INFLUENCE OF ADJUVANTS ON PHYSICOCHEMICAL PROPERTIES, DROPLET SIZE SPECTRA AND DEPOSIT PATTERNS: RELEVANCE IN PESTICIDE APPLICATIONS

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ABSTRACT;

Due to the increasing use of adjuvants in pesticide formulations, and given the fact that the function of adjuvants is not fully understood, a study was conducted in order to investigate the effect of different types of adjuvants on the physicochemical properties, atomization characteristics and deposit patterns of spray mixtures. For this study, two surfactants, two humectants and a polymeric adjuvant were used. In addition, water and two fenitrothion formulations containing polymeric adjuvants were used for the sake of comparison. The adjuvants were mixed with water in the concentartions listed in Table 2, and were then tested for physicochemical properties and atomization characteristics. The results were partially what was expected prior to conducting the tests. It was thought that the solutions of the two surfactants, Atlox 3409F and Triton X-114, would have similar properties, and that the solutions of the two humectants, propylene glycol and glycerol, would be similar to each other, but would be somewhat different as compared to the surfactants. Agrisol, the polymeric surfactant was expected to be close to the two fenitrothion formulations containing polymeric adjuvants. However, it turned out to be a median between the two surfactants and the two humectants.

A cross-section of the physicochemical properties and atomization characteristics is located in Table 7.

INTRODUCTION

Adjuvants are almost universal constituents of pesticide formulations. However, the exact function of most adjuvants is poorly understood (McWhorter, 1982), although their use is continuously increasing. The term 'adjuvant' includes a wide range of chemicals which are used to enhance biological activity, to modify droplet generation and behaviour, and to improve handling, storage and use patterns of pesticide formulations.

At present there is little information in the literature on the comparative influence of three types of adjuvants, viz., surfactants, humectants and polymers, on physicochemical properties, atomization characteristics, droplet size spectra and deposit patterns of spray mixtures. This report addresses this aspect using two surfactants, two humectants and one polymeric adjuvant. For the sake of comparison, two fenitrothion [O,O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate] formulations containing polymeric adjuvants, and water were also included in the study.

MATERIALS AND METHODS

Pesticide formulation concentrate and adjuvants used in the study are listed in Table 1, along with the names of suppliers. The percentage compositions of the ingredients used in preparing the spray mixtures are listed in Table 2.

Physicochemical properties measured were: relative viscosity, surface tension, apparent viscosity-shear rate relationship, pH and conductance. Viscosity was measured using a gravity force capillary viscometer, from 5°C to 25°C at 5°C intervals in a thermostatic bath. Viscocosity data are located in Table 3 along with the density and surface tension values for each formulation. Density was measured under the same conditions as viscosity, using a 10 mL density bottle. Surface tension measurements were conducted on each formulation using a FISHER Surface Tensiomat (Fisher Scientific, Toronto, Canada) - Model 21 instrument, inside a controlled environmental chamber of dimensions 2.2 m x 1.6 m x 2.4 m, from 5°C to 25°C at 5°C intervals. Also conducted inside the environmental chamber (at 25°C and 75 ± 5% relative humidity) were volatility tests using the blue screen method (Sundaram and Leung, 1986). The pH and conductance tests were also done at 25°C and are located in Table 7, and the viscosity-shear rate relationships in Table 6.

To determine spray characteristics, a chamber (Figure 1) was constructed for trial purposes. The chamber was made out of a plastic sheet wrapped around a metal frame of dimensions 1.25 m x 0.46 m x 0.70 m. Sprays were applied using 0.5 mL volume of each formulation, using a twin fluid atomizer (Desaga Spray Gun, Desaga, Heidleberg, Germany), located 0.92 m away from the sampling location and 0.46 m above the targets (Figure 1). The location of the atomizer was determined experimentally for providing the most uniform droplet distribution on the sampling units (Kromekote® card/glass plate units) (Randall, 1980), by conducting trial sprays with the spray mixtures, after placing the collection units at various locations. All formulations were sprayed in triplicate in order to provide a mean droplet size spectrum spray deposit and also a standarad deviation. For collection purposes, 2 Kromekote cards (10 cm x 10 cm each) and 4 glass plates (7.5 cm x 5.0 cm) were used for each spray. A time period of two minutes was allowed for each spray for impaction of the droplets upon the collection units. To aid in detection of the droplets, 0.2% or 0.05 g per 25 mL, of a tracer dye (Erio Acid Red) was added to each formulation. After spraying, the 6 Kromekote cards (2 cards x 3 sprays) for each formulation were inspected for various droplet data. These data included: number and volume median diameters (NMD and VMD respectively), maximum droplet diameter (D_{max}) and droplet density (droplets/cm^2). These data were obtained by measuring the droplet stains present on the Kromekote cards in a given area, in this case 4 x 1 cm^2 blocks on each card, or 24 cm^2 in the six cards used for each formulation. The droplet stain numbers were then pooled for each formulation, and the various parameters were then calculated. First the stain diameters were converted into aerodynamic droplet diameters by dividing the stain diameter by the spread factor of the formulation. The number and volume median diameters were found by plotting respectively the cumulative number and volume distribution values versus the droplet diameter, and finding the point at which half of the droplets fell either above or below the 50% mark.

