

67. *Addition Compounds of Gallium Tribromide with Pyridine and Piperidine.*

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Gallium tribromide forms 1:1 addition compounds with pyridine and piperidine, but no evidence was obtained for 1:2 complexes such as exist in the corresponding systems with gallium trichloride. Gallium tribromide-pyridine melts at 126° and gallium tribromide-piperidine at 139°. The densities, surface tensions, viscosities, and conductivities were measured over a range of temperature and the activation energies, Eötvös constants, and parachors were calculated. The product of the molar conductivity and viscosity is almost independent of temperature and indicates that the molten compounds are about 2% dissociated into ions.

RECENT work ¹ has shown that gallium trichloride forms a variety of addition compounds with inorganic and organic ligands, and the properties of these compounds have been compared with those of complexes with related electron-acceptors, particularly boron trichloride.² The effect of replacing chlorine by bromine has been less studied though it

¹ Greenwood, *J. Inorg. Nuclear Chem.*, 1958, **8**, 234, and references therein.

² Greenwood and Wade, *J.*, in the press.

is known³ that gallium tribromide-phosphorus oxybromide closely resembles gallium trichloride-phosphorus oxychloride. To see whether this similarity was a general feature of gallium trihalide complexes it was decided to investigate the properties of the systems which gallium tribromide forms with typical organic ligands, and pyridine and piperidine were selected.

RESULTS

The preparation of gallium tribromide⁴ and the purification of the ligands^{5,6} have previously been described. The experimental methods used to determine density, surface tension, viscosity, and conductivity have also been published in earlier papers from this laboratory.

Gallium Tribromide-Pyridine.—A partial phase diagram of the system was obtained by making up about 20 mixtures of differing compositions, sealing these into small tubes under vacuum, and then heating the samples at the rate of 1° per 10 min. until they melted. The results, shown in Fig. 1, indicate the presence of a stable 1:1 addition compound, m. p. 126° ($\text{GaCl}_3, \text{C}_5\text{H}_5\text{N}$ has an identical m. p.).⁵ The first eutectic occurs at -1° (24 moles % of pyridine),

FIG. 1. System $\text{GaBr}_3\text{-C}_5\text{H}_5\text{N}$.

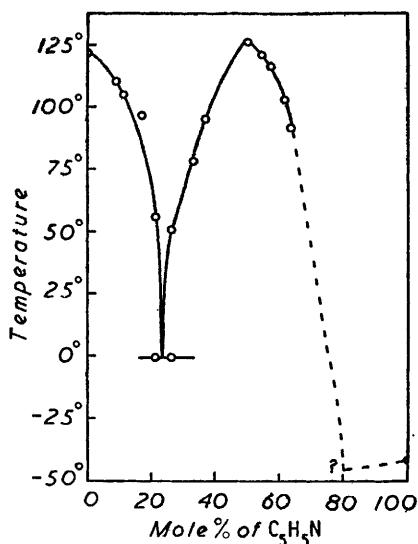
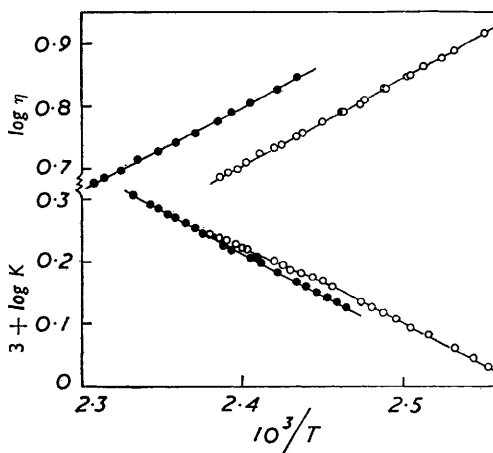


FIG. 2. Conductivity and viscosity of fused $\text{GaBr}_3, \text{C}_5\text{H}_5\text{N}$ (○) and $\text{GaBr}_3, \text{C}_5\text{H}_{10}\text{NH}$ (●).



but the second could not be determined because of a tendency for the mixtures to supercool and resolidify above 65 mole % of pyridine. There was no indication of a 1:2 complex at 66.7 moles % of pyridine or of a eutectic between this composition and the 1:1 complex at 50 moles %.

