

Solubility of Small AgI Particles in NaI and KI Solutions : Significance to Cloud Seeding

BRIANT L. DAVIS

Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, Rapid City 57701

(Manuscript received 23 August 1971, in revised form 8 November 1971)

ABSTRACT

Utilizing standard solubility data in the literature it is seen that for 2:1 mole ratio AgI:NaI (or KI) aerosol compositions only AgI particles $<0.01 \mu$ radius are in danger of complete dissolution into hygroscopically derived solution envelopes containing NaI, or KI. This condition develops only momentarily when sufficient water vapor has accreted to form a saturated solution about the AgI particle. Taking a typical AgI-NaI aerosol such as that studied by Mossop and Tuck-Lee as representative of generated aerosols, only a small part of the AgI can be dissolved under the most favorable atmospheric conditions; particles representing the median size for this aerosol, of 0.042μ radius, will lose only 35 weight percent of the AgI present. Very similar relations hold for KI-bearing aerosols.

1. Introduction

Fletcher (1968) comments upon the negligible solubility of AgI in aqueous KI solutions of 1:1 and 2:1 mole ratio AgI:KI. St. Amand *et al.* (1971a) discuss the deleterious effect of dissolution of the AgI aerosol particle and imply (p. 45) in a general way that the whole particle might dissolve under moist warm-air conditions. In a companion paper (St. Amand *et al.*,

1971b) the critical particle size for complete dissolution in pure water is calculated for large water droplets presumably brought into contact with an AgI aerosol particle. Fletcher (1970) discusses the relative roles of solution, etching of surface features, and freezing point depression of solution droplets surrounding the AgI particle.

In the short discussion to follow we present some

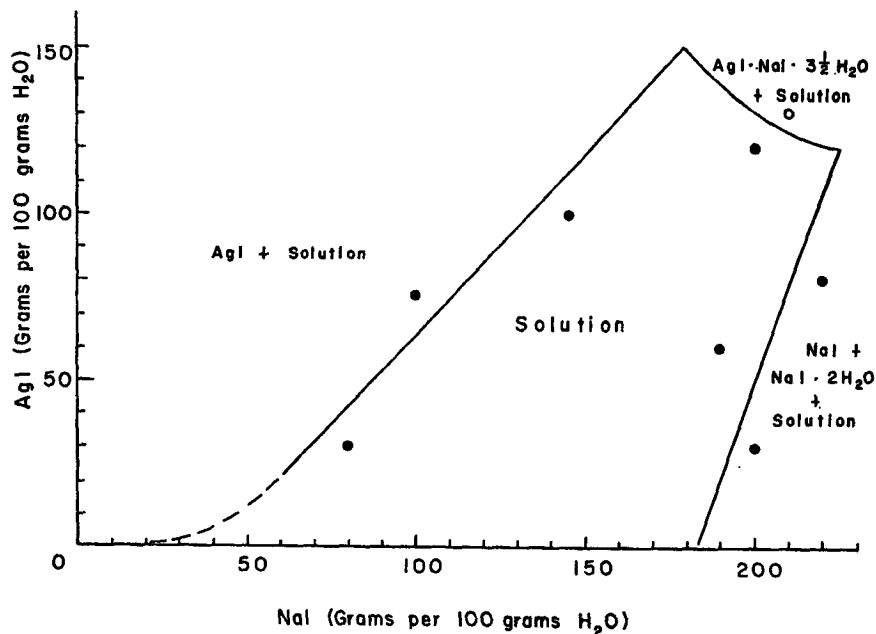


FIG. 1. Partial phase diagram of the system AgI-NaI-H₂O (after Krym, 1909). Filled circles are our laboratory checks made on boundary positions.

