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The Formulation of Dispersion Media for Some Organotin Compounds

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Abstract: ***In order to overcome the aqueous insolubility of organotin compounds, dispersion media have been formulated for tri-and di-organotin compounds based on polar and hydrocarbon solvents and a number of additives. The stability of the aqueous dispersions of the formulae were assessed using a combination of visual observations and centrifugal and transmittance measurements. The results show that stable dispersions were obtained only in the presence of the additives. The role of the additives in the stabilization mechanism has been adduced and the implications of the findings to the control of some agricultural pests have been highlighted.***

Keywords: Organotin compounds, Antifungal, Media formulation, Emulsion stability, Solubility

1. Introduction

According to a recent UN report [1], the world's population currently stands at slightly above 7 billion and is expected to reach the 8 billion mark by the year 2025. Alongside this increase is the food problem which has continued to plague several nations especially in the developing countries. Famine results from a complex interplay of national, regional and international conflicts, adverse climatic conditions such as drought and flooding, non-adaptation to modern agricultural practices including soil maintenance and loss of potential yields to pests. Reduction in output by pests alone accounts for over one-third of the total agricultural potential [2]. The problem is more severe in the tropics where high humidity and temperature combine to provide favourable conditions for the rapid growth and multiplication of pests. Chemical fertilizers have been used for long to improve soil quality and reverse this trend. To alleviate the problem of pests however requires the use of pest resistant species and/or pesticides.

An important class of pesticides is the organotin compounds. These compounds are active against a wide range of pests including weeds, mites, insects, worms, and fungi [3, 4].

Biologically active organotin compounds contain the di-and tri-organotin moieties; R_2Sn^{2+} and R_3Sn^{+} respectively where R is an alkyl or aryl group and may be mixed or unmixed. The specific organism against which the organotin is active depends on the size and structure of the R group [5] which may therefore not be altered.

One problem confronting the application of organotin compounds to agriculture is their aqueous insolubility. The solubilities in water of the most useful organotins are often less than 10ppm whereas, useful pesticide formulations require concentrations in excess of 50 ppm and sometimes as high as 250 ppm. There is need to find water compatible media that will give stable dispersions of these compounds even when diluted with water.

Several efforts have been made to utilize the anion independence of bioactivity to introduce highly hydrophilic groups that increase water solubility [6-9]. The values of aqueous solubilities reached are adequate for concentrate preparation but these reports are biased towards alkyltin compounds. There is thus need to find suitable means of dispersing tri- and di-organotin compounds in water uniformly prior to field applications. The dispersions produced must be stable enough to ensure a smooth operation of the spray equipment.

For the purpose of this work, a dispersion medium has been defined as one which absorbs the active ingredient to give a macroscopically homogeneous dispersion. On dilution with water, the solution, suspension or emulsion produced should not separate out within the time limit required for field application. On this basis, constant values of the optical and centrifugal properties of the formulae and their dilutions are expected. Stable dispersions are often prepared by the addition of surface active agents to suspension or emulsion concentrates [10-14].

In this work, we report the preparation of water-compatible media for solubilising some useful biologically active organotin compounds. The stabilities of the formulae were assessed using a combination of visual observations, transmittance and centrifugal measurements.

2. Materials and Methods

The organotin compounds were prepared by procedures similar to that already reported [9]. They include palmitates and stearates of Bu_2Sn- and the acetates (Ac), salicylates (Sa) and acetyl salicylates (As), of Ph_3Sn- (TPT), Ph_2Sn- (DPT), Bu_3Sn- (TBT), and Bu_2Sn- (DBT).
All the TPT and TBT compounds were prepared from Ph_3SnOH and Bu_3SnOH respectively and the corresponding carboxylic acid [15-17] according to the equation:

$$R_3SnOH + R'COOH \rightarrow R_3SnOCOR' + H_2O$$

Compounds of Ph_2Sn- and Bu_2Sn- were prepared from the reaction of their chlorides and the silver salts of the appropriate carboxylic acids [15-17] as shown by the following equation:

