A Study on the Solubility of Sparingly Soluble Salt. VIII. Solubility of Lead Sulfate in Various Mixed Solvents with Isodielectric Constant

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To investigate the relation between the solubility of sparingly soluble salt and the dielectric constant of the solvent, the solubility of lead sulfate was measured by the present author in the following various isodielectric solvents composed of the mixture of water with dioxane,[1] acetone,[2] glycerine,[3] ethanol[4] and methanol,[5] in the small range of change in dielectric constants of the solvents.

The observed solubility in the mixed solvent with isodielectric constant are listed in Table 1.

Table 1

Solubility of Lead Sulfate in the Isodielectric Solvents

Temp. °C.	Dielect. const.	Solubility (mol./l.×10⁶) Dioxane	Acetone	Glycerine	Ethanol	Methanol
20	80.37	142.1	142.1	142.1	142.1	142.1
	78.10	117.4	85.0	100.8	95.0	91.6
	75.90	103.8	45.0	61.0	57.0	61.0
25	78.54	148.1	148.1	148.1	148.1	148.1
	76.35	121 0	92.0	109.5	100.2	96.0
	74.10	109.2	50.8	69.2	60.2	61.8
30	76.73	154.4	154.4	154.4	154.4	154.4
	74.50	129.8	95.2	115.3	102.8	96.8
	72.35	116.2	54.4	77.4	61.7	63.8

The above date were considered by means of various theoretical relations between the solubility and the dielectric constant of the solvent. They are the Born's,[6] Davis's,[7] Flatt's[8] and (1)[3] equations.

$$\ln\frac{C_0}{C_1}=\frac{Z^2\varepsilon^2}{2RT\gamma_s}N\left(\frac{1}{D_1}-\frac{1}{D_0}\right)$$
$$-\frac{Z^2\varepsilon^2}{2kT}\sqrt{\frac{8\pi NZ^2\varepsilon^2}{10^3kT}}\left(\frac{C_1^{1/2}}{D_1^{3/2}}-\frac{C_0^{1/2}}{D_0^{3/2}}\right) \quad \ldots\ldots(1)$$

where R, N, k and ε are the gas constant, Roschmidt number, Boltzman number and electric elementary quantum, respectively; and C_0 and C_1 are the solubilities of the solutes in two media of different dielectric constants D_0 and D_1.

In conclusion, we may say that;

(1) The assumption of the constancy of solvation radius, which is assumed in the induction of the equation (1), may be admitted in the range of this research except in the case of dioxane solution, but it calls for further investigation.

(2) Even if the dielectric constant of the mixed solvent is equal, the solubility is not so. In other words, the solubility is not determined solely by the dielectric constant of the solvent.

The dioxane, which shows an extraordinarily great difference in the above two conclusions (1) and (2), is a peculiar substance that has a symmetrical structure in the molecular construction, and the dipole moment of which is almost equal to zero, its dielectric constant being very small when compared with the other solvents. As the concentration of the organic solvent in the solution is sufficiently low in each mixed solvents, the molecular association of each organic solvent itself may not exist, but the intermolecular reaction of each solvent and the water molecule must be noted. Such non-polar solvent as dioxane cannot easily approach to the solute as it is intercepted by the water molecule; consequently, the solute (lead sulfate) may be partly dissolved indirectly in the dioxane solution

(1) *J. Chem. Soc. Japan*, **68**, 81 (1947).

(2) *ibid.*, **70**, 271 (1949).

(3) *ibid.*, **70**, 407 (1949).

(4) *ibid.*, **69**, 40 (1948).

(5) *ibid.*, **68**, 29 (1947).

(6) M. Born. *Z. Physik.*, **1**, 45 (1920).

(7) Ricci and Davis, *J. Am. Chem. Soc.*, **62**, 407 (1940).

(8) Flatt and Jordan, *Helv. Chim. Acta.*, **16**, 37 (1933).

under the condition of the solvated ions. So the solubility of lead sulfate in the dioxane solution may be greater than that in the other solvents. Such effect of the dipole moment on the solubility, along with that of the change in the value of a, should become more remarkable as the concentration of the organic solvent in the mixed solvent increases, it is, therefore, desirable to extend this experiment still further. In short, the solubility of the slightly soluble salt does not solely depend upon the dielectric constant of the solvent, but it may also depend on the difference in the chemical constitution of the solvent.

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