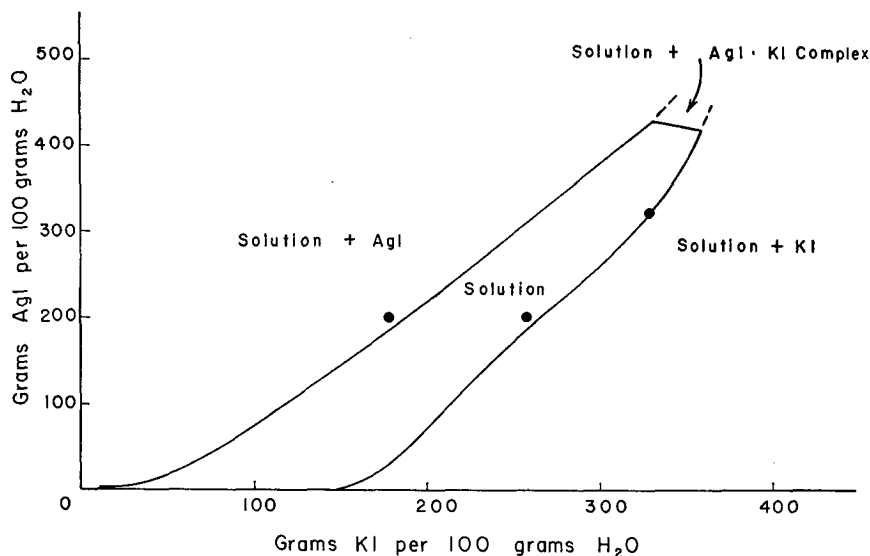


FIG. 2. Partial phase diagram of the system AgI-KI-H₂O (after Dam and Donk, 1911). Filled circles are our laboratory checks on boundary positions.

simple calculations demonstrating the solubility relations of AgI in aqueous solutions of NaI and KI, and their significance to the seeding aerosol which accretes water solely by hygroscopic action.

2. Solubility relations

The solubility data for KI, NaI and AgI in aqueous solutions has been compiled by Linke (1965). Most of the calculations to follow are based on AgI-NaI data, with AgI-KI results being similar. At 25°C a saturated aqueous solution of KI contains 8.91 moles KI per liter of H₂O, and a saturated NaI solution contains 12.20 moles NaI per liter. However, the former solution will dissolve 1430 gm AgI and the latter 1510 gm. The mole fractions of AgI in solution for the two cases are 0.0862 and 0.0866, respectively.

Figs. 1 and 2 present the plotted solubility data for the AgI-NaI-H₂O and AgI-KI-H₂O systems, respectively. Of some interest is the complex phase field AgI·NaI·3½H₂O of Fig. 1 (data from Krym, 1909) which we believe to represent either phase C or E of Davis (1969)¹ but with a hydration coefficient of 4. This phase has also been described by Burkhart *et al.* (1970) and St. Amand *et al.* (1971a) but with a hydration coefficient of 3. The filled circles in Figs. 1 and 2 represent spot checks of the data carried out in our laboratory. These results indicated essential correctness of the existing boundaries. In the original data of Krym the solid phase NaI was presumed to be in equilibrium with the solution, whereas either NaI or NaI·2H₂O, or both, may be present according to our studies.

The solubility relations of AgI in dilute NaI solutions

¹The composition for phase C of 3AgI·2NaI·*n*H₂O [proposed by Davis (1969)] is now known to be incorrect, with the proper composition being AgI·NaI:*n*H₂O, *n* between 3½ and 4.

used in the calculations below were taken from Schulz and Težak (1951). The great increase in solubility of AgI in these solutions is demonstrated by these data; for example, in pure water 3×10^{-7} gm of AgI per 100 gm H₂O will dissolve, whereas with 1 gm NaI added the solubility of AgI rises by a factor of 10³.

The phase diagrams of Figs. 1 and 2 are significant in their demonstration of complex phases existing in the region of low H₂O concentration, a fact of considerable importance in cloud seeding technology. The phase diagram of St. Amand *et al.* (1971a) presents a similar and more complete relationship (although inverted in appearance), even though much of the boundary determination is yet incomplete. The point (four-phase region) where only phase C can exist as shown by St. Amand *et al.* in their diagram can also be plotted in Fig. 1 from calculation alone because the mole ratio AgI:NaI is 1:1 with only sufficient H₂O to complete hydration.

