The Solubility of Silver Chloride and the Concentrations of Silver-Containing Species in Ethanol–Water Mixtures

by K. P. Anderson, E. A. Butler, D. R. Anderson, and E. M. Woolley

Department of Chemistry, Brigham Young University, Provo, Utah *(Received February 28, 1967)*

Values of the solubility of silver chloride at chloride ion concentrations between 10^{-5} and 10^{-1} M were determined in 0, 10, 20, 40, and 50% by weight ethanol–water mixtures using a radio tracer technique with ^{110}Ag. Values of the solubility product constant (K_{sp}), the associated silver chloride formation constant (K_0), and the dichloroargentate ion formation constant (K_1) for each solvent mixture were calculated by use of a modified least-squares analysis of the solubility data. It was found that the concentration of silver ion decreased, the concentration of associated silver chloride remained almost constant, and the concentration of dichloroargentate ion increased at a given chloride ion concentration as the per cent ethanol was increased. In other words, K_{sp} decreased from 1.76×10^{-10} to 7.77×10^{-12}, K_0 increased from 2.11×10^{3} to 4.34×10^{4}, and K_1 increased from 1.81×10^{6} to 2.28×10^{7} as the per cent ethanol was changed from 0 to 50.

Introduction

Although the solubility of silver chloride in water at various chloride ion concentrations has been extensively studied,[1-5] few investigations have been made of its solubility as a function of chloride ion concentration in aqueous–nonaqueous solvent mixtures. Several investigators[6-8] have reported the total solubility of silver chloride in mixed solvents with no excess chloride ion present. Kratohvil and Težak[3,9,10] reported values of the solubility of silver chloride at various chloride ion concentrations in mixed solvents. They calculated a value of the solubility product constant from the Ricci and Davis relationship[11] and obtained values of the equilibrium constants for all other silver-containing species in solution by drawing tangents to various parts of the solubility curves. In making those evaluations, Kratohvil and Težak assumed that the thermodynamic activity of each species was equal to its molar concentration and that only one silver-containing species was present in significant concentration at the point where the tangent was drawn.

This paper reports our investigation of the solubility of silver chloride in 0, 10, 20, 40, and 50% by weight ethanol–water mixtures at chloride ion concentrations between 10^{-5} and 10^{-1} M using a radio tracer technique with ^{110}Ag. Our purpose was to determine quantitatively the effect of the composition of the solvent on the concentrations and equilibrium constants of the silver-containing species in solution.

Experimental Section

Materials. All chemicals used were reagent grade. Solutions were prepared from doubly distilled water, which had a specific conductance of 1.3×10^{-6} ohm^{-1} cm^{-1} at 25°. Gas chromatographic analysis of the absolute ethanol used in solution preparation indicated less than 0.1% water and showed no volatile organic impurities.

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$^{110}AgNO_3$ solution (4 mcuries) was obtained from Oak Ridge National Laboratories and was used to prepare stock solutions of $AgClO_4$. The $^{110}AgNO_3$ was mixed with 0.3 g of nonradioactive $AgNO_3$ in a cyanide solution and the silver was electroplated onto platinum. The silver was then dissolved in nitric acid and fumed three times to near dryness with perchloric acid. The residue, of initial specific activity *ca.* 5×10^7 cpm/mg of Ag, was diluted to about 1.7×10^{-4} *F* $AgClO_4$ and was stored in a light-protected container.

Procedure and Equipment. The experimental procedure was similar to that of Jonte and Martin[2] and Tingey.[5] Equilibration samples were 25-ml solutions prepared in 30-ml screw-cap vials. Each cap was equipped with a cone-shaped polyethylene insert to prevent leakage. The $AgClO_4$ solution was pipetted into the vials last to minimize exposure of personnel and to prevent premature formation of insoluble species. The sealed vials were mounted on a rotating drum immersed in a water bath maintained at 25.00 ± 0.01°. After equilibration for 1 week, the samples were centrifuged 6 min at 12,300 rpm in a Sorvall SS-1 Superspeed angle centrifuge mounted in an air bath maintained at 25.0 ± 0.2°. Portions (2-ml) of each centrifuged solution were carefully withdrawn, evaporated to dryness, and analyzed for total silver content by using a thallium-activated NaI scintillation detector coupled to Tracerlab automatic counting apparatus. Twenty to thirty solubility determinations, each at a different chloride ion concentration, were made in each ethanol–water solvent mixture.

