

Binary Melting Point Studies for Boron Bromide with Some Group IV Halides and for Germanium Bromide with Silicon Bromide

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Melting point and solubility data are presented for the binary systems boron bromide-germanium bromide, boron bromide-silicon bromide, boron bromide-germanium chloride, boron bromide-silicon chloride and germanium bromide-silicon bromide. The Group IV halides with boron bromide had simple eutectics and there was no evidence of compound formation. The germanium bromide-silicon bromide system formed a continuous series of solid solutions. Comparisons of ideal and experimental solubilities have been made.

SOLID-LIQUID equilibria of the binary systems of SnBr_4 and of SnI_4 with BBr_3 have been studied by Adamsky and Wheeler (1) and the system SiBr_4 with BBr_3 by Nisel'son and Petrusevich (8). In this paper the solid-liquid equilibria of some additional Group IV tetrahalides with BBr_3 and of the GeBr_4 - SiBr_4 system have been studied by determination of liquidus curves. In the BBr_3 - SiBr_4 system the eutectic point has been more precisely determined.

EXPERIMENTAL

Materials. Electronic grade chemicals were used without further purification. The BBr_3 , GeCl_4 and GeBr_4 were reported to be 99.99+%, 99.999+%, and 99.99+%, respectively, and were obtained from Eagle-Picher Company. The SiBr_4 and SiCl_4 were reported to be 99+%, and were obtained from Stauffer Chemical Co.

Procedure. Mixtures of 2 ml. total volume were prepared

volumetrically from thermostated reagents, using a micro-syringe calibrated in 0.02 ml. divisions. All additions were made in a dry box. Conversion from volume to weight units was made using the respective densities.

The method of determining melting points which was used was similar to that reported by Collett and Johnston (2). Mixtures were sealed in Pyrex tubes immediately after making them up and the melting temperature was taken when the last crystal disappeared. The sample tubes were vigorously stirred. Thermometers used were calibrated against a thermometer calibrated by the National Bureau of Standards. Melting temperatures were read with a reproducibility of $\pm 0.1^\circ \text{C}$. A five gallon unsilvered dewar was used for the constant temperature bath and dry ice-methanol was used to obtain low temperatures. When not being measured samples were kept in the dark to minimize photochemical reactions.

Melting points were checked by time-temperature studies.

RESULTS AND DISCUSSION

Figure 1 shows the melting point-composition curves for the $\text{BBr}_3\text{-GeBr}_4$ and $\text{BBr}_3\text{-SiBr}_4$ systems with eutectics at 80.9 and 76.0 mole % BBr_3 , respectively (-53.0° and -57.5°C.). The eutectic in the $\text{BBr}_3\text{-SiBr}_4$ system found in this study differs from that previously reported as 80.0 mole % BBr_3 at -57°C. by Nisel'son and Petrusevich (8). These curves give no evidence of molecular coordination compounds. Adamsky and Wheeler (1) found from their freezing point studies that bromine in aluminum, stannic, and arsenic bromides and iodine in stannic iodide also showed no tendency to coordinate with boron in BBr_3 .

Figure 2 shows that the melting point-composition curves for $\text{BBr}_3\text{-GeCl}_4$ and $\text{BBr}_3\text{-SiCl}_4$ are also of the simple eutectic type with eutectics at 40 and 26.4 mole % BBr_3 , respectively (-74° and -80.0°C.), with no evidence of compound formation. These solutions were kept frozen until their melting points were taken and presumably before any appreciable halogen exchange reaction took place.

