

Organo-monohalogeno and Organo-monothiocyanato Mercury(II) Complexes: Tendency for further Complex Formation

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The tendency of organo-monohalogeno and organo-monothiocyanato mercury complexes to coordinate further halide and thiocyanate ions has been studied by solubility measurements in aqueous 1 M salt solutions ($\text{NaX} + \text{NaClO}_4$), and partly in a 50 vol % methanol-water solvent. The saturated solutions were analyzed polarographically. Distinct complex formation was found only in the thiocyanate and the iodide systems, and the 2nd and 3rd formation constants were determined for these systems. Further evidence for this coordination was obtained in the 2-butyl-mercuric thiocyanate system from measurements of the change in optical rotatory power of the partially resolved complex with increasing ligand concentration.

Previously, organomercury cations have been considered to form only 1:1 complexes with ligands such as halide or pseudohalide ions: formation of complexes with more than one ligand attached to the mercury atom have either been ignored or thought to be formed in undetectable concentrations.¹⁻³ On the other hand, one of us (R.B.) had found evidence from anion exchange and paper electrophoretic studies for the formation of the complexes $\text{C}_2\text{H}_5\text{Hg}(\text{SCN})_n$ ¹⁻ⁿ (with n ranging from 1 to 3) in aqueous solution, and also some evidence for negatively charged chloride complexes of $\text{C}_2\text{H}_5\text{HgCl}$ in aqueous solutions at high ligand concentration.⁴

The present work was carried out in order to clarify the situation. Complex formation between the compounds RHgX ($\text{R} = \text{ethyl, 2-butyl}$; $\text{X} = \text{Cl, Br, I, SCN}$) and the ligand ions was examined by the solubility method, in aqueous solutions (for the ethylmercury halides and thiocyanate) and in a 50 vol % methanol-water solvent (for ethyl and 2-butyl mercury thiocyanates). In this manner the influence of the ligand, the solvent and the organic radical on the formation of complexes, was examined.

EXPERIMENTAL

The bromide,⁵ iodide,⁵ and thiocyanate⁶ compounds of ethylmercury were prepared according to methods given in the literature while the chloride was obtained from L. Light and Co.

2-Butylmercuric thiocyanate, whose preparation has not been described previously, was prepared in both racemic and optically active forms by the reaction of thiocyanic acid with 2-butylmercuric hydroxide and (-)-mandelate, respectively. The thiocyanate is a rather stable compound, showing no change or decomposition if stored in the dark and becoming grey only on prolonged exposure (one month) to diffuse daylight.

Racemic 2-butylmercuric thiocyanate. 2-Butylmercuric hydroxide was obtained by a Grignard reaction of 2-butylmagnesium bromide with mercuric bromide followed by treatment of the 2-butylmercuric bromide with potassium hydroxide in acetone-methanol.⁷ An aqueous solution of thiocyanic acid (10 mmoles in 25 ml), prepared from aqueous sodium thiocyanate by cation exchange on Amberlite CG-120, H⁺, was added to a sample of 2-butylmercuric hydroxide (from 10 mmoles of the bromide) dissolved in methanol (30 ml). The thiocyanate, precipitated by dilution to about 300 ml with water, was recrystallized from methanol (25 ml) to give colourless needles, m.p. 80°. The analysis for mercury was carried out both by a volumetric and a gravimetric method. The first method consisted in the oxidation with nitric acid at high temperature in a sealed quartz tube followed by titration of the Hg(II) with EDTA.⁸ The second method involved the precipitation of [Cu pn₂][HgI₄] (pn = 1,2-diaminepropane) after oxidation to Hg(II).⁹ The analyses for C, H, and N were carried out in the microanalytical laboratory of this Institute. (Found: C 19.13; H 2.99; N 4.47; Hg 62.80. Calc. for C₄H₉HgSCN: C 19.01; H 2.87; N 4.44; Hg 63.52).

