

# Characterization of a microencapsulated marking agent for explosives by TGA

Kenneth J. Mintz\*

*Mining and Mineral Sciences Laboratories, Natural Resources Canada, 555 Booth Street, Ottawa, Ont., Canada K1A 0G1*

Received 8 December 2000; accepted 17 April 2001

## Abstract

Microencapsulation of the principal marking agent for detection of explosives, 2,3-dimethyl-2,3-dinitrobutane (DMNB), has been investigated as a means of extending the lifetime of the marking agent. DMNB sublimates from explosives, into which it has been incorporated and is detected by GC/MS. TGA was used to characterize and optimize the type and thickness of the coating. Results of various TGA tests are presented, to show that microencapsulation of DMNB is effective at substantially reducing the emission rate of DMNB, and thus increasing the lifetime for detection of explosives. As an extension to this study, a simple but novel method for measuring the permeability of DMNB vapor through various materials was developed using TGA and the solubility–diffusion model. Preliminary results for permeability through polystyrene and polyethylene are presented.

Crown Copyright © 2002 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Microencapsulation; Permeability; Explosives; DMNB

## 1. Introduction

Although some explosives, such as dynamite, can be detected directly by vapor-phase detectors, plastic explosives, which have been used extensively by terrorists, contain only explosive ingredients of very low vapor pressure. Therefore, the International Civil Aviation Organization adopted the “Convention on the Marking of Plastic Explosives for the Purpose of Detection” in 1991 (ratified in 1998) that requires the addition of one of the four specified marking agents; these have a sufficient vapor pressure that, when mixed into the explosive, allows their detection. The marking agent of choice is 2,3-dimethyl-2,3-dinitrobutane (DMNB) which is a solid at room

temperature [1]. Although the effectiveness of detection of marked explosives has been proven, the loss of marking agent by sublimation is sufficiently high, particularly for explosives that have a high surface to volume ratio, to cause concern about the shelf life for detection.

The DMNB particles remain in solid form in the finished explosive; they do not dissolve to any significant extent in the liquid phase. Thus, to a first approximation, the vapor pressure of DMNB in the explosives can be considered as the same as in free air. To be able to control the rate of sublimation, we decided to microencapsulate the individual particles of DMNB. The concept is to add a coating of polymer to reduce the rate of emission of DMNB vapor. In addition to increasing the lifetime for detection, microencapsulation offers advantages in production of marked explosives. By reducing the emission rate,

\* Tel.: +1-613-947-4274; fax: +1-613-996-9673.

E-mail address: kmintz@nrncan.gc.ca (K.J. Mintz).

the loss of DMNB during production at elevated temperatures would be reduced. This loss, which may be up to one-third, not only adds to the cost of marking explosives, but also adds to the variability of the concentration of DMNB in the final product. As well, since DMNB is classified as “toxic”, ventilation requirements during production of the explosive would also be reduced, which may make it possible to use existing production facilities without modifications. This paper deals with the characterization of microencapsulated DMNB, primarily by TGA. It should be noted that DMNB, although not formally classified as an explosive, decomposes quite strongly exothermically.

In order to characterize the process of emission of DMNB from the microcapsules on a more fundamental basis, a measurement of the diffusion through a layer of plastic was developed using TGA. Unfortunately, a sample of Parylene-C film was not available at the time of this research, so tests were carried out on polystyrene and polyethylene. These measurements are also valuable in estimating the vapor concentrations in suitcases containing marked explosives.

## 2. Experimental

The TGA was calibrated for mass and temperature before use. A 1–5 mg sample of the powder was spread out on a Pt pan. Both non-isothermal and isothermal tests were carried out.

Extensive safety tests (impact, friction and thermal) were carried out on the microencapsulated DMNB, both neat and mixed with explosives, to determine if there would be any added hazard relative to uncoated DMNB. In addition, safety tests were conducted on the empty capsules after the DMNB had completely sublimed, because of the potential concern that the empty capsules would act as sensitizers for the explosive (bubbles of air are known to increase the shock sensitivity of explosives).