Calculations. The solubility product constant, K_{sp}, associated silver chloride formation constant, K_0, and the dichloroargentate ion formation constant, K_1, are defined by eq 1, 2, and 3, respectively[2,5] in terms of the thermodynamic activities of the indicated species.

$$K_{sp} = a_{Ag^+}a_{Cl^-} \tag{1}$$

$$K_0 = \frac{a_{AgCl_{assoc}}}{a_{Ag^+}a_{Cl^-}} \tag{2}$$

$$K_1 = \frac{a_{AgCl_2^-}}{a_{Ag^+}a_{Cl^-}{}^2} \tag{3}$$

Combination of these three equations with the mass balance equation for total silver in solution gives eq 4, an expression for total molar silver concentration as a function of the equilibrium constants, thermodynamic activity coefficients, and the molar concentration of chloride ion. The activity coefficient of $AgCl_{assoc}$, γ^*_0,

$$[Ag_{total}] = \frac{K_{sp}}{[Cl^-]\gamma^*_1{}^2} + \frac{K_0K_{sp}}{\gamma^*_0} + K_1K_{sp}[Cl^-] \tag{4}$$

was assumed to be unity.[2,5] The activity coefficients of all singly charged species, γ^*_1, were assumed to be equal and were calculated from the extended Debye–Hückel expression[12]

$$\log \gamma^*_1 = -\frac{A(I)^{1/2}}{1 + Bd(I)^{1/2}} \tag{5}$$

where

$$A = 354.5(\rho/D^3)^{1/2} \tag{6}$$

$$B = 2.913 \times 10^8(\rho/D)^{1/2} \tag{7}$$

and

$$I = \frac{1}{2\rho}\Sigma C_iZ_i^2 \tag{8}$$

In eq 5–8, I is the ionic strength of the solution, ρ is the density of the solution in grams per milliliter,[13] D is the dielectric constant[14] of the mixed solvent, and d is the effective ionic diameter of the ions in solution expressed in centimeters. The value of d used in this work was 3.047×10^{-8} cm, so that $Bd = 1.000$ for water as the solvent.[12] The asterisk superscripts on the activity coefficients indicate that the standard states chosen were based upon infinite dilution in that solvent or solvent mixture in which the solubility was determined. Values of K_{sp}, K_0, and K_1 were calculated simultaneously by means of a modified least-squares treatment[15] of total silver concentration *vs.* chloride ion concentration data. The application of a relative-deviation least-squares method of data treatment permitted very small absolute deviations in the concentrations of species present in a low-concentration region to be as important in the determination of the shape of a solubility curve as much greater absolute deviations in a high-concentration region.

Results and Discussions

The solubility data and accompanying least-squares solubility curves for the solvent systems studied are shown in Figures 1 and 2. Figure 1 also shows values of $[AgCl_2^-]$, $[AgCl_{assoc}]$, and $[Ag^+]$ as a function of $[Cl^-]$ for the 9.88% ethanol system. These values were calculated from the values of K_{sp}, K_0, and K_1 given in

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[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, pp 42–92, 508–515.

[13] Values used in this work are interpolations of data from "International Critical Tables of Numerical Data," Vol. 3, 1st ed, E. W. Washburn, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 116.

[14] Values used in this work were interpolations of data from G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4132 (1932).

[15] K. P. Anderson and R. L. Snow, *J. Chem. Educ.*, in press.

