OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

FAIR USE POLICY

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

RESTRICTED

20090

DP/ID/SER.A/1631
8 March 1993
ORIGINAL: ENGLISH

STRENGTHENING OF PESTICIDE DEVELOPMENT CENTRE

DP/IND/89/128

INDIA

Technical report: Research and development in pesticide formulation*

Prepared for the Government of India
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of R. Aveyard, consultant in
pesticide formulations

Backstopping Officer: B. Sugavanam
Chemical Industries Branch

United Nations Industrial Development Organization
Vienna

---

* Mention of firm names and commercial products does not imply the endorsement of the United Nations Industrial Development Organization (UNIDO). This document has not been edited.

V.93 82583

CONTENTS

ABSTRACT

The 2 week assignment to the Institute of Pesticide Formulation Technology (IPFT) at Ugyog Vihar, Gurgaon (near Delhi) has been successful. Detailed discussions were held concerning a number of formulations which are either close to commercialisation or under development. Systems considered included 3 microemulsion concentrates, which comprise a new generation of formulations circumventing the use of large quantities of undesirable organic solvents. The active ingredients of these concentrates are Monocrotophos (an insecticide/acaricide), Butachlor (a herbicide) and Dimethoate (an insecticide/acaricide). In addition to these systems consideration was also given to a formulation for the application of a microbial pesticide to water surfaces and to a wettable powder formulation in which Malathion is absorbed in the pores of the powder.

Clearer pictures have emerged about the formulation structures, surface chemical aspects of their mode of action and some of the formulation problems which are encountered. In the case of 4 out of the 5 formulations considered, simple experimentation been suggested which should throw light on the questions posed.

In addition to consultation sessions I also gave 4 lectures/seminars to members of the Formulation Group, visited the research laboratories of the Indian Oil Corporation (and subsequently held a short consultancy session with 4 senior personnel of IOC) and gave 2 lectures at the University of Delhi, one being sponsored by the Royal Society of Chemistry, North India Section.

RECOMMENDATIONS

Detailed technical recommendations in respect of each of the various formulations have been made in the appropriate sections, and are not repeated here. I found the members of the Formulation Group, in particular Dr. P. K. Ramdas (Manager, R & D) and Dr. P. K. Patanjali (Senior Colloid and Surface Chemist) to be dynamic and resourceful. The formulation laboratory is well equipped in general and the Group is having significant successes in developing new formulations. There are however some gaps in the instrumentation which should be filled, and additionally a need for a staff member to undergo training in some fundamental aspects of surfactant science of direct relevance to the programme of the Formulation Group. I therefore make the following recommendations, which are amplified in the Annex.

1. The purchase of (a) microelectrophoresis equipment (b) a contact angle microscope and (c) a polarising microscope.

2. A member of staff of the Formulation Group should undergo six months training in surfactant science in an appropriate research laboratory.

INTRODUCTION

I have spent 2 weeks, at the request of the United Nations Industrial Development Organisation, at the Institute of Pesticide Formulation Technology (IPFT). My main duties were to assist technical personnel in the development and evaluation of pesticide formulations and to provide expert information on theoretical aspects of the surface and colloid chemistry of these formulations. Detailed discussions were held concerning 5 formulations, 3 of these being a new generation of microemulsion concentrates which avoid the use of large amounts of undesirable organic solvents which are present in the alternative emulsion concentrate formulations.

I interacted mainly with Dr. P. K. Ramdas (Manager, R & D) and Dr. P. K. Patanjali (Senior Colloid and Surface Chemist), and the important questions and problems raised were all in the area of surface and colloid chemistry, including microemulsion phase behaviour, surface monolayers on water and solid wettability. My own expertise is directly relevant to all these areas and the consultations were I believe fruitful, and a number of recommendations for future experimentation have been made.

In addition to consultancy sessions, and in accordance with the job description, I held 4 seminars in the areas of adsorption at solid/liquid interfaces, solubilisation, microemulsions and emulsions. Copies of the material covered have been given to Dr. Ramdas, and copies of a number of relevant research papers from my own research group were also taken. As well as my work at the IPFT, I also visited and held discussions with personnel at the laboratories of the Indian Oil Corporation, and delivered 2 lectures at the University of Delhi, one of the lectures being sponsored by the Royal Society of Chemistry, North India Section.

