[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

On the Solubility of Ag_2SO_4 in Various Electrolyte Media. Effects of the Solubility of Ag_2SO_4 and AgCl on the Ag, Ag_2SO_4 and the Ag, AgCl Electrodes[1]

BY M. H. LIETZKE AND R. W. STOUGHTON

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The log of the solubility products of Ag_2SO_4 on a molality basis in KNO_3, $AgNO_3$, $Mg(NO_3)_2$, $Al(NO_3)_3$, Na_2SO_4, $MgSO_4$, $CuSO_4$, $Al_2(SO_4)$, $La_2(SO_4)_3$ and $In_2(SO_4)_3$ media were plotted against the stoichiometric ionic strength. The curves were unexpectedly similar. The solubility of AgCl in HCl and $AgNO_3$ solutions was interpreted in terms of the mononuclear complexes $AgCl_2^-$, $AgCl_3^{--}$, $AgCl_4^{---}$ and Ag_2Cl^+, Ag_3Cl^{++}, Ag_4Cl^{+++}, respectively. Possible effects of increased solubility of the silver salts on the usefulness of the Ag, Ag_2SO_4 and Ag, AgCl electrodes are mentioned.

Introduction

Previous work[2] indicated that the Ag, Ag_2SO_4 (sat.) and the Ag, AgCl(sat.) electrodes offered considerable promise as reference electrodes for high temperature e.m.f. studies in aqueous solutions. The increasing solubility of Ag_2SO_4 in H_2SO_4 media with increasing acid concentration and temperature,[3] on the other hand, would appear to put upper limits on the values of these variables at which useful thermodynamic data can be obtained with the use of the Ag, Ag_2SO_4 electrode. Because of the moderately high solubility of Ag_2SO_4 in water (about 0.03*m* over a rather large temperature range) any appreciable reaction of this salt with an electrolyte in solution may be expected to complicate significantly the interpretation of thermodynamic data. In this connection it was anticipated that a study of the solubility of Ag_2SO_4 in a variety of electrolytes of different valence types even at room temperature might elucidate the general problem of such interpretations.

Data for the solubility of Ag_2SO_4 in $AgNO_3$, $Al(NO_3)_3$, $Al_2(SO_4)_3$ and $La_2(SO_4)_3$ solutions at 25° were obtained experimentally for this study, while data for the solubility of Ag_2SO_4 in $Mg(NO_3)_2$,[4] Na_2SO_4,[5] $MgSO_4$,[6] $CuSO_4$[6] and $In_2(SO_4)_3$[7] solutions were obtained from the literature. The determinations in $AgNO_3$ solutions were made because, as will be shown later, the literature values for this system[4] appeared to be inconsistent with the other data. Solubility data for AgCl in HCl, $AgNO_3$ and HNO_3 media were also obtained from the literature in order to compare the common ion effect on this salt with that on Ag_2SO_4.

Experimental

The Ag_2SO_4 used in the solubility measurements was prepared according to the method described by Archibald.[8] The $La_2(SO_4)_3$ was prepared from Fisher Scientific Company $La(NO_3)_3 \cdot 6H_2O$ by treating the nitrate with Baker analyzed concentrated H_2SO_4, fuming off the excess H_2SO_4, and igniting the $La_2(SO_4)_3$ in a muffle furnace at 500°. The $Al(NO_3)_3$, $Al_2(SO_4)_3$ and $AgNO_3$ were all Baker Analyzed Reagent grade chemicals. In each case a series of stock solutions was prepared covering the desired concentration range. Ten-ml. aliquots of the stock solutions along with an excess of Ag_2SO_4 crystals were sealed in 15-ml. centrifuge tubes and rotated at 25° for 5 days. The equilibration was carried out in the dark to prevent photodecomposition of the Ag_2SO_4.

After equilibration the solutions and the solid phase, as well as the original stock solutions, were analyzed to determine exact concentrations. In all cases included in the present work Ag_2SO_4 was the stable solid phase in equilibrium with the solution.

Results and Discussion

Values of the solubility product *S* of Ag_2SO_4 were calculated for each system on a molality basis on the assumption of complete dissociation of the Ag_2SO_4 and of the supporting electrolyte. In making the calculations the solubility data from the literature were converted, when necessary, to molalities using density data from the International Critical Tables.[9] Log *S* was then plotted against the square root of the ionic strength *I* as shown in Fig. 1. The curves were all drawn through the value of the log of the solubility product of Ag_2SO_4 in pure water[6] (represented by the lowest point). The data obtained in the course of the present study are also given in Table I.

