

A System to Measure Viscosities of Spray Mixtures at High Shear Rates

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Abstract: The viscosity of spray mixtures can greatly influence the sizes of spray droplets produced by atomizers. However, no low-cost system has been available to measure the viscosity at the high shear rates that are typical of pesticide mixtures passing through orifices of nozzles at pressures commonly used in agricultural spraying. An inexpensive system was developed to measure viscosity at shear rates up to $200\,000\text{ s}^{-1}$ for both Newtonian and non-Newtonian liquids. Viscosity measurements of Newtonian liquids with viscosities ranging from 0.87 to 9.1 mPa s indicated that the measured viscosity was within 5% of the actual value at various high shear rates up to $200\,000\text{ s}^{-1}$. As shear rate was increased, the viscosities of mixtures of water with drift control agents 'Nalco-Trol,' 'Target' and an experimental formulation decreased remained about the same, and increased respectively.

Key words: shear viscosity, measurement.

1 INTRODUCTION

Spray drift is a major concern with many agricultural pesticide applications. Adjuvants that increase viscosity are often added to spray mixtures to increase the mean droplet diameter and thus reduce spray drift. Many scientists^{1–7} have investigated the effects of such additions.

When pesticide mixtures are sprayed, they are subjected to high shear rates while passing through nozzle orifices. Newtonian liquids are defined as mixtures that maintain a constant viscosity even when subjected to a range of shear rates; non-Newtonian liquids are mixtures with viscosities that vary with a change in shear rate. Probably most agricultural spray mixtures are non-Newtonian liquids because they are made of active ingredient formulations including stabilizers and emulsifiers in addition to water or other diluents. The viscosity of non-Newtonian liquids varies with shear rate, and viscosity influences spray droplet size and, hence, spray drift and effectiveness of pesticides. Kaupke and Yates⁸ reported that the viscosity of spray mixtures with thickening adjuvants might be very high in tank mix-

tures, but the viscosity may be markedly reduced under high shear rates that occur when liquid is forced through a nozzle orifice to produce spray droplets. Yates *et al.*⁹ used a coaxial cylinder viscometer to measure the viscosities of spray mixtures of water and a drift control adjuvant (HEC/B) at shear rates ranging from 0 to 4000 s^{-1} and found that the viscosity of the mixture decreased with increasing shear rate. Bouse *et al.*¹⁰ evaluated the effects of several drift-control adjuvants on spray mixture viscosities and spray droplet sizes when the mixtures were sprayed from a nozzle. They measured viscosities at a shear rate of 73.4 s^{-1} with a Brookfield viscometer, and found that 'Nalco-Trol' and '38-F' produced the greatest increase in viscosity with increasing adjuvant concentration. Viscosity measurements of non-Newtonian liquids at low shear rates with commonly used viscometers can result in values greatly different from the viscosity of the liquid when passing through a nozzle orifice. Viscosities of agricultural spray mixtures at high shear rates representative of when liquids pass through orifices have not been reported, primarily due to the lack of an inexpensive system to measure viscosities at high shear rates.

The shear rate on a liquid passing through a nozzle orifice varies greatly with the position of the liquid within the orifice. For example, calculations of shear

