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The Independence of Isothermal Equilibria in Electrolyte Solutions on Changes in Dielectric Constant

By Arvin S. Quist and William L. Marshall

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The importance of including the molar concentration of the solvent as a variable in the equilibrium constant (K^0) is discussed. When the solvent is considered to participate actively in the equilibrium, isothermal values of K^0 are found to be independent of changes in dielectric constant of the solvent mixtures. Extensive examples are given in support of this general principle. The new principle contrasts with existing theory that considers log K (the conventional constant not containing solvent species as concentration variables) to be a linear function of $1/D$. It is shown to apply to electrolyte behavior in water, water–organic, and organic–organic solvent systems over a wide range of temperature and pressure. For example, in water–dioxane solvent mixtures where electrolytes (ions and polar molecules) are preferentially solvated by water molecules, a plot of log K (dissociation) *vs.* log C_{H_2O} in moles per liter yields a straight line of intercept K^0 and slope representing the net change in waters of solvation between equilibrium reactants and products. From the slope and an estimate of the hydration number of the ion pair, the "ion size" parameter can be calculated. Many examples in support of this new principle are presented both for homogeneous and heterogeneous equilibria.

Introduction

In an earlier communication, we have proposed a general principle that the inclusion of solvent species of variable concentration directly into the conventional equilibrium constant (K) for ion–ion-pair–solvent equilibria provides a complete constant (K^0) that is *independent* of changes in *dielectric constant* at constant temperature.[2] It is the purpose of this paper to present substantial evidence to support this principle, to show that it provides an independent method for calculating hydration numbers and ion size parameters, and to present a clearer description of solution equilibria in general.

Previously, changes in conventional, isothermal equilibrium constants involving electrolytes in aqueous–organic and organic–organic solvents have been almost universally correlated with changes in the measurable dielectric constant (D) of the solvent mixtures. The decrease in a conventional dissociation constant [expressed herein always as dissociation constants for direct comparisons and consistency] with decreasing concentration of the more polar component of a binary solvent mixture has usually been related to the simultaneous decrease in the measurable dielectric constant of the solvent mixture. Thus the Bjerrum equation,[3] relating ion-pair formation to the dielectric constant of the solvent and to ionic size, was used by Fuoss and Kraus[4] to relate log K for the ionization of tetraisoamylammonium nitrate in water–dioxane mixtures to log D. The currently accepted Denison–Ramsey–Fuoss theory[5,6] of ion-pair formation predicts

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[1] Work sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

[2] W. L. Marshall and A. S. Quist, *Proc. Natl. Acad. Sci. U. S.*, **58**, 901 (1976).

[3] N. J. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926).

[4] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

that log K should be a linear function of $1/D$, with a slope that is proportional to the ion size. The latter relationship holds moderately well for most ionization constants when the concentration of added organic solvent is not great, but the correlation (although observed over limited ranges of very low dielectric constant) is not observed over wide ranges of solvent composition.

The Denison–Ramsey–Fuoss theory of ion-pair formation is based on a sphere-in-a-continuum model and considers that the measurable dielectric constant is the controlling factor in association. However, in recent years evidence has been accumulating[7-9] to indicate that ion–solvent interaction must be considered and that the dielectric constant of the solvent mixture may not be the only significant factor in ion association. If the important factors in short-range electrostatic attractions between oppositely charged ions, ion pairs, and solvent molecules in solution are the charges on the ions and the dipole moments (assumed constant at constant temperature) of the reacting species, and if ions and ion pairs in mixed solvents are selectively solvated, then a complete, isothermal constant K^0 involving also solvent species as variables would be expected to remain constant over a large range of solvent compositions.[10] Therefore, it would appear that the Denison–Ramsey–Fuoss theory as presently derived, using the measurable dielectric constant and considering the incomplete constant K, is probably incorrect. This theory considers also that only contact ion pairs are formed in the association process.[9] Eigen[11] and Atkinson,[12] however, have demonstrated the existence of a three-step ion-association process for 2–2 electrolytes, involving stepwise removal of solvent molecules from between ions.

We propose that the activity (or concentration) of solvent molecules indeed be included, in molar concentration units,[13] as very important *variables* in the complete equilibrium constant, K^0. When this is done, it is found that the isothermal K^0 for a particular equilibrium is independent of changes in dielectric constant, whether these changes are made by varying the density of the solution system by pressurization or by adding an "inert" solvent (*i.e.*, one that does not significantly solvate the ions or polar molecules of the electrolyte), such as dioxane, to water. Tests of this general principle have shown remarkable agreement over a wide range of conditions for a variety of aqueous–organic and some organic–organic solvents at room temperature and atmospheric pressure, and also for equilibrium behavior in water alone. The agreement far surpasses that shown by existing theories that correlate the change in the incomplete equilibrium constant (not K^0) with changes in the measurable dielectric constant.

