MODEL STUDY ON THE EFFECT OF ANIONACTIVE TENSIDES ON THE PENETRATION OF PESTICIDES

By

J. Bozzay, I. Rusznák, A. Schületz* and T. Zilahi*

Department of Organic Chemical Technology, Technical University Budapest,
*CHINOIN Chemical and Pharmaceutical Products Comp., Budapest

Received January 6, 1982

Introduction

The action of surface-active agents on pesticides asserts itself above all by changing the properties of the interface between the target and the spray, including the promotion of wettability and thereby of penetration.

Earlier studies have indicated that a correlation frequently exists between wettability (contact angle), surface tension and biological activity of herbicides and certain insecticides [1, 2, 3].

Knowledge about the effect of tenside on the penetration of pesticides will be useful to find the most efficient dosage form, e.g. emulgeable concentrates, and more expedient application of the agents. Studies of this action therefore appear highly promising both from the theoretical and from the practical view.

In this paper an *in vitro* model study of the action of anionactive tensides on pesticides will be described.

Theoretical concept and experimental

The rate of resorption of pharmacologically active substances is usually controlled by diffusion resulting from the concentration gradient (passive transport).

The resorption of drugs from stomach and intestins is successfully simulated *in vitro* with the Sartorius membrane filter apparatus [4]. Relying on the results, the diffusion constant can be calculated.

Since the penetration of pesticides through the — usually lipoid — membrane of the target is a diffusion process analogous to that of drug resorption, the idea to attempt studies of pesticide penetration and the action of tensides on this process in a Sartorius apparatus appeared evident, presuming that the findings at 37 °C in this apparatus will be comparable to the effects at ambient temperature.

The lipoid membrane model of the low-energy target surface was prepared by uniform impregnation of known-mass filter paper discs with a mixture of stearic acid and sunflower oil whose composition was pre-determined to attain satisfactory pour point and contact angle values.

The actual thickness h of the lipoid layer was calculated with the formula

$$h = \frac{m}{F\varrho}, \tag{1}$$

where m is the mass of the lipoid mixture on the filter paper disc, ϱ is the density of the lipoid mixture and F is the surface area of the paper disc.

The average thickness $\bar{h}$ was obtained by calculating the arithmetic mean of the h values.

The diffusion constants k_d of the substances applied in the study were determined experimentally [4] and the corrected diffusion constants K_d, taking into account the actual thickness h relative to the average thickness $\bar{h}$ of the lipoid layer were calculated:

$$K_d = k_d \left[\frac{h}{\bar{h}}\right] \tag{2}$$

Dioxacarb [5] was chosen as pesticide model substance and sodium lauryl sulfate as anionactive tenside. The membrane diffusions of the pesticide and the tenside were studied separately, and subsequently that of the pesticide in the presence of increasing amounts of tenside.

Dioxacarb contentration was determined by UV spectrophotometry, tenside concentration by conductometry, using previously recorded calibration curves.

The c.m.c. values measured with the sodium lauryl sulfate used in our work were 1.92 g dm^{-3} at 20 °C and 2.15 g dm^{-3} at 37 °C (Fig. 1).

The membrane diffusion of dioxacarb from its solution in distilled water into distilled water was studied in the range of 0.8 g dm^{-3} to 2.2 g dm^{-3} initial concentrations. Within this range the corrected diffusion constant K_d was found to be independent of the initial concentration.

In contrast, we found that in the membrane transport of the tenside the value of the corrected diffusion constant K_d changes with initial concentration. The average of K_d values calculated from initial concentrations exceeding the c.m.c. value is about 50% less than the corresponding value calculated from concentrations lower than c.m.c. In our opinion, this result is related to the micelle structure of the tenside, since the diffusion constant of the micelles aggregated from individual molecules, that is, larger than the monomers is, according to the formula of the diffusion coefficient D [6]

$$D = \frac{RT}{N} \frac{1}{6\pi\eta r} \tag{3}$$

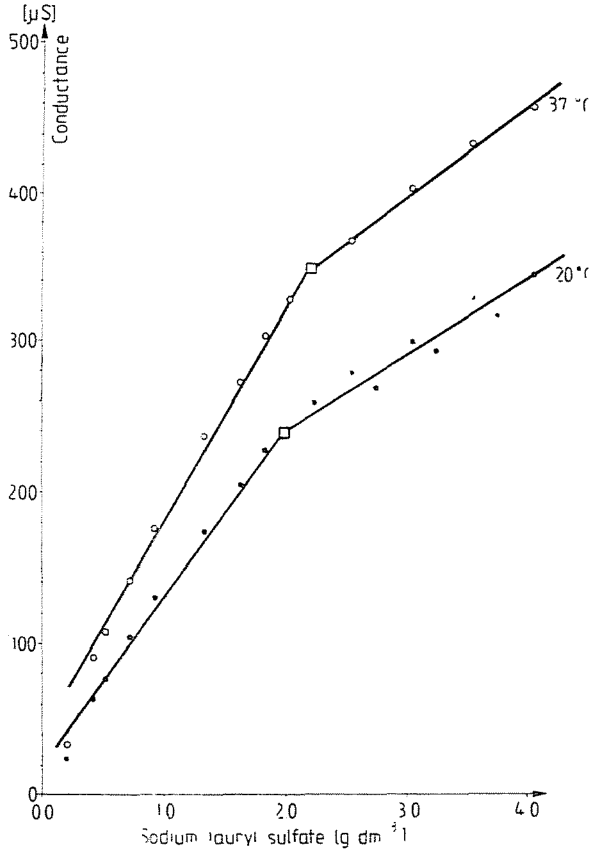

Fig. 1. Determination of the c.m.c. value of sodium lauryl sulfate by conductometry