(-)-2-Butylmercuric thiocyanate. 2-Butylmercuric (-)-mandelate prepared from 2-butylmercuric hydroxide, was partially resolved by fractional recrystallization from acetone.⁷ An aqueous solution of freshly prepared thiocyanic acid (2.5 mmoles in 20 ml) was slowly added with stirring to the partially resolved mandelate (1.024 g) in dioxan (15 ml). The thiocyanate precipitated with water (250 ml), was recrystallized from methanol (15 ml) to give colourless needles, m.p. 80°.

Reagents. Analar grade reagents were used wherever possible, otherwise the reagents were purified by recrystallization or distillation. Stock aqueous solutions of sodium halides, thiocyanate and cyanide were standardized argentometrically. Aqueous sodium perchlorate was standardized both by cation and anion exchange titrimetry, using Amberlite CG-120, H⁺, or Amberlite CG-400, Cl⁻, respectively.

Solubility measurements. The solubilities of C₂H₅HgCl, C₂H₅HgBr, C₂H₅HgI, and C₂H₅HgSCN were determined at 25° in weakly acidic solutions (C_{HClO₄} = 0.001 M) as a function of the concentration of the salts NaX (X = Cl⁻, Br⁻, I⁻, SCN⁻) in a 1 molar mixed salt medium of NaX + NaClO₄. Similarly, the solubilities of C₂H₅HgSCN and 2-C₄H₉HgSCN were determined at 25° in a 50 vol % methanol-water solvent with a 1 molar mixed salt medium of NaSCN + NaClO₄. In this case no pH adjustment was made.

All solutions were brought to equilibrium in glass or polythene bottles, which were tightly closed after the introduction of the solid organo-mercurial and were shaken in a water thermostat for 1 or 2 days. The concentrations of the saturated solutions were measured polarographically after aliquots of each solution for a particular anion were brought to the same composition. Calibration curves for each anion were composed by measuring standard solutions that had been treated in a similar manner.

The polarographic analyses were carried out with a Radiometer Polariter type PO4 using a calomel-satd. KCl electrode as anode. The oxygen was removed from the samples with oxygen-free nitrogen. The cell was thermostated at 25° and the polarograms were automatically recorded at a speed of 1.66 mV·sec⁻¹. The capillary had the following characteristics (at 25°, in distilled water and with open circuit): $m = 2.56 \text{ mg Hg}\cdot\text{sec}^{-1}$, $t = 4.0 \text{ sec per drop}$.

The organomercurials studied here show two reduction waves as have been observed for other organomercurials.¹⁰ The first wave was used for the analyses because the second wave is often too distorted to give reproducible measurements. The diffusion currents, i_d , were determined at the half-wave potentials to avoid errors in i_d due to the distortion of the waves. The maxima were suppressed with gelatine.

Table 1. Polarography of the R₂HgX compounds at 25°. Half-wave potentials $E_{1/2}$ vs. calomel-satd. KCl electr., and diffusion currents i_d referred to the half-wave potential. Composition of the solutions: R₂HgX in 1 M NaX + 1 M NaClO₄ with further additions as given in footnotes.

| Compound | $C_{R_2HgX_g}$ (mM) | First wave | | Second wave |
|--|------------------------|----------------------|---------------------|----------------------|
| | | $E_{1/2}$ (Volts) | i_d (μ A) | $E_{1/2}$ (Volts) |
| C ₂ H ₅ HgCl ^a | 1.05 | -0.85 | 3.61 | -1.37 |
| | 0.167 | -0.875 | 0.55 | -1.31 |
| C ₂ H ₅ HgBr ^b | 0.307 | -0.875 | 1.05 | -1.35 |
| | 0.051 | -0.895 | 0.165 | -1.295 |
| C ₂ H ₅ HgI ^c | 0.212 | -0.905 | 0.825 | -1.34 |
| | 0.021 | -0.935 | 0.08 | -1.28 |
| C ₂ H ₅ HgSCN ^d | 2.418 | -0.46 | 8.40 | -1.41 |
| | 0.403 | -0.465 | 1.385 | -1.335 |
| C ₂ H ₅ HgSCN ^e | 1.308 | -0.455 | 4.89 | -1.395 |
| | 0.261 | -0.47 | 0.95 | -1.32 |
| 2-C ₄ H ₉ HgSCN ^f | 1.141 | -0.41 | 4.05 | - |
| | 0.254 | -0.415 | 0.87 | - |

