Structure and Properties of Thallium(I) Formate Solutions

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The structure of thallium(I) formate aggregates in concentrated aqueous thallium(I) formate solutions was investigated by the X-ray diffraction method at 25 °C for solutions A (10.77 mol dm^{-3}) and B (3.493 mol dm^{-3}). The former solution had the density of 3.189 g cm^{-3} and the C_{H_2O}/C_{Tl} mole ratio of 2.59, where C_i represents the total concentration of species i, and was an almost saturated solution at room temperature. From the analysis of the X-ray diffraction data of solution A, thallium(I) formate was found to be present as a tetramer $Tl_4(O_2CH)_4$. The nearest interatomic distances between thallium(I) and atoms within the formate ions in the tetramer were determined as Tl–O: 2.79(1) Å and Tl···C: 3.33(2) Å. The nonbonding Tl···Tl distances within the aggregate were estimated to be 3.92(1) Å, 4.34(1) Å, and 4.79(1) Å. The Tl–OH_2 bond length was also determined to be 3.22(3) Å, which was much larger than the distance expected from the sum of the ionic radius of thallium(I) ion (≈1.4 Å) and size of a water molecule (≈1.4 Å). A comparison of the radial distribution function of solution A with that of solution B, which had the C_{H_2O}/C_{Tl} mole ratio of 13.5, indicated that the aggregate decomposed by dilution. Raman spectra of four different thallium(I) formate aqueous solutions of 3.493 to 10.77 mol dm^{-3} were measured and the frequencies of the C–O and C=O stretchings of formate ions in the solutions were compared with those of free formate ion. Band shifts of the two frequencies observed for concentrated thallium(I) formate solutions indicated the existence of bridge-type formate ions coordinated to thallium(I) ions, and the result agreed with that observed by the X-ray diffraction analysis. Densities, refractive indices, viscosities and conductivities were measured for thallium(I) formate aqueous solutions with varying concentrations.

It has been well known that some thallium(I) carboxylates are extremely soluble in water. Densities of concentrated solutions become 2—4 g cm^{-3} and thus the solutions can be used as heavy liquids for gravity concentrations of ores. The solutions also have large absorptivity for high energy beams and good transparency for visible light. Therefore, applications of the solutions to transparent shields for radiation instead of lead glasses have been examined.[1–3] Mixtures of thallium(I) carboxylates and organic scintillators may provide useful detectors of radiation beams. In this connection it is interesting to investigate structures and properties of thallium(I) carboxylate solutions.

Another interest of the structural study of concentrated solutions of thallium(I) carboxylates is concerned with an investigation in which structures of crystal hydrates are compared with those of hydrate melts. It has often been reported that a part of the structure of a crystal hydrate still remains in a concentrated solution of the salt. X-Ray diffraction data of hydrate melts of $CaCl_2\cdot 6H_2O$[4] and $Ca(NO_3)_2\cdot 3.5H_2O$[5] have been interpreted in terms of a quasi-lattice structure of the corresponding crystal hydrates. Structures of concentrated solutions of magnesium, aluminium and indium(III) with monovalent anions have been studied by means of X-ray diffraction and the liquid structure has been approximated to a quasi-close-packing lattice structure of hydrated cations.[6,7] Enderby and his coworkers' studies[8–10] on the structure of nickel(II) chloride solutions by the neutron diffraction method have suggested a quasi-lattice arrangement of hydrated nickel(II) ions in the solutions.

In the present investigation we focus our attension on the structure of thallium(I) formate aggregates formed in solution and changes in physicochemical properties of thallium(I) formate solutions with the concentration of the solute.

The crystal structure of thallium(I) formate has recently been determined by Oddon *et al.*[11] and has been found that a formate ion bridges two thallium atoms as a bidentate ligand through the two oxygen atoms and infinite -HCOO-Tl-HCOO-Tl- chains are formed in crystal. A thallium(I) ion is surrounded with four oxygen atoms within formate ions, the Tl–O distances being 2.559, 2.565, 2.736, and 3.047 Å. The coordination polyhedron of the thallium(I) ion is trigonal bipyramidal with the thallium(I) ion at one apex of the equatorial triangle plane.