The specific conductivity of fused gallium tribromide-pyridine at 1000 cycles sec^{-1} did not vary with time and was reproducible in the temperature range studied (118–147°). The results, plotted in Fig. 2, fall on a curve having two almost linear limbs, corresponding to activation energies of 6.01 kcal. mole^{-1} below 135° and 4.58 kcal. mole^{-1} above this temperature. The corresponding value for the gallium trichloride complex⁵ is 4.16 kcal. mole^{-1} . Interpolated values at 5° intervals are summarized in Table 1. At the m. p., 126°, the specific conductivity, κ (compared with that of $\text{GaCl}_3, \text{C}_5\text{H}_5\text{N}$ at the same temperature,⁵ in parenthesis) is 1.242×10^{-3} (2.725×10^{-3}) $\text{ohm}^{-1} \text{cm}^{-1}$. The molar conductivity, μ , is 0.2165 (0.4472) $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$, and the reduced conductivity, $\mu\eta$, is 1.531 (1.077) $\text{cm}^2 \text{cp ohm}^{-1} \text{mole}^{-1}$.

Viscosity results in the temperature range 119–146° were reproducible over a period of days and are shown in Fig. 2. Efflux times varied from 120 to 200 sec. The activation energy for viscous flow was 6.41 (4.47) kcal. mole^{-1} , and at the m. p. the dynamic viscosity was 7.090 cp

³ Greenwood and Worrall, *J. Inorg. Nuclear Chem.*, 1958, **6**, 34.

⁴ *Idem, ibid.*, 1957, **3**, 357.

⁵ Greenwood and Wade, *J.*, 1958, 1663.

⁶ *Idem, J.*, 1958, 1671.

(compared with 2.408 cp for $\text{GaCl}_3 \cdot \text{C}_5\text{H}_5\text{N}^5$). Interpolated values of the viscosity at 5° intervals are incorporated in Table 1.

The density of gallium tribromide-pyridine in the range $118\text{--}155^\circ$ can be represented (± 0.0006) by the equation

$$d_4^t = 2.2368 - 1.29 \times 10^{-3}(t - 120) \text{ g. ml.}^{-1}$$

This corresponds to a density of $2.2291 \text{ g. ml.}^{-1}$ and a molar volume of $174.32 \text{ ml. mole}^{-1}$ at the m. p.

TABLE 1. *Properties of molten* $\text{GaBr}_3 \cdot \text{C}_5\text{H}_5\text{N}$.

Temp.	d_4^t (g. ml. ⁻¹)	η (cp)	$10^3\kappa$ (ohm ⁻¹ cm. ⁻¹)	μ (cm. ² ohm ⁻¹ mole ⁻¹)	$\mu\eta$ (cm. ² cp ohm ⁻¹ mole ⁻¹)
120°	2.2366	8.048	1.109	0.1931	1.549
125	2.2299	7.260	1.222	0.2129	1.536
130	2.2224	6.475	1.338	0.2337	1.523
135	2.2162	5.914	1.465	0.2567	1.519
140	2.2108	5.386	1.589	0.2792	1.497
145	2.2051	4.920	1.709	0.3012	1.479

The surface tension was determined approximately by noting the difference in height of the menisci in the two limbs of the dilatometer. Its variation with temperature (± 0.9 dyne cm.⁻¹) is given by the equation

$$\gamma = 43.5 - 0.15(t - 120) \text{ dynes cm.}^{-1}$$

The corresponding equation for the molar surface free energy ($\omega = \gamma V_M^{\frac{2}{3}}$) is

$$\omega = 1364 - 4.91(t - 120) \text{ ergs mole}^{-\frac{2}{3}}$$

The Eötvös constant has the rather high value of $4.91 \text{ ergs mole}^{-\frac{2}{3}} \text{ deg.}^{-1}$ (2.34 for $\text{GaCl}_3 \cdot \text{C}_5\text{H}_5\text{N}^5$). The parachor was independent of temperature, thus providing a check on the quality of the surface-tension measurements, and had a mean value of 442.4 ± 2.5 . The value calculated for the structure $\text{C}_5\text{H}_5\text{N} \rightarrow \text{GaBr}_3$ is 432.5 .

