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Vapor Pressure of 1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol

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UT-BATTELLE

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Nuclear Science and Technology Division

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ABSTRACT

The vapor pressure of the compound 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol was measured over the temperature range 62 to 92°C using a Knudsen effusion technique. This compound, known as Cs-7SB, is the modifier component in the caustic-side solvent extraction process solvent. The vapor pressure is related to temperature by the equation

$$\ln(p/\mathrm{Pa}) = (32.202 \pm 0.265) - (12154 \pm 93)/T\ ,$$

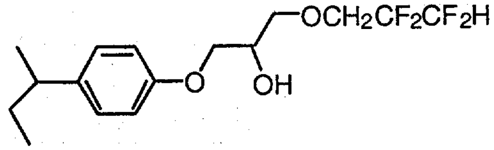
where p is the pressure, expressed in pascals; Pa is the reference pressure of 1 pascal; and T is the temperature, expressed in degrees kelvin. The derived heat of vaporization is 101.1 ± 0.8 kJ·mol^{1} at 35 1 K. Because the vapor pressures over the temperature range of 15 to 50°C were lower than the design capabilities of the Knudsen effusion apparatus, the vapor pressures at these temperature limits were obtained by extrapolation. The estimated values are 4.6 ± 0.3E−05 (3.5 ± 0.2E−07 mm Hg) and 4.5 ± 0.1E-03 Pa (3.4 ± 0.1E−05 mm Hg) for 15°C and 50°C, respectively.

1. INTRODUCTION

1.1 SCOPE OF WORK

At the Savannah River Site, the supernatant liquid and salt cake in high-level waste tanks is to be retrieved, treated, solidified, and immobilized for disposal. This requires the removal of ^{137}Cs during the processing. A complexant, calix[4]arene-bis(*tert*-octylbenzo-crown-6), known as BOBCalixC6, has been developed to extract the cesium from this supernatant waste. In addition to the crown ether extractant, the solvent mixture used contains a modifier—1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (known as Cs-7SB)—and a suppressor—trioctylamine-all dissolved in Isopar® L, a modified kerosene composed of C_{10} to C_{12} branched alkanes. The composition of the solvent mixture, as recently modified, is 0.007 *M* extractant, 0.75 *M* modifier, and 0.003 *M* suppressor dissolved in the Isopar® L solvent.'

This report d&ails the determination of the vapor pressure of the following modifier:



1.2 DESCRIPTION OF TASK

From the molecular weight of the modifier, a vapor pressure in the range of 0.1 to 1 Pa was estimated prior to any measurements. For vapor pressure determinations in this range, the Knudsen effusion method[2-4] is one of the most accurate measurement techniques available. Within the Physical Properties Research Facility (PPRF) at Oak Ridge National Laboratory (ORNL), a Knudsen torsion-weighing effusion vapor pressure apparatus is under development. When finished, the combination of torsion pendulum and weight-loss methods will give a sensitive apparatus from which both the vapor pressure and the molecular weight of the effusing molecules can be determined simultaneously. The weighing effusion method is based on the equation from the kinetic theory of gases first developed by Knudsen:[2-4]

$$p = \text{Constant}(dm/dt)\,,$$

in which dm/dt represents the mass loss per unit time from an effusion cell. The "Constant" is proportional to the orifice area, molecular weight, and the temperature of the effusing species. In the torsion-effusion experiment, the effusion cell, suspended from a long thin wire, exerts a torque on the wire as a result of the escaping molecules. That torque is directly proportional to the vapor pressure.

The ORNL PPRF effusion vapor pressure equipment has not yet been described in the scientific literature, because it continues to be developed. However, it replicates that previously described by De Kruif and Van Ginkel in 1977.[5] In this research, only the weighing effusion method was used, as the torsion portion of the apparatus is still under development. The work scope funding this task specified measuring the vapor pressure of the modifier over the temperature range of 15 to 50°C.

