The Solubility of Silver Bromate in Tetrahydrofuran-Water Mixed Solvents

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Introduction

In the previous reports regarding the investigation of the relation between solubilities of inorganic salt and dielectric constants of solvents, the solubilities of silver bromate in dioxane- and sucrose-water mixed solvents were described[1,2]. In the present work, the solubility of silver bromate in tetrahydrofuran-water mixed solvents which have a wide range of dielectric constant dependent on the composition was measured at 20°, 25° and 30°C. These data were examined using the theoretical formula[3] concerning the solubility of sparingly soluble salt and the dielectric constant of the solvent.

With regard to the investigations which use tetrahydrofuran as the solvent, few reports have appead so far. The physical properties of the tetrahydrofuran-water system have been studied by Erva[4] and Yoshioka et al.[5] Likewise, the solubility of silver bromate in this mixed solvent has not yet been measured.

Experimental

(1) **Preparation of Solute and Solvent.**—The silver bromate was prepared from the dilute solution of silver nitrate and potassium bromate by the infinite dilution method. The precipitates were recrystallized from boiling conductivity water by the modified Reedy's method[6], and stocked in the vacuum.

After the inhibitor was removed, the tetrahydrofuran (from Badische Anilin und Sodafabrik A. G.) was purified twice by fractional distillation in a special rectifier with threefold reflux tube (30 cm. in length) and glass spiral (25 cm. in length) in its inner tube. The fraction boiling at 64.5°–65.5°C was used for the present experiment. From the density determination at 25°C using a Sprengel type pycnometer, this fraction was found to have a purity of 99.15% (wt.), when calculated after Critchfield's empirical equation assuming water to be the only impurity. This grade of purity was sufficient for the present purpose.

Eleven tetrahydrofuran-water mixed solvents were prepared from the purified tetrahydrofuran mentioned above and the conductivity water (1×10^{-6} mho at 20°C), the concentrations of which are ranging from zero to 64.232 per cent by weight of tetrahydrofuran.

(2) **Determination of the Solubility of Silver Bromate.**—The mixed solvent and excess solute were placed in shaking bottles made of quartz, and sealed. The bottles were rotated in thermostats regulated within ±0.02°C of 20°, 25° and 30°C,

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[1] E. Koizumi and H. Miyamoto, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 75, 1302 (1954).

[2] E. Koizumi and H. Miyamoto, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), 77, 193 (1956).

[3] E. Koizumi, *J. Chem. Soc. Japan*, 68, 19 (1947).

[4] J. Erva, *Suomen Kemistilehti*, **28B**, 131 (1955). —By *C. A.*, 50, 6171 (1956).

[5] T. Yoshioka and M. Taniyama, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), 57, 747 (1954).

[6] J. H. Reedy, *J. Am. Chem. Soc.*, **43**, 1440 (1921).

respectively. These bottles were slowly rotated for seventy-two hours, which were sufficient to give the saturated solutions.

The solubility of silver bromate was determined volumetrically from the total silver ion using dichlorofluorescein as the indicator. To the sample to be determined was added a definite excess of sodium chloride solution (0.050 mol./l.), then the sodium chloride remaining was determined by titration with 0.025 mol./l. silver nitrate solution.

Results and Discussions

(1) **Results.**—The solubilities of silver bromate and other values are shown in Tables I, II, III and IV. The observed solubilities

TABLE I

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 20°C

T.H.F. %(wt.)	Density	Dielectric Constant	Solubility		$\log S+3$	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9982	80.37	7.28	2.62	0.8621	1.244
3.347	0.9966	78.18	6.34	2.35	0.8021	1.279
6.769	0.9952	75.88	5.72	2.18	0.7574	1.318
12.645	0.9936	71.87	4.73	1.89	0.6749	1.391
18.770	0.9909	67.39	3.97	1.68	0.5988	1.484
24.471	0.9880	62.93	3.39	1.51	0.5302	1.589
29.208	0.9853	59.12	2.93	1.37	0.4669	1.691
35.670	0.9801	52.74	2.51	1.26	0.3997	1.896
43.537	0.9719	46.78	1.90	1.05	0.2788	2.138
54.513	0.9595	37.48	1.34	0.85	0.1271	2.668
64.232	0.9461	29.71	0.99	0.73	$\bar{1}.9956$	3.366

