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THE INFLUENCE OF ACETATE AND OXALATE AS SIMPLE ORGANIC LIGANDS ON THE BEHAVIOR OF PALLADIUM IN SURFACE ENVIRONMENTS

SCOTT A. WOOD[§] AND JULIE VAN MIDDLESWORTH[¶]

Department of Geological Sciences, University of Idaho, Box 443022, Moscow, Idaho 83844-3022, U.S.A.

ABSTRACT

Acetate and oxalate are simple organic ligands that occur naturally in surface waters, groundwaters, and soils; they may play a role in the transport of palladium in such environments. Mass transfer of Pd in surface environments has implications for geochemical exploration as well as the environmental impact of the platinum-group elements. The complexation of divalent palladium and acetate was studied *via* measurement of the solubility of amorphous $Pd(OH)_2$ in 1 molal $NaClO_4$ as a function of concentration of acetate (0.0001 to 0.1 molal) at 25°C. From these data, the predominant Pd^{2+} acetate species was determined to be $Pd(ac)_2^0$ (where ac denotes the acetate anion), with a conditional stability-constant of $\log \beta_2^* = 9.3 \pm 0.3$. Palladium oxalate complexes were investigated using UV–visible spectrophotometry. Experiments were conducted at 25°C as a function of concentration of NaCl (0.1 to 2.0 molal) and oxalate (0.1 to 100 millimolal). The results demonstrate that oxalate-bearing Pd species become important at relatively low concentrations of oxalate. At 1 molal NaCl, the existence of an isosbestic point indicates an equilibrium between one oxalate-bearing Pd species and $PdCl_4^{2-}$. At lower concentrations of NaCl, more than two Pd species may be present under the experimental conditions. Calculation of speciation as a function of pH in a model soil solution shows that $Pd(ac)_2^0$ never exceeds 40% total Pd, even in the absence of oxalate and at acetate concentrations as high as 5 millimolal. At lower concentrations of acetate or in the presence of oxalate, the proportion of $Pd(ac)_2^0$ is negligible. However, $Pd(ox)^0$ appears to be an important Pd^{2+} species, predominating at low pH, with its field of predominance expanding with increasing concentration of oxalate.

Keywords: palladium, acetate, oxalate, organic ligands, solubility, complexation, absorption spectroscopy, environmental geochemistry, exploration geochemistry.

SOMMAIRE

L'acétate et l'oxalate sont de ligands organiques simples que l'on peut trouver dans la nature dans les eaux de surface, les nappes d'eau souterraine, et les sols; ils pourraient bien jouer un rôle dans le transfert du palladium dans de tels milieux. Le transfert de masses de Pd dans les milieux de surface aurait des implications pour l'exploration fondée sur critères géochimiques aussi bien que pour l'impact environnemental des éléments du groupe du platine. Nous avons étudié la complexation du palladium bivalent avec l'acétate en mesurant la solubilité du $Pd(OH)_2$ amorphe dans le $NaClO_4$ (solution de molalité 1) en fonction de la concentration d'acétate (molalité entre 0.0001 et 0.1) à 25°C. A partir de ces données, l'espèce prédominante de l'acétate de Pd^{2+} serait $Pd(ac)_2^0$ (ici, ac représente l'anion acétate), avec une constante de stabilité conditionnelle $\log \beta_2^*$ égale à 9.3 ± 0.3. Les complexes impliquant palladium et oxalate ont été étudiés au moyen de la spectrométrie dans les domaines ultraviolette et visible. Nos expériences ont été menées à 25°C en fonction de la concentration de NaCl (de 0.1 à 2.0 molal) et d'oxalate (de 0.1 à 100 millimolal). Les résultats démontrent que les complexes à Pd et oxalate deviennent importants à concentrations relativement faibles d'oxalate. Dans une solution de NaCl de molalité 1, il existe un point isosbestique qui indique l'équilibre entre un complexe à Pd et oxalate d'un part, et $PdCl_4^{2-}$. A plus faibles concentrations de NaCl, il se pourrait que plus de deux espèces contenant le Pd coexistent aux conditions expérimentales choisies. Un calcul de la spéciation en fonction du pH dans une solution modèle pour simuler un sol montre que le complexe $Pd(ac)_2^0$ ne rend compte que de 40% du Pd total au plus, même en l'absence d'oxalate et même si la concentration d'acétate atteint 5 millimolal. A concentrations d'acétate plus faibles, ou en présence d'oxalate, la proportion de $Pd(ac)_2^0$ est négligeable. Toutefois, le complexe $Pd(ox)^0$ semble être un important porteur de Pd^{2+}, étant prédominant à faible pH, et son champ de stabilité augmenterait à mesure qu'augmente la concentration d'oxalate.

(Traduit par la Rédaction)

Mots-clés: palladium, acétate, oxalate, ligands organiques, solubilité, complexation, spectroscopie d'absorption, géochimie environnementale, géochimie d'exploration.

[§] *E-mail address*: swood@uidaho.edu

[¶] *Current address*: Geomega, 2995 Baseline Road, Suite 202, Boulder, Colorado 80303, U.S.A.