Droplet density for each formulation was determined by taking the total number of droplets found on the 6 cards and dividing that number by the area measured, in this case 24 cm^2 (4 cm^2 per card x 6 cards). The maximum droplet diameter was simply the droplet size (as measured under the microscope) of the largest droplet stain observed. The minimum droplet stain diameter that was measurable by the droplet sizing technique was 8 µm, which was equivalent to the droplet diameter ranging from 3 to 5 µm; and this range was regarded as the detection limit of the droplet sizing technique used in this stduy.

To determine the spray deposit for each formulation, 4 glass plates (7.5 cm x 5 cm) were used for each spray. After spraying, each set of 4 glass plates was eluted using 5 ml of water, giving 3 samples for colorimetric analysis for each formulation. For comparison purposes, standards of 1.0%, 0.5%, 0.2%, 0.1% and 0.05%, of the formulations were run through the spectrophotometer. The spray samples were then run through the spectrophotometer and compared to the standard curve in order to obtain the percentage of formulation present. This percentage was then converted to obtain the spray volume deposit as shown in Table 7.

RESULTS AND DISCUSSION

As stated before the exact function of the various adjuvants is not fully understood, and this study was designed to explore the effects of various adjuvants. Prior to this study, it was known that surfactants were used in the spray formulations, to increase the surface adhesion of droplets, and humectants were used to decrease the volatility of pesticide fromulations, but what was not known was the effect that surfactants and humectants had upon the physicochemical properties of pesticide firmulations, spray atomization characteristics and deposit patterns. Throughout the course of this study it was found that in most instances the two surfactants were close to each other in physical characteristics, and that the two humectants were close in physical characteristics, with the exception being the viscosity-shear rate relationships, where the two formulations had different values. The viscosity density and surfaces tension values, while being different between the surfactants, the differnce between the two humectants were not greatly so.

One area of main difference was in the volatility factor (see Table 5), $R_{(Evap)}/A$ where $R_{(Evap)}/A$ is a measure of the volatility of the formulation. As should be expected, the two humectants had the lowest volatility factor, compared to the anionic (Atlo-3409-3), non-ionic (Trit-114-3) and polymeric surfactants (Agr-W-8), which had extremely high volatility factors.

Another area of difference between the surfactants was in the droplet density, and the spray volume deposit. The humectants showed a 50% increase in droplet density and a 100% increase in spray volume deposit, compared to the polymeric surfactant (Agrisol), falling in between the two groups, surfactants and humectants (see Table 7). One reason for this difference is that the decreased surface tensions of the surfactants leads to the formation of smaller droplets than those of the humectants as a result, more droplets of a smaller size were produced during atomization of the surfactant solutions. This decreased droplet spectra would lead to a smaller amount of formulation being recovered due to in-flight evaporation of the finer droplets, whereas the humectants suffer very little, if any, in-flight evaporation of droplets, which would lead to a larger droplet spectrum, and conversely a larger **spray** volume deposit. (In addition, glycerol is a highly hygroscopic material, and therefore, during falling from the released height, the small droplets would even absorb water from the ambient environment, which was maintained at 75% RH).

CONCLUSIONS

The purpose of the present study was to determine the exact effects of adjuvants upon physicochemical properties, droplet size spectra and deposit patterns of pesticide formulations. For the purposes of comparisons, water and Sumithion® /water mixtures were also used. Formulations containing anionic, non-ionic and polymeric surfactants, and humectants were tested for their physicochemical properties and atomization characteristics. It was found that by using humectants, you can expect viscosities that differ from water as the standard, not greatly in surface tension, pH and conductance.