2. CONSULTANCY AND DISCUSSIONS

The discussions and consultancy covered a number of formulations including microemulsion concentrates (MEC) containing pesticide, a formulation for the delivery of particulate microbial pesticide to water surfaces and a system in which liquid pesticide is contained within the pores of a wettable powder. The aims were, variously, to understand surface-chemical aspects associated with the application of the formulation, to understand the origin of problems associated with the preparation of formulations and to contribute ideas on the probable structure of the formulations. In some cases simple experiments were performed and in others key experiments suggested.

2.1 Formulation for the application of microbial pesticide to water surfaces

Description. The formulation consists of (by weight, here as elsewhere) 5% butanol, 20% pesticide, 10% water-insoluble surfactant (an EO/PO block copolymer - Pluronic), all in vegetable oil (assumed to contain long chain glycerides). When applied to the surface of water, the formulation spreads spontaneously, producing small lenses. The necessary surface-chemical features appear to be (a) to give a large number of small lenses which can retain the microbial particles and (b) that the lenses should be spread over a large area of surface and remain evenly spaced. The formulation is almost ready for commercialisation

Objective. The aim of the discussions (and some simple experimentation) was to arrive at a reasonable model for the surface-chemical properties of the formulation. On the basis of the model it may prove possible for example, to improve the formulation and devise effective screening procedures for the choice of suitable surfactants.

Discussion. The main question addressed concerned the nature of the surface separating the lenses, which is able to resist compression by wind impinging on the water surface and the resultant loss of lenses to the edge of the water surface. Simple experiments were carried out which clearly showed that both the vegetable oil and the surfactant spread rapidly along the surface on contact, and (importantly) the surface pressure generated was maintained. It thus appears that in the spread formulation the surface which separates the lenses is a mixed monolayer of oil and surfactant, probably exerting a substantial spreading pressure which is able to withstand compression. Butanol, like the oil and surfactant can also spread on the surface but due to its high solubility in water is lost. Its role in the formulation thus appears to be to cause violent agitation of the applied droplets (as it transfers from the oil to the water), thus breaking the droplets into much smaller lenses which are then held apart by the intervening mixed monolayer of oil and surfactant.

Recommendation. Mixed monolayers of oil and surfactant, which are insoluble, should be spread on water on a Langmuir trough (available in the Formulation

Laboratory) and surface pressure (π) - surface area (A) curves obtained by standard procedures. The probable form of the π - A curves will be as shown in Figure 1. If the equilibrium spreading pressure (ESP) exerted by the formulation is in the range indicated (i.e. on the steep part of the isotherm) the film will be incompressible, as in the proposed mechanism.

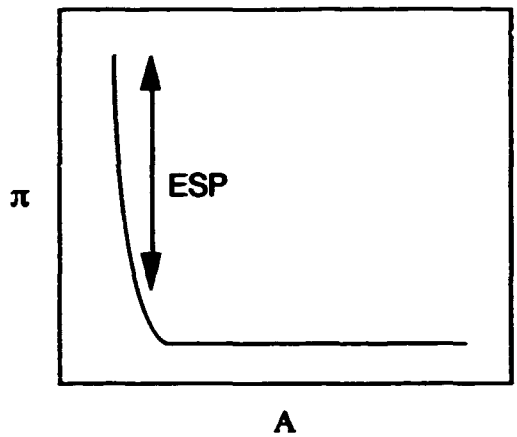

Figure 1. Possible form of π-A curve for mixed insoluble monolayer of nonionic surfactant and vegetable oil.

It is also recommended that the phase of the lenses be investigated. It may be that the lenses need to be viscous to retain their physical integrity. There is a possibility that they may be liquid crystalline in nature. When a lens of the formulation is placed on the surface of water, since the oil and surfactant cannot dissolve in the subphase, it is likely that some water will be taken up in the drop. It is well known that liquid crystal formation is common in systems containing oil, water and surfactant in combination. Liquid crystal phases can be recognised by viewing between crossed polarisers under a microscope.

2.2 Wettable powder formulation for Malathion

Description. The formulation consists of the liquid insecticide, Malathion (M) taken up in porous hydrated calcium silicate together with surfactant (as a dispersing agent). The product, which is 50% insecticide, is ultimately applied as a 5% dispersion in water. It is found that some surfactants lead to displacement of M from the solid pores when dispersed in water, which is undesirable. The formulation is almost ready for commercialisation, with a very good potential export market in Asian countries.