The X-ray diffraction method is employed in the present work for the structural determination of thallium(I) formate complexes in solution. Raman spectroscopic measurements are also carried out as a supplement to the X-ray structural analysis. Densities, refractive indices, viscosities and conductivities of thallium(I) formate solutions with varying concentrations are measured.

Experimental

Preparation and Analysis of Sample Solutions. Two kinds of test solutions (A and B) were prepared for X-ray diffraction measurements by dissolving thallium(I) formate of reagent grade in water. Solution A was an almost saturated solution of thallium(I) formate at room temperature, while solution B was about three times more dilute than solution A. Concentrations of thallium(I) ions in the solutions were determined by gravimetry as TlI. Concentrations of formate ions were estimated from the stoichiometry of thallium(I) formate. The composition of the sample solutions is listed in Table 1. Solutions used for measurements of Raman spectra, densities, refractive indices, viscosities and conductivities were prepared by diluting a stock solution of thallium(I) formate with water.

X-Ray Scattering Measurements. X-Ray scattering data were obtained at 25 °C with a JEOL θ–θ type diffractometer equipped with a Philips Mo X-ray tube (λ=0.7107 Å).

TABLE 1. THE COMPOSITION (mol dm^{-3}) AND STOICHIOMETRIC VOLUME V PER THALLIUM ATOM IN THE SOLUTIONS

	A	B
Tl	10.77	3.493
O	49.47	54.11
C	10.77	3.493
H	66.63	97.73
V/Å^3	154.2	475.4
C_{H_2O}/C_{Tl}	2.59	13.5
density/g cm^{-3}	3.189	1.720

The method of measurements and data treatments were described elsewhere.[12,13] The measured scattering angle (2θ) ranged from 2° to 140°. Times requiring to accumulate 80000 counts were recorded at each angle of 2θ. All calculations were carried out by using programs KURVLR[14] and NLPLSQ.[15]

Raman Spectroscopic Measurements. Raman spectroscopic measurements were performed by using a JEOL JPG-400D spectrometer with the use of the 5145 Å excited line of Ar$^+$ laser.

Measurements of Physicochemical Properties. Densities of thallium(I) formate solutions were measured pycnometrically. Two pycnometers were used for the measurements and the results agreed each other within 0.05%. Measurements of viscosities of solutions were carried out by using an Ubbelohde-type viscometer and water was employed as the standard. The efflux time was measured with a stop watch. Conductivities of solutions were measured by a direct current method. A conductivity cell and electrical circuits used for the measurements were essentially the same as those designed in the literature.[16] A current-supplying electrode was a platinum electrode and a TOA-type HC-205 calomel electrode was employed to measure voltage drops. The reproducibility of the conductivity measurements was within 0.3%. The temperature was kept at (25.00±0.03) °C in all the physicochemical measurements. An Atago NAR-3 Abbe-type refractometer was employed to refractive index measurements of solutions with the use of the NaD line (5893 Å). The temperature for the refractive index measurements was regulated at (25.0±0.1) °C by circulating thermostated water through the refractometer.

Results and Discussion

The observed $s \cdot i(s)$ and $(D(r)-4\pi r^2(\rho_0)$ curves, where ρ_0 denotes the average scattering density in the stoichiometric volume V per thallium atom, of the test solutions are shown in Figs. 1 and 2, respectively.

The structure of formate ion in crystal has been determined for various formates with monovalent cations. The intramolecular bond distances of a formate ion in the thallium(I) salt[11] do not appreciably differ from those in lithium,[17] sodium,[18] potassium[19] and ammonium formates.[20] Therefore, in the course of the analysis of the radial distribution functions of solutions A and B, the intramolecular bond lengths of formate ion were assumed to be the same as those in the