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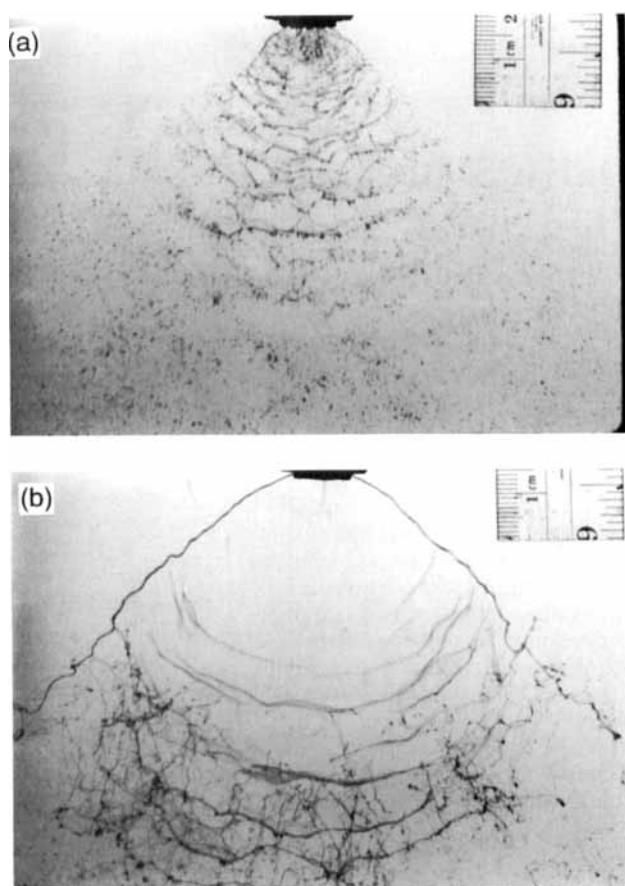


Fig. 1. Spray patterns discharged from an 8004 VH nozzle operated at 276 kPa for (a) distilled water and (b) distilled water with 'Nalco-Trol'.

rates on the liquid passing through an 8004 VH flat spray nozzle operated at 276 kPa varied from 0 s^{-1} at the center to $436\,000 \text{ s}^{-1}$ at the wall of the long axis of the orifice.¹¹ The shear rate varied from 0 s^{-1} at the center to $168\,000 \text{ s}^{-1}$ at the wall of the orifice over the short axis. Although viscosity can vary with shear rate, no known publications on viscosity of agricultural spray mixtures have reported viscosities at shear rates greater than 4000 s^{-1} .

Some drift control agents greatly influence the viscosity of the spray mixture and hence the spray droplet size delivered by nozzles. Figs 1(a) and 1(b) illustrate the effect of a drift control agent ('Nalco-Trol', Nalco Chemical Company, Naperville, IL, USA) that increases the viscosity of the mixture on the spray pattern produced by an 8004 VH nozzle tip operated at 276 kPa. The spray pattern for distilled water is shown in Fig. 1(a), and that for a mixture of distilled water and

* Trade names are necessary to report factually on available data; however, the US Department of Agriculture neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

'Nalco-Trol' ($0.55 \text{ ml liter}^{-1}$ in distilled water) in Fig. 1(b). The spray sheet of water breaks up much more rapidly than the sheet containing 'Nalco-Trol'. 'Nalco-Trol' increases the viscosity of the liquid and this tends to increase the resistance of the sheet to breaking up into small droplets. Others³ have measured spray droplet sizes for operating conditions similar to these above and indicated that volume median diameters of the sprays were 303 and $515 \mu\text{m}$ for the sprays with water only and water with 'Nalco-Trol'. Obviously, low concentrations of some drift control agents can change the physical properties of spray mixtures.

Equations to express the relationship between the mean droplet size in sprays and variables of liquid properties (such as viscosity and surface tension), flow conditions and atomizer dimensions are needed for agricultural sprays. Many droplet size equations published in the literature are of somewhat dubious value.¹² Part of this is probably due to the use of values for liquid properties which are not valid for the flow conditions. For example, when liquid passes through a nozzle orifice the shear rate is usually much higher than the maximum shear rate developed by commonly used viscometers and the viscosity of non-Newtonian liquids varies with shear rate.

Viscometers generally measure either the resistance to flow, or drag or torque produced by movement of an element through a liquid.¹³ Many configurations of viscometers are available, but most are of the following general types: rotational, float or piston, vibrating probe or capillary. The glass capillary viscometer, because of its accuracy, simplicity and cost, is often used to determine the viscosity of liquids, mostly Newtonian. Normally glass capillary viscometers are used at flow rates determined by gravity. However, some such as Cannon-Manning, vacuum, capillary viscometers (Cannon Instrument Company, State College, PA, USA) have been used with vacuum to determine the viscosities of asphalts (ASTM Standard D2171-88).