3. Calculations for dilute solutions

To consider the amount of AgI dissolved from the presence of NaI only (presently ignoring size effects), we assume a 2:1 mole ratio AgI:NaI mixture in acetone, and that the particles are spheres with the AgI and NaI components intimately mixed but not shell-core composites (Petersen and Davis, 1971). Here the weight ratio is 3.12 and the volume ratio 2.02. Knowing that $V_T = V_1 + V_2$ and that $V_T = 3.016 V_2$, where subscripts 1 and 2 refer to AgI and NaI, respectively, we calculate the masses of each component in the particle (M_1 and M_2) to be 19.8×10^{-16} and 6.36×10^{-16} gm, respectively. Of course, we must also assume here that in every particle the original solid component ratio of the solution is maintained, an as-

sumption which may not be too good except on a statistical basis.

From the Köhler curves plotted for other types of hygroscopic materials by Low (1969), we estimate that the radius of a droplet containing 10^{-15} – 10^{-16} gm NaI will be 0.3μ and maintained at equilibrium for a supersaturation of 0.1% in a cloud. The volume of such a drop is 1.1×10^{-13} cm³ and comparing this with the mass of NaI dissolved therein its density should be about 1.1 gm cm^{-3} (Call, 1961, p. 962). This results in a mass M_D of the droplet of 1.24×10^{-13} gm.

Letting M_1' represent the AgI concentration in grams per 100 grams H₂O obtained from the Schulz-Težak data (by extrapolation) for the droplet containing mass M_2 of NaI, the fraction F of available AgI dissolved in the droplet under consideration is

$$F = \frac{(M_1')(M_D)}{100 M_1}, \quad (1)$$

giving a value of 8.35×10^{-5} for 25C solubility data.

4. Calculations for saturated solutions

Shortly after release of the aerosol into humid air the NaI will take on water, forming the dihydrate NaI·2H₂O. At about 28.5% relative humidity at 25C (Davis, 1969) the dihydrate breaks down and NaI combines with some of the AgI and H₂O to form phase C (or E). At 42% and 25C the phase C complex breaks down and at this stage a saturated solution of NaI surrounds the AgI. Similar relations occur at lower temperatures according to the phase diagram of Davis.

For at least a short period of time following the breakdown of phase C the saturated aqueous solution of NaI forms, at which time the greatest ability to dissolve the AgI exists. Considering the size particle discussed in the dilute case above where $M_2 = 6.36 \times 10^{-16}$ gm and that a saturated solution contains 183 gm NaI per 100 gm H₂O (Fig. 1), there exists a droplet containing a mass M_D of 3.47×10^{-16} gm of H₂O at time of saturation. According to the Mellor tables (Call, 1961, p. 962), this solution has a density of 1.9 gm cm^{-3} . The radius of such a drop is only 5×10^{-6} cm.

According to Fig. 1, a solution containing 183 gm NaI per 100 gm H₂O is capable of completely dissolving 150 gm AgI (a small part of which may exist as phase C or E in solid form), whereas for a 2:1 mole ratio there is 574 gm per 100 gm H₂O of AgI available. Thus, slightly more than one-fourth of the total AgI in the particle is dissolved in such aerosols.

Similar relations apply to the KI-bearing aerosols. From the Linke tables a saturated solution contains 152 gm KI per 100 gm H₂O capable of dissolving 144 gm AgI at 30C. This is a 0.916 molar KI solution, but with a 2:1 AgI:KI initial mix in the aerosol there are 430 gm AgI per 100 gm H₂O available, indicating a loss of only one-third of the solid AgI. As it turns out the mole fraction of AgI in either type of solution is nearly

identical, being 0.0862 for the NaI solution and 0.0866 for the KI solution. Of course, no particle size effect on solubility is included here. Particle size effects will increase the mole fraction dissolved in the same manner for both cases, as we shall now consider.

5. Effect of small particle size

From the above size data and mass ratio (dilute solution case), the "equivalent" spherical size of the AgI component alone has a radius of 4.36×10^{-6} cm. The increase of solubility of the AgI due to its small size can be estimated from the Freundlich-Ostwald relation (Defay *et al.*, 1966, p. 269, and Dundon and Mack, 1923):

$$(1 - \alpha + n\alpha) \frac{RT}{V_m} \ln(X_r/X_\infty) = \frac{2\sigma}{r}, \quad (2)$$

with the dissociation factor $(1 - \alpha + n\alpha)$ taken from Dundon and Mack (1923). Here α is the fraction of dissociation of a molecule into n ions, and X_r and X_∞ are the mole fractions of AgI dissolved for small particles of radius r and infinite radius, respectively.