$$R_2SnCl_2 + 2AgOCOR' \rightarrow R_2Sn(OCOR')_2 + H_2O$$

2.1 Determination of Solubility of the Organotin Compounds:

Four hydrocarbon solvents; (cyclohexane, toluene, benzene and kerosene), cotton seed oil, acetone, DMSO, bis-(2-

methoxyethyl)ether, (MEE), propylene glycol (PG) and 1:1 mixtures of MEE with acetone, DMSO and PG were used for this test. All solvents except PG and cotton seed oil were redistilled before use.

A 0.05 g sample of the organotin was transferred to a test tube and 0.25 ml of acetone was added. The mixture was shaken for about five minutes and observed. If dissolution occurred (as evidenced by a clear solution), the solubility was taken to be greater than 20 % wt/vol. If not, more acetone was added to bring the nominal concentration to 15 % then 10 %, 9 %, 8 % until 1 % wt/vol. The solubility was calculated based on the volume of solvent at which complete dissolution was first observed. This procedure was repeated using acetone and the other test compounds. The entire procedure was repeated using each solvent system.

2.2 Preliminary Investigation of the Stability of Aqueous Dispersions

0.1 ml portions of the near saturated solutions were diluted to 1, 2, 4, 8, 16 and 32 ml with distilled water and observed for homogeneity. The concentrations of organotin in the mixtures at which homogeneous dispersions were obtained was recorded in each case.

2.3 Determination of the Required HLB of Toluene

Two emulsifier mixtures: potassium oleate/n-hexanol and potassium oleate/n-hexanol/tween-80 were composed to span HLB's 8-18 (the required HLB for emulsification) by applying the additivity law [18]. 100 ml of the emulsions of toluene with water were prepared using the inversion method [19].

Potassium oleate (0.381 g) and hexanol (2.619 g) were weighed out and mixed in a 150 ml stoppered flask. Toluene (10 ml) was added and the mixture was shaken until the emulsifier mixture completely dissolved. To this solution, 1 ml aliquots of distilled water were added with vigorous stirring after each addition. This continued until about 10 ml of water was added. The mixture was finally diluted to 100 ml with distilled water, homogenised and observed for 48hrs. It was then centrifuged on a bench-top centrifuge and again observed. The experiment was repeated using the second (potassium oleate/n-hexanol/tween-80) emulsifier mixture.

If segregation occurred, the emulsions were labeled U (unstable) otherwise they were S (stable). Emulsions that failed to segregate were centrifuged on a bench-top centrifuge for 5 minutes and again observed. They were labeled as C_u (unstable to centrifugation) or C_s (stable to centrifugation) based on whether or not they segregated. Milky opaque emulsions were labeled P while transparent or translucent emulsions were labeled as T. The required HLB of toluene was taken as the HLB at which stable transparent or translucent emulsions were formed.

2.4 Effects of Varying the Emulsifier Composition:

An emulsifier composition may be varied by altering the nature of the components since for each emulsifier mixture, the amount of each component is fixed by the hydrophile-lipohile balance (HLB) requirements of the solvent. The role of alcohols as co-surfactant was investigated.

Normal butanol, pentanol, hexanol and heptanol were each used in conjunction with Tween-80 to compose the emulsifier mixture for toluene. The composition of each mixture was adjusted to give an HLB of 14. To 3.0 g of the emulsifier mixture in a test tube was added 10 ml of toluene and shaken until it was completely dissolved. This gave a solution with 30 % emulsifier. The following volumes: 0.80, 0.60, 0.40, 0.30, 0.25, 0.20, 0.15 and 0.1 ml of the solution were each transferred to separate test tubes, diluted to 20 ml with distilled water and homogenised. The transmittances of the solutions were measured at each dilution as a function of time at 540 nm using a spectronic-20 spectrophotometer.