It was alos noted that the use of humectants would greatly increase the droplet density and the spray volume deposit of the formulation being studied.

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Table 1. Surfactants, humectants, polymeric adjuvant and pesticide formulation concentrate used in the study

Name	Abbreviation used	Source
Atlox® 3409F *a*	Atlo-3409	ICI Americas Inc. (Wilmington, Del., USA)
Triton® X-114 *a*	Trit-114	Rohm and Haas Canada (Westhill, Ontario, canada)
Propylene glycol *b*	PrGl	Fisher Scientific
Glycerol *b*	Gly	(Toronto, Ontario, Canada)
Agrisol® FL-100F *c*	Agr	Sumitomo Chemical (Osaka, Japan)
New Sumithion® 20F *d*	Sumi-20F	Sumitomo Chemical (Osaka, Japan)

a: Atlo-3409F is a blend of anionic and non-ionic surfactants.

b: Trit-114 is a non-ionic surfactant.

c: PrGl and Gly are both humectants.

d: Agr is a cationic polymeric surfactant.

e: Sumi-20F is a formulation concentrate of the organophosphate, fenitrothion.

Table 2. Percentage compositions of ingredients used in the spray mixtures

Liquid abbreviation	Percentage composition (v/v)		
Atlo-3409-3	Atlo-3409	3/water	97
Trit-114-3	Trit-114	3/water	97
PrGl-W-50	PrGl	50/water	50
Gly-W-50	Gly	50/water	50
Agr-W-8	Agr	8/water	92
Sumi-44.4	Sumi-20F	44.4/water	55.6
Sumi-66.7	Sumi-20F	66.7/water	33.3

Table 3. Viscosity, density and surface tension values of adjuvant solutions and pesticide formulations

Liquid abbreviation	Physical Properties at °C of				
	5	15	15	20	25
			Viscosities (mPa.s)		
Water	1.519	1.308	1.140	1.050	0.894
Atlo-3409-3	1.75	1.47	1.27	1.21	1.01
Trit-114-3	2.90	3.20	4.00	6.05	8.02
PrGl-W-50	14.1	10.4	7.60	6.72	5.08
Gly-W-50	15.6	11.6	9.07	7.95	6.15
Agr-W-8	14.2	10.6	8.92	8.35	6.89
Sumi-44.4	37.2	29.3	23.5	19.2	16.7
Sumi-66.7	95.3	76.4	58.3	50.9	38.9
			Densities (kg/ℓ)		
Water	1.0000	0.9997	0.9991	0.9982	0.9971
Atlo-3409-3	1.0016	1.0010	1.0005	0.9993	0.9981
Trit-114-3	1.0030	1.0023	1.0018	1.0016	0.9999
PrGl-W-50	1.0467	1.0424	1.0397	1.0369	1.0335
Gly-W-50	1.1469	1.1443	1.1422	1.1394	1.1371
Agr-W-8	1.0096	1.0088	1.0081	1.0073	1.0054
Sumi-44.4	1.0370	1.0362	1.0351	1.0340	1.0323
Sumi-66.7	1.0563	1.0550	1.0542	1.0527	1.0509
			Surface tensions (mN/metre)		
Water	74.9	74.2	73.5	72.8	72.0
Atlo-3409-3	30.1	30.0	29.7	29.6	29.5
Trit-114-3	30.7	30.4	30.0	29.7	29.5
PrGl-W-50	46.8	46.2	45.7	45.0	44.4
Gly-W-50	52.6	51.8	51.0	50.2	49.4
Agr-W-8	62.7	59.5	63.8	64.5	65.8
Sumi-44.4	52.2	51.7	51.0	50.0	49.2
Sumi-66.7	47.9	47.5	47.0	46.3	45.8

Table 4. Volatility determinations: Residual weight percentages 'Y' (mean values of triplicate measurements) at time 't'. Temp. = 25°C; and relative humidity = 75 ± 5 percent.