INTRODUCTION

The potential for mobility of palladium in surface environments is relevant to the use of geochemical methods of exploration (*e.g.*, soil and biogeochemical surveys) for platinum-group element (PGE) ores and to the behavior of these elements as environmental contaminants. Several authors have interpreted field evidence in terms of the mobility of Pd in soils and laterites (Fuchs & Rose 1974, Kothny 1978, Bowles 1986, 1995, Riese & Arp 1986, Taufen & Marchetto 1989, Wood & Vlassopoulos 1990, Coker *et al.* 1991, Cook *et al.* 1992, Zang *et al.* 1992, Cook & Fletcher 1993, 1994, Bowles *et al.* 1994, Salpéteur *et al.* 1995). Other authors have demonstrated uptake of PGE by plants and have suggested their possible use in biogeochemical exploration surveys (Kothny 1978, 1979, 1987, Dissanayake & Kritsotakis 1984, Dunn 1986, Riese & Arp 1986, Dunn *et al.* 1989, Hall *et al.* 1990, Rencz & Hall 1992, Roger & Dunn 1993, Fletcher *et al.* 1995). In addition, many environmental geochemists have found evidence for PGE contamination from catalytic converters in automobiles and other industrial sources in roadside dust, river sediments, sewage sludge, soil, marine sediments, and Greenland snow (Furr *et al.* 1976, Lee 1983, Dissanayake *et al.* 1984, Hodge & Stallard 1986, Esser & Turekian 1993, Lottermoser 1994, Wei & Morrison 1994, Heinrich *et al.* 1996, Ravizza & Bothner 1996, Boyd *et al.* 1997, Gregurek *et al.* 1998, Schäfer & Puchelt 1998, Barbante *et al.* 2001, Jarvis *et al.* 2001, Ely *et al.* 2001, Zereini *et al.* 2001). The implications of PGE contamination for the environment are not yet well understood, but it is known that these elements can be bioavailable and toxic (*e.g.,* Brubaker *et al.* 1975, Campbell *et al.* 1975, Hightower *et al.* 1977, Ridley *et al.* 1977, Uno & Morita 1993, Bunger *et al.* 1996, Veltz *et al.* 1996, Gebel *et al.* 1997, Artelt *et al.* 1999). Possible migration of radioactive ^{107}Pd, a long-lived ($t_{1/2} = 6.5 \times 10^6$ a) product of fission of the actinides in some forms of nuclear waste, is also an environmental concern (Brookins 1984, McKinley *et al.* 1988).

A prerequisite to the quantitative prediction of chemical mass transfer of PGE in the surface environment is knowledge of the nature and stability of aqueous PGE complexes. Thermodynamic data for complexes of Pt and Pd with most common inorganic ligands are available at standard conditions (*cf.* review by Wood 2002). However, relatively little information is available for complexes of PGE with naturally occurring organic ligands, in spite of repeated suggestions in the literature that such complexes may be quite important in surface environments (*e.g.*, Cousins & Kinloch 1976, Cousins & Vermaak 1976, Dissayanake & Kritsotakis 1984, Bowles 1986, Wood & Vlassopoulos 1990, Cook *et al.* 1992, Bowles *et al.* 1994, 1995). The main objective of this contribution is to help constrain the role of simple carboxylic acid anions (CAA) in the transport of Pd in surface environments. We use experimental methods (solubility, spectroscopy) to characterize aqueous Pd^{2+} complexes with two common CAA, acetate (CH_3COO^-) and oxalate ($C_2O_4^{2-}$), that are capable of monodentate and bidentate complexation, respectively.

BACKGROUND INFORMATION

Acetate is an aliphatic, monocarboxylic acid anion and is one of the more common of the simple CAA in surface environments. It is produced by the roots of corn, grasses, and herbs, and occurs in soil solutions at concentrations of 2×10^{-3} to 5×10^{-3} mol L^{-1} (Sposito 1989). Oxalate is a dicarboxylic acid that forms bidentate chelates with metals. It occurs in comparatively high concentrations in soil solutions (5×10^{-5} to 10^{-3} mol L^{-1}; Bruckert & Jacquin 1969, Bruckert 1970, Thurman 1985, Vance *et al.* 1996) and fresh surface waters (10^{-5} to 5×10^{-5} mol L^{-1}; Vance *et al.* 1996), and, like acetate, is exuded by the roots of some plants (Sposito 1989). Calcium and magnesium oxalate minerals have been found in a variety of surface environments, including sediments (river, lake, marine), soils, and fracture fillings in and weathered surfaces on rocks (Pecora & Kerr 1954, Gude *et al.* 1960, Hutton & Taft 1965, Hyde & Landy 1966, Lowenstam 1968, Marlowe 1970, Graustein *et al.* 1977, Tirelli 1977, Wilson *et al.* 1980, Mandarino 1983, Mandarino & Witt 1983, Campbell & Roberts 1986). The relatively common occurrence of such minerals points to the ubiquity of oxalate in surface environments. Acetate and oxalate are also important in that they represent models for other simple aliphatic mono- and dicarboxylic acid anions, and for mono- and bidentate carboxylic binding sites on more complex organic matter, such as humic and fulvic acids.