2. EXPERIMENTAL

2.1 APPARATUS AND PROCEDURE

As noted in Sect. 1.2, the apparatus is a replicate of that developed by De Kruif and Van Ginkel.[5] A summary of the equipment is given here to aid the reader. The instrument consists of a vacuum chamber that can be evacuated to <1E-04 Pa (-E-06 mm Hg) by a rotary pump/turbo pump combination. A sample cell is suspended in the vacuum chamber by a thin wire attached to an electrobalance (Cahn Model 1000). A dummy cell (identical to the sample cell) is positioned immediately below the suspended cell. The dummy cell contains a platinum resistance thermometer that is used for the temperature measurement. An electrical resistance heater, consisting of top, middle, and bottom sections, completely surrounds the sample and dummy cells. The middle heater is equipped with a thermocouple, while the top and bottom heaters are equipped with difference thermocouples and are slave to the middle heater.

Weight-loss data were obtained from the electrobalance, which produces an analog voltage output that is linearly dependent on the weight of the sample cell. This voltage is measured and digitized by a digital nanovoltmeter (Keithley Model 181). The temperature is determined by measuring the resistance of a platinum resistance thermometer (Minco) via an ac impedance bridge (Tinsley Senator). Temperature regulation is achieved using Kepco Model 0.3MAT power supplies equipped with Eurotherm Model 818 controllers. The middle Eurotherm 818 is the master temperature control device. Data collection from and control of these devices are accomplished via a computer (IBM PC/AT) equipped with a general-purpose interface bus (GPIB) card and serial ports. Determination of time is made using the internal clock of the PC. The voltmeter and ac bridge are connected to the computer via a GPIB interface. The temperature controller is connected via the RS-232 interface. The software was written using Microsoft QuickBASIC v. 4.5, and QuickBASIC routines supplied by National Instruments supplied were used for control of and communication with the GPIB devices.

When the equipment is used in the weight-loss mode, the following equation represents accurately the relationship between the vapor pressure and the rate of mass loss. with time:

$$p = (dm/dt)(1/AC)(2\pi RT/M)^{1/2} ,$$

where p is the vapor pressure of the sample, A is the area of the orifice, M is the molecular weight of the vapor, R is the gas constant, T is the temperature in Kelvin, and C is the Clausing probability factor.[6-7] The Clausing probability factor can be calculated using the expression

$$C = [1 + (3l/8r)]^{-1} ,$$

where l is the length and r is the radius of the orifice.[7]

For the vapor pressure measurements on the modifier, the molar mass used was 0.33830 $kg \cdot mol^{-1}$, based on the 1999 relative atomic masses.* The gas constant adopted by CODATA, R = 8.314472 $J \cdot K^{-1} \cdot mol^{-1}$, was used.' The effusing cell was fitted with a 0.023-mm-thick platinum disc containing a cylindrical hole of l-mm diameter. The corresponding Clausing probability factor is 0.983.

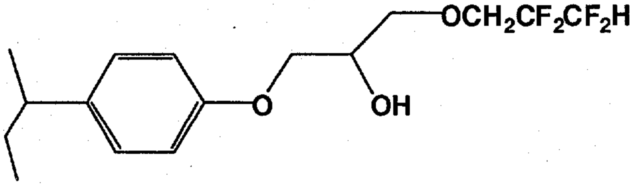
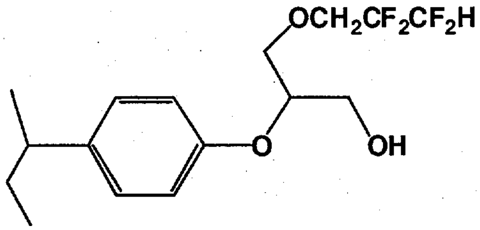
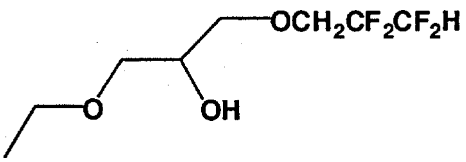
The platinum resistance thermometer used in these measurements was calibrated by comparison with a standard platinum resistance thermometer whose constants were determined at the National Institute of Standards and Technology on IPTS-68. All temperatures were measured in terms of IPTS-68 and converted to ITS-90 with increments provided in the literature."

