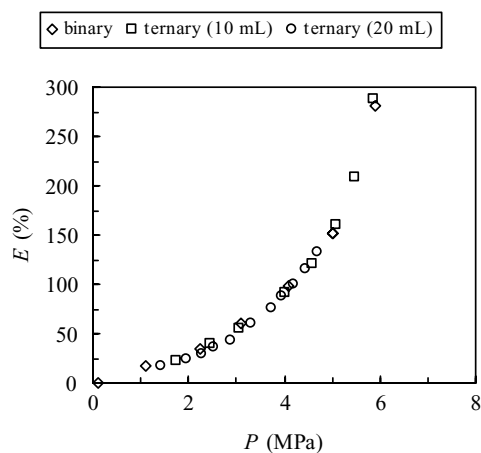


Fig. 3. Effect of 20 g/L $\text{KAu}(\text{CN})_2$ on the volumetric expansion of acetone with CO_2 at 308 K.

The volumetric expansion of pure acetone with CO_2 (binary system) in the modified apparatus is shown in Fig. 3. The expansion data for the corresponding solution initially containing 20 g/L $\text{KAu}(\text{CN})_2$ (ternary system) are also shown in this figure. Two expansion curves are presented for the ternary system, representing two different initial volumes of solution in the sight gauge (10 and 20 mL). These expansion curves only include data points for which excess solid was always observed in the sight gauge.

In a system containing two components distributed between a liquid phase and a vapour phase at equilibrium, there are two degrees of freedom according to the phase rule for nonreacting systems. At a given T and P , the compositions of the liquid and vapour phases are, therefore, fixed and cannot be arbitrarily specified. Provided that the two phases are maintained, the phase compositions are also independent of the overall composition of the system. In this situation, there is only a single value of the density of the liquid phase at the given conditions. Furthermore, the volumetric expansion of a pure solvent with CO_2 is independent of the initial volume of solvent [18].

In a ternary system with solid, liquid and vapour co-existing phases at equilibrium, there are also only two degrees of freedom. In the context of this study, the solid phase is assumed to be pure $\text{KAu}(\text{CN})_2$. If the overall composition of the system is varied at constant T and P such that the solid phase is always present, the composition of the liquid phase, and hence, its density are invariant. This means that for a solution of $\text{KAu}(\text{CN})_2$ in acetone, the volumetric expansion of the liquid phase should be independent of the initial volume of solution once precipitation has occurred at a given T and P . The data for the ternary system in Fig. 3 are consistent with this principle. It can also be seen that the data for the binary and ternary systems are in close agreement, which confirms that presence of the solute at a concentration of 20 g/L does not affect the expansion behaviour of acetone significantly. Similar findings were obtained for the DMSO and NMP solutions.

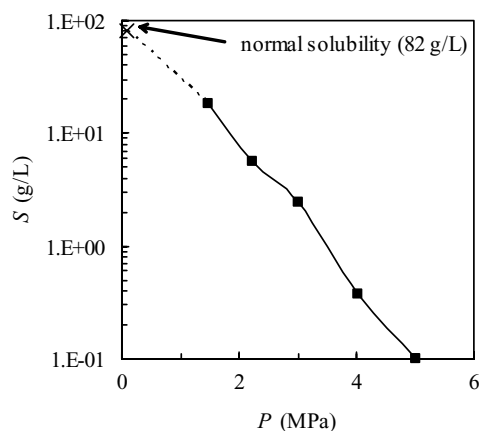


Fig. 4. Solubility of $\text{KAu}(\text{CN})_2$ in acetone expanded with CO_2 at 308 K.

