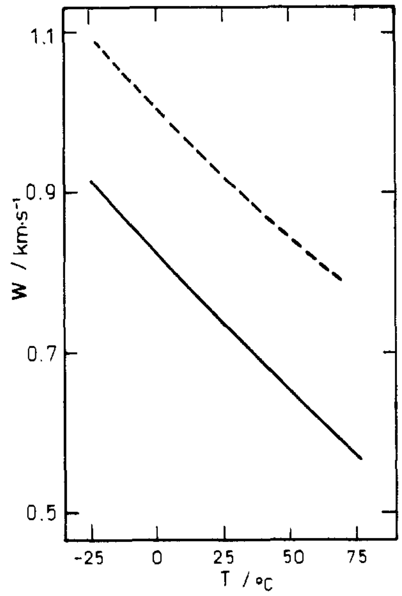

Figure 1. Speed of sound in saturated liquid CCl_3F (—) and CCl_4 (- - -) as a function of temperature.

where a, b, and c were found by an unweighted least-squares method. The coefficients and their standard deviations obtained are as follows: $a = 827.66$, $\sigma_a = 0.29$; $b = -3.0541$, $\sigma_b = 0.0145$; $c = 0.00150$, $\sigma_c = 0.00023$. The number of digits of these coefficients is given to reproduce Table I, and not all are necessarily significant. Deviations of the data from eq 1 appear to be random and less than the estimated experimental uncertainty of 0.05%. The measured values of the speed of sound are tabulated together with percent differences in Table I. Five measurements around a selected temperature on different days indicated reproducibilities better than 0.03%.

The only published data of the speed of sound in Freon 11 are those of Redkozubov (*3*) but were unavailable for comparison at the time of writing this report. Qualitatively, the data as a function of temperature show a positive curvature in contrast with those of other cryogenic fluids that have a negative curvature in their full vapor-pressure temperature ranges (*4*). However, the speed of sound data for CCl_4 published by Rowlinson (*5*) also show a positive curvature. These CCl_4 data were fitted to a quadratic expression as eq 1 and are shown together with those of CCl_3F in Figure 1.

The measured speed of sound data have been combined with the orthobaric densities represented by the equations of Benning and McHarness (*6*) to calculate adiabatic compressibilities. The latter are also shown in Table I.

Acknowledgment

We thank Dr. Jean P. Monfort for carring out the chromatographic analysis of the experimental sample for CCl_3F.

Literature Cited

(1) Greenspan, M.; Tschiegg, C. *J. Res. Natl. Bur. Std.* (*U.S.*) **1957**, *59*, 249.
(2) Younglove, B. A. *J. Acoust. Soc. Am.* **1965**, *38*, 433.
(3) Redkozubov, V. A. *Primen. Ul'traakust. Issled. Veshchestva* **1976**, *26*, 14.
(4) Tsumura, R.f Straty, G. C. *Cryogenics* **1977**, *17*, 195.
(5) Rowlinson, J. S. "Liquids and Liquid Mixtures", 2nd ed.; Butterworths: London, 1971; p 53.
(6) Benning, A. F.; McHarness, R. C. *Ind. Eng. Chem.* **1940**, *32*, 814.

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Vapor Pressures of Bromine–Quaternary Ammonium Salt Complexes for Zinc–Bromine Battery Applications

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Vapor pressures were measured for three bromine complexes: (1) tetramethylammonium bromide–bromine, (2) *N*-ethyl-*N*-methylmorpholinium bromide–bromine, and (3) trioctylmethylammonium chloride–bromine complexes. From the Clausius–Clapeyron equation, vapor pressure–temperature data obtained in the temperature range 0–40 °C were correlated to provide a least-squares curve fit. Calculated molar heats of vaporization for the three complexes listed in the preceding order are 10.0, 11.7, and 16.8 kcal/mol of bromine, respectively.