Stability constants for PGE-complexes with acetate and oxalate are rare to non-existent. One reason for this lack of data may be intense interest in the chemistry of PGE with synthetic organic compounds, which diverts attention of chemists away from more geologically relevant organic ligands. Another reason may be that, on the basis of Pearson's Hard–Soft Acid–Base (HSAB) theory (Pearson 1963), complexes between "soft" PGE ions and "hard" CAA groups are not expected to be very strong. However, some previous studies have indicated that such complexes may be strong enough to be important in surface environments. To the knowledge of the authors, Nabivanets & Kalabina (1972) reported the only available stability-constant for Pd oxalate complexes, that of $Pd(ox)^0$ ($\log \beta_1 = 8.7$; ox = oxalate anion). If this constant is correct, then the 1:1 oxalate complex is considerably stronger than the analogous chloride complex for Pd ($\log \beta_1 = 4.47$; Elding 1972). Wood *et al.* (1994) studied Pd oxalate complexes using UV–visible and FTIR spectroscopy. Their data showed strong evidence of formation of one or more Pd oxalate complexes, although stability constants were not derived. Wood *et al.* (1994) also showed that the presence of acetate increases the solubility of amorphous Pd hydroxide. Spectroscopic evidence (UV–visible, Raman) indicated that the increase in solubility is due to the formation of aqueous Pd^{2+} acetate complexes, but once again, stability constants were not determined. Some experimental effort also has been expended in studying the interaction of fulvic and humic acids with the PGE (*e.g.*, Wood 1990, Varshal 1994, Wood *et al.* 1994, Bowles *et al.* 1995). However, the data required to assess the role of geologically relevant organic ligands, particularly simple CAA, are incomplete. This study was designed to provide further information on acetate and oxalate complexes of Pd^{2+}.

EXPERIMENTAL METHODS

We investigated the stability of Pd^{2+} acetate complexes by measuring the solubility of amorphous $Pd(OH)_2(s)$ as a function of acetate concentration. The oxalate complexes were studied *via* UV–visible absorption spectrophotometry.

Solubility measurements

Solubility experiments were conducted using amorphous $PdO{\bullet}H_2O$, *i.e.*, $Pd(OH)_2(am)$, (Johnson-Matthey) as starting material. The main objectives of these solubility measurements were to detect the presence of any aqueous Pd^{2+} acetate complexes and to determine their stability constants. The experiments were not designed to determine directly the solubility of any environmentally relevant Pd phase. In order to achieve the goal of determining stability constants for Pd^{2+} acetate complexes, it was desirable to employ a phase with the following properties: 1) a sufficiently high solubility that Pd concentrations could be accurately determined with available instrumentation, and 2) sufficient reactivity that equilibrium would be approached in a reasonable time-frame (days to weeks). Because amorphous $Pd(OH)_2$ has these properties, it was chosen for this study, irrespective of whether it occurs in nature. Stability constants determined in this study can then be combined with thermodynamic data from other sources for specific Pd phases to model Pd behavior in the environment.

Examination of the $Pd(OH)_2$ before and after selected runs using X-ray diffraction (XRD) confirmed the lack of long-range order of the solid. Therefore, the amorphous solid was characterized using scanning electron microscopy (SEM) and thermal gravimetric analysis (TGA). Combined XRD, SEM or TGA failed to detect the presence of any phase other than amorphous $Pd(OH)_2$, before or after experimental runs.

All solutions employed in the experiments were prepared using chemicals of reagent grade or better, and 18-MΩ-cm de-ionized water. Buffered solutions containing equal amounts of acetic acid and sodium acetate were used in all experiments. The amount of free acetate varied from 0.0001 to 0.1 molal. Because the solutions were buffered, pH was held constant at approximately 4.4 for all solutions at 25.0 ± 0.2°C. Ionic strength was also held constant by using an excess of an inert electrolyte (1.0 molal $NaClO_4$). Solubility experiments were conducted in 60 mL, Fisher-brand, flat-bottom, borosilicate glass tubes maintained in a shaking water-bath manufactured by Precision Scientific. In order to prevent carryover of solid Pd hydroxide, all solution samples were forced through a 0.2-μm filter using a polyethylene syringe. Preconditioning of the filter was accomplished by passing through the membrane and discarding approximately 1 mL of solution prior to collection of the sample. The sample was placed in a polyethylene test tube and acidified to 2% with reagent-grade hydrochloric acid to insure that all Pd remained in solution until analysis.

Palladium concentrations were determined using a Perkin–Elmer Optima 3000 XL inductively coupled plasma – atomic emission spectrophotometer (ICP–AES) at the University of Idaho. This instrument is equipped with an axial torch, giving rise to an order-of-magnitude lower limit of detection compared to conventional radial-torch instruments. Detection limits for Pd on this instrument were between 1.9 and 3.0 μg/L, and precision was on the order of 5% or better. Total concentrations of acetate were confirmed by ion chromatography (IC) using a Dionex AI–450 work station.

In this study, pH is defined as the negative logarithm of the hydrogen-ion concentration. The pH of the buffered solutions was calculated using conditional ionization constants for acetic acid (Hac) reported by Mesmer *et al.* (1989). The calculated pH was corroborated by measurement using a combination glass pH electrode with a precision of ±0.05 pH units. The electrode was calibrated using three buffer solutions (phosphate, acetate and borate) at the same temperature and ionic strength as the experiments. Variations in activity coefficients and liquid junction potentials were minimized by making the buffer solutions as close in major-ion composition to the experimental solutions as possible. Values of pH for the buffers were obtained using experimentally determined conditional dissociation-constants of the acid (Mesmer & Baes 1974, Mesmer *et al.* 1971, 1989).