Our objective was to develop a system using the Cannon-Manning vacuum capillary viscometer to measure viscosities of agricultural spray mixtures at shear rates representative of liquids passing through nozzle orifices.

2 EQUIPMENT AND PROCEDURE

A schematic of the system assembled to measure viscosities at high shear rates is shown in Fig. 2. Basically the system contains a glass capillary, vacuum viscometer; constant temperature water bath and vacuum source.

A Cannon-Manning glass capillary vacuum viscometer (No. 4/V205) was used in the system. A schematic of the viscometer is shown in Fig. 3. Specifications of the 4/V205 Cannon-Manning vacuum viscometer used

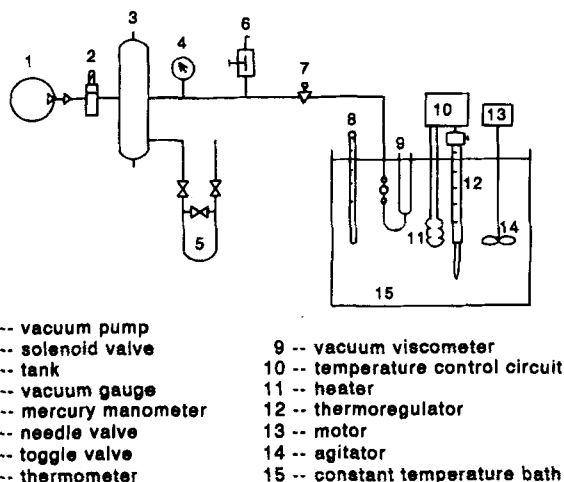


Fig. 2. Schematic of the system for measuring viscosities of liquids at high shear rates.

with the system were supplied by the manufacturer and are listed in Table 1. Values in Table 1 are not affected by temperature over the range of temperatures at which agricultural pesticides are normally applied. The sample is fed into filling tube A to ±2 mm of fill line E. Then when vacuum is applied to tube M, the efflux time for filling bulb B, the first of the two bulbs of the viscometer, is measured. While the flow continues, the efflux

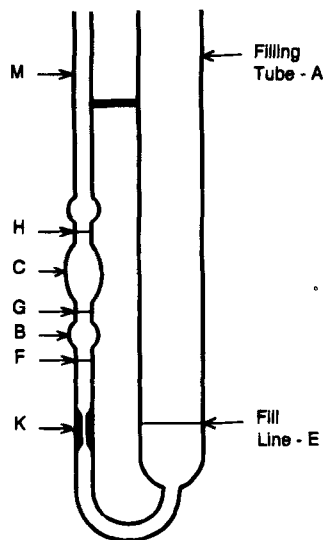


Fig. 3. Cannon-Manning vacuum viscometer. B, C are bulbs; F, G and H are lines used in timing the efflux rate, K is capillary and M is vacuum tube.

TABLE 1

Specifications of 4/V205 Cannon-Manning Vacuum Viscometer

Parameter	Bulb B	Bulb C
Calibration factor, <i>K</i> (mPa/mm Hg)	0.02251	0.00705
Bulb volume, <i>V</i> (ml)	0.50	1.68
Capillary radius, <i>r</i> (cm)	0.0088	0.0088
Liquid head, <i>h</i> (mm Hg)	2.4	4.5

time for filling bulb C is measured. A digital stop watch graduated in 0.1 s divisions and with lap/total time feature was used to measure the efflux times of the liquid when it passed between timing marks F and G, and F and H. The efflux time depends on the viscosity of the liquid and the vacuum differential. Bulbs B and C allow two viscosity measurements without recharging the viscometer.