3. Results and discussion

3.1. The effect of pressure on solubility

The solubilities of $\text{KAu}(\text{CN})_2$ in acetone and NMP expanded with CO_2 at 308 K are shown in Figs. 4 and 5, respectively. These figures show the variation in the saturation concentration of the solute in a given solvent as a function of pressure. The solubilities were obtained by expanding solutions initially containing 20 and 43 g/L $\text{KAu}(\text{CN})_2$ in acetone and NMP, respectively (see Section 2.3). At the limit of pressure for each set of data, near complete precipitation of $\text{KAu}(\text{CN})_2$ from the solution was achieved. The normal solubility of $\text{KAu}(\text{CN})_2$ is also included in each figure. The term, normal solubility, is defined here as the saturated concentration of the solute in a given solvent at ambient pressure. For DMSO, no precipitation of $\text{KAu}(\text{CN})_2$ was detected up to a pressure of 12 MPa for a solution initially containing 50 g/L of solute. Solubility data are, therefore, not presented for $\text{KAu}(\text{CN})_2$ in this solvent.

As noted earlier, the solubility values were calculated based on the assumption that the solute did not affect the expansion behaviour of the pure solvent. There are examples

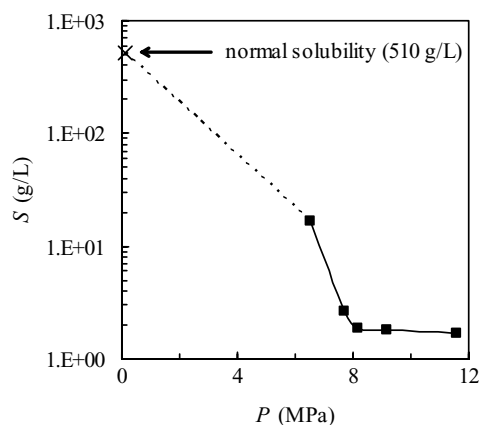


Fig. 5. Solubility of $\text{KAu}(\text{CN})_2$ in NMP expanded with CO_2 at 308 K.

in the literature, however, where phase separation of the expanded liquid phase occurs when the initial concentration of the solute in the solvent is relatively high [19,20]. This is particularly the case for solutions of $\text{KAu}(\text{CN})_2$ in NMP, as discussed in Section 3.2. There are also studies which show that CO_2 acts as a cosolvent rather than an antisolvent, at lower concentrations of the dense gas in the liquid phase, leading to an enhancement in the solubility of the solute in the solvent [19,21,22]. In Figs. 4 and 5, it cannot be assumed, therefore, that the saturation lines decrease continuously in the region of pressure between 0.1 MPa and the first solubility data point. For this reason, the saturation lines are represented by dashed lines in the relevant ranges of pressure to indicate the uncertainty in the solubility behaviour of the solute.

From Fig. 4, it can be seen that the solubility of $\text{KAu}(\text{CN})_2$ in acetone expanded with CO_2 at 4 MPa is around two orders of magnitude lower than the normal solubility of the solute. The same reduction in solubility occurs for $\text{KAu}(\text{CN})_2$ in expanded NMP when the pressure is increased to around 7 MPa (Fig. 5). These results demonstrate that carbon dioxide is an effective antisolvent for reducing the solubility of $\text{KAu}(\text{CN})_2$ in acetone and NMP. However, there are other factors that need to be considered in the determination of the optimum solvent for GAS precipitation in conjunction with the SAE process. These factors are considered in the next few sections.

3.2. The effect of initial solute concentration on the GAS process

The effect of the initial concentration of $\text{KAu}(\text{CN})_2$ on the pressure required to induce precipitation from acetone is illustrated in Fig. 6. The dashed line represents the saturation line for $\text{KAu}(\text{CN})_2$ in acetone expanded with CO_2 at 308 K and depicts the decrease in the solubility of the solute as the pressure is increased. The solid lines in Fig. 6 are operating lines representing the variation in the concentration of $\text{KAu}(\text{CN})_2$ (C_S) in response to the volumetric expansion of the solution and in the absence of precipitation. The three