As proof of proper operation of the Knudsen vapor pressure apparatus, measurements were made on a sample of high-purity phenanthrene and compared with literature data."

2.2 SAMPLES

The sample of the modifier used in the vapor pressure measurements was supplied by P. V. Bonnesen (ORNL Chemical Sciences Division) and labeled as follows: "Modifier Cs-7SB Lot No. B000894-48P." Final isolation of this material was accomplished by fractional vacuum distillation at 138–142°C, 17 ± 4 Pa (0.13 ± 0.03 mm Hg), through a short-path distillation apparatus with a S-cm-long Vigreux column. The product specification and analysis of this lot of modifier are given Table 1. The product assay was performed by gas chromatography on a Hewlett-Packard HP6850 system equipped with an HP-5MS fused silica capillary column. The modifier sample was silylated prior to injection using *N,O,*-bis(trimethylsilyl)-trifluoroacetamide, catalyzed with 1% trimethylchlorosilane. The sample of the material was used as received for the measurements reported herein and not subjected to any further purification.

Table 1. Summary of Cs-7SB product specifications and analysis of Cs-7SB modifier lot B000894-48P

Component	Allowable range (mol %)	Mol % for lot B000894-48P
Main structural isomer 	>96	97.9
Minor structural isomer 	1.1-1.4	1.2
4-*sec*-Butylphenol	<0.05	None observed
Ethanol addition product 	<1.0	0.4
All other side products and polymers	<1.6	≤0.5

The sample of phenanthrene used as a calibrant was a part of a sample that was subjected to accurate and precise thermochemical measurements during the period of time the

PPRF was located in Bartlesville, Oklahoma.[12] During the time interval prior to its use for the work reported herein, it was stored under high vacuum and sealed in borosilicate glass.

3. RESULTS

3.1 PHENANTHRENE CALIBRANT

Table 2 lists the results of the vapor pressure measurements on phenanthrene. Figure 1 compares these results with the values reported in the literature by De Kruif.” The De Kruif study is detailed, covering vapor pressure measurements on 11 polycyclic aromatics and involving comparisons of these results with a range of data reported in the literature. The agreement between the results obtained in this study and the. results reported by De Kruif lends confidence to the modifier vapor pressure results.

Table 2. Results of the Knudsen effusion vapor pressure measurements for phenanthrene

Temperature (K)	Pressure (Pa)
302.62	0.037
309.08	0.073
309.10	0.073
313.31	0.120
313.31	0.119
319.36	0.215
325.74	0.421
325.72	0.424