Introduction

Several bromine complexes are being explored as carriers of the electrochemically acitve bromine component for use in zinc bromine batteries (*1*). Vapor-pressure data for these complexes are useful in describing the operational characteristics of the battery and in estimating the release of bromine vapor in the event of an accidental spill of the complex. The gas-phase concentration of bromine vapor over the complex surface is dictated by the vapor pressure exerted by the complex at a given temperature. Vapor pressures of three complexes, tetramethylammonium bromide–bromine (TMAB–Br), *N*-ethyl-*N*-methylmorpholinium bromide–bromine (NENMMB–Br), and trioctylmethylammonium chloride–bromine (TOMAC–Br) were measured and fitted to the integrated Clausius–Clapeyron equation. The molar heat of vaporization for each of the three complexes was also calculated.

Experimental Procedure

Preparation of Bromine Complexes. The bromine complexes selected for this study are not produced commercially and were synthesized in our laboratory. The synthesis of the complexes was accomplished by the following procedures.

(1) TMAB–Br Complex: Tertramethylammonium bromide (3 mol) was dissolved in 500 mL of distilled water to obtain a saturated solution. Bromine (6 mol) was added slowly to the saturated solution of tetramethylamminoum bromide, and the mixture stirred vigorously. The stirred solution was kept still for several days in a desiccator until a yellow aqueous layer separated from a dark red liquid which was the desired TMAB–Br

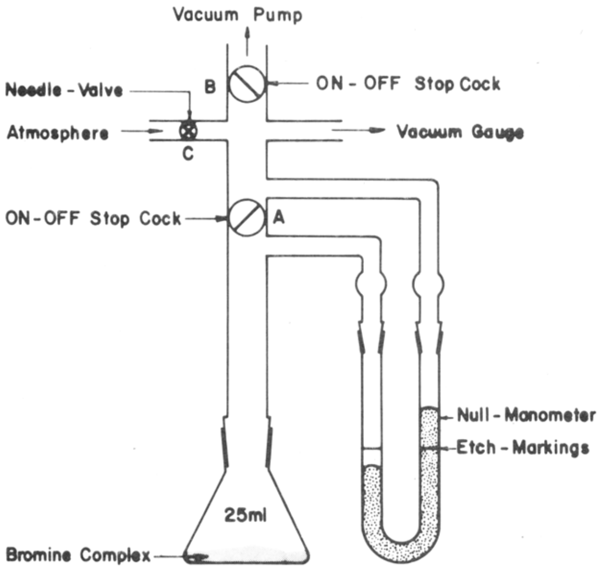

Figure 1. Pyrex glass isoteniscope used for vapor-pressure measurements.

complex. The complex was separated from the aqueous layer by using a separating funnel.

(2) NENMMB–Br Complex: A beaker containing 525 mL of a 40% aqueous solution of *N*-ethyl-*N*-methylmorpholinium bromide (NENMMB) and another beaker containing 100 mL of bromine were placed side by side in a hermetically sealed desiccator at room temperature. Gas-phase transfer of bromine to the beaker containing aqueous NENMMB solution was completed in approximately 4 days. The dark colored NENMMB–Br complex was found to have separated from the aqueous phase. The complex was separated from the aqueous layer by using a separating funnel.

(3) TOMAC–Br Complex: Bromine (1.6 mol) was added to 0.8 mol of trioctylmethylammonium chloride (TOMAC). TOMAC is a liquid at room temperature. The TOMAC–Br complex was obtained as a dark red liquid.

The overall complexation level for all three complexes was approximately 2 mol of bromine per mole of the quaternary ammonium salt; the quantity of bromine actually complexed with a fraction of the salt in the liquid phase could vary. For TMAB–Br complex, Bloch et al. (*2*) have shown that complexes with varying degrees of bromine can coexist at a given temperature; the true composition of the complexed solution can be found by the phase diagram.

Table I. Vapor Pressure of TMAB–Br Complex

temp, °C	vapor press., mmHg	temp, °C	vapor press., mmHg
0	0.7	25.5	28.7
5.1	4.3	32.0	35.6
10.4	11.0	39.5	49.0
14.7	17.4	49.7	67.0

Table II. Vapor Pressure of NENMMB–Br Complex

temp, °C	vapor press., mmHg	temp, °C	vapor press., mmHg
10	3.0	38.5	24.5
19.5	8.0	49.9	44.0
28.5	11.0	59.0	69.0