Objective. The purpose of the discussion was to identify possible mechanisms for the displacement of insecticide from pores by surfactant solution.

Discussion. There are 2 readily identifiable possibilities for the loss of insecticide from the pores. Firstly, the liquid could simply "stream" from the pores and secondly, it could be displaced by the surfactant solution. The streaming mechanism could be expected to operate in cases where the interfacial tension between insecticide and aqueous phase is very low, say < 0.1 mN/m. The displacement mechanism will be applicable in cases where the pore surfaces are more wettable by the surfactant solution than by the pesticide.

Recommendation. It is first noted that the concentration of surfactant in the vicinity of the interface between M and surfactant solution on the addition of the wettable powder to water can be very high. This should be taken into account in performing the experiments suggested below.

Appropriate tensions between M and aqueous surfactant can be readily measured using the spinning drop tensiometer available. At the time of writing the tensiometer has a fault, which needs to be rectified. In the meantime it should be possible to detect the presence of low tensions by observing if M, contained in a very narrow capillary, streams from the end when immersed in the surfactant solution. It should be noted that surfactant transfer across the liquid/liquid interface could contribute to the dispersion of M if low tensions exist.

Investigation of the displacement mechanism requires the determination of contact angles between M and the solid in the presence of aqueous surfactant. For this purpose it will be necessary to compress the solid particles into the form of a smooth solid disc. The disc will be immersed in aqueous surfactant and a drop of M placed on the solid under the solution (Figure 2). Contact angles, θ, in excess of 90° indicate that

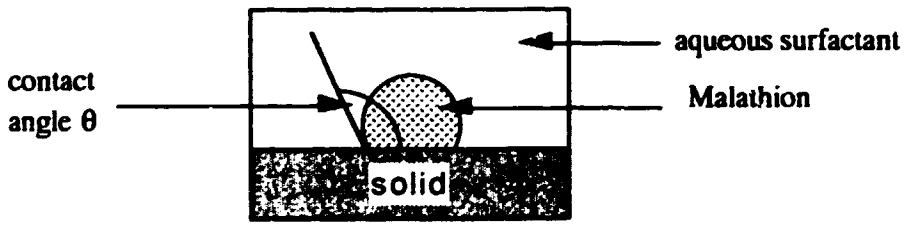

Figure 2. Malathion on solid under surfactant solution.

the solid surface is preferentially wetted by the surfactant solution and therefore that M could be displaced from the pores by the surfactant solution. The Laboratory is not currently equipped with a contact angle microscope (see Recommendations at the beginning of the report). Nonetheless, it may be possible at this stage to observe visually (using a narrow capillary) if the contact angle is greater or less than 90°.

2.3 Microemulsion concentrates (MEC)

Many effective formulations, easily prepared, are emulsifiable concentrates in which the active material is dissolved in a low cost organic solvent. There are however a number of serious disadvantages to systems containing organic solvents, which are usually highly inflammable and volatile. There are problems with storage and transportation of such systems. The solvents can also cause eye and skin irritation at the point of application and may in addition be phytotoxic. It is becoming more necessary therefore to move towards developing more complex systems which are water based. Microemulsion systems offer one way forward, but formulation problems exist at present. Discussions were held on the systems now described, and recommendations about future experimentation made.

2.3.1 Microemulsion formulation containing Monocrotophos

Description. This MEC (which is ready for commercialisation) consists of 50% Monocrotophos (MCP) (an organophosphorus insecticide/acaricide) and 50% "solvent" which is made up of 88% isopropanol (IPA), 11.5% kerosene and 0.5% surfactant (an anionic/nonionic mix). The kerosene (about 6% of the total formulation) enhances the efficacy of the formulation and appears to improve the long term chemical stability of the pesticide. The description of the formulation as a microemulsion concentrate is a little misleading since (as discussed below) it probably consists of a large volume fraction of continuous phase made up largely of IPA and MCP, in which is dispersed a low volume fraction of a kerosene-rich phase.

Objective. To gain a working picture of the structure of the formulation.