Table I: Equilibrium Constants for 0–50 wt % Ethanol–Water Mixtures

Wt % ethanol	Dielectric constant[a]	$K_{sp} \times 10^{12}$	SD,[b] %	$K_0 \times 10^{-8}$	SD,[b] %	$K_1 \times 10^{-5}$	SD,[b] %
0	78.54	176	11.0	2.11	10.0	1.81	8.3
9.88	72.87	90.4	6.4	4.61	6.1	3.76	6.3
19.99	67.00	59.9	5.3	6.16	4.5	6.57	3.4
40.12	54.93	17.0	3.5	18.6	5.9	66.4	4.6
50.02	48.99	7.77	9.2	43.4	8.6	228.0	9.9

[a] See ref 14. [b] Percentage standard deviations calculated from the weighted relative deviations of the experimental solubility data points from the least-squares solubility curves in Figures 1 and 2.

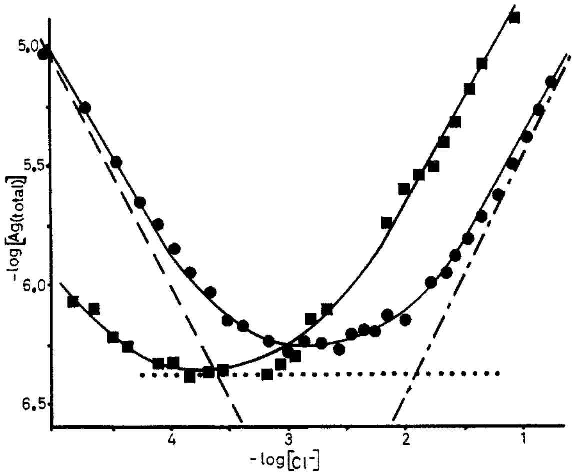

Figure 1. Solubility curves: —●—, 9.88% ethanol; —■—, 50.02% ethanol; – – – –, log [Ag^+] for 9.88% ethanol; . . . . . ., log [$AgCl_{assoc}$] for 9.88% ethanol; — · —, log [$AgCl_2^-$] for 9.88% ethanol.

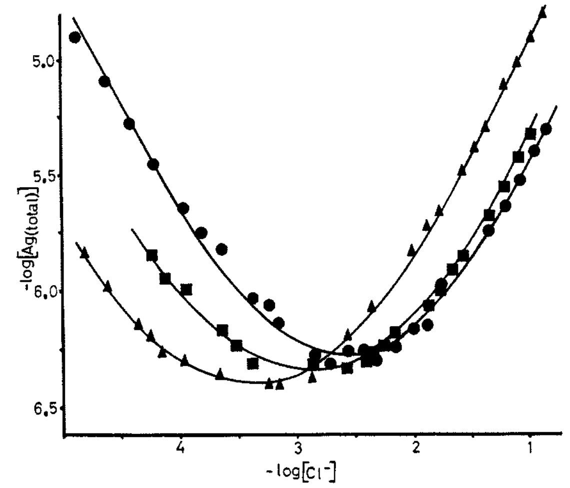

Figure 2. Solubility curves: —●—, water; —■—, 19.99% ethanol; —▲—, 40.12% ethanol.

Table I. The values of K_{sp}, K_0, and K_1 for each solvent system in Table I were calculated from the modified least-squares solubility curves in Figures 1 and 2. Since only small random deviations of the solubility data from solubility curve represented by eq 4 were observed, it was assumed that there were no appreciable concentrations of complexes of the form $AgCl_n^{1-n}$ where $n > 2$, even in 0.13 M chloride ion solutions.

Figures 1 and 2 show that the entire solubility curves were shifted toward the lower chloride ion concentrations as the per cent ethanol was increased. That is, [Ag^+] decreased, [$AgCl_{assoc}$] remained almost constant, and [$AgCl_2^-$] increased at any given value of [Cl^-]. These trends are shown quantitatively in Figure 3, where values of $-\log K_{sp}$, $\log K_0$, and $\log K_1$ are plotted *vs.* the reciprocal of the dielectric constant of the solvent. Values given by Kratohvil and Težak[9] are also shown.