Time (min)	Residual weight percents							
	Water	Atlo-3409-3	Trit-114-3	PrGl-W-50	Gly-W-50	Agr-W-8	Sumi-44.4	Sumi-66.7
0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1	95.9	94.1	95.1	95.5	97.3	94.3	97.1	97.1
2	91.4	90.4	90.4	92.6	94.8	89.8	94.8	95.2
3	88.0	86.2	86.2	89.6	92.2	83.7	92.3	93.0
4	84.0	80.7	80.9	86.0	90.4	78.9	88.0	90.9
6	75.1	73.8	73.1	82.2	86.1	68.9	83.4	85.9
8	66.7	65.7	64.4	77.3	81.9	59.1	77.9	81.5
10	58.8	56.3	57.0	73.0	79.0	49.0	72.5	76.8

Linear regression analysis of the 'Y' values against 't', provided the following equations:

1. Water: $Y = 100 - 4.15\ t$ ($R^2 = 99.9\%$)
2. Atlo-3409-3: $Y = 98.9 - 4.24\ t$ ($R^2 = 99.7\%$)
3. Trit-114-3: $Y = 99.2 - 4.31\ t$ ($R^2 = 99.8\%$)
4. PrGl-W-50: $Y = 98.1 - 2.62\ t$ ($R^2 = 98.4\%$)
5. Gly-W-50: $Y = 99.2 - 2.11\ t$ ($R^2 = 99.2\%$)
6. Agr-W-8: $Y = 99.5 - 5.08\ t$ ($R^2 = 99.9\%$)
7. Sumi-44.4: $Y = 100 - 2.76\ t$ ($R^2 = 99.8\%$)
8. Sumi-66.7: $Y = 99.8 - 2.29\ t$ ($R^2 = 99.9\%$)

Table 5. Volatility data of adjuvant solutions and pesticide formulations: Percent non-volatile components (A)[a], volatile components (B)[a], rate of evaporation (R_{Evap})[b] and volatility factor (R_{Evap}/A)[c]

Liquid abbreviation	'A'	'B'	R_{Evap}	R_{Evap}/A
Water	0.00	100.0	4.15	∞
Atlo-3409-3	3.00	97.0	4.24	141
Trit-114-3	3.00	97.0	4.31	144
PrGl-W-50	0.00	100.0	2.62	∞
Gly-W-50	59.4	40.6	2.11	3.55
Agr-W-8	3.20	96.8	5.08	159
Sumi-44.4	11.4	88.6	2.76	24.2
Sumi-66.7	18.5	81.5	2.29	12.4

a: 'A' refers to the percent non-volatile components, i.e., the amounts that did not evaporate from the plastic mesh (Sundaram and Leung, 1986), for at least 58 h after the start of the experiment; and 'B' refers to the percent volatile components (or $A + B = 100$)

b: R_{Evap} refers to the rate of evaporation, i.e., the percentage decrease of the weight of liquid film per minute, which is given by the slope of the linear regression equation listed in Table 4.

c: The volatility factor 'R_{Evap}/A' represents the degree of volatility of the adjuvant solutions and pesticide formulations, i.e., the higher the value of R_{Evap}/A, the greater the volatility. The values listed here are obtained by dividing R_{Evap} values by 'A' and then by multiplying the results by 100, so that the values would not be in very small fractions.

Table 6. Viscosity-shear rate relationships of adjuvant solutions and pesticide formulations at 25°C.

Shear rate (s^{-1})	Apparent viscosity (mPa.s) (η)							
	Water	Atlo-3409-3	Trit-114-3	PrGl-W-50	Gly-W-50	Agr-W-8	Sumi-44.4	Sumi-66.7
15	1.02	1.38	12.1	8.95	13.0	12.0	45.2	116
31	1.04	1.36	11.7	8.65	12.6	11.8	39.2	86.8
46	1.04	1.35	10.5	7.83	11.5	10.5	33.6	74.0
62	1.06	1.33	10.3	7.36	11.2	9.31	30.6	66.3
92	1.10	1.34	10.0	6.94	11.0	8.08	26.2	56.8
123	1.12	1.36	9.93	6.76	10.9	7.51	24.2	51.1
155	1.14	1.38	9.88	6.68	10.9	7.12	22.5	48.0
186	1.15	1.40	9.86	6.62	10.9	6.85	21.2	47.0
217	1.17	1.42	9.86	6.61	10.9	6.65	20.2	46.5
248	1.18	1.44	9.88	6.61	10.9	6.50	19.4	45.0
280	1.20	1.46	9.91	6.62	10.9	6.37	18.7	45.0