2.5 Preparation of Concentrates and Assessment of Stability:

The organotin compounds: Bu_2SnSa_2 and Bu_2SnAs_2 both in toluene (at HLB 14) using Potassium oleate/hexanol emulsifier mixture), were dissolved in the media to give 0.2 mol/dm^3 solutions. From the stock solutions obtained 5 ml was set aside in capped bottles for visual observations and transmittance measurements then volumes were withdrawn and diluted to give concentrations in the range 2.5-20 % (v/v). The prepared solutions were monitored visually and using centrifugal and transmittance measurements for segregation.

3. Results and Discussion

The solubilities of the compounds in the different solvents are presented in Table 1 below. The results show that these compounds are, in general, more soluble in the hydrocarbon solvents and in cotton seed oil dissolving to concentrations in excess of 20 %(w/v). In these solvents, all the prepared organotin compounds are soluble without exception. Among the polar media, DMSO dissolves the phenyltin compounds more than the alkyltin compounds. Acetone and MEE dissolve both the triphenyltin and alkyltin compounds to between 10 to 20 %(w/v) while propylene glycol has the lowest solubilising power for the compounds. However, the combination of PG with MEE has high solubilising power over a greater range of compounds than any of the other polar media.

Table 1: Solubilities of Some (a) Phenyltin and (b) Butyltin Compounds (% w/v) in selected Solvents

Compound Solvent	TPTAc	TPTSa	TPTAs	DPTAc2	DPTSa2	DPTAs2	DBTAc2	DBTPa2	TBTAc	DBTSt2
Acetone	10	20	1	2	< 1	< 1	20	10	20	20
DMSO	20	20	7	7	20	5	1	< 1	< 1	< 1
MEE	20	20	2	2	< 1	< 1	2	10	20	20
PG	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Acetone-MEE	9	20	2	3	< 1	< 1	20	10	20	20
DMSO-MEE	20	20	8	8	20	< 1	< 1	10	< 1	< 1
PG-MEE	20	20	5	8	2	3	20	10	20	20
Benzene	20	20	20	20	20	20	20	20	20	20
Toluene	20	20	20	20	20	20	20	20	20	20
Cyclohenane	20	20	20	20	20	20	20	20	20	20
Kerosene	20	20	20	20	20	20	20	20	20	20
Cotton seed oil	20	20	20	20	20	20	20	20	20	20

Key: Sa = Salicylate, As = Acetyl salicylate, Ac = Acetate, Pa = Palmitate, St = Stearate.

This is explained in terms of the solvating power of MEE molecule through two of its three oxygen atoms thereby forming stable chelate systems. In addition, the interaction of the unchelated oxygen of the MEE molecule with water is expected to enhance the dispersive tendency. Systems containing MEE are therefore expected to give more stable aqueous dispersions as observed.

Results of the preliminary investigation of the stabilities of the aqueous dispersions are given in Table 2. It is observed that when acetone is used as solvent alone, the organotin always precipitated on addition of water even at low concentrations. In the presence of MEE, stable dispersions were obtained for alkyltins at low concentrations. For DMSO solvent, the range of stable aqueous dispersions is increased while for PG, there is marked increase in solubility of the organotins. The aqueous dispersions were also found to be stable over a wider range of concentrations. These results are consistent with the idea that MEE exerts profound solvation for the organotin possibly by forming stable chelate molecules using two of its three ether oxygen atoms.

Table 2: Limiting Concentrations (% w/v) for Stable Aqueous Dispersions.