^a 0.1 M NaCN + 10⁻² M Na₂B₄O₇ + 0.015 % gelatine.

^{b,c} 0.1 M NaCN + 10⁻² M Na₂B₄O₇ + 0.010 % gelatine.

^d 10⁻² M Na₂B₄O₇ + 0.015 % gelatine.

^{e,f} 4.5 vol % CH₃OH + 0.015 % gelatine.

^g The two values given for every compound are for the most concentrated and for the most dilute solutions investigated.

Results for the standard solutions are reported in Table 1. The presence of NaCN in some samples facilitated the preparation of sufficiently concentrated stock solutions of the ethylmercuric halides. For the same reason, the stock solution of the organomercuric thiocyanates were prepared in 2 M NaSCN. All the stock solutions were stored in the dark and did not show any decomposition after several weeks.

The fact that the $E_{1/2}$ values reported in Table 1 for the second wave become more negative as the organomercurial concentrations are increased corresponds to the findings of other authors.¹⁰ The reverse dependence of $E_{1/2}$ for the first wave has not been reported previously. The polarographic reduction of 2-butylmercuric thiocyanate has not been previously reported either. It is noteworthy that the second reduction wave for this compound, which takes place between -1.4 and -1.8 V in the solvent system given in Table 1, is so distorted that it is impossible to measure the $E_{1/2}$ values.

The results of the solubility measurements are given in Table 2. Those for C₂H₅HgI must be considered only as approximate, because a gradual decomposition of the organomercurial was found to take place during the equilibration, probably due to oxidation of I₂. This occurred even if the experiments were carried out in the dark and in oxygen-free solutions. The decomposition was revealed by the increase of the total polarographic current for samples (of a saturated solution) removed at various intervals and for which the i_d differed by as much as ± 10 %.

Polarimetric measurements. The change in optical rotation of (-)-2-butylmercuric thiocyanate with the change in the concentration of thiocyanate in a 50 vol % CH₃OH-H₂O solvent with $C_{NaSCN} + C_{NaClO_4} = 1$ M, were measured with a spectro-

Table 2. Solubility determinations for the RHgX compounds in 1 M mixed $\text{NaX}-\text{NaClO}_4$ solutions at 25°. The composition of the samples analyzed polarographically are those of Table 1 for every $\text{RHgX}-\text{NaX}$ system.

