Design and Performance of a Dynamic Interfacial Tension Spinning-Drop Tensiometer

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Two standard spinning-drop tensiometers (SDT) have been modified by the addition of video equipment and an interface to a personal computer. (Since two tensiometers were available in our laboratory, both were modified. There is no reason why the system can't be set up with only one tensiometer). The computer has been fitted with a special video board and a menu-driven image enhancement and analysis program. A date-time generator accurately measures the age of the aqueous-organic interface. The operator can record droplet images for later analysis. Alternatively, the video board can "capture" a droplet image for immediate analysis. Analysis usually consists of measurement of drop length and drop width. However, interesting emulsification and solubilization phenomena can also be recorded for later study. These modifications greatly enhance the capabilities of the SDT. This new system is referred to as the tensiometer image analysis apparatus. Similar procedures can be used with air droplets to determine surface tension values. The operator can determine equilibrium interfacial tension (IFT) values with greater accuracy and in less time than is possible with the conventional SDT. Rapidly changing IFT values can be accurately determined at intervals of as little as one second. These capabilities have been used in studies of detergency, deresination of wood pulp, and deinking of waste paper. The video capture and analysis capabilities of this system are also useful in other applications.

KEY WORDS: Aqueous-organic interface; droplet image; dynamic interfacial tension; emulsification phenomena; solubilization; spinning-drop tension; surface tension values; video capture analysis capabilities.

For surfactant applications such as detergency, deresination of wood pulp and ink removal from waste paper, the process time is often less than the time required for the interfacial tension (IFT) to reach equilibrium. Measurements need to be obtained within the process time, *i.e.*, while the interfacial tension is still changing. This changing IFT is termed the dynamic interfacial tension. With the conventional University of Texas spinning-drop tensiometer (SDT) (Austin, TX), the operator determines droplet dimensions with a microscope eyepiece and a hairline indicator. This indicator is carefully moved across the droplet width by means of a small vernier gear (1). Due to the time required to do this, accurate measurements at short elapsed times are difficult. This is particularly the case when studying nonequilibrated phases.

With the modifications described below, the SDT becomes a more effective instrument for measuring interfacial tensions of liquid-liquid systems. These improvements provide improved precision in measuring equilibrium IFT. However, the greater impact is that of making the spinning-drop tensiometer a valid instrument for accurately measuring dynamic IFT.

EXPERIMENTAL PROCEDURES

Tensiometer modifications. Figure 1 is a schematic diagram of the current configuration for the two camera/two tensiometer apparatus. Table 1 is a detailed list of the components of the tensiometer image analysis (TIA) apparatus. A light-sensitive camera is mounted on the custom-made collar above the tensiometer eyepiece. The design

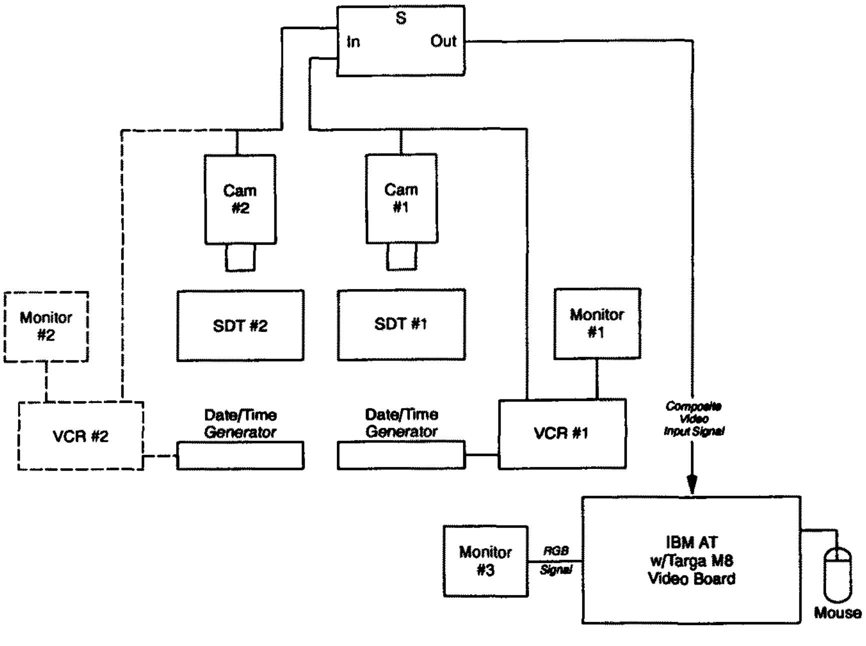

FIG. 1. Tensiometer image analysis apparatus.