The measurements of permeability of DMNB through polystyrene and polyethylene were carried out by placing DMNB in an Al pan. A small square of each was cut to just cover the pan; then the TGA was run isothermally at several temperatures. The square was weighed before and after the trial.

## 3. Results and discussion

### 3.1. Microencapsulation of DMNB

Although there are a number of methods for microencapsulation [2], the nature of DMNB (vapor pressure, exothermic decomposition, irregular surface) and the need for a thin coating, make most of them unsuitable. It should be noted that DMNB has a high permeability through most plastics. We chose the Parylene process [3], in which di-*para*-xylene is pyrolyzed in a mild vacuum to produce monomeric radicals which are deposited on the surface of the DMNB particles, where they polymerize, forming a continuous coating. The Parylene polymer is very inert, and thus would be expected to be suitable for most, if not all, explosives. The DMNB was made by Hampshire Chemical Co. and the microencapsulation was carried out by R.T. Dodge Co. A number of batches were produced with various thicknesses and different commercially available derivatives of Parylene. Only the tests on Parylene-C, which has one Cl per polymer unit are reported here. The thickness of the coating of individual particles was not measured, instead, the mass added to the DMNB was used as a measure of thickness. Reproducibility of results is one indicator of homogeneity.

Sieve tests on uncoated DMNB indicated that the mean particle size was about 150  $\mu\text{m}$  with almost none above 300  $\mu\text{m}$ ; on a sample of DMNB with nominal 2% coating, the mean particle size was about 200  $\mu\text{m}$ , with about 20% above 425  $\mu\text{m}$ . The latter may be due to two or more DMNB particles adhering together in the process, thus being coated as one. Hence, there is room for improving the process. The relatively large particles would not cause a problem for incorporating into explosives but may do so in some other anticipated applications.

The safety tests on Parylene-coated DMNB showed that, at the concentrations to be used for marking explosives, microencapsulation would not increase the hazard of the explosives.

After the microencapsulated DMNB has been heated sufficiently to sublimate all the DMNB, the capsules remain intact and are quite tough. Presumably, air crosses the membrane in the opposite direction of the DMNB so that there are no voids. Because the original particles are irregular in shape, these

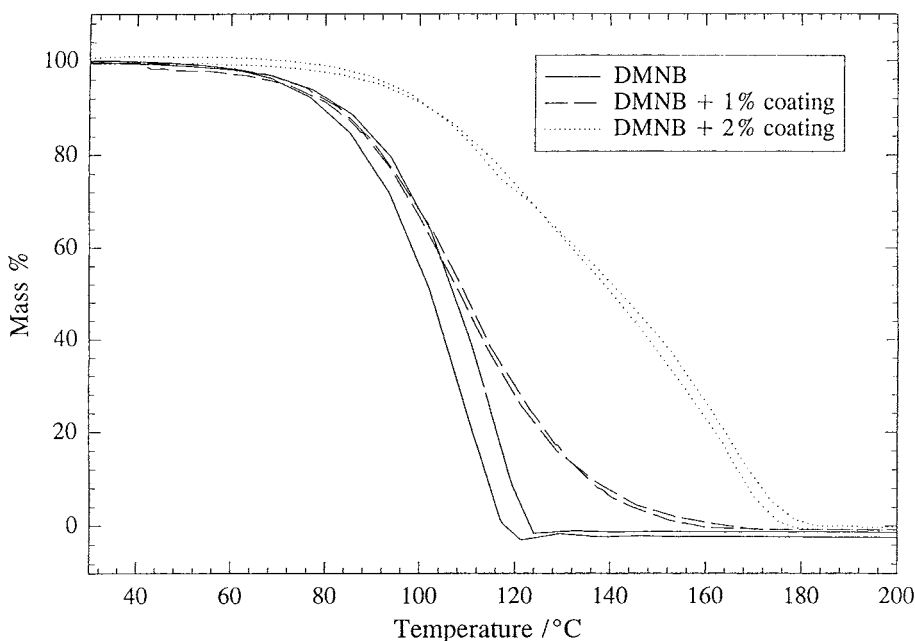


Fig. 1. TGA tests on DMNB and microencapsulated DMNB (1 mg samples,  $5\text{ }^{\circ}\text{C min}^{-1}$ ).

empty capsules are also irregular, conforming to the original shapes of the particles. As a result, the empty particles, when observed under a microscope, sparkle and display different colors.