A generalized reaction governing our solubility experiments can be written as:

$$\begin{aligned} &Pd(OH)_2(am) + n\ ac^- \\ &\quad + 2\ H^+ \leftrightarrow Pd(ac)_n^{2-n} + 2\ H_2O \end{aligned} \tag{1}$$

where ac represents the acetate anion. The conditional equilibrium-constant (K_n^*) for this reaction is given by:

$$K_n^* = \frac{m_{Pd(ac)_n^{2-n}}}{m_{ac^-}^n\, m_{H^+}^2} \tag{2}$$

The asterisk (*) here and elsewhere in this paper denotes that the equilibrium constant is a conditional one, *i.e.*, formulated in terms of concentration rather than activity. Because the ionic strength was held constant throughout the experiments, activity coefficients are approximately constant. The symbol m_i denotes the molal concentration (mol kg^{-1} H_2O) of species *i*.

Taking the logarithm of both sides of equation (2) and rearranging, one obtains

$$\log m_{Pd(ac)_n^{2-n}} = \log K_n^* - 2pH + n \log m_{ac^-} \qquad (3)$$

Differentiation with respect to m_{ac} at constant temperature and pH leads to

$$\left(\frac{\partial \log m_{Pd(ac)_n^{2-n}}}{\partial \log m_{ac^-}} \right)_{T,pH} = n \qquad (4)$$

Thus, a plot of log $m_{\Sigma Pd}$ *versus* log m_{ac} at constant temperature and pH should yield the acetate ligation number *n*. If a single complex predominates, such a plot will approximate a straight line with slope *n*, and the equilibrium constant K^o_n can be obtained from the *y* intercept.

UV–visible absorption spectrophotometry

Measurements were made at room temperature (~23°C) at the University of Idaho using a Shimadzu UV–2101PC absorption spectrophotometer and quartz cuvettes with a 1-cm path length. The spectral region scanned was from 200 to 700 nm. The scan parameters were set to the following: scan speed: very slow, slit width: 0.1 nm, sampling mode: automatic. A solution of NaCl at the same concentration as the test solution, but without Pd or oxalate, was employed in the reference cell. The spectra were smoothed using the loess smoothing routine in SigmaPlot 8.0, with a sampling proportion of 0.05.

All solutions studied contained 0.5 millimolal Pd added as K_2PdCl_4. Four series of solutions were prepared containing 0.1, 0.5, 1.0 and 2.0 molal NaCl. In each of these series, oxalate concentrations ranged from 1 to 100 millimolal (1, 5, 10, 50 and 100 millimolal). Thus, there were initially 24 solutions of varying NaCl and oxalate concentrations. However, in the 1.0 molal NaCl solutions, precipitation of sodium oxalate occurred upon increase of the concentration of oxalate to 100 millimolal. Similarly, in 2.0 molal NaCl solutions, sodium oxalate precipitated at oxalate concentrations of 10 millimolal or higher. Thus, the range of oxalate concentration investigated decreased with increasing NaCl concentration. The pH of each of the solutions was adjusted to approximately 6 using concentrated NaOH solution. This pH is above both pK_1 and pK_2 for oxalic acid (Kettler *et al.* 1991), thus insuring that the predominant oxalate species is the doubly deprotonated $C_2O_4^2$.

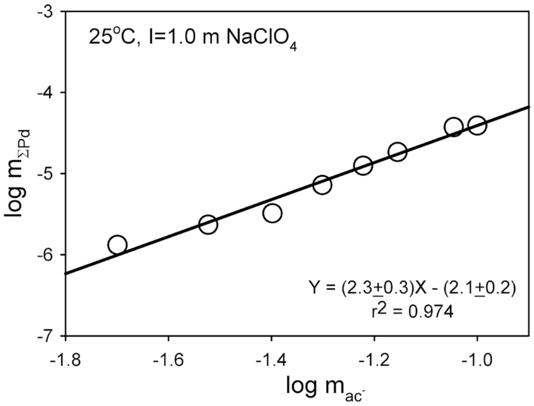


FIG. 1. Plot of the logarithm of the solubility of $Pd(OH)_2$(am) *versus* the logarithm of the free acetate concentration at 25°C in 1 m $NaClO_4$. Linear regression of the data results in the straight line shown, with the regression parameters given in the lower right-hand corner of the diagram.

RESULTS AND DISCUSSION

Solubility measurements: Pd^{2+} acetate complexes

The solubility results are given in Table 1. A plot of log $m_{\Sigma Pd}$ *versus* log m_{ac}, conforms fairly closely to a straight line with a slope of 2.3 ± 0.3. This slope is statistically indistinguishable from 2, suggesting the formation of a single, predominant Pd acetate complex with the stoichiometry $Pd(ac)_2^0$ (Fig. 1). However, on the basis of the measured slope alone, we cannot exclude the possible presence of small amounts of higher-order complexes, *e.g.*, $Pd(ac)_3^-$ or $Pd(ac)_4^{2-}$. The solubility data were subjected to non-linear regression analysis to confirm the dominant species present. Several different combinations of complexes with various stoichiometries were tested, and the species $Pd(ac)_2^0$ provided the best fit. Addition of the species $Pd(ac)^+$ together with