Aqueous Electrolyte Behavior at Supercritical Temperatures

Sodium chloride is generally considered to be completely ionized in aqueous solutions at room temperature and atmospheric pressure. However, it becomes progressively a weaker electrolyte as the temperature increases. From electrical conductance measurements on dilute NaCl solutions at temperatures to 800° and at pressures to 4000 bars,[13] conventional equilibrium constants (K) have been calculated which are related to the complete equilibrium constants as

$$\mathrm{NaCl(H_2O)}_j + k\mathrm{H_2O} \rightleftharpoons \mathrm{Na(H_2O)}_m{}^+ + \mathrm{Cl(H_2O)}_n{}^- \qquad (1a)$$

$$K^0 = \frac{a_{\mathrm{Na(H_2O)}_m{}^+}a_{\mathrm{Cl(H_2O)}_n{}^-}}{a_{\mathrm{NaCl(H_2O)}_j}a_{\mathrm{H_2O}}{}^k} = K/a_{\mathrm{H_2O}}{}^k \qquad (1b)$$

$$\log K = \log K^0 + k \log a_{\mathrm{H_2O}} \qquad (1c)$$

where K^0 is the complete constant assumed to be independent of $a_{\mathrm{H_2O}}$, K is the conventional constant that varies with $a_{\mathrm{H_2O}}$, and the a's are activities based on molar concentration units. In his studies on KCl solutions at supercritical temperatures and pressures, Franck[14] some 11 years ago showed that a plot of log K (at constant temperature) against log $C_{\mathrm{H_2O}}$ (moles per liter) gave nearly a straight line. Our own recent and extensive values of log K for NaCl show a linear relationship for similar plots.

The values of K (at a particular temperature and density) as obtained from the conductance measurements represent the values of this parameter at infinite dilution of the electrolyte. Under these conditions, the solvent has the same properties as the pure solvent and its activity can be set equal to its molar concentration. Consequently, eq 1c can be written as

$$\log K = \log K^0 + k \log C_{\mathrm{H_2O}} \qquad (2)$$

where $C_{\mathrm{H_2O}}$ refers to the molar concentration of water. Thus, if water is considered a reactant of variable concentration in the equilibrium, the linear relationship between log K and log $C_{\mathrm{H_2O}}$ is explained. Ordinarily, in studies of equilibria in aqueous solutions under the usual conditions of 25° and atmospheric pressure, the activity of water is effectively constant and is arbitrarily assigned a value of unity, whereby the equilibrium is expressed by the conventional K. However, as seen in the above example, in studies of equilibria in solutions at supercritical temperatures and pressures where wide ranges of water concentrations are encoun-

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(5) J. T. Denison and J. B. Ramsay, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

(6) R. M. Fuoss, *ibid.*, **80**, 5059 (1958).

(7) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1704, 1722 (1963).

(8) G. Atkinson and S. Petrucci, *J. Am. Chem. Soc.*, **86**, 7 (1964).

(9) G. Atkinson and S. Petrucci, *J. Phys. Chem.*, **70**, 3122 (1966).

(10) Note that the measurable dielectric constant still remains important for long-range electrostatic interactions.

(11) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93, 107 (1962).

(12) G. Atkinson and S. K. Kor, *J. Phys. Chem.*, **69**, 128 (1965).

(13) A. S. Quist and W. L. Marshall, *ibid.*, **72**, 684 (1968).

(14) E. U. Franck, *Z. Physik. Chem.* (Frankfurt), **8**, 107 (1956).

tered, it is necessary to include the activity of water as a variable in calculating the complete equilibrium constant.