A model M-18MS clear Pyrex bath with thermoregulator, heater and motor-driven stirrer (Cannon Instrument Company, State College, PA, USA) was used to maintain the liquid in the viscometer at the desired temperature. The viscometer was held vertically with a rubber stopper in the cover plate of the bath. The bath was filled with distilled water to within 2.5 cm of the top.

A vacuum system was assembled to maintain a vacuum within ±0.5 mm of the desired value up to and including 300 mm Hg. Copper tubing (6.35 mm inside diameter) was used to connect the components of the vacuum system. The vacuum system was assembled so that when vacuum in the tank was at the desired value and all valves were closed there was no loss of vacuum as indicated by the open-end mercury manometer with 1-mm graduation. A vacuum pump (Cat. No. XX6000000, Millipore Filter Co., Bedford, MA, USA) was used to create a vacuum greater than desired for the test in the 10-liter tank when the toggle valve controlling vacuum on the viscometer and needle valve were closed. The vacuum was then reduced to the desired value for the test by the needle valve.

The high shear rate viscosity (mPa s) of the sample is calculated from the measured efflux time with the following equation:^{14,15}

$$\text{Viscosity} = K(H - h)t - \frac{E}{t^2} \quad (1)$$

where *K* (mPa/mm Hg) is a calibration factor, *H* (mm Hg) is the vacuum differential, *h* (mm Hg) is the mean hydrostatic head of the liquid for a bulb, *t*(s) is the time to fill a bulb, and *E*(mPa s³) is the kinetic energy correction factor. The shear rate (s⁻¹) at the wall of the capillary is calculated with the following equation.

$$\text{Shear rate} = \frac{4V}{\pi r^3 t} \quad (2)$$

where *V* is volume (ml) of a bulb on the viscometer, and *r* is the radius (cm) of the capillary (K in Fig. 3). For a given liquid and viscometer the efflux time depends on the vacuum differential, so a change in the vacuum differential will change the shear rate on the liquid as it passes through the capillary of the vacuum viscometer.

When a liquid stream discharges at high velocity from the capillary of a viscometer, the stream carries an appreciable amount of kinetic energy. This kinetic

energy can represent a sizable portion of the total applied vacuum for the viscometer, especially at high shear rates, and the kinetic energy correction term (E/t^2) in eqn (1) can be significant. The kinetic energy correction factor, E was determined experimentally. Distilled water is a Newtonian liquid, and different values of vacuum differential on the viscometer should have no effect on the measured viscosity. The value of E/t^2 is the amount of correction required in eqn (1) to obtain the proper viscosity of the liquid. Distilled water at 25°C was used to determine the kinetic energy correction factor, E , with vacuum over the range of 50 to 300 mm Hg (10 mm Hg increments) for the Cannon-Manning vacuum viscometer. After the kinetic energy correction factor was determined using water, tests were conducted with two other Newtonian liquids with known viscosities to determine if eqn (1) was satisfactory for these liquids. We used ethanol (1.077 mPa s at 26°C¹⁶) and a viscosity standard (9.1 mPa s at 25°C, Brookfield Engineering Laboratories Inc., Stoughton, MA, USA).

The viscosities of three spray mixtures, each containing distilled water and a drift control agent, were measured at several shear rates with the 4/V205 Cannon-Manning vacuum viscometer. The viscosity of each mixture was also measured at very low shear rates with Cannon-Fenske Routine viscometers (No. 100/H983 and No. 50/T931). For measurements at very low shear rates, the only force on the liquid was gravity. The following spray drift control agents were used: 'Nalco-Trol' (Nalco Chemical Company, Naperville, IL, USA), 'Target' (Blue Ribbon Products Company, Dewitt, NY, USA), and an experimental drift control agent (BU) from Becker-Underwood, Inc., Ames, IA, USA. Concentration of the mixture with 'Nalco-Trol' was 0.55 ml of formulation per liter of distilled water. Concentrations for the mixtures with 'Target' and BU were 0.37 and 0.211 g formulation per liter of distilled water, respectively. The shear rates for all measurements were calculated from eqn (2). Viscosities of the spray mixture with 'Nalco-Trol' were measured at 20, 25, 30 and 35°C, and viscosities of the spray mixtures with 'Target' and BU were measured at 25°C.

