The Detemination of the Formation Constants of the Triiodide Ion in Water-Alcohol Mixed Solvents at Various Temperatures

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(Received April 26, 1976)

The formation constants of the triiodide ion were determined in water–alcohol mixed solvents by a spectrophotometric method at various temperatures. The formation reaction of the triiodide ion from an iodide ion and an iodine molecule is accompanied by a negative enthalpy change and a positive entropy change at various alcohol contents: $\Delta H°/\text{kJ mol}^{-1}$, -15.4 (in water) to -14.3 (in methanol) in the water–methanol system, -15.4 (in water) to -21.4 (in ethanol) in the water–ethanol system; $\Delta S_x°/\text{J K}^{-1}\text{ mol}^{-1}$, 36 (in water) to 57 (in methanol) in the water–methanol system, and about 36 at various ethanol contents in the water–ethanol system. The enthalpy term is the dominant factor in the water–ethanol mixtures, whereas the entropy term is the dominant factor in the water–methanol mixtures. In order to explain the thermodynamic behavior, the changes in the solvation properties as well as the activity coefficients of solutes must be considered in both the mixture systems.

During the course of an investigation of the effect of solvents on the rate of the oxidation of the formate ion by iodine, it became necessary to know the formation constant of the triiodide ion in mixed solvents at various temperatures. Although the formation constant has been determined in some mixed solvents[1,2] and some organic solvents[3,4] at 25 °C, it has not been determined at various temperatures in mixed solvents. The present work was undertaken in order to determine the values of the formation constant in water–alcohol mixed solvents at various temperatures. The formation constant varies with the composition of the solvents, and it has been found that the variation in the solvation properties influences the formation constant of the triiodide ion.

Experimental

Materials. The iodine, potassium iodide, ethanol (99.5%), and methanol (99.5%) were obtained from Wako Pure Chemicals Industries. The ethanol was of Wako's super special grade, while the other chemicals were of a guaranteed grade. The solutions of the iodine were prepared by dissolving exactly weighed amounts of iodine purified by sublimation in the potassium iodide solution. The presence of iodide lowers the reactivities of iodine with solvents. The potassium iodide used was dried at 120 °C overnight, and the solutions were prepared by dissolving exactly weighed amounts of the salt in mixed solvents. The water used was double-distilled from potassium permanganate in an all-glass apparatus.

Measurements. The absorbance at 355 nm was measured by using a Hitachi 101 spectrophotometer with quartz cells with a light-path length of 10 mm in a thermostated holder, and using a Valhalla Scientific digital multimeter, Model 4440, as the digital output at various temperatures. The pH and the ionic strength in the solutions were uncontrolled.

The Determination of the Formation Constant of I_3^-. The formation constant of the triiodide ion was calculated from the dependence of the absorbance at 355 nm on the concentration of the iodide of the solution containing a constant concentration of iodine (*ca.* 25×10^{-6} mol dm^{-3}).

For Reaction 1, the apparent formation constant, K_c, is given by Eq. 2:

$$I_2 + I^- \rightleftarrows I_3^- \qquad (1)$$

$$K_c = [I_3^-]/[I_2][I^-] = x/(a-x)(b-x) \qquad (2)$$

where the brackets represent the respective concentrations, a and b are the total concentrations of iodine and potassium iodide respectively, and x is the equilibrium concentration of the triiodide ion. As potassium iodide does not absorb the light at 355 nm, the absorption coefficient at 355 nm, $A(\equiv D_l/l)$, is given by Eq. 3:

$$A = \varepsilon_0(a-x) + \varepsilon_1 x \qquad (3)$$

where ε_0 and ε_1 are the molar absorption coefficients of iodine and the triiodide ion respectively, at 355 nm. From Eqs. 2 and 3,

$$\bar{\varepsilon} \equiv A/a = \varepsilon_0 + K_c b(\varepsilon_1-\varepsilon_0)/[1+K_c(a-x)+K_c b] \qquad (4)$$

As b is much larger than $(a-x)$ in the present measurements, and as ε_1 is much larger than ε_0 at 355 nm,

$$1/\bar{\varepsilon} \approx (1/\varepsilon_1 K_c)(1/b) + 1/\varepsilon_1 \qquad (5)$$

Therefore, K_c and ε_1 can be calculated by the intercept and slope of the $1/\bar{\varepsilon}$ *vs.* $1/b$ plot. All the plots were linear in various mixed solvents at $b \gg a$, and the intercept of each line was almost independent of the temperature.