For the NaCl solutions, this linear relationship was observed at temperatures from 400 to 800° and at densities from 0.30 to 0.75 g cm^{-3}. Furthermore, the values of k were essentially *constant* throughout this temperature range, indicating that j, m, and n may be primary hydration numbers. A value of K^0 can therefore be calculated with eq 2 at each temperature. This K^0 is independent of density (pressure) at constant temperature, and therefore meets one of the requirements of a "true" thermodynamic equilibrium constant.[15]

This concept of a true, isothermal equilibrium constant has been experimentally verified for several different ionization equilibria over a wide range of solution densities and over wide temperature regions. The evaluations for most of the published data for aqueous solutions at high temperatures and pressures are summarized in Table I. Since the isothermal equilibrium constants K^0 for the equilibria summarized in Table I are independent of solvent density, it became evident to us that these constants were also independent of changes in dielectric constant of the solvent. Although at 400° the dielectric constant of water decreases from 19.5 at a density of 0.8 g cm^{-3} to 4.9 at a density of 0.3 g cm^{-3},[16] the value of K^0 is constant. This observation is highly significant in demonstrating that the measurable dielectric constant of the solvent is not the determining factor in predicting the true equilibrium constant, in contrast to present theory on the variation of the conventional K.[7] In the following sections this principle is extended to include ionic equilibria in water–organic and organic–organic solvents.

Equilibrium Behavior in Water–Organic Solvents at Room Temperature

The above expectations and observations indicated that for ionic equilibria in mixed solvents the inclusion of the solvent species as reactants of variable concentration might provide equilibrium constants that were truly independent of changes in solvent composition. In the examples described above, the concentration of water was varied by changing the pressure on the solutions. The molarity of water can also be changed by adding an "inert" solvent, such as dioxane. The addition of this inert solvent does not appear to affect significantly the hydration of ions since the water molecule is much more polar than the dioxane molecule and consequently water molecules selectively solvate the ions.[17,18] Therefore, the relative hydration of ions should be nearly independent of total water concentration, and the hydration numbers in an equation like eq 1a should remain constant over a wide range of water–dioxane compositions. Kunze and Fuoss[19] have calculated conventional ionization constants for NaCl for the equilibrium represented by K in eq 1c from conductance measurements in several water–dioxane mixtures at 25°. When the ionization constants reported

Table I

Electrolyte	Solvent system	Temp, °C	Net change in waters of hydration on ionization	Lit. ref
HSO_4^-	H_2O to 4000 bars	100–300	20	*a*
H_2SO_4	H_2O to 4000 bars	400–800	11	*b*
$KHSO_4$	H_2O to 4000 bars	400–800	8.5	*a*
NaCl	H_2O to 4000 bars	400–800	10	*c*
KCl	H_2O to 2700 bars	400–750	9	*d*
HCl	H_2O to 2700 bars	400–700	9	*e*
KOH	H_2O to 2700 bars	400–700	8	*e*

[a] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **70**, 3714 (1966). [b] A. S. Quist, *et al.*, *ibid.*, **69**, 2726 (1965). [c] Reference 13. [d] Reference 14. [e] E. U. Franck, *Z. Physik. Chem.* (Frankfurt), **8**, 192 (1956).

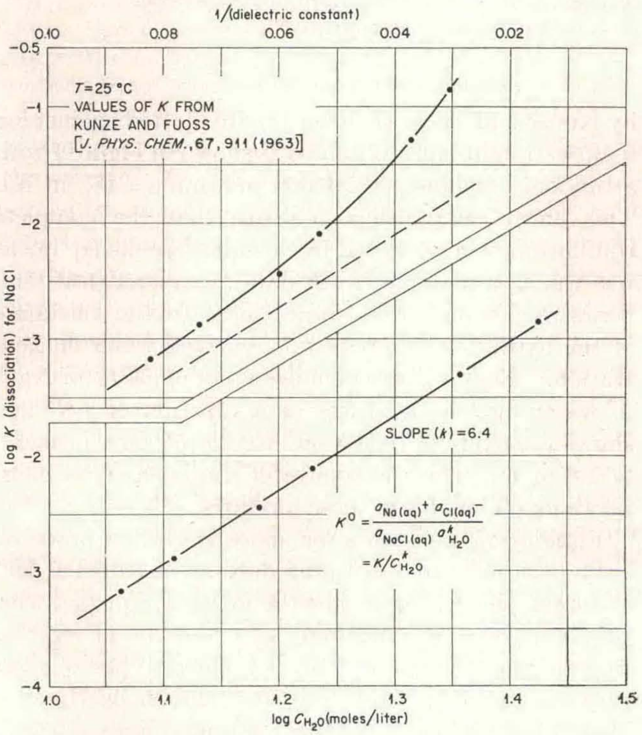

Figure 1. Log K (dissociation) of sodium chloride *vs.* log C_{H_2O} (moles per liter) in dioxane–water mixtures; also compared *vs.* 1/(dielectric constant, D); K values of Kunze and Fuoss (1963).