### 3.2. TGA tests on microencapsulated DMNB

TGA was used because it measures the mass loss as a function of time and temperature, which is the property of interest. Fig. 1 shows non-isothermal TGA tests on DMNB and 1 and 2% Parylene-C coating. Clearly, the latter is retarding the emission of DMNB by a large amount. The 1% coating has only a marginal effect, probably because there is insufficient material to coat the particles completely: any discontinuity in the coating would allow the vapor above the particle to be close to that of DMNB. The duplicate test results are given to indicate the degree of reproducibility—these are typical. DMNB tests always had considerable scatter. The reason is believed to be due to the highly irregular shape of the DMNB particles, samples of which will have significantly different surface areas. On the other hand, the reproducibility of the microencapsulated DMNB was very good; the emission from the particulates is

governed primarily by the rate of diffusion through the coating.

Isothermal tests were carried out at temperatures between 35 and 70 °C. The rate of mass loss in the initial region followed first-order kinetics to a good approximation. The rate constants, thus obtained, are plotted in Arrhenius form in Fig. 2; as expected from the non-isothermal tests, the microencapsulated samples had significantly lower rate constants than the uncoated DMNB.

In order to decrease the rate of emission further, heavier coatings (4 and 6%) of Parylene-C were applied to DMNB. Rather surprisingly, the rate constants measured were similar to those of the 2% coatings. The most likely explanation is inhomogeneity, non-uniform wall thicknesses. A second set of batches were prepared with the same masses of coatings added stepwise; evaluation has not yet been carried out by TGA on these batches, though evidence by another method indicates significant decrease in emission.

In order to characterize the emission throughout its lifetime, samples were run isothermally for much longer periods of time. Fig. 3 shows that the rate of mass loss of uncoated DMNB increases as the mass

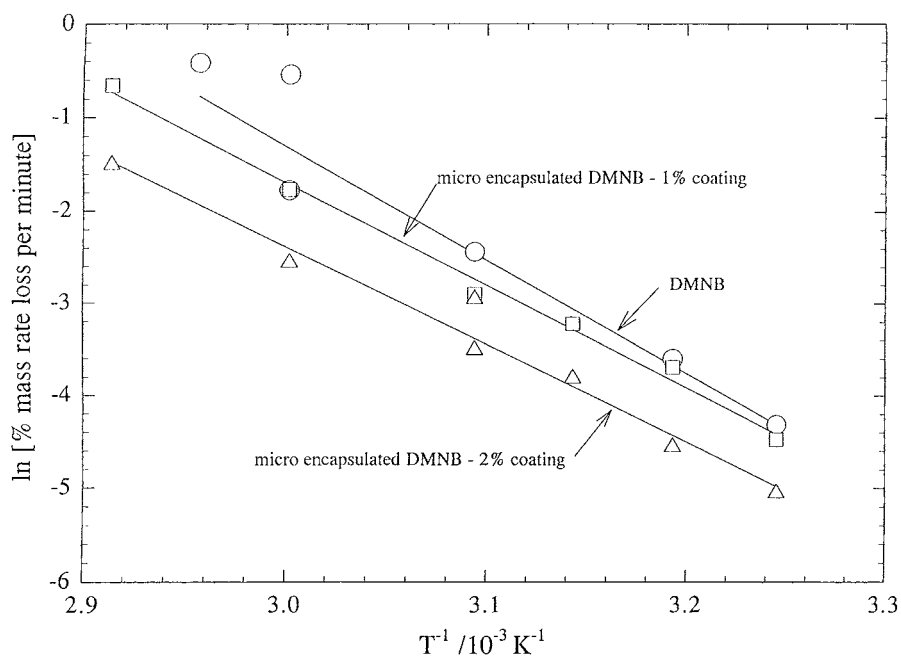


Fig. 2. Arrhenius-type plot for mass loss of microencapsulated DMNB.