TABLE 1. EXPERIMENTAL RESULTS FOR SOLUBILITY OF $Pd(OH)_2$(am) AS A FUNCTION OF FREE ACETATE CONCENTRATION AT 25°C

log m_{Pd}	log $m_{acetate}$	log m_{Pd}	log $m_{acetate}$
-5.88	-1.70	-4.90	-1.22
-5.63	-1.52	-4.73	-1.15
-5.49	-1.40	-4.43	-1.05
-5.14	-1.30	-4.41	-1.00

$Pd(ac)_2{}^0$ did not improve the fit, and a model involving $Pd(ac)^+$ alone provided an inadequate fit to the data. Regression analysis assuming the sole presence of $Pd(ac)_2{}^0$ resulted in a value of log $K_2{}^* = 6.3 \pm 0.1$ (the error representing twice the standard error of $K_2{}^*$ from the regression) for the following reaction at 1 molal $NaClO_4$:

$$Pd(OH)_2(am) + 2\ ac^- + 2\ H^+ \leftrightarrow Pd(ac)_2{}^0 + 2\ H_2O \qquad (5)$$

This regression procedure is equivalent to fitting the data shown in Figure 1 with a straight line with a slope fixed at exactly 2. Inclusion of $Pd(ac)^+$ in addition to $Pd(ac)_2{}^0$ resulted in a physically implausible, negative value for $K_1{}^*$ and only a slight increase in the value of $K_2{}^*$ (log $K_2{}^* = 6.4$). The latter is within the error of the estimate obtained assuming the presence of only $Pd(ac)_2{}^0$. These findings further suggest the insignificance of $Pd(ac)^+$ under the experimental conditions. On the other hand, inclusion of the species $Pd(ac)_3{}^-$ together with $Pd(ac)_2{}^0$ results in log $K_3{}^* = 7.1 \pm 0.4$ and log $K_2{}^* = 6.1 \pm 0.2$. Thus, the inclusion of $Pd(ac)_3{}^-$ in the speciation model has a larger effect on the value of log $K_2{}^*$ than the inclusion of $Pd(ac)^+$, but the two values of log $K_2{}^*$ overlap within their error ranges. The inclusion of $Pd(ac)_3{}^-$ in the model results in only a marginal improvement in the overall fit to the data and a comparatively large error in the estimates of both $K_2{}^*$ and $K_3{}^*$. Thus, we conclude that there are insufficient data to justify inclusion of the species $Pd(ac)_3{}^-$ in the model. However, we believe that the uncertainty in log $K_2{}^*$ should be adjusted upward to ±0.3 to reflect the effect that inclusion of $Pd(ac)_3{}^-$ in the speciation model has on the value of log $K_2{}^*$ and to account for uncertainties in measured quantities (pH, Pd concentration), which are not accounted for by the standard error of regression.

Using the value of log $K^* = -3.0 \pm 0.2$ for the reaction

$$Pd(OH)_2(am) + 2\ H^+ \leftrightarrow Pd^{2+} + 2\ H_2O \qquad (6)$$

from van Middlesworth & Wood (1999), we can derive a stability constant for $Pd(ac)_2{}^0$, *i.e.*, the conditional equilibrium constant for the reaction:

$$Pd^{2+} + 2\ ac^- \leftrightarrow Pd(ac)_2{}^0 \qquad (7)$$

log $\beta_2{}^* = 9.30 \pm 0.3$. This value is higher than the second cumulative stability-constant for Pd chloride complexes, log $\beta_2{}^* = 7.76$, determined by Elding (1972) in 1 M $HClO_4$ at 25°C. This finding suggests a relatively strong Pd acetate complex, which can compete effectively with chloride, as also was suggested qualitatively by the work of Wood *et al.* (1994). To our knowledge, no other thermodynamic data for Pd acetate complexes exist, and so a comparison of our results with previous work is not possible. The formation of a comparatively strong complex between the soft Pd^{2+} and the hard acetate anion is in apparent contradiction to Pearson's (1963) hard–soft acid–base theory. However, Pd^{2+} has been proven to form extremely strong complexes with OH^- and a variety of carboxylate ligands (Wood *et al.* 1994, van Middlesworth & Wood 1999, and references therein), which also are hard. Thus, hydroxide and carboxylate ligands appear to represent exceptions to Pearson's (1963) rule with respect to Pd^{2+}.