The unknown factors here are the dissociation factor α and the value for the solution-solid AgI surface tension σ . We can estimate the former by assuming that it should be of the same order of magnitude as the ionic character I proposed by Pauling (1960, p. 35–36) as

$$I = 1 - \exp\left[-\frac{1}{4}(Z_1 - Z_2)^2\right], \quad (3)$$

where Z_1 and Z_2 are the electronegativities of the atoms. For AgI, then, $I = 0.097$ which we can take to be equal to α .

On the other hand, following our more complete knowledge of the dissociation of other silver halides, such as AgCl, we would estimate the value of α to be near unity, i.e., the small amount of AgI dissolved is nearly completely dissociated into ions. For our present calculations we shall use $\alpha = 0.80$.

It is more difficult to assess the proper value for σ in this system in view of the lack of experimental data for AgI-H₂O. On the basis of the molar volume and hardness of AgI compared with the values of σ for a number of compounds determined from solubility measurements by Dundon (1923), we estimate σ to be about 400 ergs cm^{-2} . With 6.9×10^{-15} moles water and 7.04×10^{-22} moles AgI in our NaI-bearing droplet, we find $X_\infty = 1.01 \times 10^{-7}$. Using these data we calculate the percent increase in solubility of AgI (independent of X) as well as the absolute magnitude of X_r under the assumptions and uncertainties discussed above. The results for dilute and saturated solutions are presented in Table 1.

6. Discussion

For non-dissociating materials the dissociation factor containing α is omitted from Eq. (2). For our

4.36×10^{-6} cm AgI particle and with $\alpha=0$, we find $X_r=1.365 \times 10^{-7}$, or an increase of 34.5% over the 1.01×10^{-7} value for X_∞ . With $\alpha=0.097$ included there is a 30.6% increase and, with $\alpha=1.0$, a 16.3% increase, showing that only small errors are introduced by the uncertainty in knowledge of α . Uncertainty in σ is more serious but not intolerably so. Considering the data of Dundon (1923), there is not likely to be a greater variation in σ for AgI than about 50% from the estimated value of 400 ergs cm^{-1} . With such a variation, for a particle size of 10^{-6} cm, the exponential term ($=X_r/X_\infty$) varies from 1.4 to 2.9 about the 2.07 value obtained for $\sigma=400$. This equates to an uncertainty in X_r of 32% at the low end of the range in σ to 42% at the high end.

For a typical AgI-NaI aerosol, such as given by Mossop and Tuck-Lee (1968), few particles are smaller than 0.01μ , although smaller ones may have been lost in the collecting technique. For the actual distribution given, only a small fraction of particles would lose as much as half of the AgI present while those having the median radius of 0.042μ would lose only about 35% according to the data of Table 1. For the NaI case, particles of about 0.008μ will completely dissolve. These smaller particles are also of little significance in practical cloud seeding operations.

The effect of lowered temperature is to reduce slightly the amount of AgI in solution. For example, at 0C a saturated solution of KI contains 127.6 gm KI which is able to dissolve only 100 gm AgI, leaving 72.5% free AgI in an initial 2:1 mole ratio mixture.

Considering the above calculations and solubility data for both saturated and dilute solutions of NaI and KI in water containing AgI, it is here concluded that at no time during ascent of the seeding aerosol (2:1 mole ratio AgI:NaI) is even a major portion of the AgI aerosol dissolved by its own hydrospectically derived water envelope. The amount dissolved is certainly insignificant after short residency within the cloud itself, and only in the event of capture of the particle by large cloud droplets will the average aerosol particle become dissolved (St. Amand *et al.*, 1971b). Some of these conclusions are borne out by Davis (1969) for *in situ* x-ray diffraction measurements on collected aerosols of these compositions under a

carefully controlled atmosphere having vapor pressures of H_2O varying from near zero to saturation values. The chemical complexing, however, *does* significantly reduce the amount of free AgI in the aerosol, there being 100% reduction for AgI-NaI aerosols of 1:1 mole ratio for sufficient reaction time allowed. The AgI particle *in either case* is considerably modified by "aging" processes as to surface properties and amount of stored strain energy from quenching. As contrasted to the solubility question, we consider these processes to be of first-order significance in their known negative effect upon the nucleation properties of AgI.