Gallium Tribromide-Piperidine.—The phase diagram of the system was not investigated, but the m. p. of the 1 : 1 compound was $139\text{--}141^\circ$ (cf. piperidine $^6 - 10.4^\circ$, gallium tribromide $^4 122.5^\circ$, and $\text{GaCl}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$ 134° ⁶). The properties of this complex were determined and are shown in Fig. 2 and Table 2. The specific conductivity was measured between 133° and 156° , and at 139° was 1.503×10^{-3} (1.969×10^{-3}) ohm⁻¹ cm.⁻¹ (values in parentheses refer to $\text{GaCl}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$ at its m. p.⁶). The molar conductivity is 0.2821 (0.346) cm.² ohm⁻¹ mole⁻¹, and the reduced conductivity 1.931 (1.63) cm.² cp ohm⁻¹ mole⁻¹. The plot of $\log \kappa$ is linear and leads to an activation energy of 6.58 (5.61) kcal. mole⁻¹.

TABLE 2. *Properties of molten* $\text{GaBr}_3 \cdot \text{C}_5\text{H}_{10}\text{NH}$.

Temp.	d_4^t (g. ml. ⁻¹)	η (cp)	$10^3\kappa$ (ohm ⁻¹ cm. ⁻¹)	μ (cm. ² ohm ⁻¹ mole ⁻¹)	$\mu\eta$ (cm. ² cp ohm ⁻¹ mole ⁻¹)
135	2.1104	7.347	1.389	0.2597	1.908
140	2.1043	6.714	1.533	0.2875	1.930
145	2.0970	6.156	1.676	0.3152	1.930
150	2.0910	5.586	1.829	0.3452	1.943
155	2.0851	5.149	1.993	0.3775	1.949
160	2.0771	4.732			

The viscosity was determined over the temperature range $138\text{--}160^\circ$ with outflow times varying between 125 and 175 sec. The activation energy of viscous flow calculated from the linear plot of $\log \eta$ was 6.09 (~ 6.06) kcal. mole⁻¹. The dynamic viscosity at the m. p. was 6.844 (4.713) cp.

Density in the temperature range $133\text{--}160^\circ$ follows the equation (± 0.0006):

$$d_4^t = 2.1105 - 1.33 \times 10^{-3}(t - 135) \text{ g. ml.}^{-1}$$

The density at the m. p. is $2.1052 \text{ g. ml.}^{-1}$ and the molar volume $187.45 \text{ ml. mole}^{-1}$.

Surface tension, γ , and molar surface free energy, ω , can be represented in the same temperature range by the equations

$$\gamma (\pm 0.5) = 44.4 - 0.14(t - 135) \text{ dynes cm.}^{-1}$$

$$\omega (\pm 30) = 1462 - 7.63(t - 135) \text{ ergs mole}^{-\frac{2}{3}}$$

The Eötvös constant is very large, 7.63, to be compared with 2.34 erg mole⁻³ deg.⁻¹ for gallium trichloride-piperidine. The parachor is 480.1 ± 1.5 (calc. for C₅H₁₁N → GaBr₃, 469.0).

DISCUSSION

No new features emerge from these results, and the interpretation of the data follows the lines indicated for the gallium trichloride complexes.^{5,6} The great similarity between all four complexes is notable, the major differences being in the larger activation energies and Eötvös constants of the bromo-compounds. The specific conductivity of the bromo-complexes is slightly less than that of the corresponding chloro-compounds but, because of their rather larger viscosity, the product $\mu\eta$ is slightly greater. If normal ionic migration velocities are assumed, the values of the reduced conductivity indicate that the complexes of gallium tribromide with pyridine and piperidine are about 2% dissociated into ions.

Before this work only three systems containing gallium tribromide had been investigated. Ammonia apparently forms several addition compounds,⁷ the stable 1 : 1 adduct melting at 124°. More recently gallium tribromide-dimethyl ether, m. p. 8.5°, and gallium tribromide-trimethylamine have been prepared and the latter ligand also forms an unstable 1 : 2 complex at low temperatures.⁸ The present work, together with that on gallium tribromide-phosphorus oxybromide,³ shows that the complexes of gallium tribromide closely resemble those of gallium trichloride, and further investigations on these lines seems unlikely to add further to our knowledge of the structure and properties of these complexes.

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⁷ Klemm, Tilk, and Jacobi, *Z. anorg. Chem.*, 1932, **207**, 188, 190; Johnson and Parsons, *J. Phys. Chem.*, 1932, **36**, 2587.

⁸ Van Dyke and Crawford, *J. Amer. Chem. Soc.*, 1950, **72**, 2829.