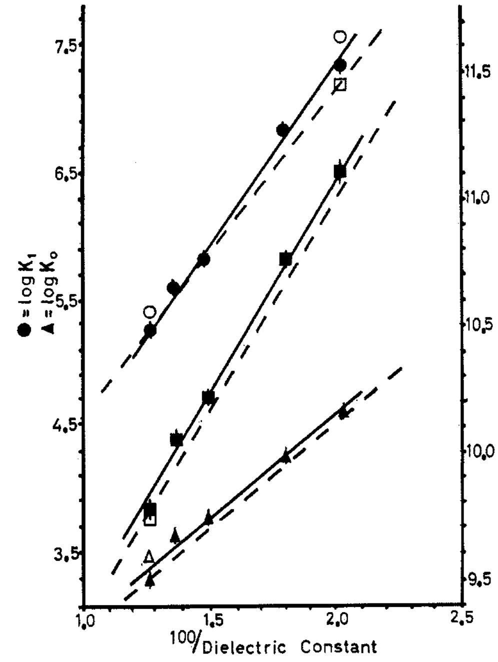

Figure 3. Log K *vs.* 100/D: ■, ▲, and ●, experimental values; □, △, and ○, values reported by Kratohvil and Težak;[10] – – – –, values predicted by Born's equation;[16] ———, least-squares fits of experimental points according to eq 9.

An equation derived by Born[16] which considers electrostatic interactions has the general form

$$\log K' = M\left(\frac{1}{D'} - \frac{1}{D''}\right) + \log K'' \qquad (9)$$

When applied to equilibria involving ions, K' and K'' are the equilibrium constants in media of dielectric constant D' and D'', respectively, and M involves values for the radii of the ions. The solid lines in Figure 3 were obtained from least-squares analyses of the data in Table I. The broken lines were obtained from the Born equation by using values of 1.26, 1.81, and 4.88 A (the crystallographic radii) for the radii of silver ion, chloride ion, and dichloroargentate ion, respectively. Table II gives values of M for eq 9 for the lines in Figure 3. The linear relationship predicted by Born is apparent from Figure 3 and Table II.

Table II: Values of M in Equation 9

Equilibrium constant	Measured M values[a]	AD,[b] %	Calcd M values[c]	% difference
K_{sp}	−171.4	5.36	−162.9	−5.22
K_0	161.9	5.85	162.9	−0.61
K_1	275.8	8.76	254.5	+8.37

[a] From least-squares fit of the data in Table I according to eq 9. [b] Percentage average deviations calculated from the relative deviations of the experimental values of the constants from the least-squares line. [c] Calculated from Born's equation[16] using values of 1.26, 1.81, and 4.88 A for the radii of silver ion, chloride ion, and dichloroargentate ion, respectively.

As illustrated in Figure 1, about two-thirds of the total silver present at the solubility minimum is in the form of $AgCl_{assoc}$, whereas the remaining one-third is about equally distributed between the species Ag^+ and $AgCl_2^-$. As shown in Figure 3, Kratohvil and Težak[9] reported higher values for the concentrations of $AgCl_{assoc}$, Ag^+, and $AgCl_2^-$ in water than determined in this study. Their method involved the determination of equilibrium constants by the construction of tangents to the solubility curve, a tacit assumption that at the minimum in the curve only $AgCl_{assoc}$ is present while at each extremity of the curve only one charged species is present. These investigators also assumed that all activity coefficients were unity.

Further investigation of various other solvent and slightly soluble salt systems should prove helpful in providing quantitative explanations of the effects of the dielectric constant of the solvent and the nature of the nonaqueous component on the concentrations of the various species present in solution and on the values of the constants for the equilibria among these species.

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