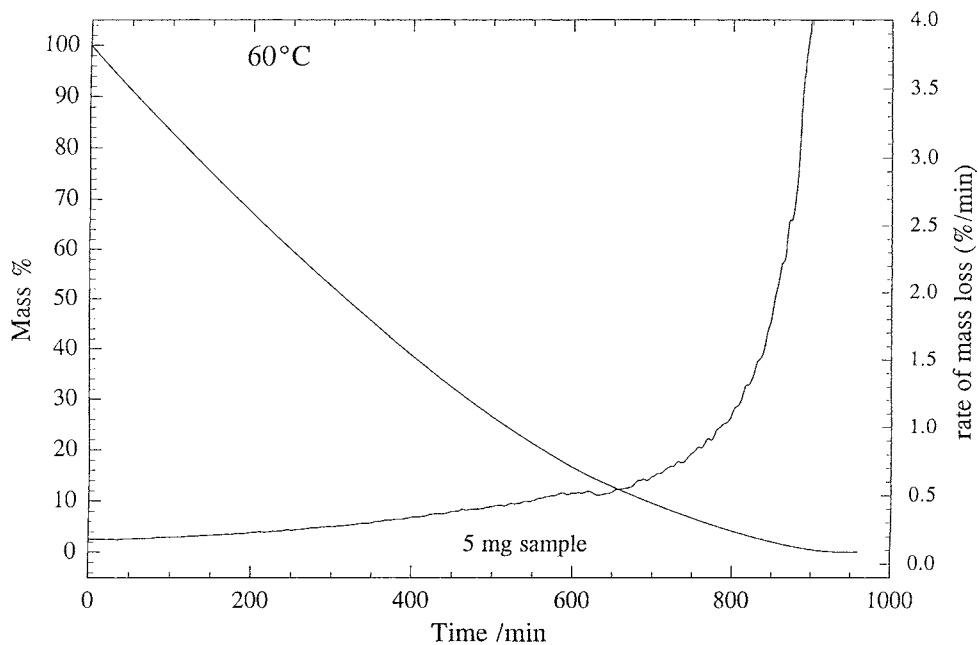


Fig. 3. Mass loss and rate of mass loss of DMNB at 60°C.