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TABLE 1

Components of the Tensiometer Image Analysis Apparatus (TIA)[a]

Quantity	Unit
2	University of Texas Model 500 spinning-drop tensiometers
2	Javelin Model JE-7262 NEWVICHIP CCD cameras
1	Panasonic Model AG-1230 videocassette recorder
1	Panasonic Model WJ-810 Time-Date Generator
1	World Video Model CHR-14 high resolution color/black & white monitor
1	IBM PC-AT equipped with a 1.2 MB hard drive, two 360KB 5.25 in. floppy disk drives, a math co-processor, Vega Video-7 EGS graphics, Microsoft serial mouse, and IBM enhanced color display
1	Archer video selector

[a] Company sources: Javelin (Torrance, CA). Panasonic (Secaucus, NJ). World Video (Boyertown, PA); Archer (Meyer Instruments, Inc., Houston, TX).

of the electrical connections permits simultaneous operation of two camera/tensiometer systems. The cameras send a composite video signal that is split. One cable carries the signal to a videocassette recorder (VCR) for real time recording. The other cable carries the same signal to a switch box.

The signal from this switch box goes to the Targa® M8 video graphics board (Truevision, Inc., Indianapolis, IN) installed on an IBM PC-AT® personal computer (Boca Raton, FL). The video image enhancement (see below) is accomplished with the Targa board and transmitted as a red-green-blue (RGB) signal to a high-resolution monitor. Thus, the operator can display the Targa board image for enhancement and measurement.

The monitor has the added feature of accepting a composite signal. This allows it to double as Monitor #1 when the operator wishes to examine the image from the other camera. When necessary, the live droplet image can be monitored to keep the oil drop within the camera's field of view. The date/time generator superimposes the current date and time onto the video images on both legs of the video system.

Video board. The heart of the system is the Targa M8 video graphics board. This computer board accepts a composite video signal from a camera or VCR. A droplet image is "captured" or stored in video RAM as a series of numbers. These numbers correspond to level of grayness (white = 255, black = 0) of the image. The video board has the power to perform sophisticated mathematical manipulations of the image as directed by the JAVA® software (Scientific Corp., Corte Madera, CA). These manipulations usually involve expanding the gray scale. This results in bright areas of the image becoming brighter and dark regions even darker. As a result, droplet edges are more clearly defined. This plus image magnification makes measurement of droplet width and length more precise.

The Targa board transmits the image as an RGB signal to a high-resolution monitor. The operator can view a droplet while the video board enhances the image. Due to the enormous number of bit manipulations that take place on the board, an AT class or faster IBM-compatible computer is recommended.

Computer software. JAVA is a menu-driven computer program that uses the powerful capabilities of the Targa board. JAVA accepts live or still video images from camera or VCR, or digital image files. Thousands of calculations are necessary to alter an entire monitor screen. Therefore, the operator uses a Microsoft Mouse pointer to define a smaller, more specific "area of interest" of the captured image. Processing only the area of interest reduces calculation time.

Having captured an image and defined an area of interest, the user can perform several differant operations. The image can be enhanced in a variety of ways depending on the application. Objects or grey areas can be counted; distances, areas, or angles can be measured. An on-screen scale permits conversion of measured length units to micron distances. This conversion or calibration factor may be entered into the software. The conversion factor is dependent on the magnification power of the tensiometer eyepiece. An image also can be mapped with X-Y coordinates, thus making relative positions measurable. The data generated by these measurements are written to a spreadsheet. The operator can generate plots from the spreadsheet data. Transforms can be written to manipulate the data mathematically. The user can calculate average values, standard deviation, standard error, and 95% and 99% confidence levels. Data can be exported to disk in ASCII format for later inclusion in Lotus or other software. The operator can print the data or store them on disk.

Additional equipment. The following equipment has also been used: gas purifier for drying the air used to maintain test temperature across the length of the tensiometer sample tube; water bath to control temperature of air used to maintain temperature across length of the sample tube; spinning-drop tensiometer sample tubes, caps, rubber O-rings, and 1/4″ septa.

Method summary. For simplicity, the procedures are presented here for a one camera/one tensiometer operation.

A constant flow of heated air provides better temperature stability across the sample tube at elevated temperatures. At lower operating temperatures, an unheated air stream cools the tensiometer and minimizes temperature gradients across the tube. The air flows through a gas purifier for drying and then through the constant-temperature bath before entering the tensiometer. The water bath is heated to the desired test temperature before beginning the IFT experiment.