Acknowledgments. I acknowledge the helpful discussions and laboratory assistance of Yi-Hsiung Chen and L. R. Johnson. This research was supported by the National Science Foundation under Grant GP-18243.

REFERENCES

- Burkardt, L. A., W. G., Finnegan, F. K. Odencrantz and P. St. Amand, 1970: Pyrotechnic production of nucleants for cloud modification, Part IV: Compositional effects on ice nuclei activity. *J. Wea. Modification*, **2**, 65-76.
- Call, F., 1961: Sodium iodide. *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. II, Suppl. II, New York, Wiley, 956-979.
- Dam, W. van, and A. D. Donk, 1911: Equilibrium in the system: Silver iodide, potassium iodide and water. *Chem. Weekblad.*, **8**, 846-855.
- Davis, B. L., 1969: Chemical complexing of AgI-NaI aerosols. *J. Atmos. Sci.*, **26**, 1042-1048.
- Defay, R., I. Prigogine and A. Bellemans, 1966: *Surface Tension and Adsorption*. New York, Wiley, 432 pp.
- Dundon, M. L., 1923: Surface energy of several salts. *J. Amer. Chem. Soc.*, **45**, 2658-2666.
- , and E. Mack, Jr., 1923: The solubility and surface energy of calcium sulphate. *J. Amer. Chem. Soc.*, **45**, 2479-2485.
- Fletcher, N. H., 1968: Ice nucleation behavior of silver iodide smokes containing a soluble component. *J. Atmos. Sci.*, **25**, 1058-1060.
- , 1970: On contact nucleation. *J. Atmos. Sci.*, **27**, 1098-1099.
- Krym, V., 1909: The conditions of the solubility of silver iodide in sodium iodide. *Zh. Russ. Fiz. Khim. Obshchestva*, **41**, 382-385.
- Linke, W. F., 1965: *Solubilities of Inorganic and Metal Organic Compounds*, Vol. 2. New York, Amer. Chem. Soc., 1914 pp.
- Low, D. H., 1969: A theoretical study of nineteen condensation nuclei. *J. Rech. Atmos.*, **5**, 65-78.
- Mossop, S. C., and C. Tuck-Lee, 1968: The composition and size distribution of aerosols produced by burning solutions of AgI and NaI in acetone. *J. Appl. Meteor.*, **7**, 234-240.
- Pauling, L., 1960: *The Nature of the Chemical Bond*, 3rd ed. Ithaca, Cornell University Press, 644 pp.
- Petersen, R. L., and B. L. Davis, 1971: Determination of crystallite size and anelastic strain in various types of generator effluent. *J. Geophys. Res.*, **76**, 2886-2890.
- St. Amand, P., W. G. Finnegan and L. Burkardt, 1971a: Understanding of the use of simple and complex ice nuclei generated from pyrotechnics and acetone burners. *J. Wea. Modification*, **3**, 31-48.
- , L. Mathews, D. Reed, L. Burkardt and W. Finnegan, 1971b: Effects of solubility of AgI nucleation effectiveness. *J. Wea. Modification*, **3**, 106-110.
- Schulz, K., and B. Težak, 1951: Solubility of silver iodide in aqueous solutions of potassium iodide and sodium iodide. *Arhiv Kemi*, **23**, 200-205.

TABLE 1. Solubility of AgI in 2:1 solutions* of AgI:NaI and AgI:KI for small particles.

r (cm)	Dilute NaI		Saturated NaI		Saturated KI	
	X_r/X_∞	X_r	X_r	C	X_r	C
$>10^{-4}$	1.000	1.01×10^{-7}	0.086	0.640	0.087	0.614
1×10^{-5}	1.075	1.09×10^{-7}	0.093	0.694	0.094	0.668
5×10^{-6}	1.156	1.17×10^{-7}	0.099	0.744	0.100	0.720
1×10^{-6}	2.069	2.09×10^{-7}	0.178	1.462	0.179	1.410
5×10^{-7}	4.278	4.32×10^{-7}	0.368	3.940	0.372	3.835

* σ (AgI solution) = 400 ergs cm^{-2} , $\alpha=0.80$ and $T=25\text{C}$. The symbol C represents the number of moles AgI dissolved per 100 gm H_2O .