The viscosity of each sample was measured only after the viscometers with test liquid were in the constant temperature bath for at least 30 minutes. The viscometer was cleaned after measurement by rinsing with distilled water and then acetone (Pesticide Grade). It was then dried by forcing clean, dry, filtered air through it. The viscometers were also cleaned with chromic/sulfuric acid cleaning solution before use with different liquids.

3 RESULTS AND DISCUSSION

The kinetic energy correction term (E/t^2) in eqn (1) varies with the applied vacuum. The effect of vacuum

on the kinetic energy correction term, E/t^2 for distilled water at 26°C is shown in Fig. 4. For both bulbs, B and C, E/t^2 increased with an increase in the value of vacuum differential. For example, when the vacuum differential was 300 mm Hg, the filling time for bulb C was 16.4 s and E/t^2 was 0.296 mPa s or about 34% of the total value of the viscosity. When the vacuum differential was 50 mm Hg the filling time was 91.2 s, and E/t^2 was only 0.0176 mPa s, or about 2% of the total value of the viscosity.

The kinetic energy correction factor, E , needed in eqn (1) was correlated with the vacuum differential H and the hydrostatic head h . Based on viscosity measurements of distilled water at 26°C and 26 values of vacuum differential with the 4/V205 Cannon-Manning vacuum viscometer, a relationship between E and $H - h$ of the form shown in eqn (3) fit the data very well.

$$E = \frac{A_0 + A_1(H - h) + A_2(H - h)^2}{[B_0 + B_1(H - h) + B_2(H - h)^2]^3} \quad (3)$$

where A_0 , A_1 , A_2 , B_0 , B_1 and B_2 are constants. To determine the energy correction factor (E), the value for viscosity of water (0.8705 mPa s at 26°C¹⁶) was used along with K and h values from Table 1. From the regression for bulb B, $A_0 = -0.00384$, $A_1 = 0.0000914$, $A_2 = 0.0000003$, $B_0 = 0.004415$, $B_1 = 0.0007639$, $B_2 = -0.00000035$ and the coefficient of determination (R^2) was 0.99897. From the regression for bulb C, $A_0 = -0.00057$, $A_1 = 0.0000105$, $A_2 = 0.00000017$, $B_0 = 0.00066$, $B_1 = 0.000262$, $B_2 = -0.0000002$ and R^2 was 0.9992. The constants (A_0 , A_1 , A_2 , B_0 , B_1 and B_2) could also be determined from eqn (3) with experimental data for at least six pairs of values for E (from eqn (1)) and $H - h$ determined with water or another liquid with known viscosity. Then simultaneous equations in the form of eqn (3) could be solved to determine the constants.

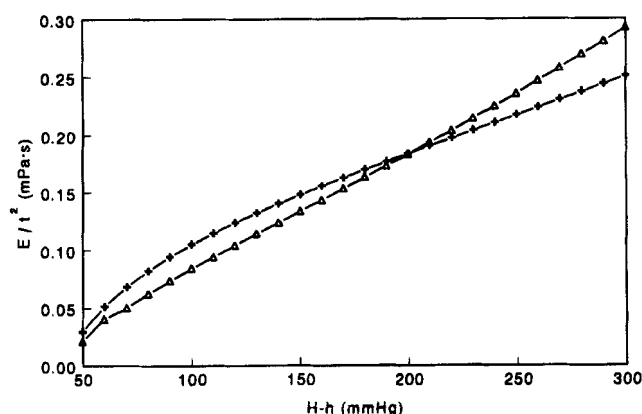


Fig. 4. Effect of vacuum differential on kinetic energy correction term, E/t^2 , for 4/V205 Cannon-Manning vacuum viscometer with distilled water. (+) Bulb B, (Δ) Bulb C.