Results and Discussion

The iodine solution in methanol and ethanol has an absorption band with a maximum absorbance near 355 nm.[1,5] However, the absorbance at 355 nm is not proportional to the concentration of iodine. This band is ascribed to a small amount of the triiodide ion formed by the reaction of iodine with alcohol.[5,6] The formations of I_5^-, I_7^-, I_9^-, *etc.* are neglected because of the low concentration of iodine in the present work (for example, $\log([I_5^-]/[I_2]^2[I^-])=1.8$ in ethanol[2]).

In aqueous solutions, Reaction 1 is accompanied by Reactions 6 and 7:[7-10]

$$I_2 + H_2O \rightleftarrows HIO + I^- + H^+ \qquad (6)$$

$$3I_2 + 3H_2O \longrightarrow IO_3^- + 5I^- + 6H^+ \qquad (7)$$

At pH≈7, Equilibrium 6 may be neglected.[9,10] Reaction 7 is sufficiently slow in the presence of excess potassium iodide.[9] In fact, the absorbance at 355 nm did not vary for 24 h in an iodine solution containing an excess of potassium iodide.

Table 1 gives the values of the apparent formation constants of the triiodide ion, K_c. The constant increases when the temperature is lowered and the alcohol content is increased. The values of K_c obtained in the present work are compared with those of other workers in

Table 1. The formation constant, K_c, of the triiodide ion in water–alcohol mixed solvents

Mole fraction of alcohol	$10^{-3}\times K_c$/mol^{-1} dm^3			
Methanol				
0.00	1.01±0.01 (9.5 °C)	0.73±0.00 (25.0 °C)		0.55±0.02 (38.0 °C)
0.10	1.25±0.04 (11.0 °C)	0.98±0.02 (22.1 °C)	0.88±0.00 (30.0 °C)	0.72±0.02 (37.4 °C)
0.18	2.07±0.05 (10.0 °C)	1.69±0.06 (19.5 °C)	1.35±0.04 (29.0 °C)	1.20±0.10 (37.7 °C)
0.31	4.10±0.04 (11.1 °C)	3.25±0.03 (21.2 °C)	2.64±0.04 (30.8 °C)	2.34±0.02 (37.4 °C)
0.47	7.57±0.03 (10.0 °C)	5.98±0.05 (20.8 °C)	5.06±0.20 (29.0 °C)	4.51±0.23 (37.4 °C)
0.64	10.4 ±0.1 (11.3 °C)	8.56±0.03 (21.0 °C)	7.39±0.04 (28.8 °C)	6.29±0.09 (38.1 °C)
0.82	14.1 ±0.0 (10.3 °C)	11.0 ±0.1 (20.9 °C)	9.66±0.01 (28.9 °C)	7.86±0.01 (39.0 °C)
0.99	16.0 ±0.1 (11.8 °C)	13.6 ±0.2 (20.0 °C)	10.9 ±0.1 (31.0 °C)	9.59±0.02 (38.6 °C)
Ethanol				
0.07	2.05±0.08 (12.0 °C)	1.66±0.05 (20.5 °C)	1.34±0.06 (29.5 °C)	1.17±0.04 (37.0 °C)
0.13	5.54±0.02 (11.2 °C)	4.44±0.10 (19.0 °C)	3.63±0.03 (27.0 °C)	2.86±0.03 (37.0 °C)
0.24	12.7 ±0.1 (11.0 °C)	10.8 ±0.2 (18.0 °C)	7.80±0.07 (29.0 °C)	6.26±0.10 (37.2 °C)
0.38	21.4 ±0.5 (11.0 °C)	15.7 ±0.7 (20.0 °C)	12.2 ±0.5 (30.0 °C)	10.0 ±0.3 (37.0 °C)
0.55	27.5 ±0.4 (9.5 °C)	20.0 ±0.2 (18.2 °C)	15.4 ±0.2 (27.5 °C)	11.9 ±0.3 (37.0 °C)
0.76	32.8 ±1.0 (8.0 °C)	22.6 ±0.5 (19.2 °C)	17.0 ±0.4 (30.0 °C)	14.1 ±0.6 (36.0 °C)
0.98	35.1 ±0.8 (10.0 °C)	28.7 ±0.2 (17.0 °C)	20.7 ±0.2 (28.0 °C)	15.1 ±0.2 (39.0 °C)