TABLE I

SOLUBILITY OF Ag_2SO_4 IN $AgNO_3$, $Al(NO_3)_3$, $Al_2(SO_4)_3$ AND $La_2(SO_4)_3$ SOLUTIONS AT 25°

Added electrolyte	*m* added electrolyte	*m* Ag_2SO_4
$AgNO_3$	0.00983	0.0238
	.0174	.0211
	.0268	.0180
	.0448	.0130
$Al(NO_3)_3$	0.00527	0.02950
	.01029	.03180
	.03014	.03923
	.05035	.04493
	.1005	.05595
	.3044	.08166
	.4787	.1022
	.8774	.1382
$Al_2(SO_4)_3$	0.00221	0.02741
	.00531	.02692
	.01030	.02664
	.03048	.02644
	.05072	.02672
	.1010	.02785
	.2712	.03091
$La_2(SO_4)_3$	0.001999	0.02733
	.004938	.02747
	.009819	.02769

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) M. H. Lietzke and R. W. Stoughton, THIS JOURNAL, **75**, 5226 (1953); M. H. Lietzke and J. V. Vaughen, *ibid.*, **77**, 876 (1955).

(3) M. H. Lietzke and R. W. Stoughton, *ibid.*, **78**, 3023 (1956).

(4) W. D. Harkins, *ibid.*, **33**, 1807 (1911).

(5) M. Barre, *Compt. rend.*, **150**, 1321 (1910).

(6) G. Åkerlöf and H. C. Thomas, THIS JOURNAL, **56**, 593 (1934).

(7) M. H. Lietzke and R. W. Stoughton, *ibid.*, **78**, 4520 (1956).

(8) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, Inc., New York, N. Y., 1942.

(9) "International Critical Tables," First Edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1936.