After the kinetic energy correction factor (E) was established, several measurements of the viscosity of distilled water at shear rates from 6500 to 200 000 s^{-1} indicated measurement errors were less than 3%. For water flow through the capillary of the 4/V205 viscometer with shear rate of 200 000 s^{-1} , the Reynolds number is about 830 and within the region for laminar flow. The system with the 4/V205 viscometer is capable of measuring viscosities at shear rates representative of shear rates of liquids passing through orifices for a very large number of agricultural and industrial spray applications. Most pesticide applications are for weed control, and fan pattern nozzles are often used for herbicide applications. For example, the mean velocity of liquid at the orifice of an 8002 fan pattern nozzle (Spraying System Co., Wheaton, IL, USA) operated at 276 kPa is about 20 $m s^{-1}$, and the calculated mean shear rate on the liquid for these conditions is about 116 000 s^{-1} .

Repeatability of viscosity measurements with the system was very good. For example, three measured viscosities of distilled water from bulb B at 26°C with 300 mm Hg vacuum (shear rate = 200 000 s^{-1}) were 0.8787, 0.8460 and 0.8787 mPa s. At 50 mm Hg vacuum (shear rate = 6500 s^{-1}) the measured viscosities were 0.8665, 0.8856 and 0.8742 mPa s. The main experimental error occurred in measuring the time required for the liquid to pass through bulb B. Another test to determine if temperature influenced the kinetic energy correction factor (E) indicated that E was not affected by liquid temperatures of 20 and 35°C. For example, the measured viscosities of distilled water at 20°C were 1.011 and 1.018 mPa s for shear rates of 32 000 and 174 000 s^{-1} , respectively; and the measured viscosities of distilled water at 35°C were 0.712 and 0.713 mPa s for shear rates of 44 000 and 207 000 s^{-1} , respectively. Published viscosities for distilled water¹⁶ are 1.002 mPa s at 20°C and 0.7194 mPa s at 35°C.

The accuracy of eqn (1) for use with other Newtonian liquids was also determined. Generally, the viscosities of pesticide spray mixtures discharged through hydraulic

nozzles are within 0.8 to 10 mPa s. Pure ethanol has a viscosity¹⁶ of 1.077 mPa s at 26°C regardless of shear rate. The experimental viscosities, shear rates and filling times of 100% ethanol at 26°C for various values of vacuum differential for both bulb B and bulb C of the 4/V205 Cannon-Manning, vacuum viscometer are given in Table 2. Viscosities were calculated from eqns (1) and (3), and the shear rates from eqn (2). All viscosities were very close to 1.077 mPa s at shear rates from 30 400 to 171 000 s^{-1} . Relative to 1.077 mPa s, the greatest error in the measurement of viscosity for 100% ethanol was 3.2% at a shear rate of 89 682 s^{-1} with bulb B, and 4.6% with bulb C at a shear rate of 94 946 s^{-1} .

The experimental viscosities, shear rates and efflux times of a 9.1 mPa s viscosity standard at 25°C for various vacuum differentials for both bulb B and bulb C of the 4/V205 Cannon-Manning, vacuum viscometer are shown in Table 3. An agricultural spray mixture with viscosity as high as 9.1 mPa s would be extremely rare. We used the 9.1 mPa s viscosity standard to determine the accuracy of eqn (3) with a liquid with high viscosity relative to agricultural spray mixtures. Table 3 indicates that experimental viscosities of the viscosity standard varied little with shear rates and were always very close to 9.1 mPa s. The greatest error in the measurement of viscosity of the viscosity standard was only 1.9% at 100 mm Hg vacuum with bulb C. With the 9.1 mPa s viscosity liquid, the shear rate was only 23 192 s^{-1} with 300 mm Hg vacuum on the viscometer. The system has been used with 500 mm Hg vacuum in other tests and is limited to 500 mm Hg vacuum by the scale on the mercury manometer.