Fig. 1. Ramadan *et al.*[1] assigned the absorption bands at 360 and 294 nm to the iodine molecule, and obtained the molar absorption coefficient of the iodine molecule, ε_0, from the absorbance of the iodine–alcohol–water systems. However, this assignment is questionable, because the absorbances at 360 and 294 nm are not proportional to the concentration of iodine. The absorption bands may be ascribed to a small amount of the triiodide ion formed by the reaction of iodine with the alcohol.[6] The difference between the present results and those reported by Barraqué *et al.*[2] (Fig. 1) may be attributed to the difference in methods. Barraqué *et al.* used a potentiometric method.

Table 2 gives the values of the standard thermodynamic functions, $\Delta H°$, $\Delta S_c°$, and $\Delta G_c°$, of Reaction 1 and the molar absorption coefficient, ε_1, of the triiodide ion. In order to compare the formation constant in mixed solvents, it is necessary to use a measure which is independent of the conventional scale. For a solute A, the chemical potential, μ(A), is represented by either Eq. 8 or Eq. 9:

$$\mu(\mathrm{A}) = \mu_c°(\mathrm{A}) + RT\ln(C_\mathrm{A}/C°) + RT\ln y_\mathrm{A} \qquad (8)$$

$$\mu(\mathrm{A}) = \mu_x°(\mathrm{A}) + RT\ln x_\mathrm{A} + RT\ln f_\mathrm{A} \qquad (9)$$

where x_A is the mole fraction of A, C_A is the concentration of A, y_A, and f_A are the activity coefficients in

Table 2. The equilibrium characteristics and the absorption coefficient of the formation of triiodide in water–alcohol mixed solvents at 25 °C

Mole fraction of alcohol	$\Delta H°$ / kJ mol^{-1} (±0.4)	$\Delta G_c°$ / kJ mol^{-1} (±0.6)	$\Delta S_c°$ / JK^{-1} mol^{-1} (±2)	$\Delta G_x°$ / kJ mol^{-1} (±0.5)	$\Delta S_x°$ / JK^{-1} mol^{-1} (±3)	$10^4\times\varepsilon_1$[a)] / mol^{-1} dm^3 cm^{-1} (±0.2)
Methanol						
0.00	−15.4	−16.3	3	−26.3	36	2.5
0.10	−15.0	−17.0	7	−26.7	39	2.7
0.18	−14.8	−18.1	11	−27.6	43	2.7
0.31	−15.7	−19.8	14	−29.0	45	2.7
0.47	−14.0	−21.4	25	−30.3	55	2.8
0.64	−13.9	−22.3	28	−30.9	57	2.6
0.82	−14.8	−22.9	27	−31.2	55	2.7
0.99	−14.3	−23.3	30	−31.3	57	2.8
Ethanol						
0.07	−16.6	−18.1	5	−27.8	38	2.5
0.13	−18.7	−20.4	6	−29.8	37	2.6
0.24	−20.1	−22.5	8	−31.5	38	2.7
0.38	−21.1	−23.6	8	−32.1	37	2.6
0.55	−22.0	−24.1	7	−32.1	34	2.6
0.76	−21.5	−24.5	10	−32.0	35	2.7
0.98	−21.4	−24.8	11	−31.9	35	2.5

a) At 355 nm.