| No. | Dilution ^a | $i_d(\text{av.})$ (μA) | C_{NaX} (M) | Solubility S (mM) | $\frac{(S/S_0)-1}{C_{\text{NaX}}}$ |
|--|-----------------------|--|-------------------------|------------------------|------------------------------------|
| $\text{C}_2\text{H}_5\text{HgCl}$ in $\text{NaCl}-\text{NaClO}_4$ aqueous solution. pH = 3. | | | | | |
| 1 | 4:1 | 3.50 | 0.00 | 4.07 | — |
| 2 | 4:1 | 3.29 | 0.15 | 3.83 | — |
| 3 | 4:1 | 3.24 | 0.35 | 3.77 | — |
| 4 | 4:1 | 3.20 | 0.60 | 3.72 | — |
| 5 | 4:1 | 3.25 | 0.80 | 3.79 | — |
| 6 | 4:1 | 3.12 | 1.00 | 3.64 | — |
| $\text{C}_2\text{H}_5\text{HgBr}$ in $\text{NaBr}-\text{NaClO}_4$ aqueous solution. pH = 3. | | | | | |
| 1 | 4:1 | 0.78 | 0.00 | 0.916 | — |
| 2 | 4:1 | 0.575 | 0.15 | 0.676 | — |
| 3 | 4:1 | 0.62 | 0.30 | 0.728 | — |
| 4 | 4:1 | 0.66 | 0.45 | 0.772 | — |
| 5 | 4:1 | 0.67 | 0.60 | 0.788 | — |
| 6 | 4:1 | 0.755 | 0.80 | 0.890 | — |
| 7 | 4:1 | 0.81 | 1.00 | 0.944 | — |
| $\text{C}_2\text{H}_5\text{HgI}$ in $\text{NaI}-\text{NaClO}_4$ aqueous solution. pH = 3. | | | | | |
| 1 | 1.25:1 | 0.24 | 0.00 | 0.077(= S_0) | — |
| 2 | 2:1 | 0.16 | 0.20 | 0.083 | 0.39 |
| 3 | 2:1 | 0.19 | 0.40 | 0.098 | 0.68 |
| 4 | 2:1 | 0.25 | 0.60 | 0.130 | 1.15 |
| 5 | 2:1 | 0.29 | 0.80 | 0.152 | 1.22 |
| 6 | 2:1 | 0.32 | 0.90 | 0.168 | 1.31 |
| 7 | 2:1 | 0.36 | 1.00 | 0.184 | 1.39 |
| $\text{C}_2\text{H}_5\text{HgSCN}$ in $\text{NaSCN}-\text{NaClO}_4$ aqueous solution. pH = 3. | | | | | |
| 1 | 4:1 | 2.817 | 0.00 | 3.34(= S_0) | — |
| 2 | 4:1 | 3.37 | 0.20 | 3.98 | 0.96 |
| 3 | 4:1 | 4.36 | 0.40 | 5.12 | 1.33 |
| 4 | 4:1 | 5.51 | 0.60 | 6.48 | 1.57 |
| 5 | 4:1 | 6.46 | 0.70 | 7.56 | 1.80 |
| 6 | 4:1 | 6.95 | 0.80 | 8.12 | 1.79 |
| 7 | 6.66:1 | 4.52 | 0.90 | 8.90 | 1.85 |
| 8 | 6.66:1 | 5.22 | 1.00 | 10.23 | 2.06 |
| $\text{C}_2\text{H}_5\text{HgSCN}$ in $\text{NaSCN}-\text{NaClO}_4$, 50 vol % $\text{CH}_3\text{OH}-\text{H}_2\text{O}$. | | | | | |
| 1 | 16.66:1 | 3.88 | 0.00 | 17.29(= S_0) | — |
| 2 | 33.33:1 | 2.67 | 0.20 | 23.83 | 1.89 |
| 3 | 33.33:1 | 3.57 | 0.40 | 32.00 | 2.13 |
| 4 | 33.33:1 | 4.72 | 0.60 | 42.17 | 2.40 |
| 5 | 66.66:1 | 2.83 | 0.80 | 50.67 | 2.41 |
| 6 | 66.66:1 | 3.61 | 1.00 | 64.33 | 2.72 |
| $2\text{-C}_4\text{H}_9\text{HgSCN}$ in $\text{NaSCN}-\text{NaClO}_4$, 50 vol % $\text{CH}_3\text{OH}-\text{H}_2\text{O}$. | | | | | |
| 1 | 16.66:1 | 2.71 | 0.00 | 12.83(= S_0) | — |
| 2 | 33.33:1 | 2.04 | 0.20 | 19.42 | 2.57 |
| 3 | 33.33:1 | 2.88 | 0.40 | 27.17 | 2.79 |
| 4 | 33.33:1 | 3.88 | 0.60 | 36.50 | 3.07 |
| 5 | 66.66:1 | 2.47 | 0.80 | 46.83 | 3.31 |
| 6 | 66.66:1 | 3.14 | 1.00 | 59.33 | 3.62 |

^a Dilution with respect to the saturated solution of the sample analyzed polarographically.

polarimeter Perkin-Elmer model 141, using a mercury arc source and a 10 cm cell with quartz windows, which was thermostated at 25°.