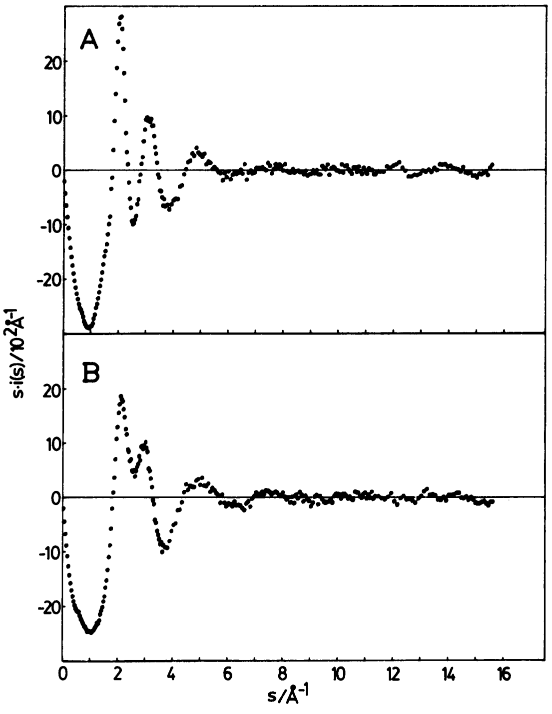

Fig. 1. The reduced intensities multiplied by s for solutions A and B.

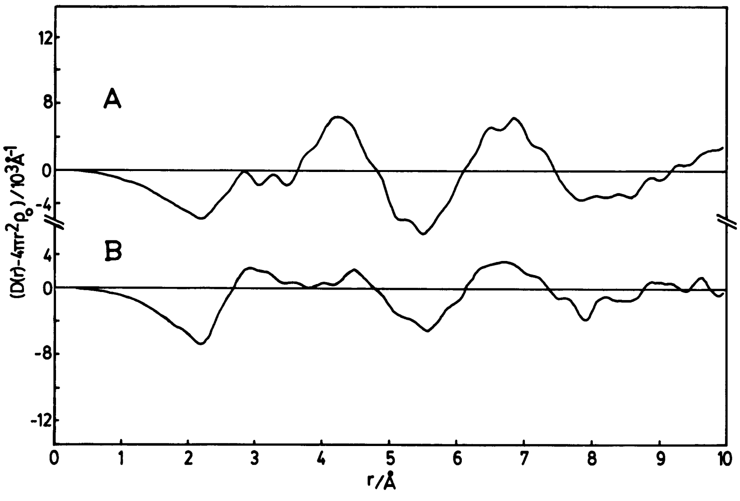

Fig. 2. The $(D(r)-4\pi r^2\rho_0)$ curves for solutions A and B.

thallium(I) formate crystal.[11] The temperature factors of atom-pairs within formate ion were taken from the electron diffraction data of the formic acid monomer in the gas phase.[21]

Structure of Thallium(I) Formate Aggregates in Solution A. The $s\cdot i(s)$ curve of solution A showed a sharper peak at 2.1 Å^{-1} and a deeper minimum at 2.5 Å^{-1} than the curve of solution B (see Fig. 1), and the radial distribution curve of solution A (Fig. 2) had a large and broad peak around 4.3 Å, which was not observed in the radial distribution curve of solution B.

The broad peak around 1.2 Å was composed of peaks owing to the O–H bonds within water molecules and the C–H and C$\overset{\cdots}{-}$O bonds within formate ions. The second peak appearing at about 2.8 Å could be ascribed to the Tl–O bonds as was expected from the sum of their ionic radii. The hydrogen bonded O$\cdots$O interactions within bulk water might contribute to the peak, but the contribution should be so small in such a concentrated thallium(I) formate solution that the O$\cdots$O peak might be neglected in the course of the analysis of the radial distribution curve. The area of the peak gave the frequency factor of 3 for the Tl–O bond. If a thallium atom was combined with three formate ions, the nonbonding Tl$\cdots$C distance should appear at about 3.2 Å. Therefore, the third peak observed at about 3.2 Å in Fig. 2 was attributed to be mainly due to the Tl$\cdots$C distance within the thallium(I) formate aggregate.

The fourth peak around 4.3 Å was considered to be constructed by, at least, three peaks, because the broad peak had shoulders at both sides of the maximum. The large area of the peak could not well be explained in terms of the nonbonding Tl$\cdots$O interactions and was only explainable by the existence of Tl$\cdots$Tl interactions in the aggregate. By the trial-and-error method the peak could be divided into three peaks centered at 3.9, 4.4, and 4.8 Å, and the frequency factors of each peak corresponded to 0.5 (Tl$\cdots$Tl) pairs, which indicated that each thallium(I) ion in the aggregate interacted with three thallium(I) ions with different distances (Fig. 3).