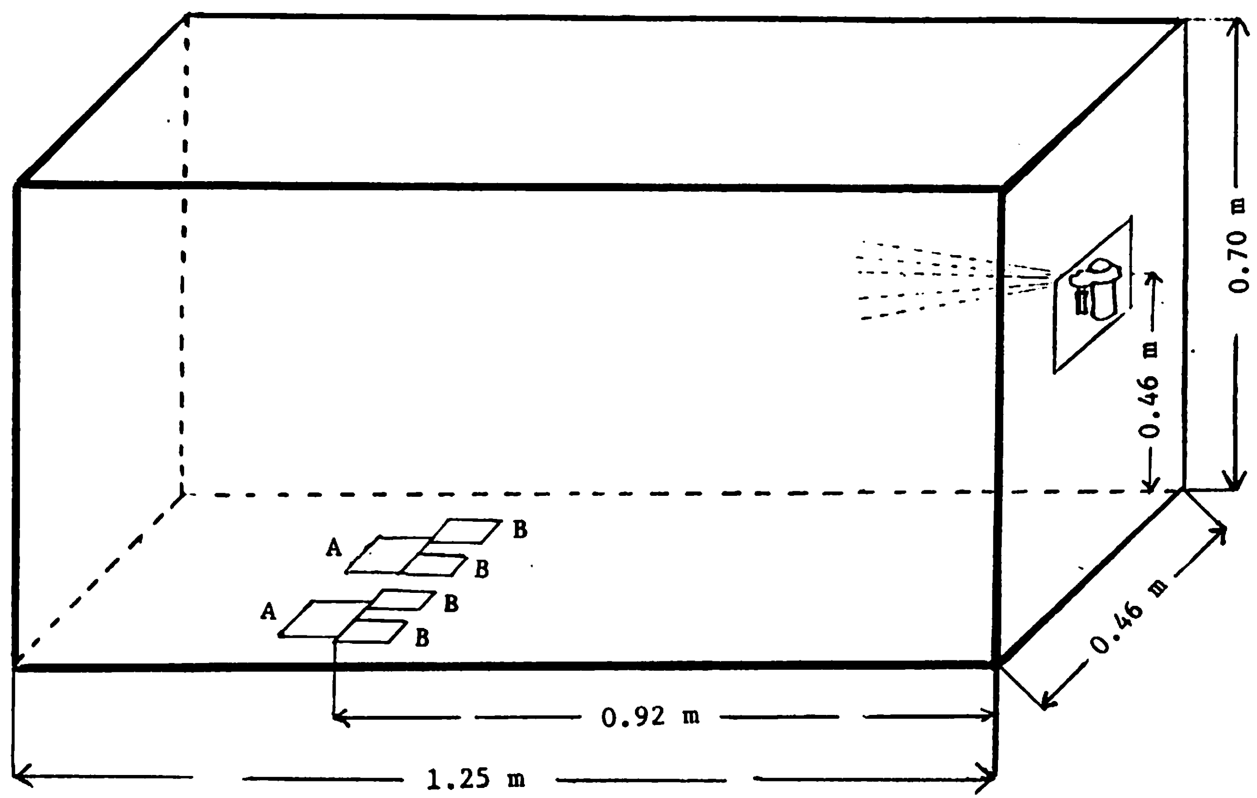
The degree of pseudoplasticity is proportional to the reduction in apparent viscosity, RAV, of liquids used in the study. The values of RAV are obtained from $\eta_{max} - \eta_{min}$, which are listed below.

1. Water: RAV (mPa.s) = 0.18
2. Atlo-3409-3: RAV (mPa.s) = 0.13
3. Trit-114: RAV (mPa.s) = 2.24
4. PrGl-W-50: RAV (mPa.s) = 2.34
5. Gly-W-50: RAV (mPa.s) = 2.10
6. Agr-W-8: RAV (mPa.s) = 5.63
7. Sumi-44.4: RAV (mPa.s) = 26.5
8. Sumi-66.7: RAV (mPa.s) = 71.0

Table 7. Droplet characteristics, spray volume deposits and physicochemical properties of adjuvant solutions and pesticide formulations at 25°C and 75 ± 5 % relative humidity.