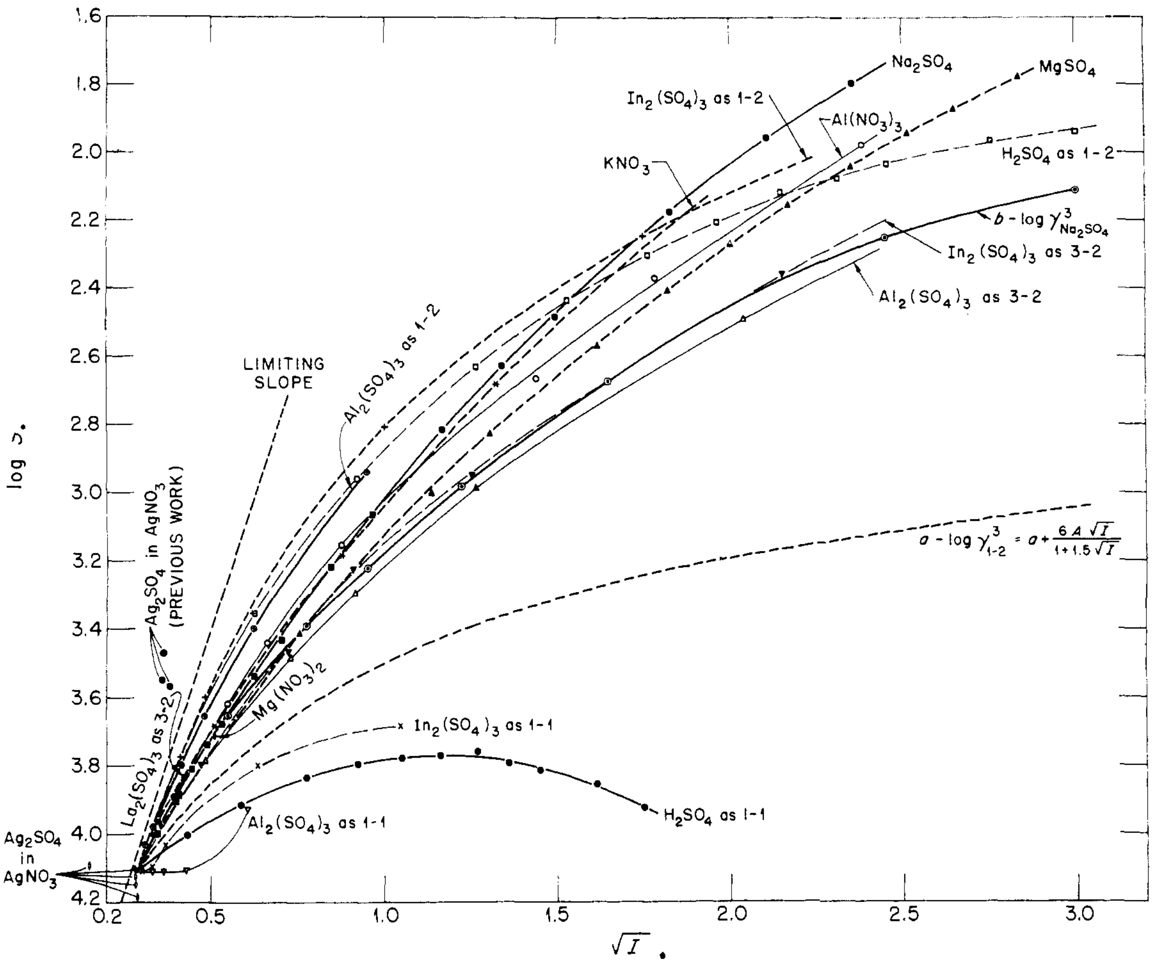

Fig. 1.—The apparent solubility product of Ag_2SO_4 in various electrolyte media.

As can be seen in Fig. 1 the solubility products on a molality basis vary in a surprisingly similar manner with the stoichiometric ionic strength whether or not the "supporting electrolyte" contains sulfate ions. The solubility data of Ag_2SO_4 in $AgNO_3$ solutions obtained in this study appear to be generally consistent with the other data, while the values obtained by Harkins[4] fall considerably above the limiting slope. It is interesting to note that the ionic strength in this case is essentially independent of $AgNO_3$ concentration.

For purposes of comparison, plots of log $\gamma_\pm^3$ for Na_2SO_4[10] and a generalized average activity coefficient function are also shown in Fig. 1. These two curves were shifted vertically to make them go through the point representing the solubility product of Ag_2SO_4 in pure water. The generalized average activity coefficient function (equation 2) was obtained by calculating log $\gamma_\pm^3$ for a 1–2 electrolyte from equation 1 which relates log γ of an ion to the ionic strength I, the charge of the ion Z_i, and the Debye–Hückel limiting slope A. The factor 1.5 in the denominator of equation 1 was suggested by Scatchard[11] as being more useful in many cases than the value unity used by Guggenheim.

$$\log \gamma_i = -\frac{AZ_iI^{1/2}}{1 + 1.5I^{1/2}} \qquad (1)$$

For a 1–2 electrolyte

$$\log \gamma_\pm^3 = -\frac{6AI^{1/2}}{1 + 1.5I^{1/2}} \qquad (2)$$

As can be seen the activity coefficient of Na_2SO_4 varies with its stoichiometric ionic strength in a manner very similar to that in which the activity coefficient of Ag_2SO_4 varies with the stoichiometric ionic strength in the various mixed electrolyte solutions. Two interesting conclusions can be drawn concerning all the curves based on the assumption of complete dissociation: (1) they all lie closer to the limiting law slope than do most activity coefficient curves, and (2) they are surprisingly close together compared to activity coefficient curves for strong electrolytes picked at random (after multiplication by the proper factors to correct for different valence types).

These two statements can be seen clearly to be true by noting the position of the hypothetical "average" 1–2 electrolyte curve, denoted as $a - \log\gamma^3_{1-2}$ in Fig. 1, or by an actual comparison with a plot of strong electrolyte activity coefficients.

Originally it had been hoped that some qualitative conclusions concerning the degree of dissocia-

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(10) R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948).

(11) G. Scatchard, private communication.

tion of electrolytes such as the 3–2 sulfates might result from inspection of the curves in Fig. 1. For this reason the 3–2 sulfates were assumed to dissociate "completely" on three separate bases

$$3\text{–}2 \quad M_2(SO_4)_3 = 2M^{+3} + 3SO_4^{--}$$
$$1\text{–}2 \quad M_2(SO_4)_3 = 2MSO_4^{+} + SO_4^{--}$$
$$1\text{–}1 \quad M_2(SO_4)_3 = MSO_4^{+} + M(SO_4)_2^{-}$$