The results of a typical experiment are reported in Table 3.

TREATMENT OF DATA

From Table 2 it can be seen that the systems $C_2H_5HgCl-NaCl$ and $C_2H_5HgBr-NaBr$ do not show significant changes in solubility with changes of $NaCl$ and $NaBr$ concentrations. Thus, under these conditions further complex formation is insignificant. However, we cannot exclude the formation of higher ethylmercury-chloride and ethylmercury-bromide complexes, which may well exist for ligand concentrations greater than 1 M. In fact, a noticeable difference in solubility for C_2H_5HgBr in 4 M $NaClO_4$ ($S = 0.66$ mM) and in 4 M $NaBr$ ($S = 1.20$ mM) was observed at 25°.

For the other systems examined, the solubility noticeably increased with the increase of the ligand concentration, showing that formation of the complexes $RHgX_n^{1-n}$ had taken place. The n values and the stability constants were obtained as follows.

The solubility, *i.e.* the total concentration of the chemical species $RHgX_n^{1-n}$, assuming no complexes with n higher than 3, is given by the equation:

$$S = S_0 + [RHgX_2^-] + [RHgX_3^{2-}] \quad (1)$$

in which $S_0 = [RHgX]$, *i.e.*, the solubility of $RHgX$ in 1 M $NaClO_4$, in the absence of ligand. It is assumed that the concentrations of the cationic species, RHg^+ , are negligible even at low ligand concentrations, as would be expected from a consideration of the known high values of K_1 for $RHgX$ compounds.¹

Introducing the stability constants in eqn. (1), and rearranging we get:

$$[(S/S_0) - 1]/[X^-] = K_2 + K_2K_3[X^-] \quad (2)$$

in which K_2 and K_3 are the stepwise stability constants for the complexes $RHgX_2^-$ and $RHgX_3^{2-}$.

Table 3. Optical rotations of a sample of partially resolved (–)-2-butylmercuric thiocyanate in 50 vol % CH_3OH-H_2O at 25°. $C_{NaSCN} + C_{NaClO_4} = 1$ M, wavelength = 364 m μ , cell length 10 cm.

| No. | C_{NaSCN} (M) | C_{RHgSCN} (M) | $\alpha_{obs.}$ (degrees) | $-10\alpha_{obs.}/C_{RHgSCN}$ |
|-----|--------------------|---------------------|------------------------------|-------------------------------|
| 1 | 0.00 | 0.00897 | –0.108 | 120.4 |
| 2 | 0.05 | 0.00897 | +0.112 | 124.9 |
| 3 | 0.10 | 0.00897 | –0.1135 | 126.5 |
| 4 | 0.30 | 0.01345 | –0.178 | 132.3 |
| 5 | 0.50 | 0.01345 | –0.188 | 139.8 |
| 6 | 0.70 | 0.01345 | –0.195 | 145.0 |
| 7 | 0.85 | 0.01345 | –0.201 | 149.4 |
| 8 | 1.00 | 0.02242 | –0.345 | 153.9 |

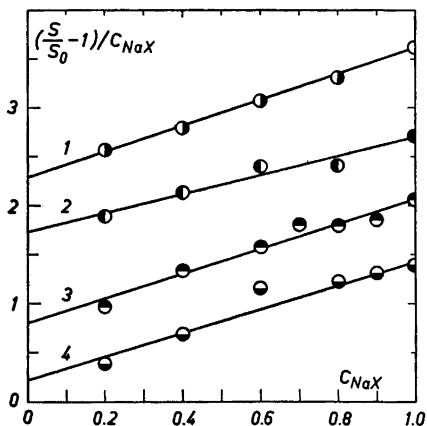


Fig. 1. Solubility plots for RHgX in 1 M mixed solutions of $\text{NaX} + \text{NaClO}_4$ at 25°C : $2\text{-C}_4\text{H}_9\text{HgSCN}$ in 50 vol % CH_3OH 1, $\text{C}_2\text{H}_5\text{HgSCN}$ in 50 vol % CH_3OH 2, $\text{C}_2\text{H}_5\text{HgSCN}$ in water 3, $\text{C}_2\text{H}_5\text{HgI}$ in water 4.