Table III. Vapor Pressure of TOMAC–Br Complex

temp, °C	vapor press., mmHg	temp, °C	vapor press., mmHg
0.8	1.5	24.9	56.0
5.4	7.5	29.9	67.5
9.8	17.0	34.9	101.0
15.2	30.0	39.9	120.5
19.9	44.5		

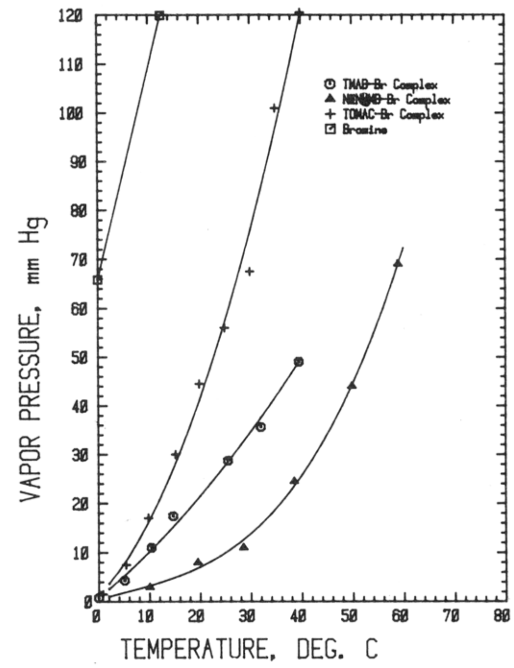

Figure 2. A comparision of vapor pressures of bromine–quaternary ammonium salt complexes with pure bromine.

Measurement of Vapor Pressure. An isoteniscope fabricated from Pyrex glass and shown in Figure 1 was used for vapor-pressure measurement. The isoteniscope consists of a sample flask and a null-manometer using mercury. The null-manometer contains mercury at the etch markings, which also serves as a reference during vapor-pressure measurement. The temperature of the apparatus and its contents is controlled by immersing it in a Pyrex glass temperature-controlled bath. Pressure in the apparatus is monitored by the Wallace and Tiernan Model 14417 absolute pressure gage. Approximately 10 mL of the bromine complex is taken in the sample flask which is then coupled to the main body of the apparatus. The apparatus assembly is immersed in the temperature-controlled bath, and the complex sample is frozen in the flask at −20 °C. Once sample freezing is assured, stopcocks A and B are opened and the apparatus is evacuated to ~5 mmHg; this pressure is the residual pressure. Stopcocks A and B are closed, thereby sealing the test sample in the container, which is coupled to the left arm of the null-manometer while the right arm is in contact with the pressure gage. The bath temperature is raised to some desired level, and the apparatus and its contents are maintained at that level for ~1 h. Temperature rise causes depression of the mercury level in the left arm of the null-manometer. The needle valve, C, is opened slowly to admit air into the apparatus such that mercury levels in both arms of the null-manometer are on the same plane, that is, at the etch markings. The gage pressure minus the residual air pressure noted previously provides the vapor pressure of the sample at a given temperature.

To verify that pressures measured were in fact due to the vapor pressure of the complex only, a check of vapor pressure reversibility was carried out with NENMMB–Br complex. Vapor pressures were the same when measured with both increasing and decreasing temperature.

Results and Discussion

Vapor-pressure data for the three complexes, TMAB–Br, NENMMB–Br, and TOMAC–Br, are presented in Tables I, II, and

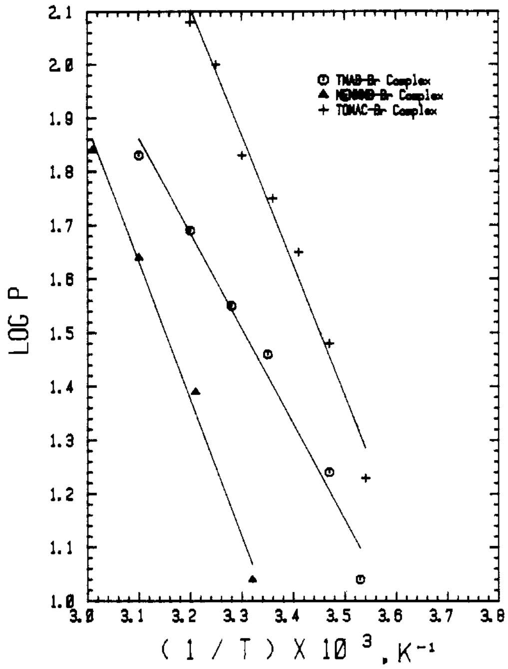

Figure 3. Vapor pressures of bromine-quaternary ammonium salt complexes.