Measurements	Adjuvant solutions and pesticide formulations							
	Water	Atlo-3409-3	Trit-114-3	PrGl-W-50	Gly-W-50	Agr-W-8	Sumi-44.4	Sumi-66.7
Droplet data: [a]								
1. NMD (µm)	30	13	18	38	37	23	15	21
2. VMD (µm)	49	57	56	56	56	53	51	63
3. D_{max} (µm)	114	178	168	150	144	130	125	200
4. Droplets/cm^2	82	187	238	279	342	198	341	186
Deposit data: [b]								
1. Spray volume deposit (ml/m^2)	0.096	0.175	0.186	0.385	0.595	0.335	0.382	0.323
2. Deposit ratio (relative to water)	1.00	1.82	1.94	4.01	6.20	3.49	3.98	3.36
Physicochemical properties:								
1. Viscosity (mPa.s)	0.894	1.01	8.02	5.08	6.15	6.89	16.7	38.9
2. Surface tension (mN/metre)	72.0	29.5	29.5	44.4	49.4	65.8	49.2	45.8
3. Volatility factor [c]	∞	141	144	∞	3.55	159	24.2	12.4
4. $\eta_{max} - \eta_{min}$ [c] (mPa.s)	0.18	0.13	2.24	2.34	2.10	5.63	26.5	71.0
5. pH	6.5	5.7	6.7	7.9	6.5	3.7	5.8	5.8
6. Conductance (Ω^{-1}) x 10^6	8.56	311	126	1.02	7.84	66.7	255	202

a, b and *c:* For the explanation of these terms, see the text.



A: Kromekote® cards (10 cm x 10 cm)

B: Glass plates (7.5 cm x 5.0 cm)