COMPOUND	SOLVENTS						
	Acetone	**DMSO**	**MEE**	**Acetone//MEE**	**DMSO//MEE**	**PG//MEE**	**Hydrocarbons**
Ph_3SnAc	-	0.4	0.7	-	0.7	0.7	TWO-PHASE MIXTURE
Ph_3SnSa	-	0.7	-	-	0.7	0.7	
Ph_3SnAs	-	0.7	-	-	0.7	0.7	
Ph_2SnAc_2	-	0.7	-	-	0.7	0.7	
Ph_2SnSa_2	-	*	-	-	-	-	
Ph_2SnAs_2	-	0.6	-	-	0.5	0.5	
Bu_2SnAc_2	-	-	-	0.1	-	-	
Bu_2SnPa_2	-	-	-	0.1	-	-	
Bu_3SnAc	-	-	-	0.1	-	-	
Bu_2SnSt_2	-	-		0.1	-	-	

* Gives uncoagulated precipitate.

The low stability of the diphenyltin salicylates and acetylsalicylates dispersions may also relate to this phenomenon. There is possibility of interaction of the phenolic oxygen in these compounds with the organotin moiety. If this happens, it would produce fairly stable chelate molecules whose interaction with the solvent and other additives such as MEE would be reduced. Two such groups saturate the coordination number of Sn in dipheyltin compounds whereas one group would be unable to saturate Sn in triphenyltin compounds. The extra coordination valence could be taken up by MEE. This would account for the higher stability of the aqueous dispersions of the Ph_3Sn- compounds as compared to the Ph_2Sn- compounds.

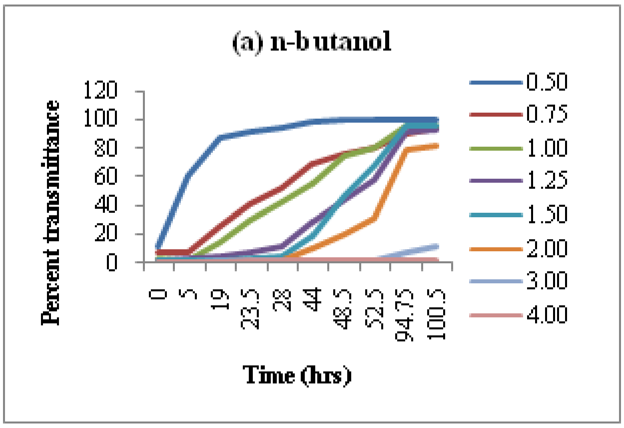
Table 3: The Character of the Toluene/Water emulsions

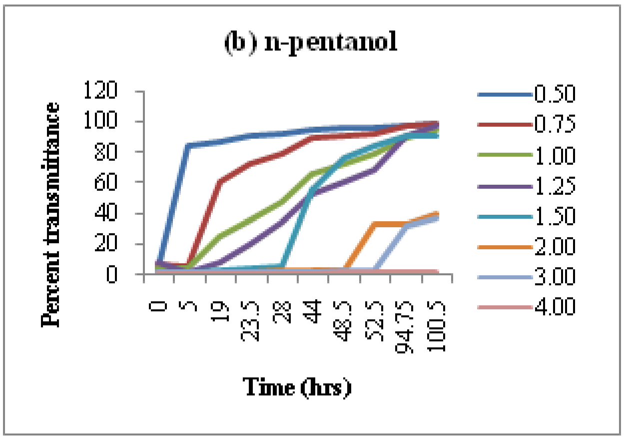
HLB	EMULSIFIER	
	Potassium Oleate/Hexanol	Potassium oleate/ Hexanol/Tween-80
8	SPC_u	SPC_s
9	SPC_u	SPC_s
10	SPC_u	SPC_s
11	SPC_u	SPC_s
12	SPC_u	SPC_s
13	SPC_S	STC_s
14	STC_S	STC_s
15	STC_S	STC_s
16	STC_S	STC_s
17	SPC_S	STC_s
18	SPC_S	STC_s
Required. HLB	14-16	13-18