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[15] W. J. Moore, "Physical Chemistry," 3rd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, p 174.

[16] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 3165 (1965).

[17] T. W. Davis, J. E. Ricci, and C. G. Sauter, *J. Am. Chem. Soc.*, **61**, 3274 (1939).

[18] A. Fratiello and D. C. Douglass, *J. Chem. Phys.*, **39**, 2017 (1963).

[19] R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, **67**, 911 (1963).

$$\mathrm{Bu_4N\ picrate_{(solv)}} + k(\mathrm{C_6H_5NO_2}) + p(\mathrm{CCl_4}) \xrightleftharpoons{K_d{}^0} \mathrm{Bu_4N^+{}_{(solv)}} + \mathrm{picrate^-{}_{(solv)}} \quad (3a)$$

$$K_d{}^0 = \frac{a_{\mathrm{Bu_4N(solv)}}{}^{+}a_{\mathrm{picrate(solv)}}{}^{-}}{a_{\mathrm{Bu_4N\ picrate(solv)}}C^k{}_{\mathrm{C_6H_5NO_2}}C^p{}_{\mathrm{CCl_4}}} \quad (3b)$$

$$= K/(C^k{}_{\mathrm{C_6H_5NO_2}}C^p{}_{\mathrm{CCl_4}}) \quad (3c)$$

where $K_d{}^0$ is now the complete constant and k and p represent the net (selective) changes in solvation in the reaction equilibrium of solvents $C_6H_5NO_2$ and CCl_4, respectively. By a method of least squares, values of k of 7.7 and p of 0.61, respectively, were obtained that provided a fit to the conventional K's of ±15%, within the experimental precision of the K's, over the entire range of compositions (but not including pure nitrobenzene, where eq 3 cannot apply).

Solubility Equilibria in Aqueous Solution

In accordance with the concept of water as a necessary concentration variable, a complete solubility product equilibrium for the dissolution of an anhydrous salt may be written as

$$\mathrm{MA(s)} + r\mathrm{H_2O} = \mathrm{M(H_2O)_m{}^+} + \mathrm{A(H_2O)_n{}^-} \quad (4a)$$

$$K_{sp}{}^0 = \frac{a_{\mathrm{M(H_2O)}m}{}^{+}a_{\mathrm{A(H_2O)}n}{}^{-}}{a_{\mathrm{MA(s)}}a^r{}_{\mathrm{H_2O}}} \quad (4b)$$

where the activity of the solid phase is a constant and may be set equal to unity at all temperatures and pressures, and where the solute is completely ionized in solution. When the solute remains undissociated in solution, the solubility equilibrium may be written as

$$\mathrm{MA(s)} + j\mathrm{H_2O} = \mathrm{MA(H_2O)}_j\mathrm{(aq)} \quad (5a)$$

$$K_s{}^0 = \frac{a_{\mathrm{MA(H_2O)}j\mathrm{(aq)}}}{a_{\mathrm{MA(s)}}a^j{}_{\mathrm{H_2O}}} \quad (5b)$$

Equations 4 and 5 are related by the complete equilibrium constant for the dissociation of the neutral species in solution

$$\mathrm{MA(H_2O)}_j\mathrm{(aq)} + (r - j)\mathrm{H_2O} = \mathrm{M(H_2O)_m{}^+} + \mathrm{A(H_2O)_n{}^-} \quad (6a)$$

$$K_d{}^0 = \frac{a_{\mathrm{M(H_2O)}m}{}^{+}a_{\mathrm{A(H_2O)}n}{}^{-}}{a_{\mathrm{MA(H_2O)}j}a_{\mathrm{H_2O}}{}^{(r-j)}} \quad (6b)$$

Dickson, Blount, and Tunell[22] have measured the solubility of anhydrous $CaSO_4$ in water from 100 to 275° and at pressures to 1000 bars. When the logarithm of the molar solubility of $CaSO_4$ is plotted against log C_{H_2O}, at 250°, a straight line is obtained. If it is considered that $CaSO_4$ is nearly completely ionized under these conditions[23] a hydration change of 28 is calculated according to the equilibrium of eq 4b. Since the solid phase is anhydrous, this number, although large, corresponds to the sum of the hydration numbers of the calcium and sulfate ions and not to the net change of hydration numbers between the solvated ion pair and the ions as listed in Tables I and II. When the solubility data for NaCl at 600°[24] are treated in a similar manner, the graph shown in Figure 4 is obtained. At low solution densities where NaCl exists nearly completely in the form of neutral species[13] and eq 5b would be expected to apply predominantly, the slope of the line gives a hydration number of approximately 2 for this neutral species. At higher solution densities, NaCl has been observed to ionize appreciably, and so the slope of the line approaches that number equal to $^1/_2$ the sum of the hydration numbers of the sodium and chloride ions. In Figure 4 the densities of the solutions have been assumed to be those of pure water, a reasonable assumption at low solubilities but invalid for the concentrated solutions. This causes the graph to become nonlinear at high concentrations of water where the solubility of NaCl is quite large. If at high solubilities the mean activity coefficient of NaCl would change markedly with changing water concentration, nonlinearity could occur also from this effect. However, at solution saturation, this coefficient would be expected to remain constant as discussed in the next section.