On the basis of the analysis of the radial distribution curve of solution A, calculated intensities and radial distribution curves drawn from model structures of various thallium(I) formate aggregates were compared with the experimental values. A dimer or a trimer structure was not acceptable because of their too small frequency factors for Tl$\cdots$C and Tl$\cdots$Tl interactions, and the area of the peak around 4.3 Å calculated by assuming a pentamer or a hexamer was too large compared with the peak area obtained by the experiment. The tetramer model depicted in Fig. 4 gave calculated intensities which satisfactorily agreed with observed ones over the s-range of 2—16 Å^{-1} (see Fig. 5). The radial distribution curve drawn on the basis of the structural model thus proposed well explained the large peak found at 3.5—5 Å with two shoulders at the both side of the peak as seen in Fig. 3.

The least-squares method was applied to the $s\cdot i(s)$ curve for the refinement of the structural parameters of the tetramer by taking into account the formation of Tl–OH$_2$ bonds at each thallium(I) ion. The refinement was carried out over the range $s \geq 2.5$ Å^{-1}. All the

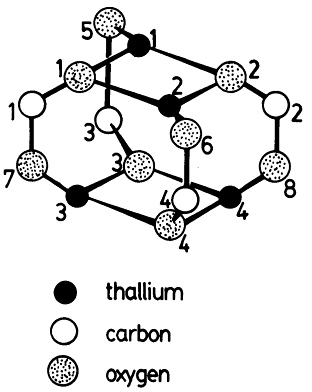

Fig. 4. The structure of Tl$_4$(O$_2$CH)$_4$ complex in solution.

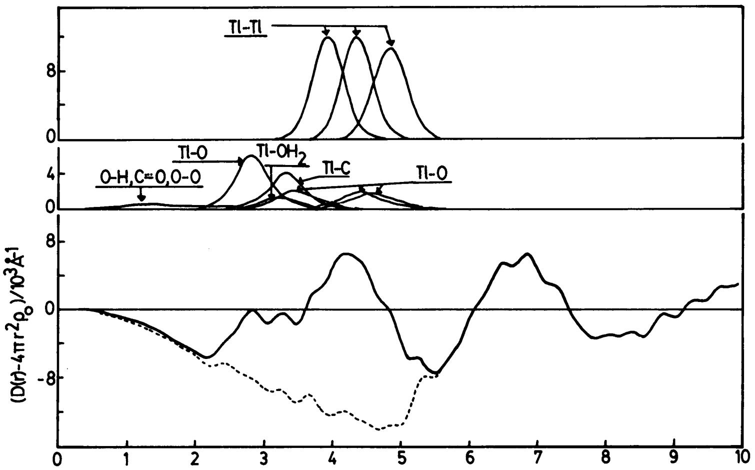

Fig. 3. The $(D(r)-4\pi r^2\rho_0)$ curve for solution A. The dashed line represents the residual curve after subtraction of the theoretical peaks calculated for the O–H bond within water molecule, C–H, C$\cdots$O, and O$\cdots$O pairs within formate ion and Tl–O, Tl–OH$_2$, Tl$\cdots$C, Tl$\cdots$O, and Tl$\cdots$Tl interactions within Tl$_4$(O$_2$CH)$_4$.

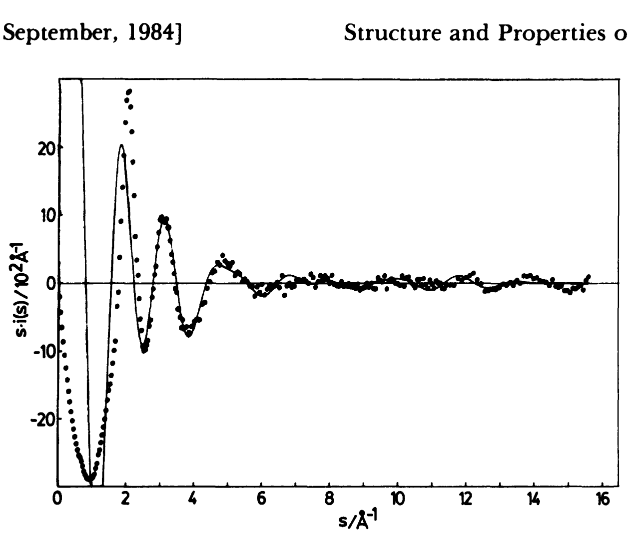

Fig. 5. The $s \cdot i(s)$ values for solution A. The observed curve is shown by circles and calculated one by the solid line.