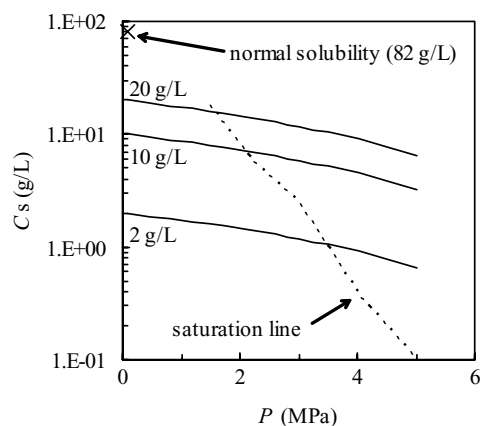


Fig. 6. Effect of the initial concentration of $\text{KAu}(\text{CN})_2$ on the pressure required to induce precipitation from acetone at 308 K.

operating lines depict different initial concentrations of $\text{KAu}(\text{CN})_2$ in acetone (2, 10 and 20 g/L).

In order to induce precipitation of the solute, the pressure must be increased until the saturation concentration of the solute equals the concentration of the solute in the expanded solvent, i.e. the saturation line and the operating line must intersect. For an initial concentration of 20 g/L $\text{KAu}(\text{CN})_2$ in acetone, the pressure must be increased to around 1.5 MPa before precipitation occurs. As the initial solute concentration decreases further, the separation between the saturation line and the operating line increases and even greater pressures are required to induce precipitation. It should also be apparent that once precipitation has been initiated, the concentration of the solute in solution follows the path defined by the saturation line, as the system pressure is increased further.

Another scenario in which the initial solute concentration affects the GAS process is if the concentration of the solute is very high. A comparison of the volumetric expansions of pure NMP and an 80% saturated solution of $\text{KAu}(\text{CN})_2$ in NMP is presented in Fig. 7. The normal solubility of $\text{KAu}(\text{CN})_2$ in NMP is around 510 g/L at 308 K. The volumetric expansion data for the 80% saturated solution were measured using the procedure described above. For such high solute concentrations, the volumetric expansion of the solution is very different to that observed for the pure solvent. For example, the volumetric expansion of the solution at 7 MPa is around 43%, well below that for the pure solvent (279%).

At approximately 7.4 MPa, the formation of two immiscible liquid phases was observed in the sight gauge. The upper liquid phase was initially present as a thin but distinct line. As the pressure was increased, the upper liquid phase expanded rapidly while the lower liquid phase contracted. The upper liquid phase was assumed to be a CO_2 -rich phase while the lower liquid phase was assumed to be an NMP-rich phase. Due to the immiscibility of $\text{KAu}(\text{CN})_2$ with CO_2 , it was also assumed that the solute was present mainly in the lower liquid phase. In Fig. 7, the volumetric expansion of the combined liquid phases, relative to the initial volume of solution, is

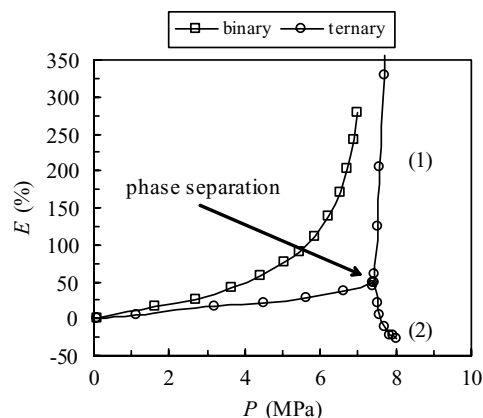


Fig. 7. Comparison of the volumetric expansions of pure NMP (binary) and an 80% saturated solution of $\text{KAu}(\text{CN})_2$ in NMP (ternary) with CO_2 at 308 K.

represented by the upper branch (1) of the expansion data for the 80% saturated solution. The lower branch (2) represents the volumetric expansion of the lower liquid phase, again relative to the initial volume of solution.