FIGURE 1

Enclosure for spray application, and location of the atomizer and sampling units

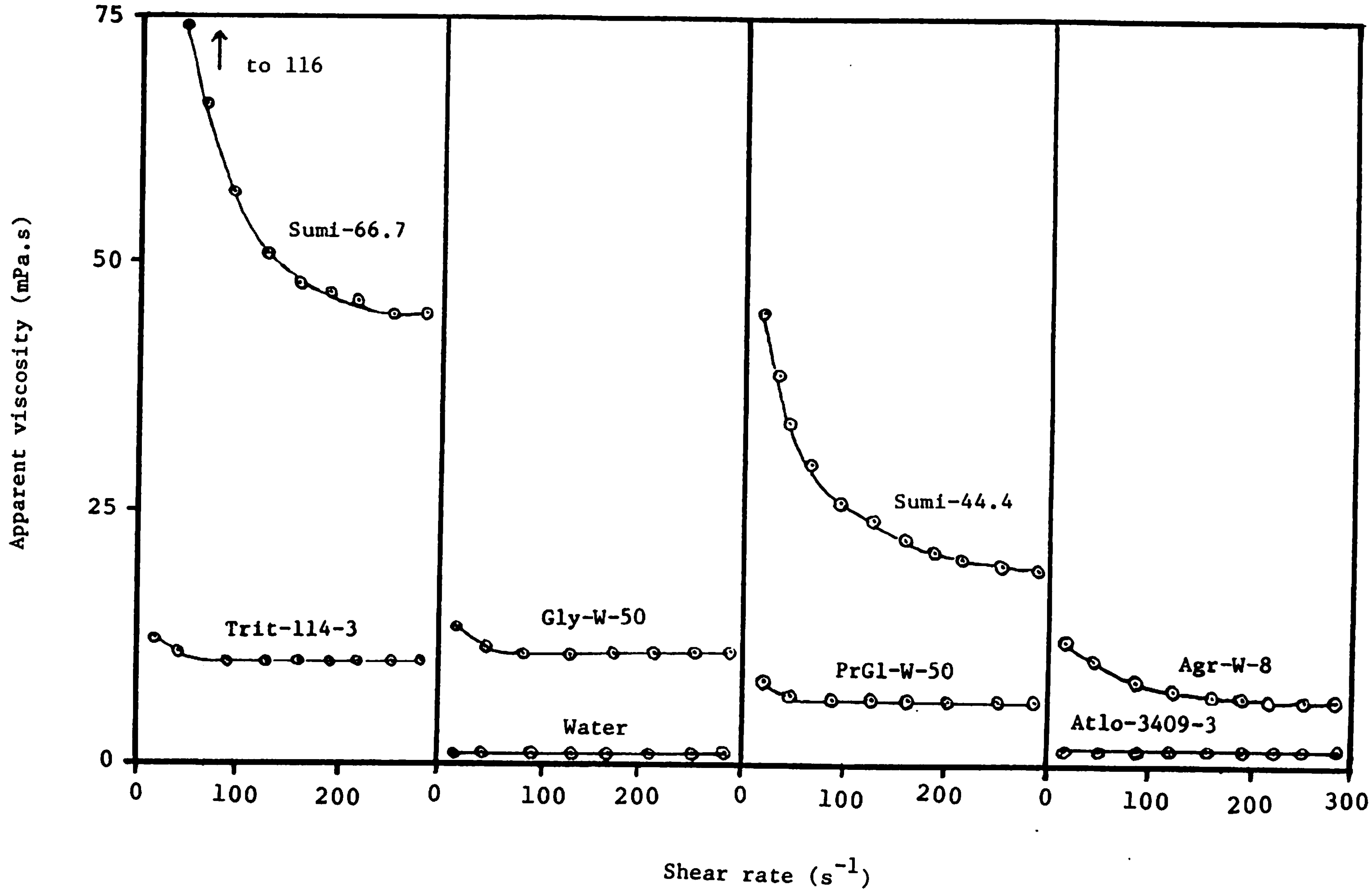


FIGURE 2

Apparent viscosity-shear rate relationships of adjuvant solutions, pesticide formulations and water at 25°C