When the $\text{BBr}_3\text{-GeCl}_4$ and $\text{BBr}_3\text{-SiCl}_4$ systems were held at room temperature a depression of their melting points was observed after about two days, indicating that halogen exchange reactions took place. The melting points became constant at a maximum depression of about 1°C. after approximately five days. The depression was only observ-

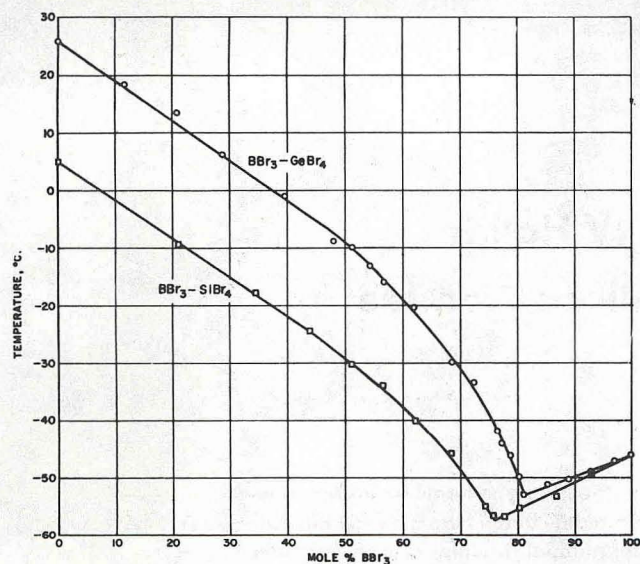


Figure 1. Melting point-composition curves for $\text{BBr}_3\text{-GeBr}_4$ and $\text{BBr}_3\text{-SiBr}_4$

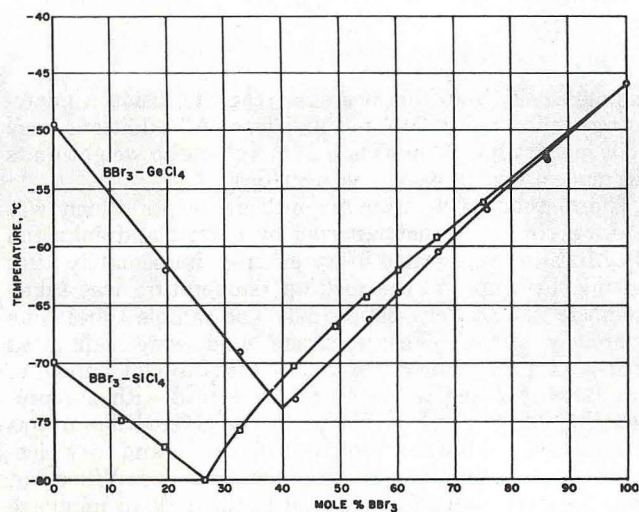


Figure 2. Melting point-composition curves for $\text{BBr}_3\text{-GeCl}_4$ and $\text{BBr}_3\text{-SiCl}_4$

able in solutions close to 1:1 mole ratio, indicating a mass action effect on the halogen exchange reaction. Infrared spectroscopy measurements of vapors above these solutions showed BCl_3 to be present (7) confirming a halogen exchange reaction. In similar studies by Delwaulle (3) of the solidification behavior of mixtures of GeCl_4 and GeBr_4 , mixed halides were observed as reaction products by Raman spectroscopy and the melting points of the solutions were also found to be changed.

If the tetrahalides in BBr_3 studied obeyed the ideal thermodynamic solubility equation (5, 10):

$$\log N = \frac{\Delta H_f}{2.303R} [1/T_0 - 1/T]$$

their heats of fusion, ΔH_f , could be determined from the slopes of the curves obtained by plotting $\log N$ as a function of $1/T$, where N is the mole fraction of the respective tetrahalide at the liquidus temperature T , and T_0 the melting point of pure tetrahalide. This equation assumes negligible solid solubility of BBr_3 in the tetrahalides and that heats of fusion are independent of temperature, namely that ΔC_p (fusion) is zero.

Curves obtained by plotting $\log N$ vs. $1/T$, determined for N as pure tetrahalide to the eutectic composition, can be seen in Figure 3. These curves have been compared with those calculated from the ideal solubility equation using the reported heats of fusion of the respective tetrahalides. The limiting slope of the experimental curve as $N \rightarrow 1$ should correspond to the ideal slope. The experimental GeBr_4 curve can be seen to approach closely the ideal solubility curve.