interatomic distances and temperature factors were floated as independent variables. Frequency factors of atom-pairs within the model were fixed at values estimated from the model, except for the frequency factor for the Tl-OH_2 bonds. The agreement between calculated and experimental $s \cdot i(s)$ values was sufficient in the range $s \geqq 2.5$ Å^{-1} (Fig. 5). The frequency factor for the Tl-OH_2 bond was estimated to be 0.7, which suggested that one water molecule combined with each thallium(I) ion in the tetramer, and therefore, the thallium(I) ion has the coordination number of 4. However, the Tl-OH_2 bond distance was much larger than the distance expected from the sum of the ionic radius of thallium(I) ion (≈1.4 Å) and the size of a water molecule (≈1.4 Å), the result suggesting a weak interaction between a thallium(I) ion and a water molecule.

In crystal of thallium(I) formate, the coordination number of the thallium(I) ion is four, and the thallium(I) ion is located at a corner of a triangle plane which is constructed with two oxygen and one thallium atoms, and other two oxygen atoms are situated above and below the plane. The model derived from the structure in the crystal did not give $s \cdot i(s)$ values which sufficiently fitted the experimental values.

The structural parameters finally obtained for the tetramer are listed in Table 2.

Structure of Solution B. The radial distribution curve of solution B did not give the large peak which had been observed in solution A, and therefore, the result showed that the thallium(I) formate tetramer did not exist as the predominant species in solution B and the aggregate decomposed by dilution. An asymmetrical peak at about 2.8 Å suggested the formation of bonds between thallium(I) and oxygen atoms in the solution, but the radial distribution curve was not explainable by assuming the formation of a simple 1:1 complex between thallium(I) and formate ions. In solution B there might be some complexes coexisting, but the radial distribution curve could not be analyzed without knowledge of formation constants for thallium(I) formate complexes, which had not been found in the literature. The conclusion which we can derive from the radial distribution curve is that the thallium(I) formate tetramer is not a predominant form in a relatively dilute solution, but can be the main species in a solution of extremely high concentration.

Raman Spectra. In Table 3 are summarized frequencies for vibrations found in Raman spectra of aqueous thallium(I) formate solutions of 3.493, 5.924, 8.528, and 10.77 mol dm^{-3}, as well as those observed in Raman and infrared spectra of thallium(I) formate crystal[11,22] and an aqueous potassium formate solution.[23]

Coordination types of carboxylato groups within complexes have been discussed on the basis of the change in the frequencies of the C–O ($\tilde{\nu}_2$) and C=O ($\tilde{\nu}_4$) stretching vibrations in the complexes by comparing with those in free carboxylate ions.[24] When a carboxylate ion coordinates to a metal ion as a unidentate ligand, $\tilde{\nu}$(C–O) and $\tilde{\nu}$(C=O) shift to lower and higher frequencies, respectively, than those in free ion. Thus the separation ($\Delta\tilde{\nu}$) between the two frequencies in the unidentate complexes becomes about 300—350 cm^{-1}, which is much larger than that in free ion (230—250 cm^{-1}). In the case of the formation of chelate complexes in which carboxylate ions coordinate to metal ions as a bidentate ligand, the $\tilde{\nu}$(C–O) band shifts toward the higher frequency side, while the $\tilde{\nu}$(C=O) band shifts toward the lower side, and

TABLE 2. RESULTS OF THE LEAST-SQUARES REFINEMENTS OF SOLUTION A

Parameter values refined were bond distances(r), temperature factors(b), and frequency factors(n).