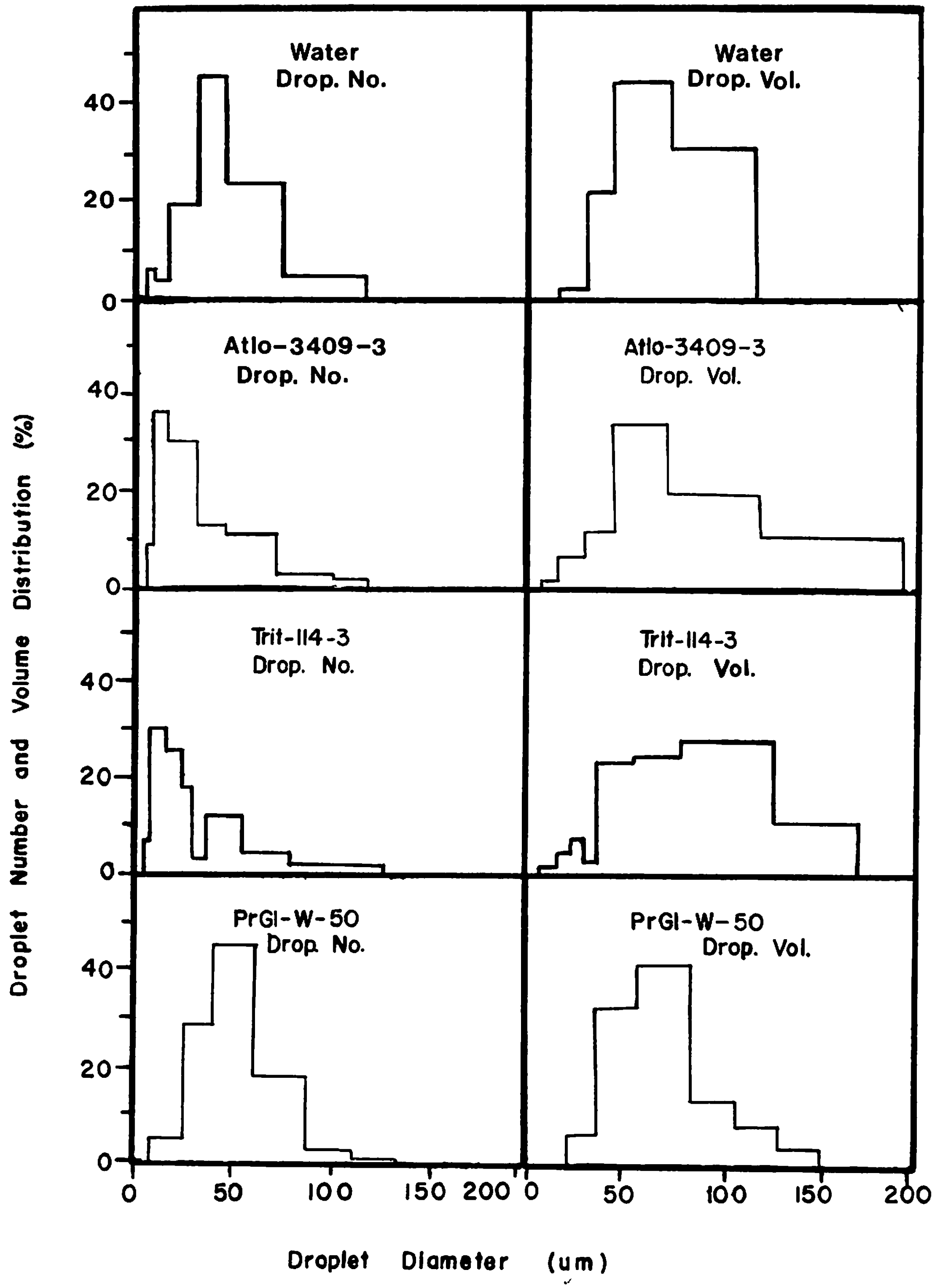


Figure 3

Percentage Distribution of Droplet Number and Volume According to Size Category

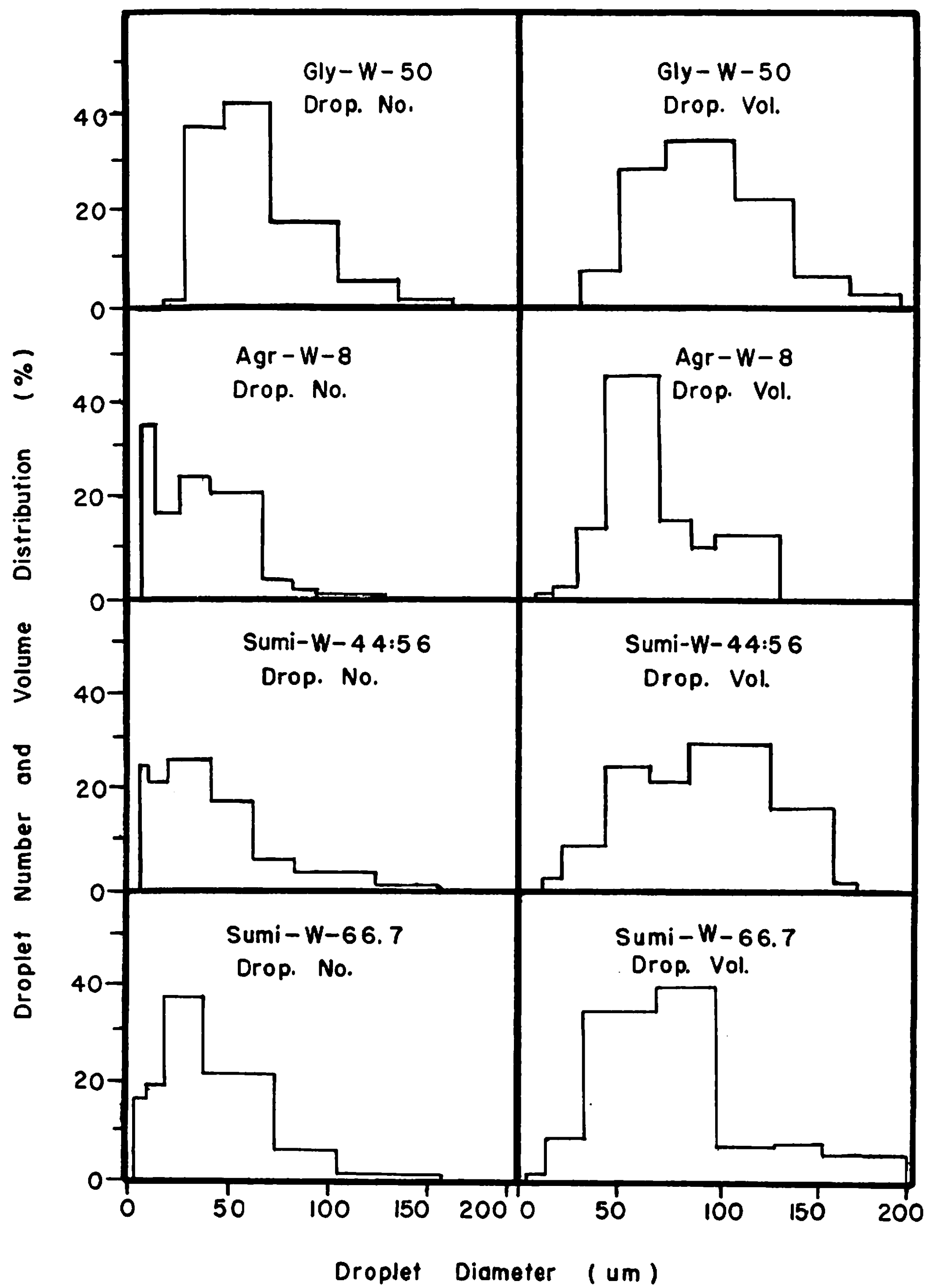


Figure 4

Percentage Distribution of Droplet Number and Volume According to Size Category