Values of S and I were then determined on each of these three bases. As can be seen from Fig. 1, basis 3–2 gives the best agreement with the other curves. Basis 1–2 causes deviations from the other curves in a direction consistent with greater association or complexing of either the Ag^+ or SO_4^{--} (or both) up to an ionic strength of about 2.3 (*i.e.*, an $I^{1/2}$ of about 1.5). Basis 1–1 shows effects entirely unlike the 1–1 salt KNO_3. At least in the case of $In_2(SO_4)_3$ it is surprising that the three different bases do not cause more widely differing curves. Apparently the ionic strength effect and the common ion effect approximately cancel each other when a comparison of the three bases is made. It is not believed that the fact that basis 3–2 gives best agreement with the other curves should be interpreted as indicating that the principal species in solution are M^{+3} and SO_4^{--}. For example, in a previous paper,[7] evidence was presented to show that $In_2(SO_4)_3$ is by no means completely dissociated into In^{+3} and SO_4^{--} ions in the concentration range indicated.

In the case of the solubility of Ag_2SO_4 in H_2SO_4 media two bases of dissociation were considered

$$1\text{–}2 \quad H_2SO_4 = 2H^+ + SO_4^{--}$$

and

$$1\text{–}1 \quad H_2SO_4 = H^+ + HSO_4^-$$

It is known that the second equation more nearly represents the principal species in H_2SO_4 solutions in the concentration range of interest than does the first. According to Fig. 1 basis 1–2 indicates an activity coefficient for Ag_2SO_4 which varies with ionic strength almost exactly as it does in $Al_2(SO_4)_3$ and $In_2(SO_4)_3$ media on basis 1–2. Such a close similarity in these three different cases is surprising. When H_2SO_4 is treated as a strong 1–1 electrolyte the plot of the Ag_2SO_4 activity coefficient varies with ionic strength in a manner distinctly different from the other curves in Fig. 1 and similar to some of the 1–1 halide curves.

It would be interesting to calculate S and I for the Ag_2SO_4–H_2SO_4 system on an actual ionic basis using the data of T. F. Young[12] for the values of the concentration quotient K for HSO_4^- dissociation as a function of ionic strength calculated from the actual ionic concentrations in pure H_2SO_4 solutions. However, both the calculation and its interpretation would be complicated since the ionic strength on this basis must be calculated by a reiterative process; the equilibrium quotients vary, in general, with species in solution as well as with ionic strength (especially at higher values of the latter); and, as shown in Fig. 1, log S appears to be to a good approximation a function of the stoichiometric ionic strength alone. The calculation may be even further complicated by the existence of Ag^+-SO_4^{--} complex ions.

A calculation similar to the one just discussed was carried out in an attempt to calculate Ag_2SO_4 solubilities in H_2SO_4 media more accurately than was done previously.[3] The previous calculation involved the assumptions that (1) only the species Ag^+, H^+, HSO_4^- and SO_4^{--} existed in solution, (2) that S and K varied with ionic strength (calculated from actual ionic concentrations) in a manner predictable by equation 1, and (3) that only A in equation 1 varied with temperature or dielectric constant. In the current calculation assumption (2) was altered in that log S was assumed to vary with I (in this calculation I being determined by the actual ionic concentrations) in a manner represented by the average of the curves in Fig. 1 where the supporting electrolytes were assumed to dissociate completely into their simple ions, *i.e.*, basis 1–2 for H_2SO_4, basis 3–2 for $Al_2(SO_4)_3$, etc. The log S curve at any other temperature was assumed to be given in terms of that at 25° by equation 3

$$\log S(t,I) = \frac{A(t)}{A(25°)} \log S(25°, I) \qquad (3)$$

The variation of K with I (on an ionic concentration basis) at 25° was obtained from the data of Young[12] and the relation given by equation 3 was also assumed to hold for log K, *i.e.*

$$\log K(t,I) = \frac{A(t)}{A(25°)} \log K(25°,I) \qquad (4)$$

These calculations were carried out for 25 and 150° and for 0.1, 0.5 and 1.0*m* H_2SO_4 based on the solubilities in pure water. Contrary to expectation the agreement with the experimental values was not noticeably better than in the previous calculations. Nor was better agreement obtained when similar calculations were made in which I was calculated from the stoichiometric concentrations of the ions.