Interaction	$2.5<s/Å^{-1}<15.0$			$4.5<s/Å^{-1}<15.0$		
	r/Å	b/Å^2	n	r/Å	b/Å^2	n
Tl_1-O_1	2.81(1)	0.007(1)	3.0[a]	2.79(1)	0.008(1)	3.0[a]
Tl···C_1	3.31(2)	0.008(1)	3.0[a]	3.33(2)	0.009(1)	3.0[a]
Tl_1···O_8	3.43(4)	0.008(2)	1.0[a]	3.50(4)	0.009(2)	1.0[a]
Tl_1···Tl_2	3.92(1)	0.015(1)	0.5[a]	3.92(1)	0.014(1)	0.5[a]
Tl_1···Tl_3	4.35(1)	0.015(1)	0.5[a]	4.34(1)	0.015(1)	0.5[a]
Tl_1···O_3	4.39(7)	0.013(4)	1.0[a]	4.31(7)	0.009(4)	1.0[a]
Tl_1···O_7	4.53(8)	0.019(5)	1.0[a]	4.34(8)	0.010(5)	1.0[a]
Tl_1···Tl_4	4.83(1)	0.021(1)	0.5[a]	4.79(1)	0.021(1)	0.5[a]
Tl_1-OH_2	3.18(3)	0.011(4)	0.7(2)	3.22(3)	0.014(5)	0.8(2)

a) The values were kept constant during the calculation.

TABLE 3. RAMAN AND INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF FORMATE ION[a]

	Thallium(I) Formate						Potassium Formate Solution[e]
	Solution/mol dm^{-3}				Crystal		
	3.493	5.924	8.528	10.77	(I)[c]	(II)[d]	
$\tilde{\nu}_1$	2828	2821	2815	2810	2786	2775	2803
$\tilde{\nu}_2$	1356	1350	1350	1347	1351 1333	1342	1351
$\tilde{\nu}_3$	768	769	772	765	758	759	760
$\tilde{\nu}_4$	1573	1567	1564	1562	1590	1572 1606	1585
$\tilde{\nu}_5$	1388	1379	1382	1379	1387 1406	1357	1383
$\tilde{\nu}_6$	1070	1067	1064	1064	—	—	1069
$\Delta\tilde{\nu}$[b]	217	217	214	215	(248)		234

a) $\tilde{\nu}_1$: C-H stretching, $\tilde{\nu}_2$: Symmetric OCO stretching, $\tilde{\nu}_3$: Symmetric OCO deformation, $\tilde{\nu}_4$: Asymmetric OCO stretching, $\tilde{\nu}_5$: Asymmetric OCO deformation, $\tilde{\nu}_6$: Out-of-Plane deformation. b) $\Delta\tilde{\nu}$ represents the separation between $\tilde{\nu}_2$ and $\tilde{\nu}_4$. c) Ref. 24. d) Ref. 11. e) Ref. 25.

therefore, the $\Delta\tilde{\nu}$ value becomes smaller by 70—100 cm^{-1} than that of free carboxylate ions. In the bridge-type coordination, on the other hand, the values of the $\tilde{\nu}$(C-O) and $\tilde{\nu}$(C=O) frequencies do not appreciably differ from those in free carboxylate ions and thus the $\Delta\tilde{\nu}$ value remains in the region 200—250 cm^{-1}.

As seen from Table 3, the frequencies of the C-O and C=O stretchings for the thallium(I) formate complex in the solutions are about 1350 and 1570 cm^{-1}, respectively, and the $\Delta\tilde{\nu}$ value is 214—217 cm^{-1}. Therefore, we concluded that the formate ions within the complex existing in the solutions coordinate to thallium(I) ion with the bridge-type. The conclusion derived from the Raman spectra supports the result obtained in the X-ray diffraction measurement.

Physicochemical Properties of Thallium(I) Formate Solutions. Densities ρ and refractive indices n_D measured in thallium(I) formate solutions with varying concentrations are plotted against the concentration (Fig. 6). The plots gave almost straight lines over a wide range of concentration, and no clear indication was obtained for the complex formation between thallium(I) and formate ions beginning at a specific concentration of the solute.

In Fig. 7 are shown absolute viscosities η, specific viscosities η_{SP}, and kinematic viscosities ν of thallium(I) formate solutions as a function of the concentration of the solute. The absolute and specific viscosities monotonously increased with the concentration of thallium(I) formate. However, the kinematic viscosity of the solution first decreased and then increased with the concentration. The kinematic viscosity of thallium(I) formate solution was lower than that of water even in 9 mol dm^{-3} thallium(I) formate solution.

