THE BOILING POINT AND MOLAR ENTHALPY OF VAPORIZATION OF FLUORINT FC-70 $N(C_5F_{11})_3$
Determined by static-sample and DSC methods

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Abstract

$N(C_5F_{11})_3$ (Fluorint FC-70) has been chosen as the test material to compare the chemico-physical data obtained by static-sample and DSC methods.

The normal boiling point, the molar enthalpy of vaporization, and the constants of the Antoine equation of fluorint FC-70 are reported.

DSC can be developed into a simple and rapid routine instrument to determine the enthalpy of vaporization as well as the boiling point of liquid, particularly at relative high temperature.

Keywords: boiling point, DSC, enthalpy of vaporization, fluorint FC-70, vapour pressure, 1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N,N-bis(undecafluoropentyl)-1-pentanamine

Introduction

Although calorimetry gives direct and good result in determining the heat of vaporization, many indirect methods have been used for various reasons. Difficulties usually exist in determining the boiling points, vapour pressures, and heats of vaporizations of some compounds with high boiling point both directly and indirectly.

A static-sample type of ebulliometer, which provides a simple way to obtain a series of vapour pressures at different temperatures with an accuracy adequate for evaluating the heat of vaporization, was employed. DSC method was also employed, as it will be useful for compounds at even higher temperature and lower vapour pressure.

1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N,N-bis(undecafluoropentyl)-1-pentan-amine (Fluorint FC-70) is widely used in the electronic industry. The compound was

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chosen for its non-hazardous and inert property, with its high boiling point. The boiling point and the heat of vaporization are two of its important specifications.

The results from the two methods reported here are in good agreement with each other. The static-sample method gives accurate results and good reproducibility, while the DSC method is simpler and more rapid, and can be developed as a comparable routine method.

Experimental

Material

1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N,N-bis(undecafluoropentyl)-1-pentanamine (Fluorint FC-70), a product of 3 M Company, was redistilled. The purity was checked by GC-IR and NMR.

Apparatus

The key part of the ebulliometer is an isoteniscope as shown in Fig. 1. It was partly filled with the purified liquid sample, and connected to vacuum system via a ballast bulb [1, 2]. The isoteniscope was immersed in a high temperature thermostat, precisely controlled with YCC-1612AP temperature programmer (a product of Xiamen Yu Guang Electronic Institute, Fujian, China), with a fluctuation of ±0.1°C. A digital thermometer, Type 2575 of Yokogawa Electronic Works, Japan, was employed. An U-type mercury manometer was used.

Once the sample is heated, the gas dissolved in the liquid will be evolved. The operation was repeated until the sample was free of any dissolved gas, and the sample was distributed properly among the three tubes. Equilibrium was established between the gas and liquid phases. When the liquid heights in tubes B and C are at the same horizontal level, the pressure of the vapour in tubes A and C is equal to that above tube B, and hence can be easily measured with the manometer. By adjusting the temperature of the thermostat and the pressure of the vacuum system, a series of vapour pressures and the corresponding temperatures can be obtained.

Du Pont 1090B was employed to make DSC curves. Indium was taken as the calibration standard. A hermetically sealed pan with a hole size of 0.4 mm was used as the container for the liquid sample in a dynamic nitrogen atmosphere. The amounts of the sample used were 5.41 to 9.89 mg, with alumina as the reference substance. The heating rates chosen were 20 and 50 deg·min^{-1}.

Results and discussions

Relationship between vapour pressure and boiling temperature

The temperature range measured by static-sample method was at 198 to 218°C, which covered a vapour pressure change from 460 mmHg to ambient at-

to vacuum and manometer system

water →

vapour + air —

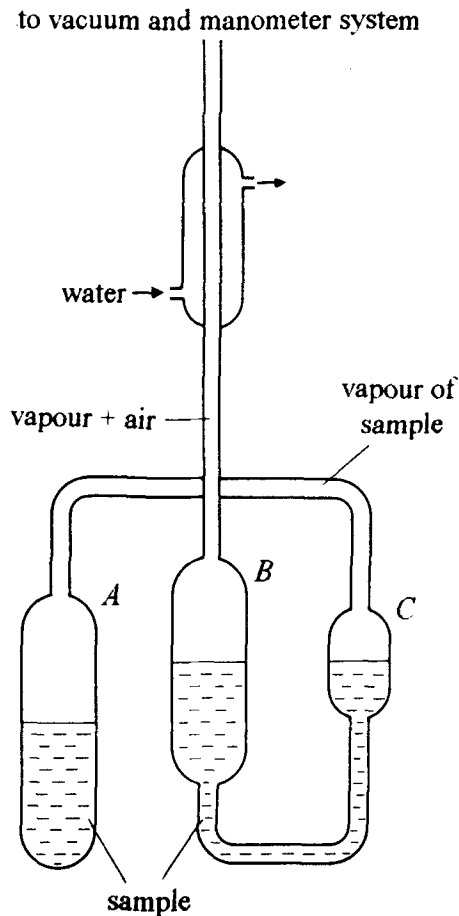vapour of sample

A *B* *C*

sample

Fig. 1 Schematic diagram of the isoteniscope of the ebulliometer

mosphere (the highest was 768.54 mmHg). The statistical results gave a relationship as follows:

$$\ln(p/\text{mmHg}) = 18.8916 - 6001 \times \text{K}/T$$

or

$$\ln(p/\text{Pa}) = 23.7844 - 6001 \times \text{K}/T$$

Although the relationship is obtained empirically, only two constants are necessary. Since the 5 plots of $\ln p$ vs. $1/T$ are perfect straight lines in such a narrow temperature region, the empirical constant C in the Antoine equation can be taken as 273.15. The relationship becomes a simplified Clausius-

Clapeyron equation if the molar volume of the liquid is negligible and the vapour is considered as a perfect gas. The normal boiling point and the molar enthalpy of vaporization can be thereby calculated:

$$T_{b.p.} = (489.6\pm0.4) \text{ K or } t_{b.p.} = (216.4\pm0.4)°C$$

$$\Delta_v H_m = (49.9\pm0.4) \text{ kJ·mol}^{-1}$$

Exactly speaking, the $\Delta_v H_m$ value here is an average molar enthalpy of vaporization at 198 to 218°C.

The results of DSC

In fact, the liquid sample begins to evaporate at room temperature in a very low rate. An asymmetric curve with a 'front tongue' due to the slow evaporation is the typical shape of the endotherm. It deviates from the baseline as long as the heat flow, associated with the sample entering the vapour phase, is large enough to be detected. The baseline always deflects after the endothermic peak because of the difference of the heat capacities between alumina and the empty sample pan. This results with larger error in the integration for the peak area. Reducing the hole size of the sealed DSC pan and increasing the heating rate will be helpful to keep the straight baseline longer. However, operating conditions, such as the hole size, heating rate, and amount of the sample, are dependent upon the properties of the sample to be determined, and should be maintained constant. Taking all these into account, the operation conditions have been chosen as mentioned above. Thus, the baseline began to deviate at about 185°C in our thermograms. The values of the extrapolated onset temperature t_e, and the heat of vaporization $\Delta_v H_m$ shown below are the statistical results of ten runs each:

Heating rate	t_e /°C	$\Delta_v H_m$/kJ·mol^{-1}
20 deg·min^{-1}	217.7±4.8	47.0±2.7
50 deg·min^{-1}	219.3±3.7	54.0±3.1

Conclusions

The boiling point, enthalpy of vaporization and the relationship between p and T of Fluorint FC-70 are as follows:

$$T_{b.p.} = (489.6\pm0.4) \text{ K or } t_{b.p.} = (216.4\pm0.4)°C$$

$$\Delta_v H_m = (49.9 \pm 0.4) \text{ kJ·mol}^{-1}$$

$$\ln(p/\text{Pa}) = 23.7844 - 6001 \times \text{K}/T$$

DSC method is hopeful as a simple and comparable routine method to estimate the enthalpy of vaporization as well as the boiling point of a liquid. However, the effects of variations in experimental conditions on the shape of the endotherm are serious. It is suggested that some pretestings, and comparison of the results with the data available should be undertaken, and then the experimental conditions can be chosen and fixed.

1,1,2,2,3,3,4,4,5,5,5-undecafluoro-N,N-bis(undecafluoropentyl)-1-pentanamine (Fluorint FC-70), a product of 3 M Company, was redistilled. The purity was checked by GC-IR and NMR.

References

1 D. P. Shoemaker, C. W. Garland and J. W. Nibler, Experiments in Physical Chemistry, 5th edn., McGraw-Hill Book Company, 1989, p.225.
2 Fudan University, Experiments in Physical Chemistry, Vol. 1 (in Chinese), Higher Education Press, Beijing 1979, p. 55.
3 G. W. Thomason, Chem. Rev., 38 (1946) 1.

Zusammenfassung — Zum Vergleich der mittels konventioneller und DSC-Methoden erhaltenen chemischphysikalischen Daten wurde die Testsubstanz $N(C_5F_{11})_3$ (Fluorint FC-70) gewählt.

Der normale Siedepunkt, die molare Verdampfungsenthalpie und die Konstanten der Antoine-Gleichung von Fluorint FC-70 wurden beschrieben.

DSC kann zu einem einfachen und schnellen Routinegerät zur Bestimmung der Verdampfungsenthalpie und auch des Siedepunktes von Flüssigkeiten, speziell bei hohen Temperaturen entwickelt werden.