Discussion. The mutual solubilities of the various components are an important factor in understanding the structure of the formulation. Kerosene dissolves in IPA at least up to 11.5%, although the pair are probably not completely miscible (the mutual solubilities should be determined). MCP is completely miscible with IPA, in which it has good chemical stability. Kerosene and MCP have low mutual solubilities. In the absence of surfactant the system is 2-phase, with a minor phase separating with a strong smell of kerosene. A possible form of the phase diagram for the formulation in the absence of surfactant, based on the observations made on solubilities, is shown in Figure 3. A simple view of the role of the surfactant is that it serves to solubilise (as swollen micelles or microemulsion droplets) the minor phase which is probably largely kerosene.

Recommendation. Information about the composition of the minor phase should be obtained. Extraction by water will remove both IPA and MCP, and the remaining liquid will be kerosene. If the minor phase is largely kerosene then a simple picture of the role of surfactant is that it solubilises kerosene in a mixture of IPA and MCP (the continuous phase).

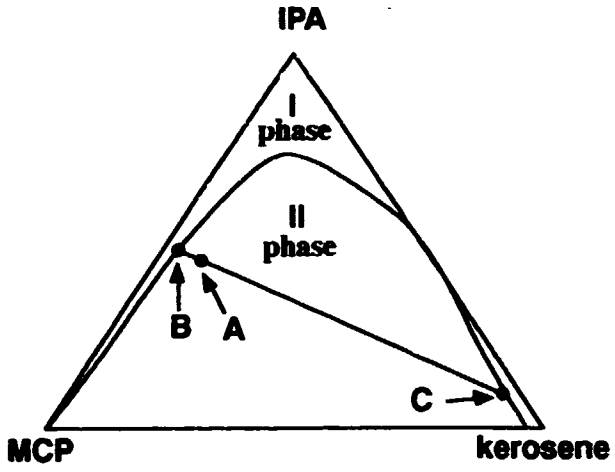

Figure 3. **The formulation (in absence of surfactant) lies at A. The separating phases lie at the ends of the tie line. The minor phase at C is expected to be largely kerosene. The phase of high volume fraction (at B) will contain mainly MCP and IPA.**

The following experiment should throw light on the structure of the formulation. Prepare a sample of the formulation but without surfactant and separate the minor phase. Make up various concentrations of surfactant in the major ("solvent" or continuous) phase, and determine how much of the minor phase can be solubilised as

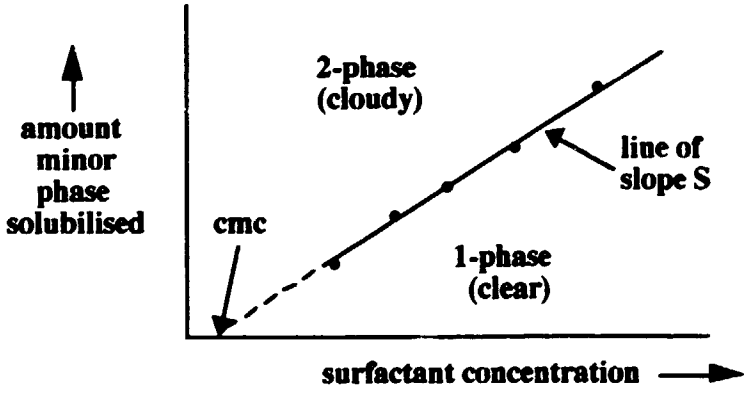

Figure 4. **Solubilisation of minor phase in major phase containing different amounts of surfactant (see text).**

a function of surfactant concentration before phase separation occurs. The results may be of the form shown in Figure 4. For a pure solvent and oil in the presence of a single pure surfactant the significance of the plot in Figure 4 is as follows. The slope of the (probably) straight line, S, is given by

$$S = \text{[amount solubilised] / ["micellised" surfactant]}$$

The value of S is simply related to the radius, r_c, of the core of the microemulsion droplets by the expression

$$r_c = 3 S v / A$$

where v is the molecular volume of solubilisate, and A the molecular area of the surfactant (chain) at the core surface.

In applying this approach to the MCP formulation rough estimates will have to be made of the surfactant molecular weight (to calculate the surfactant molarity in Figure 3) and the area per molecule, A. The volume v might reasonably taken as that of kerosene.

A simple experimental set up is shown in Figure 5.