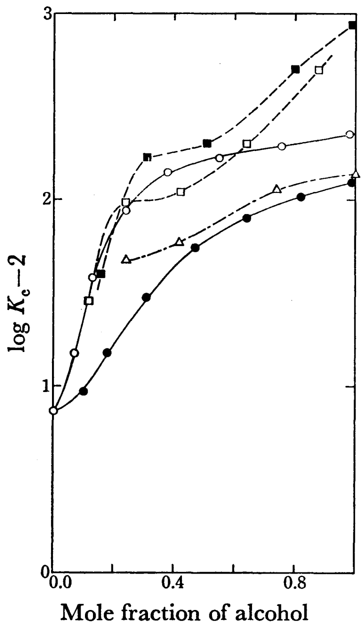

Fig. 1. Effects of the alcohol content on the formation constant of the triiodide ion at 25 °C. Open marks: water–ethanol mixture, closed marks: water–methanol mixture. Circle: the present work, square: by Ramadan *et al.*,[1] Triangle: by Barraqué *et al.*[2]

the respective concentration scale, and C° is the standard concentration, selected as 1 mol dm^{-3} in the present work. At an infinite dilution,

$$\mu_x^\circ(\mathrm{A}) = \mu_c^\circ(\mathrm{A}) + RT\ln\{(C_\mathrm{A}/C^\circ)/x_\mathrm{A}\} \tag{10}$$

Since $x_\mathrm{A}\approx C_\mathrm{A}(x_\mathrm{B}M_\mathrm{B}+x_\mathrm{C}M_\mathrm{C})/\rho$ in the B–C mixed solvents,

$$\mu_x^\circ(\mathrm{A}) = \mu_c^\circ(\mathrm{A}) + RT\ln\{\rho/(x_\mathrm{B}M_\mathrm{B}+x_\mathrm{C}M_\mathrm{C})C^\circ\} \tag{11}$$

where M_B and M_C are the molar masses of B and C respectively, while ρ is the mass of the 1 dm^3 solution. Since $\Delta G_c^\circ=\mu_c^\circ(\mathrm{I}_3^-)-\mu_c^\circ(\mathrm{I}_2)-\mu_c^\circ(\mathrm{I}^-)$ for Reaction 1,

$$\begin{aligned}\Delta G_x^\circ &= \mu_x^\circ(\mathrm{I}_3^-) - \mu_x^\circ(\mathrm{I}_2) - \mu_x^\circ(\mathrm{I}^-)\\ &= \Delta G_c^\circ - RT\ln\{\rho/(x_\mathrm{B}M_\mathrm{B}+x_\mathrm{C}M_\mathrm{C})C^\circ\}\end{aligned} \tag{12}$$

Since $\Delta H_c^\circ=\Delta H_x^\circ(=\Delta H^\circ)$ and $\Delta S_c^\circ=(\Delta H_c^\circ-\Delta G_c^\circ)/T$,

$$\begin{aligned}\Delta S_x^\circ &= (\Delta H_x^\circ-\Delta G_x^\circ)/T\\ &= \Delta S_c^\circ + R\ln\{\rho/(x_\mathrm{B}M_\mathrm{B}+x_\mathrm{C}M_\mathrm{C})C^\circ\}\end{aligned} \tag{13}$$

Table 2 shows also the values of ΔG_x° and ΔS_x° at 25 °C.