Many drift control agents increase the viscosity of spray mixtures and hence median droplet size produced by nozzles. Figure 5 shows the effect of shear rate on apparent viscosity of mixtures of water with 'Nalco-Trol', 'Target' and an experimental drift control agent (BU). The three drift control agents have different chemistries and each of their mixtures with water resulted in different changes in viscosity with shear rate. Viscosity of the mixture with 'Nalco-Trol' decreased rapidly with

TABLE 2
Viscosity of Ethanol at 26°C at Various Shear Rates in 4/V205 Cannon-Manning Vacuum Viscometer

Vacuum (mm Hg)	Bulb B			Bulb C		
	Fill time (s)	Shear rate (s^{-1})	Apparent viscosity (mPa s)	Fill time (s)	Shear rate (s^{-1})	Apparent viscosity (mPa s)
50	30.6	30 392	1.082	100.4	30 876	1.075
100	15.35	60 586	1.055	49.7	62 374	1.072
150	10.37	89 682	1.043	32.65	94 946	1.028
200	8.05	115 528	1.062	25.4	122 047	1.039
250	6.6	140 909	1.67	20.9	148 325	1.031
300	5.65	164 602	1.077	18.1	171 271	1.033

TABLE 3
Viscosity of a Viscosity Standard at 25°C at Various Shear Rates in 4/V205
Cannon-Manning Vacuum Viscometer

Vacuum (mm Hg)	Bulb B			Bulb C		
	Fill time (s)	Shear rate (s ⁻¹)	Apparent viscosity (mPa s)	Fill time (s)	Shear rate (s ⁻¹)	Apparent viscosity (mPa s)
50	258.2	3602	9.101	873.4	3578	9.198
100	121.7	7642	8.983	391.8	7912	8.926
150	79.4	11713	8.983	257.7	12029	9.067
200	60.8	15296	9.085	196.9	15744	9.181
250	48.4	19215	9.061	154.3	20091	9.034
300	40.1	23192	9.023	127.6	24295	8.991

increased shear rate from 7.77 mPa s at 9.7 s⁻¹ to 3.3 mPa s at 20 000 s⁻¹ and then slowly decreased to 2.67 mPa s at 125 000 s⁻¹. Viscosity of the mixture with 'Target' changed little with shear rate and was 2.38 mPa s at 37 s⁻¹ and 2.39 mPa s at 113 000 s⁻¹. Viscosity of the mixture with the Becker-Underwood experimental drift control agent (BU) increased with shear rate. Viscosity of this mixture was 1.85 mPa s at 42 s⁻¹ and 3.92 mPa s at 115 000 s⁻¹. Figure 5 indicates that viscosity of mixtures of water and drift control agent can vary greatly with shear rate and chemistry of the drift control agent. Mixtures of each of the three drift control agents with water all had higher viscosities than water at shear rates up to 115 000 s⁻¹.

Pesticides are applied over a very wide range of temperatures but no literature is known that indicates the effect of temperature on spray droplet size or viscosity, with mixtures containing drift control agents. Figure 6 illustrates the effects of temperature and shear rate on the viscosity of mixtures of water and 'Nalco-Trol' at temperatures of 20, 25, 30 and 35°C. The graph indicates that over the range of shear rates used, the viscosity at 35°C was about 30% less than at 20°C. Since

pesticides along with drift control agents are applied over a very wide range of temperatures, research is needed to determine the effects of temperature changes of mixtures with drift control agents on spray droplet sizes.

A second Cannon-Manning vacuum viscometer (4/V162), similar to the 4/V205 viscometer, was acquired and calibrated with distilled water. We also found that it provided accurate values of viscosities for ethanol and the 9.1 mPa s viscosity standard over a wide range of shear rates. For both viscometers, three liquids and a wide range of shear rates, the maximum error was 4.6%, but it was generally much less than this. Probably most of the error is due to timing the liquid between lines on the viscometer tube. This error could be reduced with an automatic sensor and timing system.