TABLE II

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 25°C

T.H.F. %(wt.)	Density	Dielectric Constant	Solubility		$\log S+3$	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9971	78.54	8.59	3.09	0.9340	1.273
3.347	0.9954	76.34	7.62	2.83	0.8820	1.310
6.769	0.9938	74.00	6.83	2.61	0.8344	1.351
12.645	0.9912	69.92	5.81	2.33	0.7642	1.430
18.770	0.9886	65.56	4.88	2.07	0.6884	1.525
24.471	0.9846	61.09	4.23	1.90	0.6263	1.637
29.208	0.9808	57.24	3.67	1.72	0.5647	1.747
35.670	0.9750	50.98	2.90	1.46	0.4624	1.962
43.537	0.9669	45.25	2.31	1.28	0.3636	2.210
54.513	0.9593	36.28	1.53	0.98	0.1847	2.756
64.232	0.9408	28.72	1.13	0.83	0.0531	3.482

TABLE III

SOLUBILITY OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT AT 30°C

T.H.F. %(wt.)	Density	Dielectric Constant	Solubility		$\log S+3$	$1/D\times100$
			$S\times10^3$	$S'\times10^4$		
0.	0.9957	76.73	10.02	3.59	1.0009	1.303
3.347	0.9937	74.58	8.99	3.34	0.9538	1.341
6.769	0.9921	72.34	8.08	3.09	0.9074	1.382
12.645	0.9893	68.34	6.82	2.74	0.8338	1.463
18.770	0.9860	63.95	5.62	2.39	0.7497	1.564
24.471	0.9821	59.56	4.79	2.15	0.6803	1.679
29.208	0.9780	55.85	4.12	1.94	0.6149	1.791
35.670	0.9727	49.70	3.28	1.66	0.5159	2.012
43.537	0.9640	44.01	2.55	1.42	0.4065	2.272
54.513	0.9498	35.18	1.77	1.14	0.2480	2.843
64.232	0.9361	28.00	1.43	1.10	0.1553	3.571

TABLE IV

SOLVATION RADIUS OF SILVER BROMATE IN TETRAHYDROFURAN-WATER MIXED SOLVENT

T. H. F. %(wt.)	20°C		25°C		30°C	
	$A\times10^8$	$B\times10^8$	$A\times10^8$	$B\times10^8$	$A\times10^8$	$B\times10^8$
3.347	0.773	0.758	0.789	0.774	0.968	0.956
6.769	0.907	0.895	0.988	0.975	1.024	1.013
12.645	0.994	0.983	1.148	1.141	1.154	1.148
18.770	1.135	1.128	1.251	1.248	1.246	1.242
24.471	1.296	1.294	1.433	1.438	1.400	1.403
29.208	1.165	1.166	1.549	1.559	1.503	1.510
35.670	1.743	1.745	1.755	1.777	1.910	1.932
43.537	1.878	1.899	1.966	1.997	2.265	2.302
54.513	2.354	2.402	2.354	2.405	2.390	2.447
64.232	2.463	2.541	2.949	3.050	3.076	3.208

of silver bromate in tetrahydrofuran-water mixed solvents at 20°, 25° and 30°C are listed in the fourth column ($S\times10^3$ mol./l.) and in the fifth column ($S'\times10^4$ mole fraction) of Table I, II and III, respectively. The probable error of observed solubility is $\pm0.02\times10^{-3}$ mol./l. Further, the observed densities of the tetrahydrofuran-water system are given in the second column of Tables I and III. The densities listed in Table II were obtained by applying Critchfield's experimental equation. The probable error of the observed density is $\pm0.9\times10^{-5}$g./cc. The dielectric constants (D) at 20°, 25° and 30°C are those from the data of Critchfield[7].

(2) The Relation between the Solubility and the Dielectric Constant.—The relation between the solubility (S) and the dielectric constant (D) is shown graphically in Figs. 1 and 2. In Fig. 2, these curves are approximated by straight lines in the region of higher dielectric constant (about 60–80), in the range of concentration smaller than about twenty per cent by weight of tetrahydrofuran, while in the whole range of concentration we can see the smoothly continuous curves.

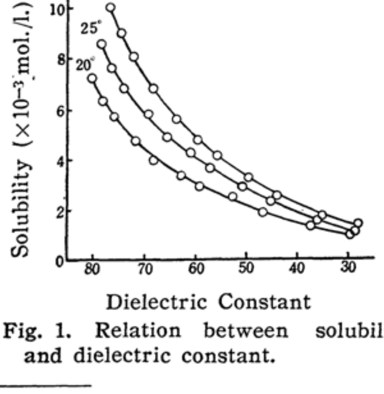

Fig. 1. Relation between solubility and dielectric constant.