III. The data are also plotted in Figure 2 together with bromine vapor-pressure data reported by Weast (*3*). The data show that, at a given temperature, vapor pressures follow the order bromine > TOMAC-Br > TMAB-Br > NENMMB-Br. This illustrates that complexing of bromine with quaternary ammonium salts reduces the concentration of bromine vapor over the complex surfaces.

The integrated Clausius-Clapeyron equation relates vapor pressure to temperature:

$$\log P = -0.434(\Delta H_v/R)(1/T) + \text{constant} \qquad (1)$$

where P is the pressure in mmHg, T is the temperature in Kelvin, R is the universal gas constant, and ΔH_v is the molar heat of vaporization. The value of the constant depends in part on the units used for pressure. The vapor-pressure data for the three bromine complexes are replotted in Figure 3, which shows that the log P vs. $1/T$ relationship for the three bromine complexes is linear.

The best-fit lines to represent the vapor pressure-temperature relationship for a complex and the calculated molar heat of vaporization are as follows:

(1) TMAB-Br complex

$$\log P = (-2.184 \times 10^3)(1/T) + 8.692 \qquad (2)$$

The coefficient of determination for the calculated line is 0.927. ΔH_v = 9.996 kcal/mol.

(2) NENMMB-Br complex

$$\log P = (-2.551 \times 10^3)(1/T) + 9.544 \qquad (3)$$

The coefficient of determination for the calcualted line is 0.990. ΔH_v = 11.67 kcal/mol.

(3) TOMAC-Br complex

$$\log P = (-3.675 \times 10^3)(1/T) + (1.402 \times 10^1) \qquad (4)$$

The coefficient of determination for the calculated line is 0.881. ΔH_v = 16.82 kcal/mol. In eq 2-4, pressure is given in mmHg, and temperatures in Kelvin. The heat of vaporization for the TMAB-Br complex, 9.996 kcal/mol of bromine, is in reasonably good agreement with approximately 11 kcal/mol reported by Bloch et al. (*2*).

Acknowledgment

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Literature Cited

(1) Bellows, R. J.; Eustace, D. J.; Grimes, P.; Shropshire, J. A.; Venero, A. F. *Proc.—Int. Power Sources Symp.* **1979**, *11*, 301-312.
(2) Bloch, R.; Farkas, L.; Schnerb, J.; Winogron, F. *J. Phys. Chem.* **1949**, *53*, 1117-25.
(3) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 50th ed.; The Chemical Rubber Company: Cleveland, OH, 1969, D-170.

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Sorption of SF_6 by Activated Charcoal

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Sorption isotherms for SF_6 on activated charcoal were obtained between −83 and 100 °C in the pressure range of 0.13 mPa to 100 kPa (1 μtorr to 750 torr) by microgravimetric techniques. Charcoal uptakes as high as 0.80 g of SF_6 per gram of charcoal were observed with isosteric heats of sorption values ranging from −6.0 to −7.5 kcal/(g-mol).

Introduction and Background

Sulfur hexafluoride (SF_6) is an important gaseous dielectric, with significant utility in the electric power industry. This gas possesses a high dielectric strength, about twice that of air or carbon dioxide, and has excellent arc quenching characteristics due to the rapid recombination of dissociated molecules and a large electron attachment cross section (~0.48 nm). The latter property permits the absorbed electron energy to be stored in the vibrational levels of the SF_6 molecules and the formation of stable negative ions of low mobility. The removal of free electrons through the formation of negative ions makes it possible to achieve higher voltage levels before an arc across the potential gradient between surfaces is produced. In addition, considerable decomposition may occur in the SF_6 without significant loss of dielectric strength.

As a consequence of these properties, SF_6 is used as an insulating gas in high-voltage transformers, circuit breakers and waveguides, and linear and electrostatic accelerators. Large quantities are used in the latter applications. For example, the

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