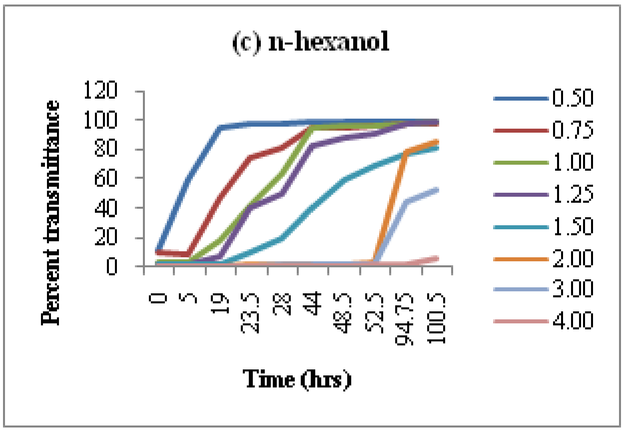
Results of the investigation of the required HLB of toluene using two emulsifier mixtures; potassium oleate/hexanol and potassium oleate/hexanol/tween-80 are presented in Table 3. Table 3 shows that transparent or translucent emulsions were obtained for these two emulsifier systems over the HLB range of 14-16 and 13-18 respectively. On diluting with water, the dispersions formed at HLB 14 and 15 were translucent, had no tendency to cream and were bluish in appearance. These properties are those of micro-emulsions. This view is supported by observations from the centrifugal tests that no phase separation occurred after 5 minutes of centrifuge.

Fig. 1(a-d) shows transmittance plots as a function of time for toluene emulsions employing tween-80 and four alcohols: n-butanol (a), n-pentanol (b), n-hexanol, (c) and n-heptanol (d) as co-surfactants. The emulsifier mixtures were composed to give the HLB of toluene. In all cases, the transmittance of the dispersions increased with time. The higher the transmittance value, the more disperse the system and the more stable it is since unstable systems will segregate through creaming or coalescence. This is a strong evidence for presence of thermodynamically stable systems called micro-emulsions. The results also show that, while all the alcohols may be used, n-hexanol appears to be more effective over a wider range of concentrations (heptanol is the least) and it appears there might be little point in using alcohols of longer chain length.

The role of alcohols in these formulations has been explained as resulting from the interposition of their molecules between Teen-80 molecules enhancing the lateral attraction within the droplets of the emulsion thereby increasing film elasticity, strength and stability.







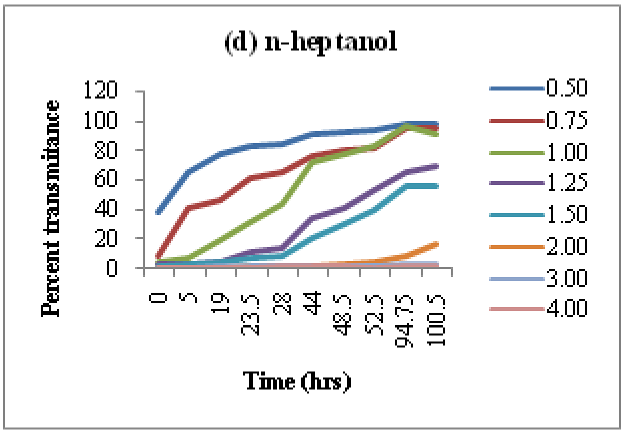


Figure 1: Tranmittance-time Graghs for Four Emulsifier Formulations Showing the Effect of Alcohol Chain Length on the Stabilization of Toluene-water Emulsions

Under this condition, the droplets form spontaneously giving rise to the thermodynamically stable micro-emulsions.

Two concentrates were prepared using this formulation. The transmittance measurements for these concentrates are presented in Table 4 for Bu_2SnSa_2 (a) and Bu_2SnAs_2 (b). Their dilutions were also monitored through transmittance measurements and the data is presented in Fig. 2 (a) and (b).