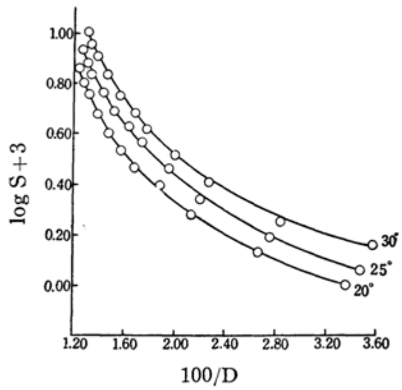

Fig. 2. Relation between logarithm of solubility and reciprocal of dielectric constant.

When the concentration of tetrahydrofuran in solution is relatively low, and provided that the molecular association of the solvent does not exist, the relation between the observed solubility and the dielectric constant of solvent was expressed by the following theoretical equation (I)[3]

$$ln\frac{C_0}{C_1}=\frac{Z^2\varepsilon^2}{2RTr_s}N\Big(\frac{1}{D_1}-\frac{1}{D_0}\Big)-\frac{Z^2\varepsilon^2}{2kT}\sqrt{\frac{8\pi NZ^2\varepsilon^2}{10^3kT}}\Big(\frac{C_1^{\frac{1}{2}}}{D_1^{\frac{3}{2}}}-\frac{C_0^{\frac{1}{2}}}{D_0^{\frac{3}{2}}}\Big) \qquad \text{(I)}$$

where N, R, T, Z, k and ε are the Roschmidt number, gas constant, absolute temperature, valency, Boltzman number, and electric elementary quantum, respectively, C_0 and D_0 are the solubility of the solute in water and the dielectric constant of water, C_1 and D_1 are the solubility of the solute in tetrahydrofuran-water mixed solvents and the dielectric constant of these solvents.

In the equation, as C_0 and D_0 are constant at constant temperature, assuming the solvation radius r_s being constant, neglecting the second term as it is very small compared with the first, the logarithm of solubility of the electrolyte should be reciprocally proportional

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[7] F. E. Critchfield, J. A. Gibson and J. L. Hall, *J. Am. Chem. Soc.*, 75, 6044 (1953).

to the dielectric constant. The theoretical equation (I) agrees almost exactly with the experimental results shown in Fig. 2 in the region of higher dielectric constant.

On the other hand, no linear relation was found in the wide range of the dielectric constant of concentrated tetrahydrofuran-water mixed solvents. Undoubtedly, the equation (I) is in such a case incorrect due to the approximations adopted in its theoretical treatment. Since the equation was derived to investigate the relation between the solubility of sparingly soluble salt and the dielectric constant of the solvent, it is not satisfactory for this investigation.

Generally speaking, the solubility of the inorganic salt does not merely depend upon the dielectric constant of the solvent, but it may also depend on the chemical constitution of the solvent. Thus, in a more improved treatment, the intermolecular reaction of the solvent (tetrahydrofuran) and water should be considered. Also to know the effect of polarization of the solubility of inorganic salt in the mixed solvents, the dipole moment of the solvent should be taken into account. Further investigations are necessary in regard to these point.

(3) **Calculation of Solvation Radius.**—The solvation radius (r_s) of silver bromate in these mixed solvents, was calculated by using values of observed solubility. The solvation radius is about 1 Å at each temperature in the solvent of high water concentration. These are listed in Table IV, the values in column (A) were calculated by the equation (I), the values in column (B) by the equation without the second term of the equation (I). The effect of the second term increases with the decrease of the dielectric constant, in a non-linear range of curve in Fig. 2. The solvation radius of this solvent is smaller than in the case of any other previous reports[1,2].

Summary

To investigate the relation between the solubility of inorganic salts and the dielectric constants of solvents, the solubility of silver bromate in tetrahydrofuran-water mixed solvent was determined at 20°, 25° and 30°C, respectively. The logarithm of solubility is almost reciprocally proportional to the dielectric constant of the solvent in the region of the higher dielectric constant. But no linear relation was found in that of the lower dielectric constant of tetrahydrofuran-water mixed solvent.

Also, the solvation radius of silver bromate was calculated applying the above-mentioned data. The solvation radius is about 1 Å at each temperature.

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