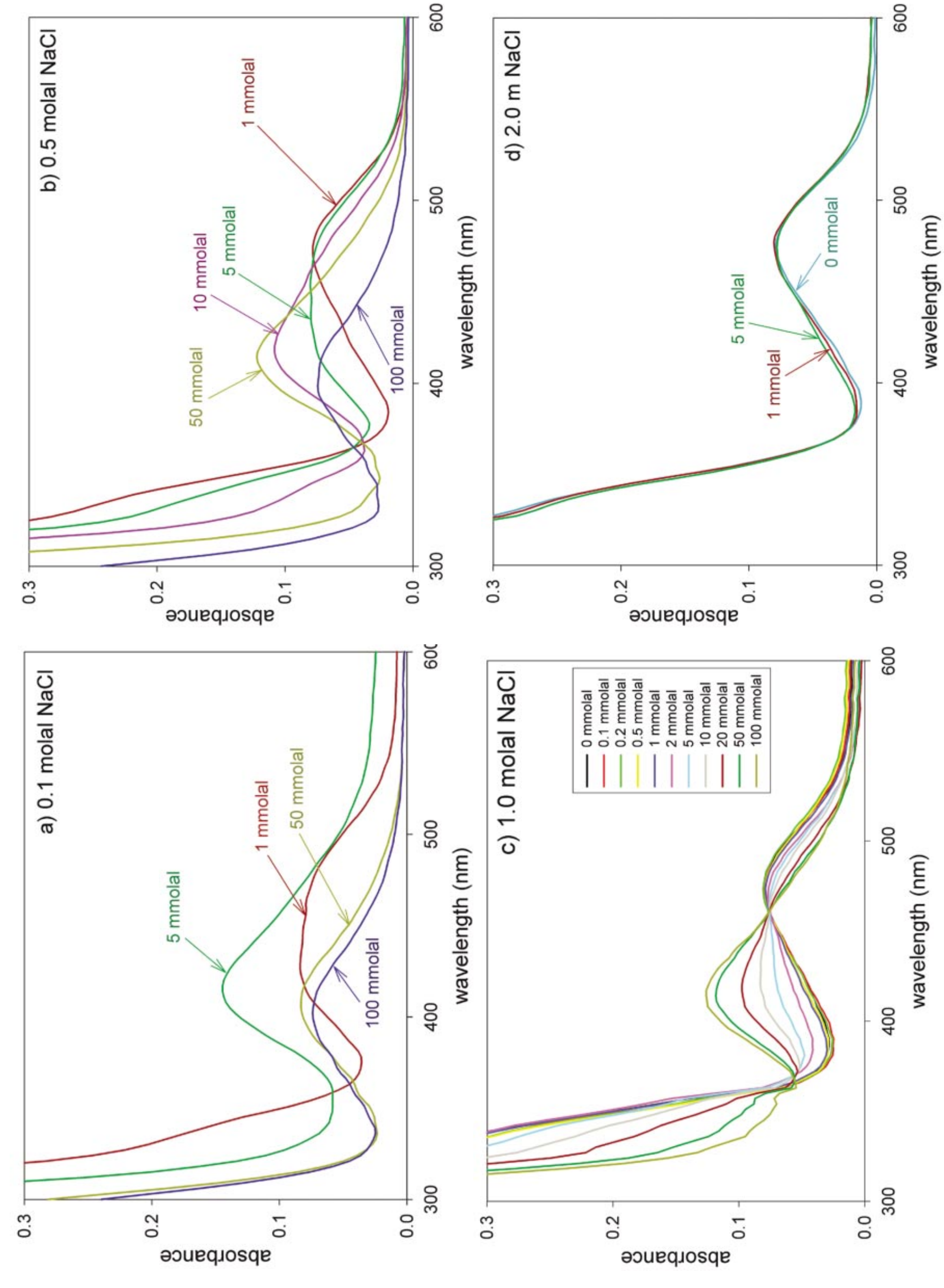
It is possible that the predominant complex in the solubility experiments is actually a mixed hydroxy-acetate complex. Our experiments were not conducted as a function of pH, so this possibility cannot be ruled out. Thus, the interpretation of our solubility data may require revision as additional experimental data become available.

UV–visible absorption spectrophotometry: Pd^{2+} oxalate complexes

Figure 2 shows the visible spectra resulting from *d–d* transitions (electronic transitions among *d*-orbitals on the Pd^{2+} ion) for solutions containing 0.5 millimolal Pd at various NaCl and oxalate concentrations. At 0.5 millimolal Pd, the bands in the UV range (arising from charge-transfer transitions, *i.e.*, electronic transitions between orbitals on the metal and orbitals on the ligand) are too intense to obtain reliable absorbances. Thus, data collected at λ greater than 300 nm are not shown. Spectra at λ = 600 to 700 nm are featureless, yielding no further information, and also are not shown.

Figure 2a shows that, at 0.1 molal NaCl and 1 millimolal oxalate, there is a very broad band that stretches from about 400 to 500 nm. This band may represent the sum of at least two individual bands. With an increase in oxalate concentration to 5 millimolal, the band becomes narrower and somewhat more intense, and the maximum shifts to lower wavelength. Further increases in oxalate concentration lead to a decrease in intensity and a decrease in the wavelength of the maximum. Similar behavior is seen at 0.5 molal NaCl (Fig. 2b), except that at 1 millimolal oxalate, the band is relatively narrow and has a maximum at about 480 nm, whereas the very broad band does not appear until oxalate concentration increases to 5 millimolal. Moreover, none of the bands in this region of the spectrum ever attains the intensity of the band in Figure 2a (at 5 millimolal oxalate). These spectral data suggest the conversion of a Pd^{2+} chloride species to one or more species containing oxalate as the concentration of oxalate increases.