Table 4: Transmittance/Time Variation for Bu_2SnSa_2 and Bu_2SnAs_2 Concentrates in Toluene Stabilized with Potassium oleate/Hexanol Emulsifier Mixture

		Time (hrs)			
		0	**96**	**216**	**1320**
Transmittance	Bu_2SnSa_2	76	76	73	66
	Bu_2SnAs_2	67	75	64	62

The data of Table 4 shows that over the period of 55 days monitored, a significant change in transmittance of the formula was observed. However, this leveled up after about 10 days. These formulae are indeed solutions hence are a convenient basis for agricultural applications.

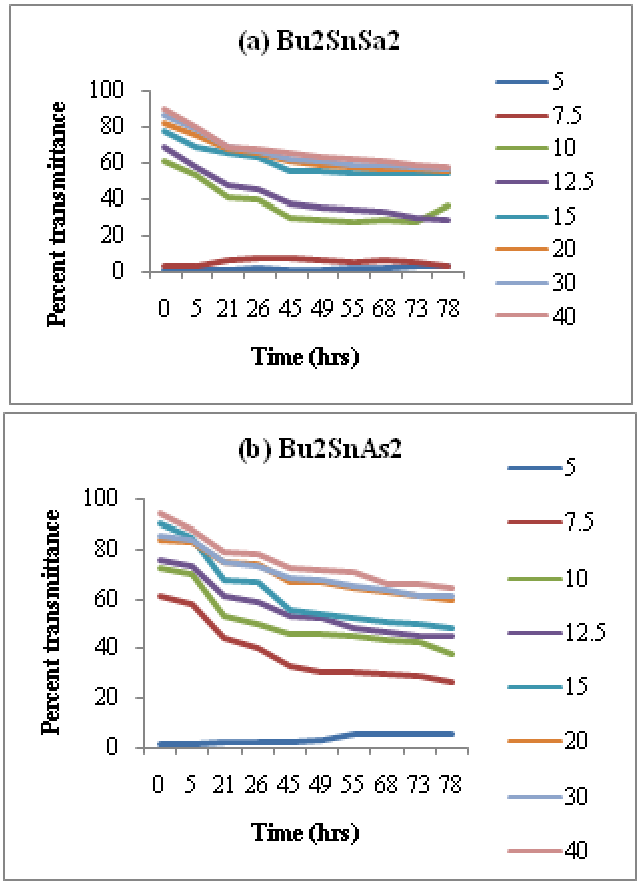


Figure 2: Variation of Transmittance with Time for Eight Dilutions of Bu_2SnSa_2 (a) and Bu_2SnAs_2 (b) Concentrates with Water

The dilutions of the formulae gave transmittance values shown in Fig. 2a and 2b for the salicylate and acetylsalicylate respectively. These figures show a marked deviation from the profiles expected on the basis of Fig.1 and indicate the ability of the organotin compounds to alter the surface tension of toluene and therefore its required HLB. However, considering that formulae are applied immediately after dilution, this is not expected to adversely affect the formulae. In addition, the decrease in transmittance with time levels up after about 40 hrs and within the period of observation, no precipitation occurred. These thermodynamically unstable dispersions may thus be used for this purpose as earlier defined.

4. Conclusion

The organotin compounds tested are known to possess antifungal activity and are commonly adopted for treatment of fungal infections where oral and mammalian non-toxicities are not critical requirements. Among the formulae based on polar media, mixed solvent systems containing bis-(2-methoxyethyl) ether were found suitable for phenyltin compounds since they yielded un-coagulated dispersions.

Dispersions in the non-polar media required emulsification. The role of the alcohol and soap in the stabilization of emulsions indicates that alcohols of medium chain length (4-7 carbon atoms) may be used with n-hexanol having the best co-surfactant property. It was observed that while the media were stable, the introduction of the active ingredient required consideration in order to arrive at thermodynamically stable systems. Dispersions of Bu_2SnSa_2 and Bu_2SnAs_2 in toluene were found to be thermodynamically unstable but did not precipitate within the period studied. These can thus be used for field applications of the test agents. The formulae may therefore be used to protect non-consumable agricultural products, such as seed yams and wood.

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