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Note

PHYSICO-CHEMICAL STUDIES IN WATER + DIOXANE MIXTURES: SOLUBILITY PRODUCT AND RELATED THERMODYNAMIC QUANTITIES OF SILVER BROMATE

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In continuation of our study on the determination of the solubility of sparingly soluble silver salts in mixed aqueous media [1] (water + dioxane), we now report the solubility product and related thermodynamic quantities of silver bromate in water +10, +20, and +40 mass% of dioxane at 20, 25, 30 and 35°C.

EXPERIMENTAL

Silver bromate and anhydrous sodium perchlorate were prepared according to the standard procedures given in the literature [2]. The solvent mixtures of various mass percentages were made as described in our earlier articles [1,4].

The solubility was determined by the method described earlier [1,5—8]. The solute contents were analysed by the iodometric determination of the bromate using 0.01 M sodium thiosulphate solution and a calibrated microburette. The sodium thiosulphate solutions were standardised against potassium dichromate. The titrations were accurate to ±0.2%.

RESULTS AND DISCUSSION

As described earlier [1,5—8], the hypothetical solubility, s^0, of silver bromate was obtained by extrapolating the function $\log s'$ defined by

$$\log s' = \log s - \frac{AI^{1/2}}{1 + Ba^0I^{1/2}} = \log s^0 - bI \qquad (1)$$

to ionic strength $I = 0$ (here, $I = c + s$), where s is the solubility in mole l^{-1} determined experimentally at any sodium perchlorate molarity, c. A and B are the Debye—Huckel constants and are known [9] over the temperature range under investigation in water +10, +20, and +40 mass% of dioxane, and a^0 is the ion-size parameter. As before, $\log s^0$ is the intercept, and b is the slope of a plot of the middle terms of eqn. (1) vs. the ionic strength, I, when extrapolated to $I = 0$ assuming proper values of a^0 are chosen. As usual [10], the values of a^0 were obtained and were found to be 4.5, 5, and 5 Å in water +10, +20, and +40 mass% of dioxane, respectively.

The solubilities of silver bromate at rounded molarities (e.g. c = 0, 0.01, 0.02, etc. mole l^{-1}) were calculated by using the usual equation [1,5—8] of the form

$$\log s = \log s^0 + \frac{AI^{1/2}}{1 + Ba^0I^{1/2}} - bI \tag{2}$$

where the symbols have their usual significance. The method of calculation was exactly the same as that described in our earlier articles [5—8]. The solubility product, K_s, has been calculated from the relation, $K_s = (s')$ [2], where s' is the solubility of silver bromate at c = 0 mole l^{-1}. The values of K_s at various temperatures were fitted by the method of least squares to an equation of the form

$$-\log K_s = \frac{A}{T} + B + CT \tag{3}$$

where T is the thermodynamic temperature in degrees Kelvin. The parameters A, B, and C in eqn. (3) are presented in Table 1 for various water + dioxane compositions. The average deviation between the observed (experimental) values and the values calculated from eqn. (3) for different media is within ±0.0005 logarithm units.

The mean activity coefficients of silver bromate calculated at rounded molarities [5—8] by means of the following equations

$$sf_\pm = s^0 \tag{4}$$

$$\log f_\pm = -\frac{AI^{1/2}}{1 + Ba^0I^{1/2}} + bI \tag{5}$$

$$\log f_\pm = -AI^{1/2} \tag{6}$$

show that there is good agreement between these values but beyond ca. 0.01 molar the values calculated by eqn. (6) show deviation from those calculated from eqns. (4 and 5).

The various thermodynamic quantities ΔG^0, ΔH^0, ΔS^0, and ΔC_p^0 for the dissolution process of silver bromate in different water + dioxane mixtures have been evaluated from the usual relations at temperatures ranging from 20 to 35°C using the parameters A, B, and C of eqn. (3). These values at

TABLE 1

Parameters of eqn. (3)

Mass% of dioxane	A	B	C
10	—36 139	232.4	—0.3831
20	—16 545	98.9	—0.1549
40	+24 017	—203.8	+0.3448

TABLE 2

Standard thermodynamic quantities of the dissolution process, $AgBrO_3$ (s) → Ag^+ (solvated) + BrO_3^- (solvated) in water and water + dioxane mixtures at 25°C

Mass% of dioxane	$\Delta G^0 \times 10^{-3}$ (J mole^{-1})	$\Delta H^0 \times 10^{-3}$ (J mole^{-1})	ΔS^0 (J mole^{-1} deg^{-1})
0	24.40	48.96	82.43
10	17.29	31.97	49.28
20	17.50	44.61	90.96
40	20.99	35.55	49.69

TABLE 3

Standard thermodynamic constants for the transfer of silver bromate from water to water + dioxane mixtures at 25°C

Mass% of dioxane	$\Delta G_t^0 \times 10^{-3}$ (J mole^{-1})	$\Delta H_t^0 \times 10^{-3}$ (J mole^{-1})	ΔS_t^0 (J mole^{-1} deg^{-1})
10	−7.11	−16.99	−33.15
20	−6.90	−4.35	+8.53
40	−3.41	−13.41	−32.74

25°C are presented in Table 2 along with that available in water [6] for the sake of comparison. It is observed that ΔG^0 does not change much on passing from water to water + dioxane media, whereas there are appreciable changes in ΔH^0 and ΔS^0 values. This indicates that the dissolution process is less energy consuming and the dissolved state is less disordered in water + dioxane media than in water.

The thermodynamic quantities, ΔG_t^0, ΔH_t^0, and ΔS_t^0 for the transfer of 1 mole of silver bromate from water to the mixed solvents of various compositions have been derived from the usual relations [11], and these values at 25°C are shown in Table 3. The values of ΔG_t^0 appear to be negative for all compositions, increasing sharply to more positive value for +40 mass% of dioxane. The negative values of ΔG_t^0 lend support to the view that silver bromate is less stabilized by solvation with water molecules in mixed solvents than in water. Further, the negative values of ΔH_t^0 and ΔS_t^0 indicate that the mixed solvent becomes less associated than pure water, pointing to the fact that the net amount of order created by the silver and bromate ions is more in the water + dioxane media than in water.

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