No precipitation was observed in either liquid phase up to a pressure of 8 MPa. This was attributed to a combination of the relatively low concentration of the solute in the upper liquid phase and the absence of the antisolvent effect in the lower liquid phase. The contraction of the lower liquid phase itself was probably due to the transfer of NMP into the CO₂-rich liquid phase. The unusual phase behaviour which can arise at high solute concentrations inevitably means that operating lines, such as those shown in Fig. 6, cannot be constructed accurately if they are based on volumetric expansion data for the pure solvent. This also highlights that volumetric expansion data for pure solvents are of limited value in the design of GAS processes and that measurements of phase compositions are required to understand the effect of the antisolvent on the solubility of the solute in the solvent.

3.3. The effect of the dielectric constant of the solvent on the GAS process

Dipolar aprotic solvents are the preferred organic solvents in the SAE process, mainly due to their ability to solubilise the salts of metal-cyanide complexes. As an example, consider the solubility data in Table 1. Among the various dipolar aprotic solvents, the normal solubility of KAu(CN)₂ increases with an increase in the dielectric constant of the solvent. Note, however, that the solubility of KAu(CN)₂ in NMP and DMSO is much greater than that for water, even though the dielectric constant for water is higher. This is due to the strong interaction between these solvents and Au(CN)₂⁻, a large polarisable anion. This feature is not evident in the solubility data for KCN.

Since the presence of water in the solvent can adversely affect the GAS process, as discussed in Section 3.4, it is of interest in this work to consider the SAE process conducted without water. An important consideration in the selection of a dipolar aprotic solvent which is suitable for this purpose is that the solvent must support a sufficient concentration of a counter-ion, such as CN⁻, in order for the desorption of Au(CN)₂⁻ from activated carbon to proceed. The low solubility of KCN in acetone necessitates the use of this solvent in combination with water. In the case of NMP and DMSO, it is actually possible to dissolve sufficient quantities of KCN without the use of water. In other words, dipolar aprotic solvents with relatively high dielectric constants are preferred in the SAE process conducted without water.

However, in a typical SAE process, the resulting concentration of KAu(CN)₂ in the solution is between 10 and 20 g/L. For such dilute solutions, in comparison with the normal solubilities of KAu(CN)₂ in NMP and DMSO, precipitation of KAu(CN)₂ from the expanded solution may not occur or may require relatively high pressures. An example of this situation is illustrated in Fig. 8. The dashed line in Fig. 8 represents the

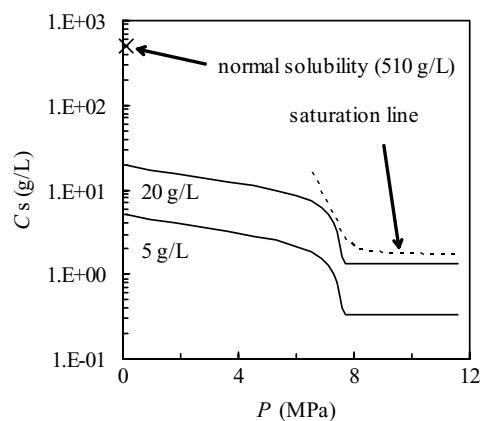


Fig. 8. Effect of the initial concentration of KAu(CN)₂ on the pressure required to induce precipitation from NMP at 308 K.

saturation line for KAu(CN)₂ in NMP expanded with CO₂ at 308 K. The operating lines (solid lines) depict different initial concentrations of KAu(CN)₂ in NMP and show the rapid decrease in the concentration of the solute as the solution undergoes expansion (neglecting precipitation). In this case though, the operating lines become independent of pressure at $P > 8$ MPa, due to the formation of a single phase.