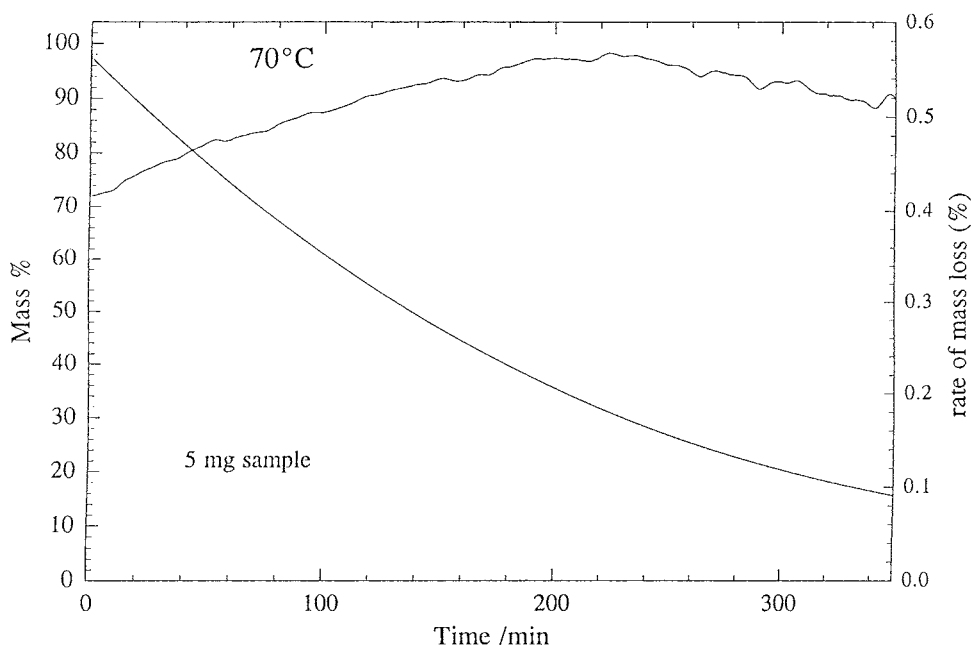


Fig. 4. Mass loss and rate of mass loss of microencapsulated DMNB at 70 °C.

loss increases, particularly close to the end. A possible explanation: as particles of DMNB decrease in size due to sublimation, the surface area/mass ratio increases, which causes an increase in the specific rate of sublimation. A theoretical calculation, assuming that the rate of sublimation is directly proportional to surface area, produced the same shape of curves as Fig. 3. On the other hand, Fig. 4 shows that the fractional rate of mass loss of microencapsulated DMNB with 1% coating remains more or less the same throughout its lifetime. The microcapsules are observed to remain a constant size even after all the DMNB has been depleted. Therefore, it is probable that the rate-determining step is the permeation through the coating. For heavier coatings, the rate of mass loss decreases with time; this decrease may be attributed to inhomogeneity of the coating. As time progresses, the thinner-walled capsules lose their DMNB, leaving behind the thicker-walled capsules, which would have intrinsically slower emission rates. This change in rate is observed to increase with the isothermal temperature applied, up to the highest temperature used, 100 °C (Fig. 5). Hence, there may be a long-lasting residual emission even after exposure to high temperatures.

The TGA experiments (initial rates of emission) have been confirmed by direct measurement of DMNB vapor in another laboratory [4]; the precision of the latter tests is much less than those of TGA. These tests also showed that the emission rates from DMNB with 4 and 6% coatings, produced by the stepwise process, were much smaller than from 2%, as predicted.

These results show that microencapsulation of DMNB can provide a much-increased lifetime for detection. The emission rate must not be allowed to decrease indefinitely, otherwise there will be insufficient DMNB vapor to be detected. The data obtained from TGA tests can be used to estimate optimum coating thicknesses.

### 3.3. Permeability tests

The assumptions are that, DMNB in the pan remains at close to its saturation pressure at the set temperature; on the outside of the material, the partial pressure is assumed to be close to zero. The solubility–diffusion model is used: DMNB dissolves in the material on the inside, then diffuses through the material and finally evaporates on the outside. The