The specific conductivity κ of thallium(I) formate solutions had a broad maximum around 7 mol dm^{-3}, although the molar conductivity Λ of the solutions monotonouly decreased with the concentration (Fig. 8). The Walden products $\Lambda\eta$ of thallium(I) formate solutions are plotted against the concentration in Fig. 9. Walden products of lithium nitrate[25] and chlorate[26] solutions, in which the cation is highly hydrated and thus no contact ion-pair formation is expected, decreased and then increased after passing through a minimum at about 8 mol dm^{-3}. Silver nitrate, which was known to form the contact ion-pair in concentrated solutions,[27] had the Walden product which had a minimum at about 4 mol dm^{-3}.[28] The values of the

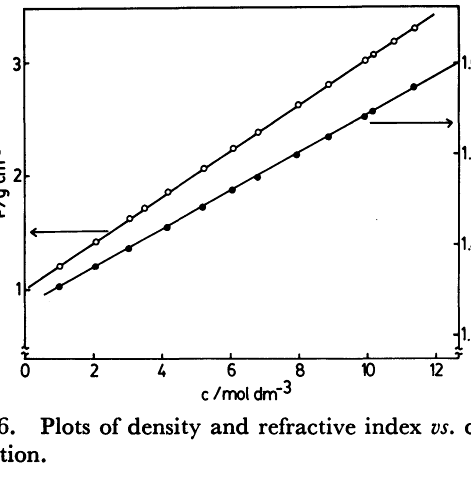

Fig. 6. Plots of density and refractive index *vs.* concentration.

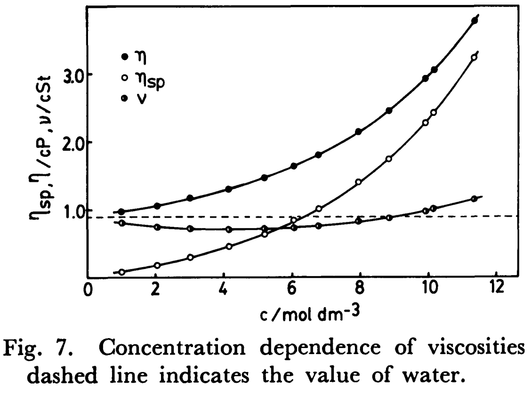

Fig. 7. Concentration dependence of viscosities. The dashed line indicates the value of water.

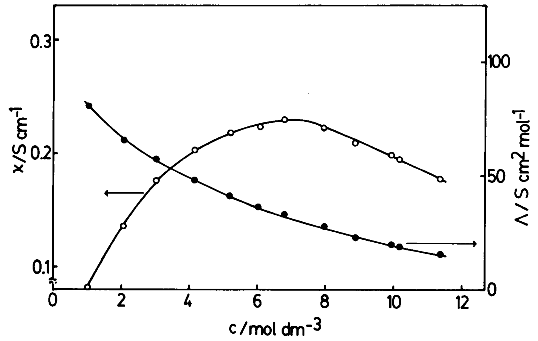

Fig. 8. Concentration dependence of conductivities.

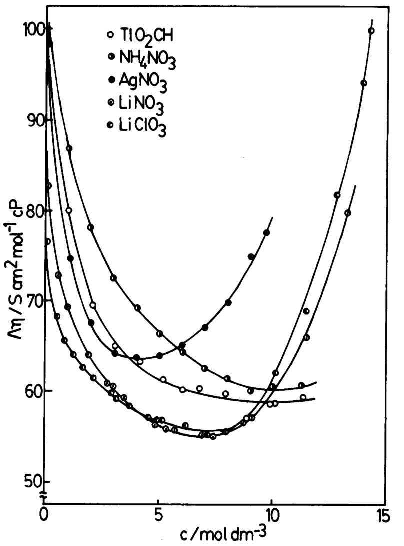

Fig. 9. Walden products of thalluim(I) formate, ammonium nitrate, silver nitrate, lithium nitrate, and lithium chlorate solutions.