If NaCl concentration is increased to 1.0 molal NaCl, two isosbestic points can be observed, one near 380 and one near 470 nm (Fig. 2c). An isosbestic point, where absorbance is independent of oxalate concentration, is an indication of the existence of an equilibrium between


a) 0.1 molal NaCl
5 mmolal
1 mmolal
50 mmolal
100 mmolal
b) 0.5 molal NaCl
1 mmolal
5 mmolal
10 mmolal
50 mmolal
100 mmolal
c) 1.0 molal NaCl
0 mmolal
0.1 mmolal
0.2 mmolal
0.5 mmolal
1 mmolal
2 mmolal
5 mmolal
10 mmolal
20 mmolal
50 mmolal
100 mmolal
d) 2.0 m NaCl
0 mmolal
5 mmolal
1 mmolal
absorbance
0.0
0.1
0.2
0.3
wavelength (nm)
300
400
500
600

two species only. It appears that there are two main bands, near 415 and 480 nm. With increasing concentration of oxalate, the intensity of the former increases at the expense of the latter. The spectra at concentrations of oxalate from 0 to 1 millimolal are similar to that reported by Elding (1972) for $PdCl_4^{2-}$, suggesting that $PdCl_4^{2-}$ is the predominant species in these solutions. The existence of isosbestic points is strong evidence for the progressive transformation from $PdCl_4^{2-}$ to a *single* oxalate-bearing Pd species with increasing concentration of oxalate. However, the data are too limited to determine whether this single oxalate-bearing species is a simple Pd oxalate complex, a mixed Pd chloride–oxalate complex, or a mixed Pd hydroxy-oxalate complex. Figure 2c demonstrates that oxalate-bearing complexes of Pd begin to form even at very low oxalate-to-chloride ratios. At 1 molal NaCl, significant differences in the spectra are observed at oxalate concentrations as low as 2 millimolal, and it appears that almost complete conversion to the oxalate-bearing species occurs at 50 millimolal oxalate, where chloride is still approximately 20 times higher in concentration.

As mentioned above, in 2.0 molal NaCl solutions, concentrations of oxalate higher than 5 millimolal resulted in the formation of a precipitate, presumably sodium oxalate. Thus the range of oxalate concentration is rather limited at the highest NaCl concentration. Figure 2d shows that there is relatively little change in the spectra with increasing oxalate from 0 to 5 millimolal. As expected, the higher concentration of NaCl stabilizes $PdCl_4^{2-}$, such that relatively little conversion to oxalate-bearing species can occur over the limited range of concentration of oxalate that could be investigated.

Importance of Pd oxalate and acetate complexes in soil solutions

In order to determine the importance of Pd oxalate and acetate complexes relative to Pd chloride and hydroxide complexes in a "typical" soil solution at 25°C, the distribution of Pd among the following species was calculated (Fig. 3): Pd^{2+}, $Pd(ac)_2^0$, $Pd(ox)^0$, $PdCl^+$, $PdCl_2^0$, $PdCl_3^-$, $PdCl_4^{2-}$, $PdCl_3OH^{2-}$, $Pd(OH)_2^0$ and $Pd(OH)_3^-$. The stability constant for $Pd(ox)^0$ from Nabivanets & Kalabina (1972) and that for $Pd(ac)_2^0$ quoted above were employed. The required stability-constants for the Pd chloride complexes come from Elding (1972), and those for the Pd hydroxychloride and hydroxide complexes come from van Middlesworth & Wood (1999). Acid dissociation constants for acetate and oxalate were taken from Mesmer *et al.* (1989) and Kettler *et al.* (1991), respectively. The concentrations of total chloride, acetate and oxalate employed in the calculations are given in the caption to Figure 3 and represent typical concentrations of these anions in soil solutions (*cf.* Wood 2000).

Figure 3 shows that relative to oxalate and hydroxide complexes, Pd acetate complexes are subordinate, and probably do not play an important role in soils. Even at 5×10^{-3} molal total acetate (the maximum concentration reported in soil solutions) and 0 molal oxalate, $Pd(ac)_2^0$ never accounts for more than 40% of total Pd in solution (Fig. 3e). On the other hand, palladium oxalate complexes could be the predominant dissolved Pd species in some acidic, organic-matter-rich soils. At 2×10^{-6} molal total oxalate, $Pd(ox)^0$ is the dominant species only at pH less than 3.5, but at 10^{-3} molal total oxalate $Pd(ox)^0$ is the dominant species at pH less than 5. However, it should be kept in mind that these calculations do not take into account competition with other cations, *e.g.*, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, *etc*., for oxalate, which might reduce the importance of oxalate complexation of Pd. Nevertheless, our results show that multidentate carboxylate anions like oxalate may play a role in mobilizing Pd, especially at low pH, and they provide a framework for interpreting experiments involving more complex organic matter, such as fulvic and humic acids.

CONCLUSIONS

Acetate and oxalate are ubiquitous simple organic ligands in the surface environment, and they represent analogues for more complex organic ligands. The stability constant of the Pd^{2+} acetate complex, $Pd(ac)_2^0$, has been determined on the basis of measurements of the solubility of $Pd(OH)_2(am)$ as a function of the concentration of free acetate. The resultant conditional stability-constant, $\log \beta_2^* = 9.30 \pm 0.3$, shows that $Pd(ac)_2^0$ is a stronger complex than the corresponding Pd^{2+} chloride complex. UV–visible spectrophotometric measurements confirm that oxalate forms strong complexes with Pd^{2+}. At 1.0 molal NaCl, the conversion of $PdCl_4^{2-}$ to an oxalate-bearing species is indicated by the spectrophotometric data. Calculations of the distribution of Pd^{2+} among chloride, hydroxide, acetate and oxalate complexes for typical soil solutions show that in spite of the relatively high stability-constant for $Pd(ac)_2^0$, this complex never accounts for a dominant percentage of total Pd at acetate concentrations likely in soils. On the other hand, Pd oxalate complexes predominate under acidic pH conditions at oxalate concentrations within the range possible for soil solutions. Although these calculations are simplistic (they ignore competition by other cations and Pd complexation by humic and fulvic acids), they do demonstrate that organic ligands can be important in governing the behavior of Pd in the surficial