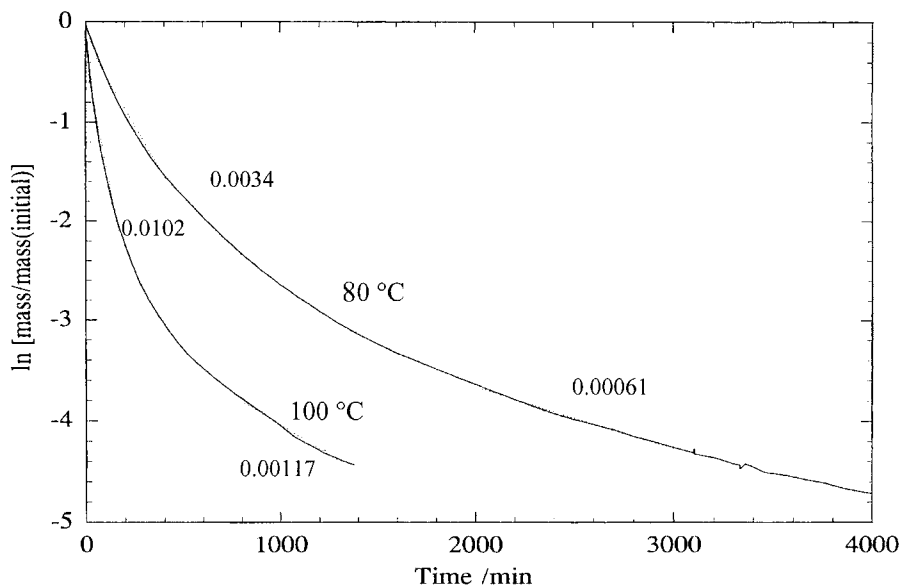


Fig. 5. Isothermal TGA tests on microencapsulated DMNB with 2% coating (first-order rate constants at different locations shown on graph).

flux,  $J$ , is given by [5]

$$J = DS \frac{P_i - P_o}{l} \quad (1)$$

where,  $D$  is the diffusion coefficient inside the membrane,  $S$  the solubility (Henry's law) coefficient,  $P_i$  the partial pressure of DMNB inside the membrane,  $P_o$  the partial pressure of DMNB outside the membrane, and  $l$

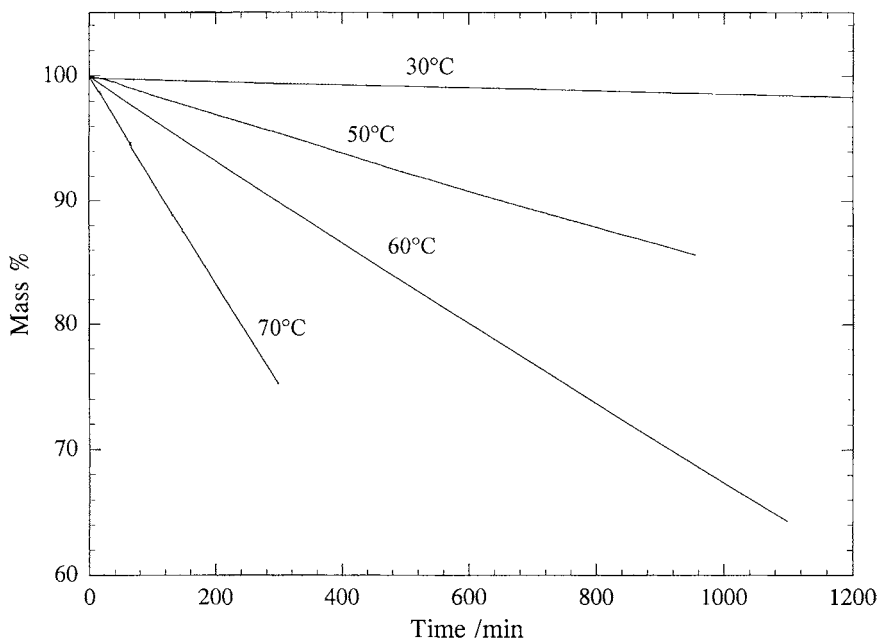


Fig. 6. Isothermal TGA tests on DMNB with 0.08 mm thick low-density polyethylene.