In contrast to the Ag_2SO_4 system where possible complexing of Ag^+ or SO_4^{--} with ions of the supporting electrolyte cannot be deduced definitively from the solubility data, the solubility of AgCl in electrolyte solutions containing a common ion shows a dramatic behavior. From the data of Forbes[13]; Pinkus and Timmermans[14]; Pinkus, Frederic and Shepmans[15]; and Pinkus and Shepmans[16] for the solubility of AgCl in HCl, $AgNO_3$ and HNO_3, respectively, the solubility products were calculated on a molality basis and on the basis of complete dissociation into simple ions. A plot of log S was then made against the square root of the stoichiometric ionic strength as shown in Fig. 2. In the case of HNO_3 media log S approaches the Debye–Hückel limiting slope at low ionic strengths and deviates at higher ionic strengths in a manner expected from the behavior of strong 1-1 electrolyte activity coefficients. In the cases of HCl and $AgNO_3$ media the deviations from the limiting law slope clearly show strong complexing. Further the two curves are, surprisingly enough, almost coincident which strongly implies complexing

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[12] T. F. Young, private communication.

[13] G. S. Forbes, THIS JOURNAL, **33**, 1937 (1911).

[14] A. Pinkus and A. M. Timmermans, *Bull. soc. chim. belg.*, **46**, 46 (1937).

[15] A. Pinkus, S. Frederic and R. Shepmans, *ibid.*, **47**, 304 (1938).

[16] A. Pinkus and R. Shepmans, *ibid.*, **47**, 337 (1938).

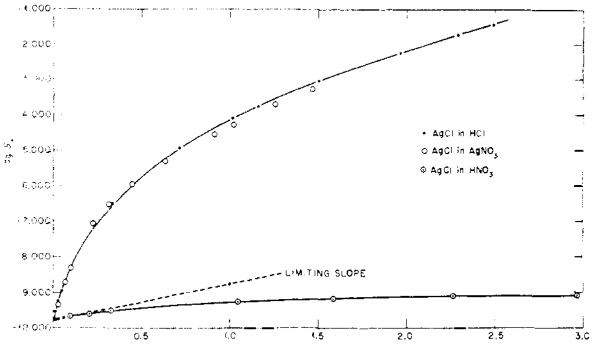

Fig. 2.—The apparent solubility product of AgCl in HCl, HNO_3 and $AgNO_3$ media.

(with excess Ag^+ or Cl^-) that is both symmetrical and that takes place to the same degree in both cases.

Some idea of the extent of complexing may be obtained in the AgCl–HCl system by making the assumption that only mononuclear complexes exist and then plotting the data in the form of log S *vs.* log m_{HCl}. On the basis of this assumption the observed S in terms of the molal solubility s and the species assumed to exist is given by

$$S = (m + s)s \qquad (5)$$

when $m \gg s$

$$S = ms = m([Ag^+] + [AgCl]_{(aq)} + [AgCl_2^-] + [AgCl_3^=] + \ldots) \qquad (6)$$

Letting S_i (where $i = 1, 2, \ldots n$) represent the molality solubility quotients for the assumed ionic equilibria

$$\underline{AgCl} = Ag^+ + Cl^- \quad S_0$$

$$\underline{AgCl} = AgCl_{(aq)} \quad S_1$$

$$\underline{AgCl} + Cl^- = AgCl_2^- \quad S_2$$

$$\cdots\cdots\cdots\cdots\cdots\cdots \quad \cdots$$

$$\underline{AgCl} + (n - 1)Cl^- = AgCl_n^{-n+1} \quad S_n$$

equation 6 becomes

$$S = S_0 + mS_1 + m^2S_2 + \ldots m^nS_n \qquad (7)$$

If a single silver species predominates in any HCl concentration range then the slope of a log S *vs.* log m curve in that region gives the number of chlorides in the predominant species, and an extrapolation of that slope to $m = 1$ gives the appropriate log S_i. For an accurate treatment of the data corrections would have to be made for activity coefficient changes throughout the region under consideration. However, for a qualitative interpretation it may be assumed that activity coefficient changes are of the order of magnitude of the changes in the AgCl–HNO_3 curve with ionic strength and hence may be neglected.

In general, more than one species may exist to an appreciable extent in any region and hence the slope will give an average of i. The simplest interpretation where the slope lies between i and $i + 1$ is to assume that $AgCl_i^{-i+1}$ and $AgCl_{i+1}^{-i}$ are the principal species. If such an interpretation is made it appears that $AgCl_2^-$, $AgCl_3^{--}$ and $AgCl_4^{---}$ become significant species above about 0.002, 0.1 and 1 m HCl, respectively. Since there is no extended region where the slope is equal to a single integral value of i it appears that more than one species is important throughout the whole range studied except perhaps at the lowest ionic strength values. Consistent with the interpretation given here is that of Barney, Argersinger and Reynolds[17] who interpreted their solubility data to give a $Ag^+/AgCl_2^-$ ratio of about unity at 0.0015 m KCl.