Figure 2 shows the dependence of these quantities on the mole fraction of alcohol. The values of ΔH° are nearly constant in the methanol–water mixtures, whereas in the ethanol–water mixtures they increase remarkably on the addition of the first portions of ethanol and become nearly constant beyond the 0.4 mol fraction. On the other hand, the values of ΔS_x° are nearly constant in the ethanol–water mixtures, while they increase in the methanol–water mixtures. The values of ΔS_c° increase with the ethanol content, whereas those of ΔS_x° are constant (Table 2). The increase in ΔS_c° may be due to the neglect of the entropy change on the mixing of the solvents.

Two factors can explain the variations in ΔS_x° and ΔH° with the alcohol content: one is the variation in the activity coefficients of the solutes with the alcohol content, and the other is the variation in the solvation properties with the alcohol content. The activity coefficients of I_3^- and I^- are nearly the same in a given solvent, because the two ions are univalent. The activity coefficient of I_2 will be close to unity because it is a neutral molecule. Even if the activity coefficient varied from 1.0 to 0.5 with the alcohol content, the difference in ΔG_x° would be only about 2 kJ mol^{-1}. Thus, the activity coefficients of solutes cannot explain the effects of the solvent on ΔG_x°.

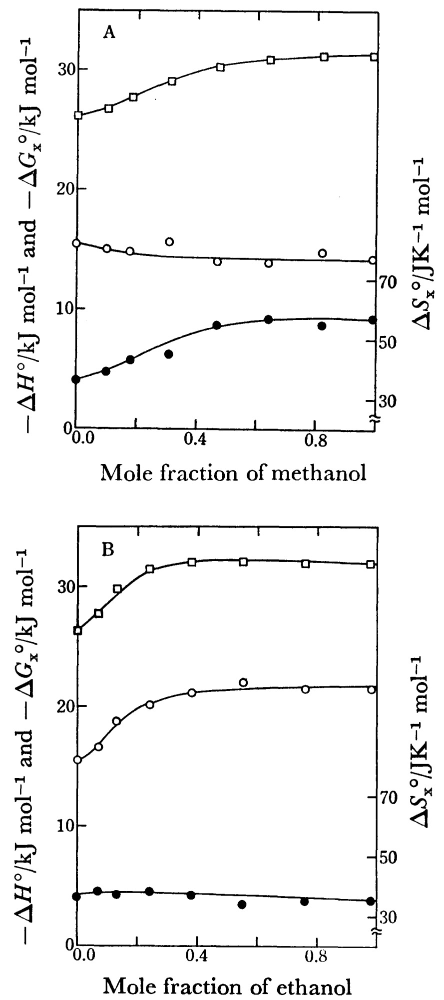

Fig. 2. The standard thermodynamic functions of the formation of the triiodide ion in water–alcohol mixed solvents. A: water–methanol mixtures, B: water–ethanol mixtures. □: ΔG_x°, ○: ΔH°, ●: ΔS_x°.

Next, the variation in the solvation properties, such as the structure of the solvation shell and the specific solvation, must be considered in both the mixture systems. ΔH° and ΔS_x° in Fig. 2 reflect the solvation energy of each solute and the structure of the solvation shell of each solute respectively, because μ_x° is based on the infinite dilution. For example, the curves of ΔH° in Fig. 2 indicate that the difference in the solvation energy between the reactants and the product in Reaction 1 is nearly constant in the methanol–water system, while it increases on the addition of a small amount of ethanol to water in the ethanol–water system. Ramadan *et al.*[1] ascribed the marked change in K_c by the addition of a small amount of organic solvents to the rearrangement of the structure of the solvent and a subsequent change in its solvation properties. In order to make it clear why ΔS_x° is the dominant factor in the methanol–water system, while ΔH° is the dominant factor in the ethanol–water system, we need to know the structure of the solvation shell of each solute and the transfer-free energy of the solutes in various solvents. Thus, in order to explain the thermodynamic behavior of Reaction 1 in the two mixture systems, the changes in the solvation properties as well as the activity coefficients of the solutes must be considered.

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