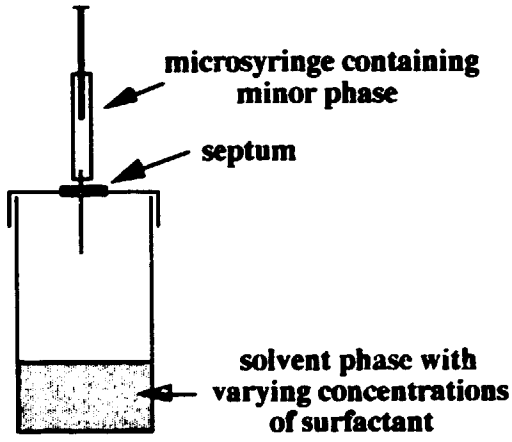

Figure 5. **Simple experimental set-up to determine solubilisation of minor phase in "solvent" phase, and hence estimate microemulsion droplet radii. Ideally the solution should be continuously mixed (magnetic stirrer) and thermostatted.**

2.3.2 Microemulsion formulation containing Dimethoate.

Description. The formulation consists of Dimethoate (DM) 37%, water 54%, surfactant (anionic/nonionic mix) 7%, which is high, and diacetone alcohol (DAA) 2%. The system is believed to be an oil (DM)-in-water microemulsion since it mixes with water

without phase separation. DM is a low melting (50°C) solid; it may be a supercooled liquid in the formulation which is formed at high temperature. Alternatively its melting point might be reduced by water and/or DAA. Without DAA the formulation is 3-phase. This formulation is still under development.

Objective. The purpose here has been to understand the factors which determine the range of temperature over which the formulation remains as a single phase microemulsion.

Discussion. It is suggested that the formulation be considered in terms of a Shinoda-type of phase diagram in which phase behaviour is depicted as a function of oil to water ratio in systems containing an overall fixed amount of surfactant. The ordinate of the diagram (shown in Figure 6) is some HLB variable (e.g. T, [cosurfactant]). Unfortunately the effect of temperature is the opposite for ionic and nonionic surfactant systems, and the surfactant used in the formulation is an (anionic + nonionic) mixture.

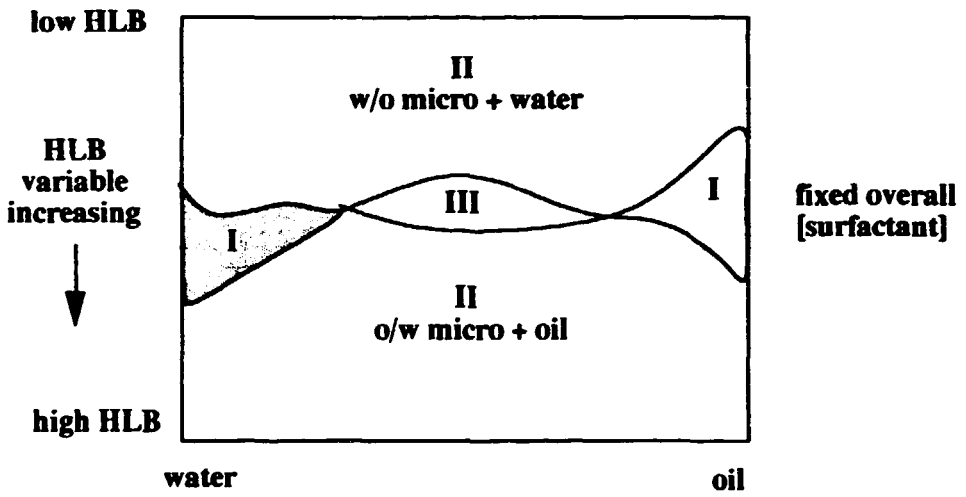

Figure 6. Shinoda type of phase diagram. The shaded area is a single phase o/w microemulsion. Roman numerals refer to the number of coexisting phases

Two problems face the formulator. It may be required to move the whole single phase region to higher or lower temperatures. It may also be desirable to increase the existing area of a single phase region (without simply using more surfactant).

With regard to the first problem it should be possible to shift the 1-phase region *en masse* by addition of a short chain alcohol (e.g. butanol). Usually addition of such a cosurfactant will tend to favour the formation of w/o microemulsions in equilibrium with excess water which, in the presence of a nonionic surfactant would lower the temperature range of the single phase regime.