The similarity between the AgCl–HCl and AgCl–$AgNO_3$ curves suggests the existence of species like Ag_2Cl^+, Ag_3Cl^{+2} and Ag_4Cl^{+3} in the presence of excess Ag^+ at approximately the same ionic strength values where $AgCl_2^-$, $AgCl_3^{--}$ and $AgCl_4^{---}$ appear to exist in the presence of excess Cl^-. Actually, in either or both systems polynuclear complexes may exist. Additional information is needed to settle the question definitively.

Berne and Leden[18] interpreted the solubility data for AgCl in chloride media and in $AgNO_3$ media in a manner consistent with that given above. Moreover, MacDougall[19] has shown impressive solubility evidence for the existence of the positive silver acetate complex $Ag_2(C_2H_3O_2)^+$ in solutions containing excess silver ion.

While the effect of the complexing described above on the solubility of AgCl at room temperature is not sufficiently great to alter appreciably an HCl or a $AgNO_3$ medium, the situation may be much more unfavorable to interpretation of Ag, AgCl (sat.) electrode results at elevated temperatures. It is known, for example, that the solubility of AgCl in pure water increases about tenfold in raising the temperature from 25 to 100°. If then the complex formation constants were temperature independent the solubility in HCl or $AgNO_3$ media would be about 10 times higher at 100° than it is at 25°. Actually the complex formation tendency may increase with temperature, and the solubility probably continues to increase with temperature above 100°. Thus it will be necessary to investigate the solubility of AgCl in water and in media containing a common ion at elevated temperatures before interpretation of e.m.f. data under such conditions can be taken seriously.

Conclusions

The molality solubility product of Ag_2SO_4 appears to a good approximation to be a function of the stoichiometric ionic strength alone. The fact that this is true to an ionic strength of over unity in widely different media and in the presence or absence of a common ion is difficult to explain. Nothing can be concluded definitively concerning the existence of complex ions from the solubility data alone, although at least in the case of $In_2(SO_4)_3$ considerable complexing was previously shown to obtain. Reasonable and surprisingly similar curves are obtained whether $In_2(SO_4)_3$ is assumed to dissociate "completely" as a 3-2, a 1-2, or a 1-1 electrolyte. Apparently, in this case, the common ion effect and the ionic strength effect

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[17] J. E. Barney, II, W. J. Argersinger, Jr., and C. A. Reynolds, THIS JOURNAL, **73**, 3785 (1951).

[18] E. Berne and I. Leden, *Svensk Kem. Tidskr.*, **65**, 88 (1953).

[19] F. H. MacDougall, *J. Phys. Chem.*, **46**, 738 (1942).

cancel each other to a first approximation. In contrast, the solubility of AgCl in the presence of either common ion clearly shows complexing. Interestingly enough the complexing of Ag^+ by Cl^- and of Cl^- by Ag^+ appear to be remarkably similar. The large extent of this complexing at room temperature combined with the known increasing solubility of AgCl in water with temperature suggest the necessity of obtaining AgCl solubilities in media containing a common ion before making definitive interpretations concerning thermodynamic data involving the Ag, AgCl (sat.) electrode in such media.

Acknowledgment.—We wish to express our appreciation to P. F. Thomason and co-workers of the Ionic Research and Development Group of the Analytical Chemical Division of the Oak Ridge National Laboratory for all analytical work in connection with our solubility program.

OAK RIDGE, TENN.

[CONTRIBUTION FROM THE JOHNSON FOUNDATION FOR MEDICAL PHYSICS, UNIVERSITY OF PENNSYLVANIA]

Some Phase Relationships in the Three-component Liquid System CO_2–H_2O–C_2H_5OH at High Pressures

BY LOUIS C. W. BAKER[1] AND THOMAS F. ANDERSON

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Phase diagrams for the liquid system CO_2–H_2O–C_2H_5OH are reported covering the temperature range 10 to 50° at pressures from 3000 lb./in.^{2} down to the vapor pressures of the respective mixtures. Liquid–vapor critical data are included. In most respects the diagrams are typical of systems wherein one component (C_2H_5OH) is completely miscible with each of the other two components while the latter are only sparingly soluble in one another. However, for ternary mixtures containing a given $C_2H_5OH:H_2O$ molar ratio, isobaric temperature rise causes first an increase and later a decrease in the extent of the region wherein only one liquid phase exists. The temperature of maximum extent of the region of one liquid phase increases with increasing pressure and decreases with increasing $C_2H_5OH:H_2O$ molar ratio. These effects are attributable to temperature-dependent variation in the extent of molecular association.