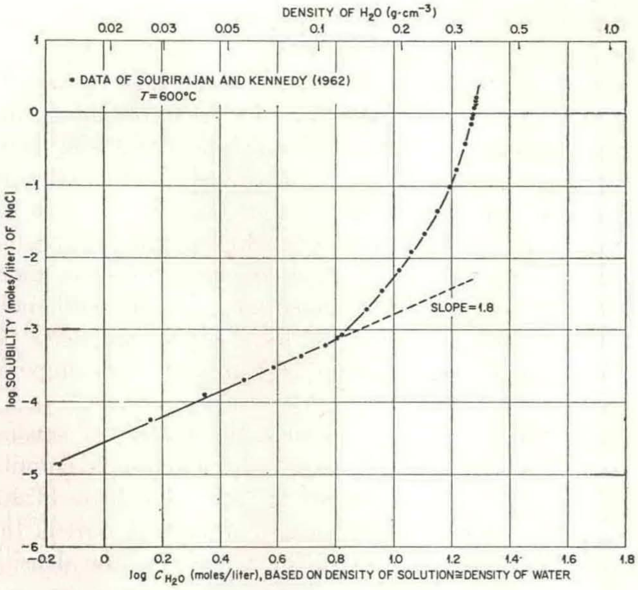

Figure 4. Logarithm of the molar solubility of NaCl *vs.* log molar concentration of water at 600°.

The solubilities of inorganic salts in water–organic solvent mixtures also exhibit the two types of behavior shown by eq 4a and 5a. Ricci and coworkers have measured the solubilities of several salts in water–dioxane mixtures; among these are AgAc,[17] Ag_2SO_4,[17] Ba-

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(22) F. W. Dickson, C. W. Blount, and G. Tunell, *Am. J. Sci.*, **261,** 61 (1963).

(23) W. L. Marshall and R. Slusher, *J. Phys. Chem.*, **70,** 4015 (1966).

(24) S. Sourirajan and G. C. Kennedy, *Am. J. Sci.*, **260,** 115 (1962).

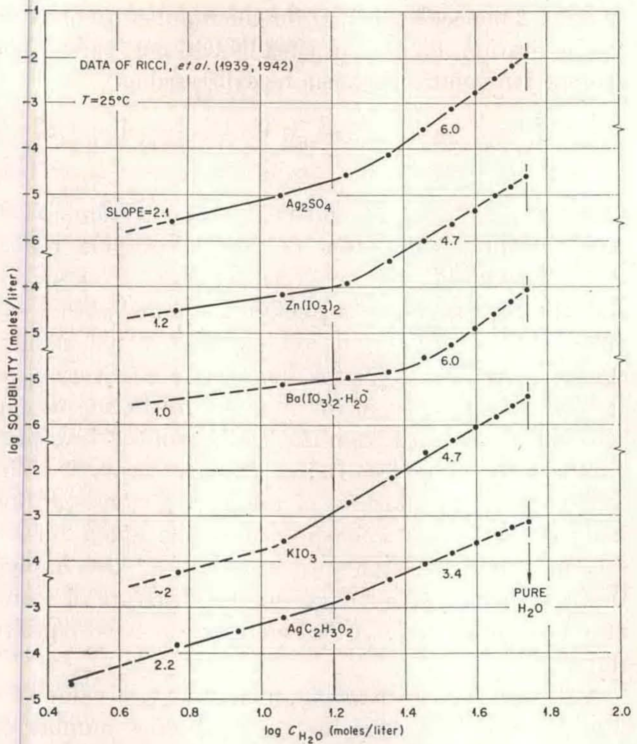

Figure 5. Log solubility (moles per liter) for several salts *vs.* log C_{H_2O} in dioxane–water mixtures at 25°; data of Ricci, *et al.* (1939, 1942). (Added in proof: add +0.4 and −0.2 to log solubilities for Ag_2SO_4 and $Zn(IO_3)_2$, respectively; corrected upper slopes = 5.7 for both Ag_2SO_4 and $Ba(IO_3)_2 \cdot H_2O$, and 3.2 for $AgC_2H_3O_2$.)