FIG. 2. Visible absorbance spectra showing *d–d* transitions for 0.5 millimolal Pd^{2+} as a function of oxalate concentration at constant NaCl concentrations at 25°C. The NaCl chloride concentrations are: a) 0.1 molal, b) 0.5 molal, c) 1.0 molal, d) 2.0 molal.

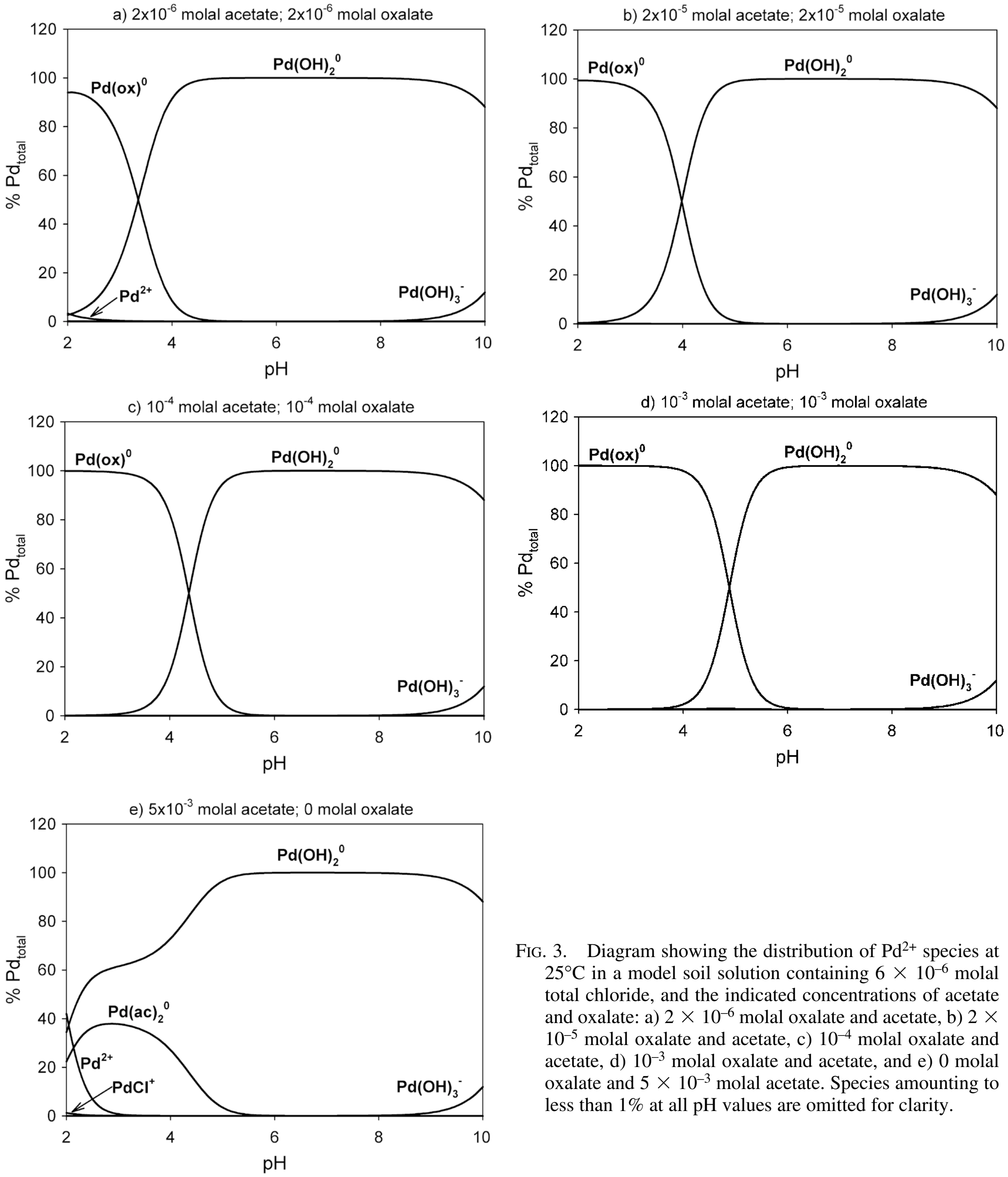


FIG. 3. Diagram showing the distribution of Pd^{2+} species at 25°C in a model soil solution containing 6×10^{-6} molal total chloride, and the indicated concentrations of acetate and oxalate: a) 2×10^{-6} molal oxalate and acetate, b) 2×10^{-5} molal oxalate and acetate, c) 10^{-4} molal oxalate and acetate, d) 10^{-3} molal oxalate and acetate, and e) 0 molal oxalate and 5×10^{-3} molal acetate. Species amounting to less than 1% at all pH values are omitted for clarity.

environment, and that additional work on organic complexes of Pd is warranted.

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