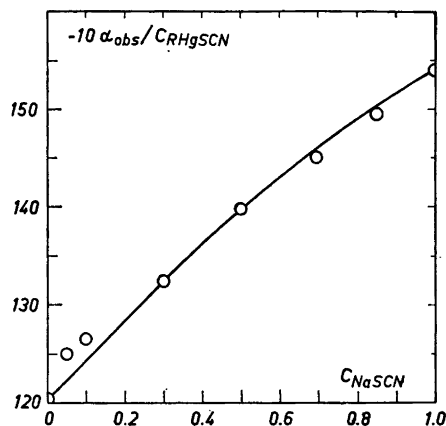


Fig. 2. Plot of the quantity $-10\alpha_{\text{obs.}}/C_{\text{RHgSCN}}$ (given in Table 3) as function of C_{NaSCN} . Experimental points \circ . Solid curve calculated with $K_2 = 2.30$, $K_2K_3 = 1.30$ and the following values for the molecular rotation of the partly resolved complexes $(-)\text{-}2\text{-C}_4\text{H}_9\text{Hg}(\text{SCN})_n^{1-n}$: $[M]_1 = -120.4$, $[M]_2 = -136.1$, $[M]_3 = -211.0$.

As $[\text{X}^-] = C_{\text{NaX}}$ with sufficient approximation (owing to the low solubilities), then a plot of $[(S/S_0)-1]/C_{\text{NaX}}$ versus C_{NaX} should give a straight line, with intercept $= K_2$ and slope $= K_2K_3$.

The plots of $[(S/S_0)-1]/C_{\text{NaX}}$ vs. C_{NaX} for the $\text{RHgSCN}-\text{NaSCN}$ ($\text{R} = \text{C}_2\text{H}_5$ or $2\text{-C}_4\text{H}_9$) and $\text{C}_2\text{H}_5\text{HgI}-\text{NaI}$ systems are shown in Fig. 1. Our assumptions are confirmed by the fact that these plots are straight lines. Thus n in the complexes $\text{C}_2\text{H}_5\text{Hg}(\text{SCN})_n^{1-n}$, $2\text{-C}_4\text{H}_9\text{Hg}(\text{SCN})_n^{1-n}$, $\text{C}_2\text{H}_5\text{HgI}^{1-n}$ ranges from 1 to 3. The stability constants calculated from Fig. 1 are reported in Table 4.

It is noteworthy that the constants for $\text{C}_2\text{H}_5\text{Hg}(\text{SCN})_n^{1-n}$ measured by anion exchange⁴ in aqueous solution at 25° and at varying ionic strength are of the same order of magnitude as those obtained in this work; *i.e.* $K_2 \sim K_3 \sim 1.8$.

The $(-)\text{-}2\text{-C}_4\text{H}_9\text{HgSCN}-\text{SCN}^-$ system was further studied by examining the change of its optical rotation as a function of the concentration of SCN^- . For the visible mercury lines there was only a slight change in the optical rotation with the thiocyanate concentration, but a significant change was found for the mercury line at $364\text{ m}\mu$. The optical rotations measured at this wavelength in a 50 vol % methanol-water solvent are given in Table 3, and in Fig. 2 the quantity $-10\alpha_{\text{obs.}}/C_{\text{RHgSCN}}$ is plotted vs. C_{NaSCN} .