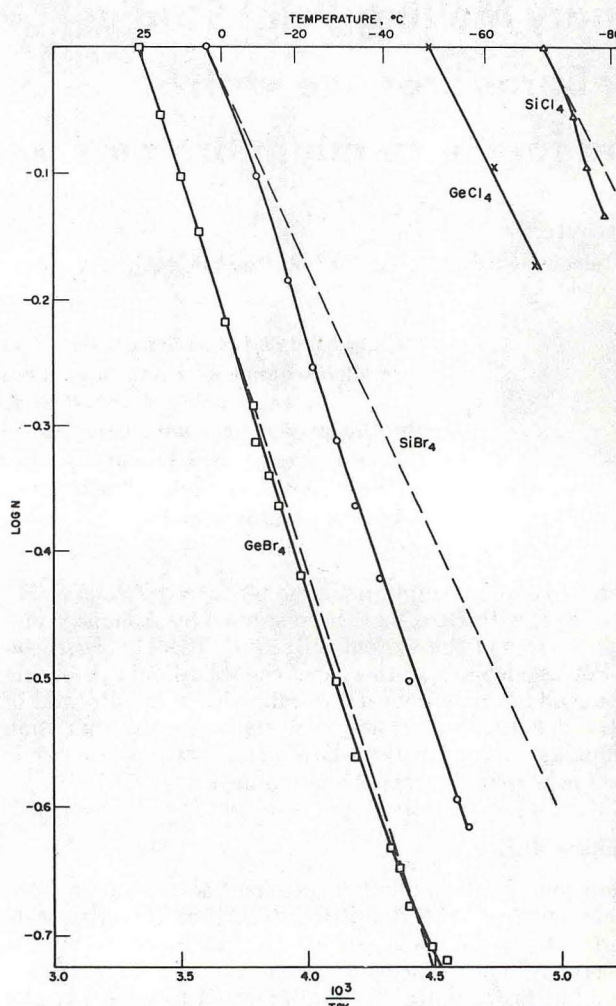


Figure 3. The solubility of GeCl_4 , GeBr_4 , SiCl_4 and SiBr_4 in BBr_3 : ----, ideal; —, experimental

Experimental solubility values were not obtained close enough to $N \rightarrow 1$, however, to obtain independent estimates of heats of fusion. The heats of fusion used for calculation were 2.9 ± 0.5 (6) 2.00 (4) and 1.84 (9) kcal./mole for GeBr_4 , SiBr_4 and SiCl_4 respectively. The heat of fusion for GeCl_4 was not available in the literature for comparison.

The GeBr_4 - SiBr_4 melting point-composition curve shown in Figure 4 is seen to be bowed upward slightly above a linear curve between the melting points of the pure components, indicating that a continuous series of solid solutions are formed in this system. The ideal liquidus and

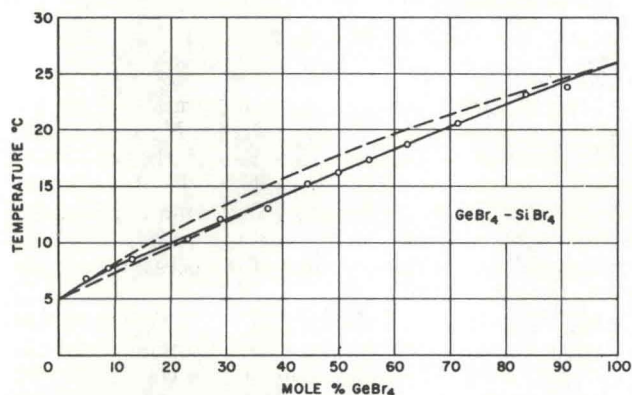


Figure 4. Experimental liquidus curve for GeBr_4 - SiBr_4 compared with calculated ideal liquidus and solidus solid solution curves: —, ideal; ---, experimental

solidus solid solution curves have been calculated (5) for this system and compared with the experimental liquidus curve in Figure 4.

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