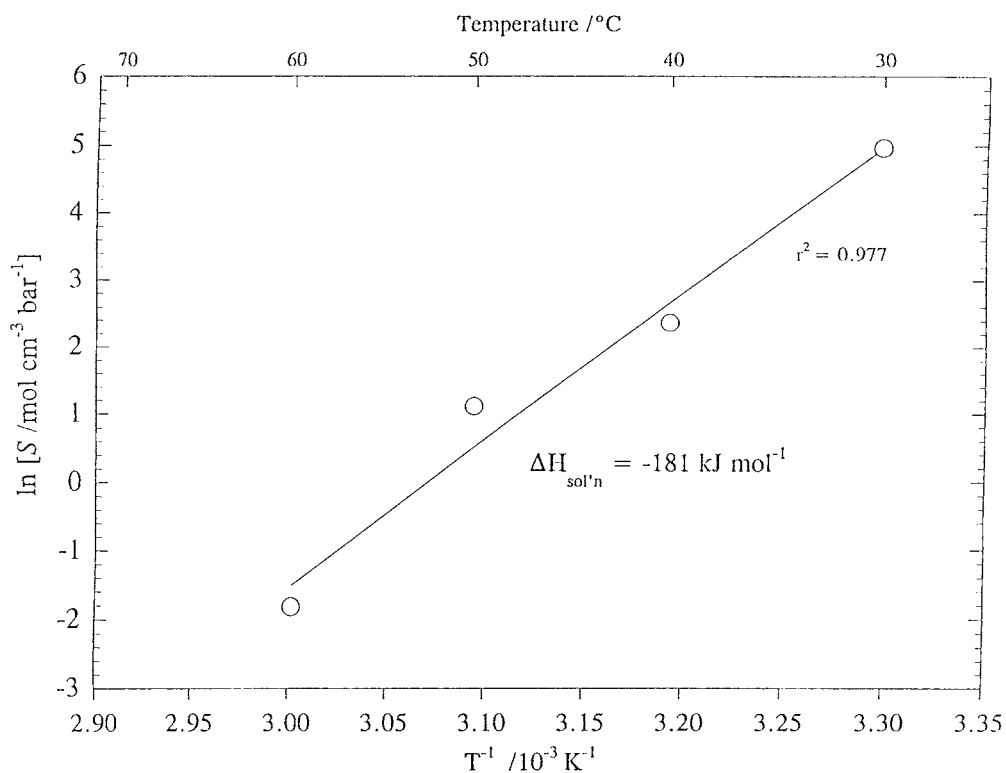


Fig. 7. The variation with temperature of the solubility coefficient of DMNB in polystyrene, as derived from isothermal TGA trials.

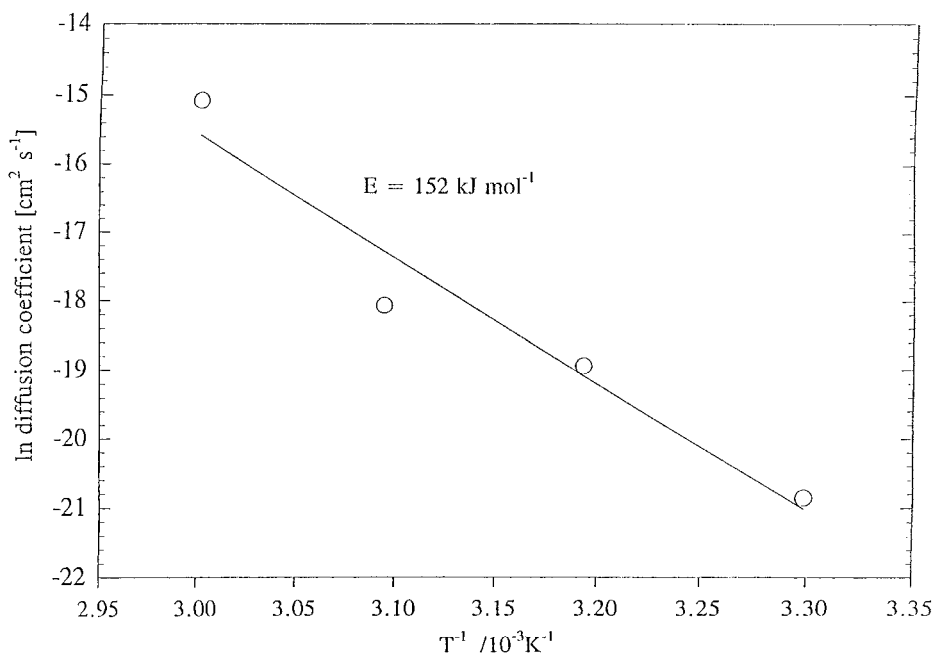


Fig. 8. The variation with temperature of the diffusion coefficient of DMNB through polystyrene, as derived from isothermal TGA trials.

the thickness of the membrane. The permeability coefficient,  $\mathcal{P}$ , is the product of  $D$  and  $S$ .