$(IO_3)_2 \cdot H_2O$,[17] KIO_3,[25] and $Zn(IO_3)_2$.[25] For most of these salts, when the logarithm of molar solubility is plotted against the logarithm of water molarity, the straight line that is observed at high water concentrations in all cases undergoes a change in slope at moderately low water concentrations, as shown in Figure 5. In this figure, the slope at very low concentrations of water approaches that corresponding to the hydration number of the neutral molecules (eq 5b). At high water molarities the slope approaches a value related to the sum of the hydration numbers of the ions. For silver sulfate, this sum is equal to three times the slope since the product of the ion concentrations is proportional to the cube of the solubility of silver sulfate. Table III summarizes the results of our interpretation of some of the solubility measurements contained in the literature, where H_2O in $Ba(IO_3)_2 \cdot H_2O$ is included in the total.

Constancy of Electrolyte Activity Coefficients in Saturated Water–Organic Mixtures

Ricci and Davis[26] have mentioned several systems in which the activity coefficients of an electrolyte in its saturated solution, based on the use of the Debye–Hückel limiting law with the measured dielectric constants of the solvent mixtures, are nearly constant and independent of the nature of the water–organic solvents. For example, the mean ionic activity coefficient of silver acetate in saturated solution at 25° was found to remain essentially constant in water and in several compositions of ethanol–water, acetone–water, and dioxane–water. Since all of these solutions contain water, on the basis of the concepts in this paper we may write for the complete solubility product equilibrium

Table III

From solubilities		Temp, °C	Total waters of hydration of ions in solution	Lit. ref
$CaSO_4$	Water to 1000 bars	250	28	*a*
KIO_3	Water–dioxane	25	9.4	*b*
$Zn(IO_3)_2$	Water–dioxane	25	14.1	*b*
AgAc	Water–dioxane	25	6.4	*c*
Ag_2SO_4	Water–dioxane	25	17.1	*c*
$NaNO_3$	Water–dioxane	25	3.2	*d*
$Ba(IO_3)_2 \cdot H_2O$	Water–dioxane	25	18.1	*c*

[a] Reference 22. [b] Reference 25. [c] Reference 17. [d] B. Selikson and J. E. Ricci, *J. Am. Chem. Soc.*, **64**, 2474 (1942).

$$AgAc(s) + rH_2O = Ag(H_2O)_m^+ + Ac(H_2O)_n^- \quad (7a)$$

$$K_{sp}^0 = \frac{a_{Ag(H_2O)_m^+}a_{Ac(H_2O)_n^-}}{a_{AgAc(s)}a^r{}_{H_2O}} = \frac{K_{sp}}{a^r{}_{H_2O}} \quad (7b)$$

If the activity of solid silver acetate (a constant) by convention is taken to be unity, if the activity of water is set equal to its molar concentration (a reasonable assumption for these solutions of low concentrations), and if the conventional K_{sp} is expressed by

$$K_{sp} = a_{Ag(H_2O)_m^+}a_{Ac(H_2O)_n^-} = Q_{sp}f_\pm^2 \quad (8a)$$

then eq 7b may be written as

$$\log Q_{sp} = \log K_{sp}^0 + r \log C_{H_2O} - 2 \log f_\pm \quad (9)$$

For saturated solutions of silver acetate in acetone–water, ethanol–water, and dioxane–water at relatively high water concentrations we have obtained the following relationships from the experimental data

$$\frac{\partial \log Q_{sp}}{\partial \log C_{H_2O}} = r = 6.0, 5.4, 6.4 \text{ (respectively)} \quad (10)$$

Since

$$\frac{\partial \log K_{sp}^0}{\partial \log C_{H_2O}} = 0 \quad (11)$$

(the true, isothermal equilibrium constant is invariant), then

$$\frac{\partial \log f_\pm}{\partial \log C_{H_2O}} = 0 \quad (12)$$

for these systems, which is what Ricci and others have

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(25) J. E. Ricci and G. J. Nesse, *J. Am. Chem. Soc.*, **64**, 2305 (1942).

(26) J. E. Ricci and T. W. Davis, *ibid.*, **62**, 407 (1940).