In order to understand how one might increase the area of the single phase region it should be realised that the two phase boundaries enclosing the region arise from different causes. For example if Figure 6 refers to phase behaviour in a nonionic surfactant system and if T is plotted as the ordinate, the upper temperature boundary of the o/w microemulsion region is the so-called "cloud point" boundary and arises as a result of inter-droplet attractions. The lower boundary is determined by the "spontaneous" curvature of the surfactant layer stabilising the droplets. To increase the area of the region in this case it would be necessary to decrease the attraction (increase the repulsion) between droplets to push the cloud point boundary up. To shift the solubilisation boundary down it would be necessary, by say adding an appropriate surfactant or cosurfactant, to decrease the spontaneous curvature of the monolayers.

The above discussion presents a framework within which the problem can be considered. There is no doubt however that the problem is a complex one, not least because the formulation of interest contains both ionic and nonionic surfactants.

2.3.3 Microemulsion formulation containing Butachlor

Description. Butachlor (B) is a water-insoluble herbicide oil which is hydrolytically stable. The basic formulation is 50% B, 40% water and 10% mixed anionic/nonionic surfactant. In order to make this mixture single phase it is necessary to add NaCl (6% in the water). This formulation spontaneously emulsifies in water but if the NaCl concentration is increased to 7% in water it is found that spontaneous emulsification with water does not occur.

Objective. The aims of the discussion were threefold: (i) to consider the nature of the formulation in the absence of salt; (ii) to suggest why addition of NaCl produces a single phase microemulsion; (iii) to understand why further addition of salt leads to a loss of spontaneous emulsification with water.

Discussion. In the absence of NaCl the formulation forms an emulsion on mixing. This probably consists of a microemulsion together with excess oil (B) or water. Since NaCl apparently increases the solubilisation to give a single phase it is probable the microemulsion phase is of the o/w type. Salt addition decreases the effective surfactant head group size (for both ionic and nonionic surfactants) which increases the solubilising power. The microemulsion type should be determined (see under Recommendations).

Addition of salt beyond 6% in water could invert the microemulsion type to w/o, which is not expected to readily emulsify in water unless the oil/water interfacial tension is low and some mass transfer across the interface occurs.

Recommendation. The microemulsion type existing before the addition of NaCl can readily be determined by mixing the components and noting the position of the interface after allowing the system to settle (Figure 7). The (possible) inversion of microemulsion type on increasing the NaCl concentration from 6% to 7% in water can be tested by measuring the conductivities of the systems.

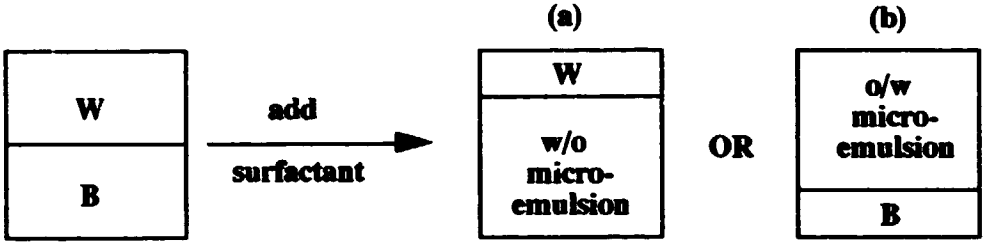

Figure 7. **Interface positions for (a) formation of w/o microemulsion and (b) o/w microemulsion.**

3. LECTURES

Four lectures were delivered to the Formulation Group at IPFT, covering areas relevant to the work of the Group.

3.1 Adsorption at the solid/liquid interface

The nature of solids was first discussed, including types encountered, origins of surface charge and surface area and porosity. Following a description of the electrical nature of solid/liquid interfaces and the forces responsible for surfactant adsorption, examples of isotherms for the adsorption of ionic and nonionic surfactants were given.

3.2 Microemulsions

Here, modern ideas about the nature of microemulsion systems were presented.The inter-relationship between oil/water interfacial tensions and microemulsion droplet size and type was described, and explained in terms of surfactant monolayer curvature requirements and the molecular packing factor. The ways in which variations in salt concentration and temperature (which are important practical variable) influence microemulsion behaviour were explained.