inversely proportional to the radius *r* of the assumedly spherical particle. (In Formula (3) R is the universal gas constant, T the thermodynamic temperature, N the Avogadro number and η the viscosity of the medium.)

In our studies on the joint penetration of the active agent and the tenside we used solutions with a constant initial pesticide concentration $c_{ip} = 1.0$ g dm^{-3} and varying tenside concentrations.

The values K_d of the corrected diffusion constant of dioxacarb *versus* initial concentration of the tenside are presented in curve 3 of Fig. 2. For orientation, the conductance values measured to determine the c.m.c. values of sodium lauryl sulfate solutions (Curve 1) and surface tension data from the literature [7] (Curve 2) are also plotted in Fig. 2.

The figure indicates a significant change of the K_d value of the active agent in the vicinity of the c.m.c. value of the tenside: up to this value K_d increases (diffusion accelerates) and begins to decrease (diffusion decelerates) after the vicinity of the c.m.c. value. From the comparison of the course of the

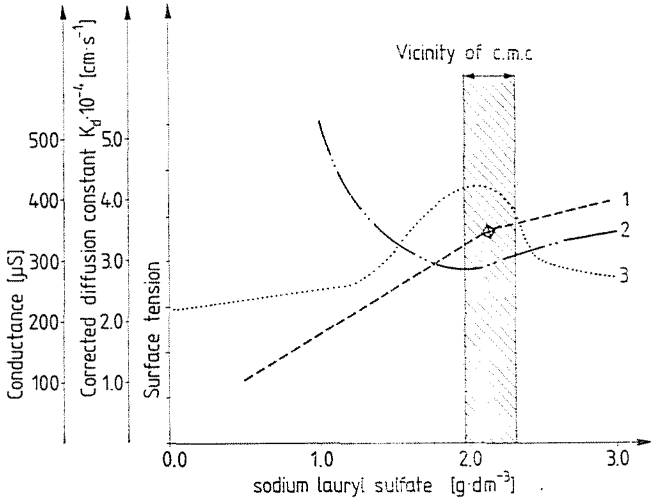

Fig. 2. The penetration of dioxacarb and other parameters *versus* sodium lauryl sulfate concentration. 1 — Measured conductance of sodium lauryl sulfate, 2 — surface tension of sodium lauryl sulfate (from [7]), 3 — measured corrected diffusion constant K_d of dioxacarb

K_d value of the pesticide with that of the surface tension of the tenside one may conclude that the penetration of pesticides is significantly affected by surface-active substances, mainly by virtue of wetting the surface of the lipoid membrane. Improvement of penetration will be attained in applying the tensides at concentrations lower than their c.m.c. range, that is, it is due to the effect of individual tenside ions and not to that of micelles formed from them.

Summary

The membrane transport of dioxacarb in the presence of anion-active sodium lauryl sulfate was studied *in vitro*. The Sartorius apparatus designed for resorption studies was found useful to provide data for the evaluation and characterization of the trends of pesticide transport. It was stated that the anion-active tenside — mainly by virtue of the wetting action of the individual tenside ions — improves penetration up to the vicinity of the c.m.c. value, while at tenside concentrations exceeding the c.m.c. value the diffusion constant decreases. The trend of the corrected diffusion constants is reverse to the change of the surface tension of the tenside solution.

References

1. Valkenburg, W.: Pesticide Formulations. Dekker, New York 1973.
2. Andriska, V.—Bozzay, J.: Fundamentals of the Technology of Pesticide Preparations.* BMETI, Budapest, 1978.
3. Jensen, L. L.: J. Agr. Food Chem. **12**, 223 (1964).

---

* In Hungarian.

4. Sartorius Membranfilter. Sartorius.
5. WORTHING, C. R.: The Pesticide Manual. 6th Ed. British Crop Protecion Council, Nottingham 1979.
6. ERDEY-GRUZ, T.—SCHAY, G.: Theoretical Physical Chemistry.* Tankönyvkiadó, Budapest 1954.
7. BECHER, P.: Emulsions.* Műszaki Könyvkiadó, Budapest 1965.

Dr. József BOZZAY
Prof. Dr. István RUSZNÁK
H-1521 Budapest

Aranka SCHÜLETZ
Tibor ZILAHI
Chinoin Chemical and Pharmaceutical Products Co.,
Budapest H-1045