The flux is calculated from the experimental change in mass:

$$J = \frac{dm}{dt} \frac{1}{A} \quad (2)$$

where  $A$  is the area of the plastic in contact with DMNB vapor and  $m$  the mass of DMNB. The experimental values of the change of mass with time is shown in Fig. 6 for several temperatures. As predicted from the model, the data fall very close to straight lines:  $r^2$  varies from 0.9993 at 30 °C to 0.9999 at 70 °C. These data can be used directly for estimating the flux through any thickness of low-density polyethylene. An Arrhenius-type plot of  $\ln$  flux versus reciprocal temperature yielded a good straight line, making it possible to estimate fluxes at other temperatures by extrapolation. Values of  $\mathcal{P}$  can be calculated using the vapor pressures of DMNB determined by Elias [6].

The TGA tests with 0.25 mm thick polystyrene produced similar variation of mass loss with time, except that the permeability was greater. These trials showed a reversible increase in mass of the polystyrene during the TGA trials (except that there was no detectable gain at the highest temperature, 70 °C), which can be attributed to the solubility of DMNB in polystyrene. The values of  $S$  were calculated from the increases in mass using the vapor pressures of DMNB. An Arrhenius plot of  $\ln S$  versus reciprocal temperature yielded a straight line (Fig. 7), and a heat of solution of  $-181 \text{ kJ mol}^{-1}$ . Finally, the diffusion coefficients can be calculated from the solubility and permeability coefficients, with the slope yielding the activation energy (Fig. 8). Because of the uncertainties in the other two quantities, the diffusion coefficients have substantial uncertainties.

#### 4. Conclusions

TGA offered a way to, first demonstrate the usefulness of microencapsulation in reducing the emission rate of the marking agent DMNB for explosives, then in quantifying the effect so as to be able to select the

appropriate coating to tailor the emission rate for any particular application. Although there is a substantial cost associated with the microencapsulation process, this can be offset by reducing the quantity of marking agent required, as well as reduction of the cost of handling the DMNB in the explosives factory. A fairly broad distribution of the thickness of the coating may have an advantage over a narrow distribution in allowing some DMNB to remain after exposure to quite high temperatures, and thus, the explosive remains detectable. Tests have shown that, due to diffusion, the quantity of DMNB varies throughout the explosive; this variability increases with time, and may cause detection problems if the explosive is broken into pieces before use. If microencapsulated DMNB is used, there will be little variability in the concentration of DMNB throughout the explosive (provided, of course, that it is mixed-in properly when made).

The simple method of measuring of permeability using TGA may be a good method for evaluating candidate microencapsulant materials, as well as generating data to be used for modeling detection agent concentration around suitcases containing marked explosives.

#### Acknowledgements

This work was carried out under the Canada/USA Agreement on Cooperative Research and Development Concerning Counterterrorism. The author also thanks Dr. Lorne Elias for useful discussions.

#### References

- [1] D.E.G. Jones, R.A. Augsten, K.K. Feng, *J. Thermal Anal.* 44 (1995) 547.
- [2] J.I. Kroschwitz, M. Howe (Eds.), *Encyclopedia of Chemical Technology*, John Wiley and Sons, New York, 4th Edition, 1995, Vol. 16, pp. 628–651.
- [3] *Method and Apparatus for Microencapsulation*, US Patent 4,508,760 (1985).
- [4] Lorne Elias, JENEL TVD, Ottawa, Canada, unpublished work, 1999.
- [5] M. Grayson, D. Eckroth (Eds.), *Encyclopedia of Chemical Technology*, John Wiley and Sons, New York, 3rd Edition, 1981, Vol. 15, pp. 92–94.
- [6] Lorne Elias, National Research Council of Canada, Ottawa, Canada, unpublished work, 1990.