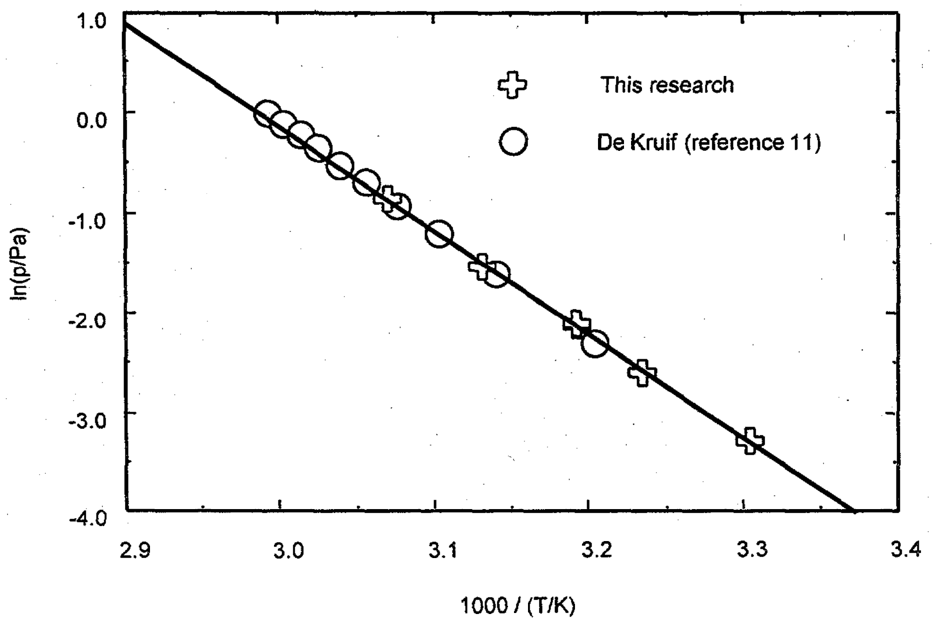


Fig. 1. Comparison of the vapor pressure measurements for phenanthrene obtained in this research with those reported in the literature by De Kruif." The straight line represents a linear fit of the data obtained in this study.

3.2 MODIFIER VAPOR PRESSURE MEASUREMENTS

Table 3 lists the results of the vapor pressure measurements on the modifier, Cs-7SB. The measurements cover the temperature range 60 to 90°C. Figure 2 contains a plot of the vapor pressure as a function of temperature.

Table 3. Results of the Knudsen effusion vapor pressure measurements for the modifier, Cs-7SB

Temperature (K)	Pressure (Pa)
335.60	0.018
344.45	0.046
356.57	0.152
365.75	0.357

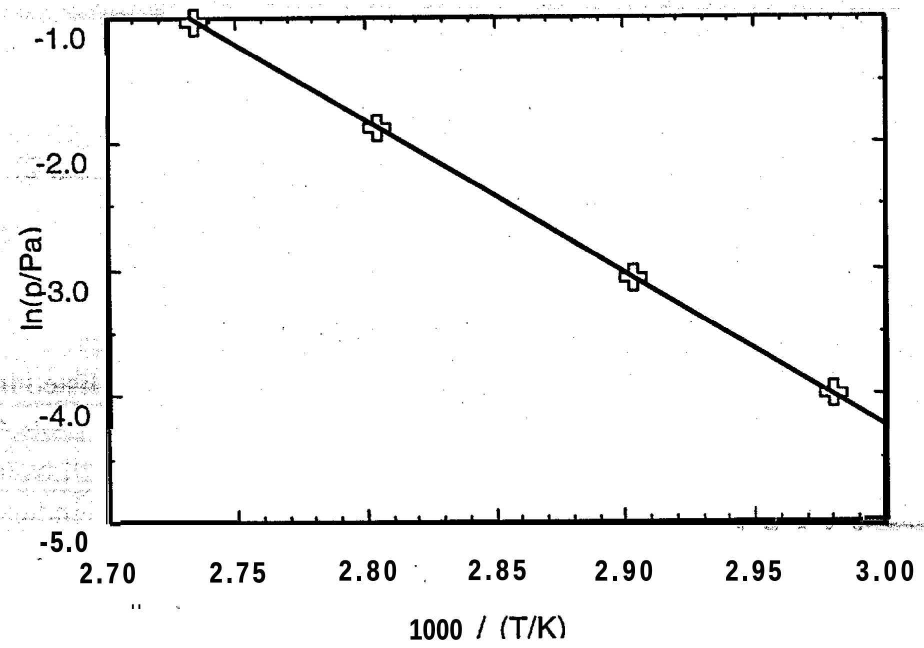


Fig. 2. Plot of the vapor pressure measurements of the modifier, Cs-7SB.