The properties of liquid carbon dioxide solutions have received relatively little study[2] although the liquid has potentialities for considerable interest as a solvent. The linear CO_2 molecule has no over-all dipole moment and the liquid has a very low dielectric constant.[3] However, the ends of the molecule are undoubtedly considerably more negative than its center, offering opportunities for hydrogen bonding and other forms of molecular association. It is challenging to consider the following facts, for example: (1) water is practically insoluble in liquid CO_2, although the solid $CO_2 \cdot 8H_2O$ is stable, at elevated pressures, at temperatures up to 8° and perhaps higher[4–6]; (2) this paper shows ethyl alcohol to be miscible with liquid CO_2, marked diminution in total molal volume taking place upon mixing[4,7]; (3) measurements with the propyl and butyl alcohols indicate rapidly decreasing solubility with increasing carbon chain length[7]; but (4) glycerol is practically insoluble in liquid CO_2.[8] Several examples of minimum critical solution temperatures have been reported for liquid CO_2 solutions of organic substances.[7]

This paper reports phase diagrams, determined with moderate accuracy, for the liquid system CO_2–H_2O–C_2H_5OH, at temperatures from 10 to 50° and at pressures from 3000 lb./in.^{2} down to the vapor pressures of the mixtures. Liquid–vapor critical data, within that range of conditions, are included. The results are potentially useful in the "critical point drying method" for electron microscope specimens.[9] The experimental approach has novel features.

Pure water and pure liquid CO_2 exhibit very limited mutual solubility. However, the latter was found to be completely miscible with absolute ethyl alcohol, as anticipated on the basis of frag-

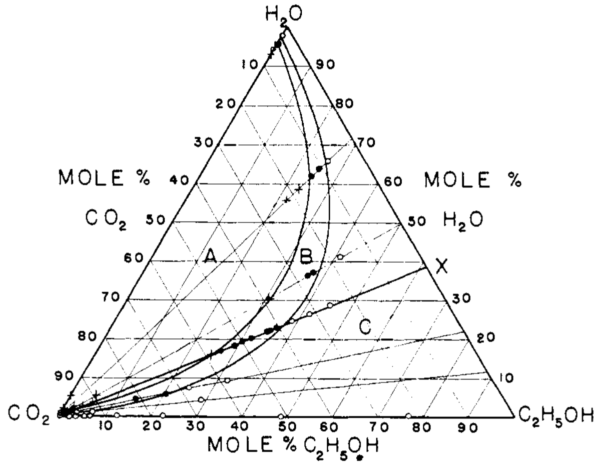

Fig. 1.—Within the ranges of conditions cited: A, area of two liquid phases; C, area of one liquid phase; B, area of one or two liquid phases depending upon temperature and pressure. Experimental points are indicated.

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[1] Department of Chemistry, Boston University, Boston 15, Massachusetts.

[2] E. L. Quinn and C. L. Jones, "Carbon Dioxide," Am. Chem. Soc. Monograph No. 72, Reinhold Publ. Co., New York, N. Y., 1936, p. 94–112.

[3] F. Linde, *Wied. Ann.*, **56**, 546 (1895); H. Riegger, *Ann. Phys.*, **59**, 753 (1919); W. Herz, *Z. physik. Chem.*, **103**, 269 (1922); F. G. Keyes and J. G. Kirkwood, *Phys. Rev.*, **36**, 754 (1930).

[4] W. Hempel and J. Seidel, *Ber.*, **31**, 2997 (1898).

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[7] E. H. Büchner, *Z. physik. Chem.*, **54**, 665 (1906).

[8] E. L. Quinn, *Ind. Eng. Chem.*, **20**, 735 (1928).

[9] T. F. Anderson, *J. Appl. Phys.*, **21**, 724 (1950); *Trans. N. Y. Acad. Sci.*, [II] **13**, 130 (1951).