It is clearly observed in Fig. 8 that the large discrepancy between the normal solubility of KAu(CN)₂ and the initial solute concentration of 20 g/L KAu(CN)₂ restricts the intersection of the saturation and operating lines to relatively high pressures. For a dipolar aprotic solvent which has a higher dielectric constant than NMP, the expected increase in the normal solubility of KAu(CN)₂ would lead to a shift in the saturation line in an upward direction. Under these conditions, the separation between the saturation and operating lines makes it difficult to induce precipitation, even at relatively high pressure. This is analogous, for example, to the separation between the saturation line and the operating line for 5 g/L KAu(CN)₂ in Fig. 8. This may partly explain why no precipitation of KAu(CN)₂ was observed when DMSO was used as the solvent.

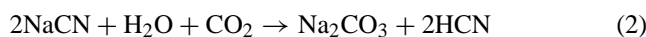
In contrast to the SAE process, dipolar aprotic solvents with relatively low dielectric constants are, therefore, more attractive for precipitating KAu(CN)₂ from solutions initially containing 10–20 g/L of solute (see Fig. 6 for example). The preceding considerations suggest that the use of mixtures of dipolar aprotic solvents may provide a means of tuning the dielectric constant to satisfy the requirement of counter-ion solubility in SAE while minimising the required operating pressure in the GAS process.

3.4. The effect of water on the GAS process

The presence of water in the solvent often leads to phase separation of the liquid phase under high pressure. This typically leads to the formation of a distinct aqueous phase. Under such conditions, the solute concentrates in the aqueous layer, preventing the precipitation and subsequent recovery of the

solute [7]. In this work, the effect of water on the GAS process was investigated in experiments on the precipitation of NaCN from DMSO. The DMSO used was not dried in the manner described in Section 2.1 and contained around 1 wt.% water. An amount of 10 ml of solution containing 8 g/L NaCN was placed in the precipitation chamber. The precipitate was analysed for sodium using atomic absorption spectroscopy.

Near quantitative recovery of the solute was observed in the range of pressure from 2 to 7 MPa. This result was not consistent with the behaviour observed in other experiments in which the mass of precipitated solute increased gradually with increasing pressure. The precipitate was therefore collected and analysed by X-ray diffraction. It was found that the dominant species in the precipitate was Na_2CO_3 . Based on these results, it was proposed that the following reaction occurred:



Ehrenstein et al. [25] have proposed a similar reaction during the precipitation of metal acetates from a solution of ethanol and water. Carbon dioxide reacts with the water in the solvent to form H_2CO_3 and the dissociation of this weak acid leads to the formation of CO_3^{2-} . Na_2CO_3 is insoluble in DMSO and precipitates immediately upon the formation of CO_3^{2-} . Since there is an abundance of CO_2 in the liquid phase, this process continues until all of the Na is depleted. This accounts for the apparent quantitative recovery of the solute at low pressure. The formation of HCN during the precipitation of Na_2CO_3 is undesirable in view of the toxicity of this species. Thus, while CN^- is a good counter-ion for the SAE process for recovering $\text{Au}(\text{CN})_2^-$, there is a significant safety issue associated with its use in GAS precipitation if the solvent contains traces of water.

4. Conclusion

Carbon dioxide is an effective antisolvent for reducing the solubility of $\text{KAu}(\text{CN})_2$ in acetone and NMP. The operating pressure required to initiate the precipitation of $\text{KAu}(\text{CN})_2$ from the dipolar aprotic solvents considered generally increases with an increase in the dielectric constant of the solvent. The presence of water in the solvent adversely affects the recovery of $\text{KAu}(\text{CN})_2$ when CO_2 is used as the antisolvent. This is due to the precipitation of carbonate salts, in preference to the target solute, upon the reaction between CO_2 and water. In contrast to the GAS process, dipolar aprotic solvents with relatively high dielectric constants are preferred in the SAE process conducted without water. In considering the requirements of both processes, the use of mixtures of dipolar aprotic solvents may provide a means of tuning the dielectric constant to satisfy the requirement of counter-ion solubility in the SAE process while minimising the required operating pressure in the GAS process.

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