Walden products of ammonium nitrate[28] and thallium(I) formate simply decreased with the concentration. It is still not clear what the minimum of the Walden product indicates, and no reliable theory has been proposed for explaining physicochemical properties in concentrated aqueous solutions. Therefore, it is not conclusive from the measurements of the physicochemical properties at which concentration thallium(I) formate begins to form the aggregates. Probably the aggregates gradually form with the increase in the concentration of the solute, and they may exist to some extent, besides mononucleic thallium(I) formate complex, even in a solution of relatively low concentration of the solute.

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References

1) A. Kusumegi, K. Kondo, Y. Watase, Y. Yoshimura, and K. Miyake, *Nucl. Instrum. Methods*, **185**, 83 (1981).

2) A. Kusumegi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **60**, 234 (1982).

3) A. Kusumegi, K. Kondo, Y. Watase, Y. Yoshimura, K. Miyake, Y. Hemmi, J. Haba, and K. Hara, *Nucl. Instrum. Methods*, **196**, 231 (1982).

4) G. Licheri, G. Piccaluga, and G. Pinna, *J. Am. Chem. Soc.*, **101**, 5438 (1979).

5) R. Caminiti, A. Musinu, G. Paschina, G. Piccaluga, and G. Pinna, *Z. Naturforsch., A*, **36**, 831 (1981).

6) M. A. Marques and M. I. D. B. Marques, *Proc. K. Ned. Akad. Wetensch. Ser. B*, **77**, 286 (1974).

7) M. I. D. B. Marques, M. I. Cabaço, M. A. S. Oliveira, and M. A. Marques, *Chem. Phys. Lett.*, **91**, 222 (1982).

8) R. A. Howe, W. S. Howells, and J. E. Enderby, *J. Phys. Chem.*, **7**, L111 (1974).

9) G. W. Neilson, R. A. Howe, and J. E. Enderby, *Chem. Phys. Lett.*, **33**, 284 (1975).

10) J. E. Enderby, *Proc. R. Soc. London, Ser. A*, **345**, 101 (1975).

11) Y. Oddon, A. Tranquard, and B. F. Mentzen, *Inorg. Chim. Acta*, **48**, 129 (1981).

12) H. Ohtaki, M. Maeda, and S. Ito, *Bull. Chem. Soc. Jpn.*, **47**, 2217 (1974).

13) H. Ohtaki, T. Yamaguchi, and M. Maeda, *Bull. Chem. Soc. Jpn.*, **49**, 701 (1976).

14) G. Johansson and M. Sandström, *Chem. Scr.*, **4**, 195 (1973).

15) T. Yamaguchi, Doctor Thesis, Tokyo Institute of Technology, March (1978).

16) L. A. King and F. R. Duke, *J. Electrochem. Soc.*, **111**, 712 (1964); F. R. Duke and L. Bissell, *ibid.*, **111**, 717 (1964).

17) A. Enders-Beumer and S. Harkema, *Acta Crystallogr., Sect. B*, **29**, 622 (1973).

18) W. H. Zachariasen, *J. Am. Chem. Soc.*, **62**, 1011 (1940); P. L. Markila, S. J. Rettig, and J. Trotter, *Acta Crystallogr., Sect. B*, **31**, 2927 (1975).

19) J. W. Bats and H. Fuess, *Acta Crystallogr, Sect. B*, **36**, 1940, (1980); B. F. Mentzen and Y. Oddon, *Inorg. Chim. Acta*, **43**, 237 (1980).

20) I. Nahringbauer, *Acta Crystallogr., Sect. B*, **24**, 565 (1968).

21) I. L. Karle and J. Karle, *J. Chem. Phys.*, **22**, 43 (1954).

22) J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Spectrochim. Acta*, **20**, 847 (1964).

23) K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

24) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Wiley, New York (1978), p. 230; J. D. Donaldson, J. F. Knifton, and S. D. Ross, *Specrochim. Acta*, **21**, 1043 (1965).

25) A. N. Campbell, G. H. Debus, and E. M. Kartzmark, *Can. J. Chem.*, **33**, 1508 (1955).

26) A. N. Campbell and W. G. Paterson, *Can. J. Chem.*, **36**, 1004 (1958).

27) T. Yamaguchi, G. Johansson, B. Holmberg, M. Maeda, and H. Ohtaki, *Acta Chem. Scand.*, in press.

28) A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.*, **33**, 887 (1955).