Our experiments indicate that the viscosities of mixtures of water and drift control agents used to alter droplet size can vary greatly with shear rate and some with temperature. The system described in this paper enables measurements of viscosities of spray mixtures at high shear rates representative of spray application con-

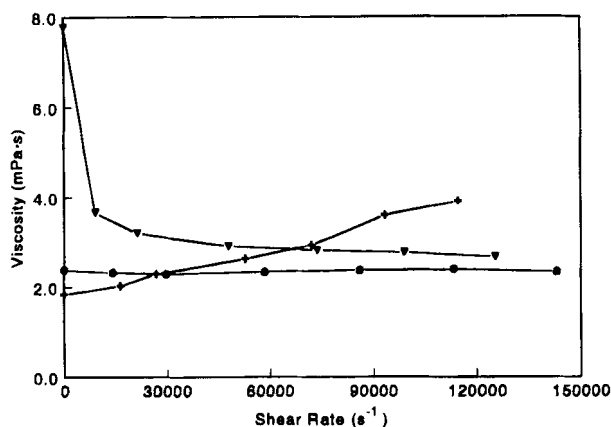


Fig. 5. Effect of shear rate on the apparent viscosities of spray mixtures of distilled water with (▼) 'Nalco-Trol', (●) 'Target' and (+) an experimental drift control agent (BU) at 25°C.

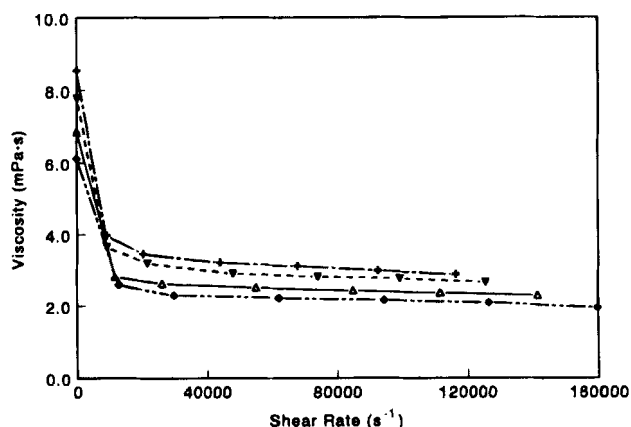


Fig. 6. Apparent viscosity of a spray mixture of water and 'Nalco-Trol' at various shear rates for ambient temperatures of (+) 20, (▼) 25, (△) 30 and (◆) 35°C.

ditions when mixtures are forced through nozzle orifices to produce droplets. The system described in this paper has been used to measure viscosities at high shear rates of spray mixtures containing various adjuvants.¹⁷

4 CONCLUSIONS

1. An inexpensive system using a Cannon-Manning vacuum viscometer was developed to measure viscosities at high shear rates, up to $200\,000\text{ s}^{-1}$, of both Newtonian and non-Newtonian liquids.

2. For Newtonian liquids with viscosities ranging from 0.875 to 9.1 mPa s, and a wide range of shear rates, the maximum error in measurement of viscosity was 4.6%.

3. The effect of shear rate on viscosity of water-drift control agent mixtures varied with chemistry of the drift control agent. Viscosity of the mixture with 'Nalco-Trol' decreased from 7.77 to 2.67 mPa s as shear rate increased from 9.7 to $125\,000\text{ s}^{-1}$, while viscosity of the mixture with 'Target' remained around 2.38 mPa s as shear rate increased from 37.6 to $185\,000\text{ s}^{-1}$. However, the viscosity of the mixture with an experimental drift control agent (BU) increased from 1.85 to 3.92 mPa s as shear rate increased from 42 to $115\,000\text{ s}^{-1}$.

4. The viscosity of mixtures of water and 'Nalco-Trol' decreased as temperature increased. At 35°C the viscosity was about 30% less than at 20°C over a wide range of shear rates.

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