4. CONCLUSIONS

4.1 PHENANTHRENE COMPARISON

Figure 1 shows the agreement between the measured vapor pressures for phenanthrene and the reported data of De Kruif.[11] The results obtained here and reported in Table 2 can be represented by the integrated Clausius-Clapeyron equation:

$$\ln(p/\text{Pa}) = A - B/T ,$$

where Pa is the reference pressure of 1 pascal. The slope of the straight line obtained by plotting $\ln(p/\text{Pa})$ vs $1/T$ is the enthalpy of sublimation or vaporization (at the mean temperature of the range of the measurements) divided by the gas constant R. Plotting $\ln(p/\text{Pa})$ vs $1/T$ for the phenanthrene data reported in Table 2 (see Fig. 1) yields

$$\ln(p/\text{Pa}) = (3\,1.17\,1 \pm 0.777) - (10437 \pm 244)/T ,$$

with a correlation coefficient of 0.9997. The uncertainty values are the 95% confidence interval. The derived enthalpy of sublimation is 86.8 ± 2.0 kJ·mol^{-1} at 31.4 K. De Kruif[11] reports an enthalpy of sublimation of 90.5 ± 1 at 325.03 K for phenanthrene using a more extensive representation of the variation of vapor pressure with temperature.

4.2 MODIFIER DISCUSSION

Plotting ln(p/Pa) vs l/T for the modifier data reported in Table 3 gives (see Fig. 2)

$$\ln(p/\mathrm{Pa}) = (32.202 \pm 0.265) - (12154 \pm 93)/T\ ,$$

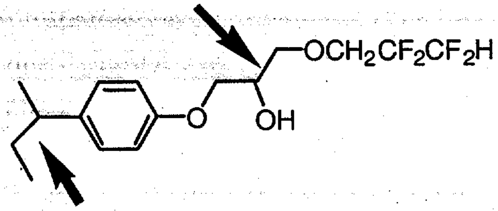
with a correlation coefficient >0.9999. The derived enthalpy of vaporization is 101.1 ± 0.8 $\mathrm{kJ \cdot mol^{-1}}$ at 35 1 K. For the convenience of the reader, the results listed in Table 3 for the vapor pressure of the modifier are repeated in several units in Table 4. The vapor pressure was so low at 60°C that it was not possible to obtain meaningful results below that temperature. Extrapolation of the linear ln(p/Pa) vs l/T plot would indicate a vapor pressure of approximately 4.6 ± 0.3E-05 Pa (3.5 ± 0.2E-07 mm Hg) at 15°C and 4.5 ± O.lE-03 Pa (3.4 ± O.lE-05 mm Hg) at 50°C. Measurements in this pressure region would require an ultra high-vacuum system attached to the effusion equipment.

Table 4. Results of the Knudsen effusion vapor pressure measurement for the modifier, Cs-7SB, given in several units

Temperature (K)	Temperature (°C)	Temperature (°F)	Pressure (Pa)	Pressure (mm Hg)
335.60	62.45	144.41	0.018	1.35E-04
344.45	71.30	160.34	0.046	3.45E-04
356.57	83.42	182.16	0.152	1.14E-03
365.75	92.60	198.68	0.357	2.68E-03

Extrapolation of the linear plot to the product purification temperature yields a pressure of 16.2 ± 0.7 Pa (0.12 ± 0.01 mm Hg), which compares well with the observed pressure of 17 Pa (0.13 mm Hg). This agreement observed with the extrapolation to higher temperatures lends credence to the estimated vapor pressure at the lower temperatures.

The measurements reported above represent the "worst-case scenario" for calculations related to the fire safety of the caustic-side solvent extraction process with respect to the vapor pressure of the modifier. There are two chiral centers in 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol. The arrows in the following drawing denote the optical centers. The vapor pressure measurements were made on a mixture of optical isomers. Such mixtures have vapor pressures in excess of that of an optically pure isomer. Therefore, the reported measurements are in excess of that of any one of the pure enantiomers and represent the most volatile state for assessments related to contributions from the modifier to the fire hazard of the caustic-side solvent extraction process.



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