The observed rotation $\alpha_{\text{obs.}}$ measured in a 10 cm cell is related to the molecular rotation of the individual complex species by eqn. (3)

$$10\alpha_{\text{obs.}} = \sum_{n=1}^{n=3} [M]_n [\text{RHg}(\text{SCN})_n^{1-n}] \quad (3)$$

The molecular rotation of a substance could be defined as

$$[M] = \frac{10^2 \alpha_{\text{obs.}}}{C \times l}$$

where C is the molar concentration of the compound and l the cell length in cm. $[M]_1 = -120.4$, the molecular rotation for the partly resolved (–)-2- C_4H_9HgSCN , was obtained from the solution containing no added SCN^- . $[M]_2$ and $[M]_3$ were calculated from eqn. (3) for solutions 5 and 8 (see Table 3) using the values of K_2 and K_3 obtained above. The values obtained were $[M]_2 = -136.1$, and $[M]_3 = -211.0$. Using these values for the molecular rotations and the stability constants, the curve for $-10 \alpha_{\text{obs.}}/C_{RHgSCN}$ vs. C_{NaSCN} was recalculated by means of eqn. (3) and is given by the solid curve in Fig. 2. The good correspondence between the experimental points and the calculated curve provides support for the values of the formation constants obtained by the solubility method.

DISCUSSION

The mercury(II) ion has a very pronounced coordination number of two. For example, for the mercury(II) thiocyanate system,¹¹ $(K_1K_2)^{1/2}$ ($= 10^{8.7}$ l-mole⁻¹) is much greater than $(K_3K_4)^{1/2}$ ($= 10^{1.9}$ l-mole⁻¹).¹² This is also found for the iodide system¹³ for which the corresponding values are $(K_1K_2)^{1/2} = 10^{11.9}$ and $(K_3K_4)^{1/2} = 10^{3.0}$. For the organomercury systems the first ligand is bound strongly. Thus $K_1 = 10^{6.1}$ for methylmercury thiocyanate and $K_1 = 10^{8.7}$ for methylmercury iodide.^{1,2} The strong carbon-mercury σ -bond increases the tendency to linear complex formation,¹⁴ but as shown in this paper, it is possible for two more ligands to coordinate.

It can be seen from Table 4 of this paper that in the alkylmercuric thiocyanate systems in 50 vol % methanol-water mixture, the values K_2 and K_2K_3 are almost the same for ethyl and 2-butyl, showing practically no influence of the change in the aliphatic radical attached to the mercury atom on complex formation.

A comparison of the constants for the $C_2H_5Hg(SCN)_n^{1-n}$ system in aqueous solution and in 50 vol % aqueous methanol shows that, while $K_2K_3 \sim 1$ is

Table 4. Stepwise stability constants of organomercury(II) thiocyanate and iodide complexes at 25° and at a total electrolyte ($NaX + NaClO_4$) concentration = 1 M, obtained by the solubility method.

| Compound | Solvent | K_2 | K_2K_3 | K_3 |
|----------------------------|------------------------|-------|----------|-------|
| $C_2H_5Hg(SCN)_n^{1-n}$ | H_2O , pH = 3 | 0.80 | 1.27 | 1.59 |
| $C_2H_5Hg(SCN)_n^{1-n}$ | 50 vol % CH_3OH-H_2O | 1.73 | 0.97 | 0.56 |
| 2- $C_4H_9Hg(SCN)_n^{1-n}$ | 50 vol % CH_3OH-H_2O | 2.30 | 1.30 | 0.565 |
| $C_2H_5HgI_n^{1-n}$ | H_2O , pH = 3 | 0.215 | 1.21 | 5.63 |

almost the same in both cases, K_2 is higher in the methanol-water solution, and that in this solvent $K_2 > K_3$, while the contrary is true in the aqueous solution. The latter seems to be a typical behaviour of these complex systems in water, as $K_3 > K_2$ also for the $C_2H_5HgI_n^{1-n}$ complexes in aqueous solution.

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