3.3 Solubilisation

A major theme in this lecture was the relationship between solubilisation and micelle shape, solution viscosity and, in the case of nonionic surfactants, cloud points. The second part of the lecture dealt with the principles underlying the stability (with respect to phase separation) of single phase microemulsions. In particular the origins of phase separation at the solubilisation and the cloud point phase boundaries were explained, in order to give a basis for the modification of phase behaviour in formulations.

3.4 Emulsions

An overview was given of the inter-droplet interactions which determine emulsion stability and physical properties. The major part of the lecture was concerned with describing the modern understanding of the important hydrophile-lipophile balance (HLB) concept. Surfactant HLB is used very widely by formulation scientists.

ANNEX

A.1 Recommendations for new equipment to be purchased by UNIDO

Various aspects of the work of the Formulation Group are concerned with the adsorption of surfactant on solids and with the wettability of solids. Valuable information in these areas can be gained from microelectrophoresis of solid particles in surfactant solutions and from the determination of contact angles of surfactant solutions with solids. In addition, phase behaviour, and in particular the formation of liquid crystalline phases in a number of formulations can be of great importance. For these reasons, I recommend the purchase of the following equipment.

(a) Microelectrophoresis equipment.

Rank Brothers, High Street, Bottisham, Cambridge, England CB5 9DA.

Mark II elecrophoresis apparatus;	£4,430
TV attachment	£770
Prism attachment	£700
TOTAL	£5,900 (+ shipping)

(b) Kruss contact angle (microscope) meter

From Camtel Sciences, 27 Alexander Road, Stotfold, Hitchin, Hertfordshire, England SG5 4NA.

Meter G1	£5763
Stand for drive and syringe holder, G23	£695
TOTAL	£6458 (+ shipping)

(c) Nikon Polarising microscope

From Nikon UK, Haybrook, Halesfield 9, Telford, Shropshire England TF7 4EW

Alphphot body MDA 154AA YS-POL	£559
Intermediate tube MDB 25300	£538
Dia-polariser MDN 11920	£40
3 of 30W lamps MXA 20451	£36
2x MCK 30101 CFWE 10x eyepiece	£48
Strain free condenser MDL 11300	£183
CF PO 4x objective MSC 30040	£56
CF PO10x objective MSC 30100	£84
CF PO 40x objective MSC 30401	£140
Trinocular "FJ" MBB 13140	£366
1/4 lambda & tint plate MDV 1030	£268
TOTAL	£2318 (+ shipping)

Total cost of equipment = £14,676

A.2 Recommendations for training programme

Microemulsions constitute a new generation of formulations. There have been considerable advances in the fundamental understanding of microemulsion behaviour in the last decade. It is highly desirable that a member of staff of the Formulation Group should spend 6 months or more receiving training in modern, relevant aspects of surfactant science and microemulsion behaviour. I would be happy to host someone in my own Laboratory, or I could suggest other possibilities if required.

Before commencing a training programme, the person involved should undertake some directed reading. A relevant research programme would then need to be agreed between Dr. P. K. Ramdas of the IPFT and the leader of the host laboratory.

A.3 People met during the visit

Institute for Pesticide Formulation Technology.

My main interactions were with Dr. P. K. Ramdas (R & D Manager) and Dr. P. K. Patanjali (Senior Colloid and Surface Chemist).

Research Laboratories of Indian Oil Corporation, Delhi.

I visited these laboratories for a morning. Subsequently 4 members of staff attended 2 lectures given by me at the University of Delhi (Chemistry Department), and afterwards I had a short consultancy session on microemulsions with Dr. A. K. Batnager (General Manager), Dr. A. A. Gupta (Deputy Manager, Research), Dr. M. M. Rai (Senior Research Manager) and K. K. Swami (Research Officer).

University of Delhi, Department of Chemistry.

Here I gave 2 lectures, one of them sponsored by the Royal Society of Chemistry, North India Section. I also held discussions with Dr. Maitra and members of his research group.

UNIDO COMMENTS

The report gives a high level advisory services for preparing modern pesticide formulations for the benefit of the Indian market. The author has looked into the bio-pesticide formulation which spreads on the surface of water. He has applied his theoretical knowledge to control the thickness of the film so that it does not break up.

The second formulation of malathion w.p. could be ideally developed for commercialization after studying storage stability tests. They should also look into the possibility of using water soluble satches for small scale application especially in public health outlets.

The author's experience in applying theory to practical development could be very useful to IPFT for developing high-tech formulations.