The spinning-drop tensiometer is fitted with the appropriate eyepiece. (Most operators prefer the 5X eyepiece to the 10X eyepiece because more of an elongated droplet is within the field of view.) The test temperature and rotation frequency (usually 11–12 ms/rev is adequate) are pre-set to the desired values with the main power switch off. Frequency should not be set higher than 12 mm/rev because of buoyance effects (2)

The operator turns on the monitor, the camera, the computer and its monitor. The VCR is turned on and a tape installed. The speed setting is placed on "slow", and the VCR stopwatch is reset. The operator loads the JAVA image analysis program into random access memory.

An empty sample tube is placed in the spinning-drop tensiometer. The operator turns on the power and the strobe. The air flow is set on the "low" setting.

The apparatus is now prepared for the start of the experiment.

Method summary—sample preparation. Standard methods of equipment cleaning and sample preparation are used. The water/oil ratio is typically 100–300:1.

The VCR stopwatch is started upon injection of the nonaqueous phase into the sample tube which is already filled with aqueous phase. The sample tube is immediately inserted in the tensiometer, and the instrument motor is turned on to the pre-set rotation speed. The operator positions the camera to capture the droplet image.

Method summary—image capture and enhancement. Either live or recorded images may be used for data acquisition. The date/time generator ensures that the droplet age is known accurately. The user captures an image by means of the frame grabber function of the image analysis software. The entire image can be enhanced. Alternatively, the operator processes only a portion of the image. Image enhancement whitens the lighter shades of gray and darkens the darker shades. This enhanced contrast makes it easier to define droplet boundaries and measure droplet dimensions accurately.

After image enhancement, the operator can magnify the image two, four or eight times. The user then manipulates a computer mouse to measure width and, if necessary, length of the enlarged droplet image.

Method summary—IFT determinations. The operator makes at least six width measurements at various positions on the droplet to ensure an accurate and representative average value. (The user determines droplet length only if it is less than four times the width.) Magnification and image enhancement permit the droplet boundary to be determined accurately, usually to ± 6 microns. This enhances the accuracy of the measurement and improves the precision as well. The measurements made of the drop image are based on previously determined calibration factors within the software. The software calculates an average value and various statistical functions.

Measurement accuracy is only as good as the calibration. The calibration used for the 10× eyepiece is based on a known distance measured by the SDT's Filar micrometer. The calibration for the 5× eyepiece is measured directly on the scale built into the Filar micrometer eyepiece.

The image is then unfrozen. The operator advances the videotape to the next time at which an IFT is to be determined.

To measure equilibrium IFT, the operator continues this process until the IFT reaches an equilibrium value. Operationally, this occurs when there is a $< 1\%$ difference in droplet width between successive measurements taken sixty minutes apart. For dynamic IFT measurements, the operator performs the experiment for a pre-selected length of time that approximates a given surfactant end use or until the system reaches equilibrium.

Another computer program has been written by C.W. Yates and K.H. Raney (Shell Development Company, Houston, TX) to calculate interfacial tension. Input data are droplet width and length measurements, density of both phases, and refractive index of the external phase.

If any interesting visual phenomena occur or if one wishes to calculate additional IFT values at times intermediate to previously calculated values, the VCR tape can be replayed. Data can be taken or photographs made at any time desired.

Surfactants used in IFT studies. The α-olefin sulfonates were synthesized on a bench-top or a pilot scale by reaction of commercial highly linear NEODENE® olefins with sulfur trioxide vapor in a falling film reactor. The NEODENE olefins are commercial products manufactured by Shell Chemical Company (Houston, TX).

Alcohol ethoxylates are referred to by the acronym AE XY-Z. XY is the range of hydrophobe carbon numbers. Z is the average number of ethoxylate units. For specific ethoxylates, XY and Z are single values, *i.e.*, AE 12-4. There are 12 carbon atoms in the hydrophobe and four ethoxylate groups comprise the hydrophile. AE 1215-9 contains a range of 12–15 carbon atoms in the hydrophobe and an average of 9 ethoxylate groups. The specific alcohol ethoxylates were purchased from Nikko Chemical Comkpany (Tokyo, Japan). AE 1215-18 was synthesized in our laboratories by the potassium hydroxide-catalyzed reaction of ethylene oxide with a $C_{12\text{-}15}$ alcohol, NEODOL 25, manufactured by Shell Chemical Company. The other alcohol ethoxylates are manufactured commercially by Shell Chemical Company under the NEODOL® tradename.

Ether sulfates of alcohol ethoxylates are referred to by the acronym AES. Otherwise the nomenclature scheme is the same as described above for alcohol ethoxylates. These surfactants were prepared in our laboratory by falling-film sulfation of the corresponding alcohol ethoxylates from Shell Chemical Company.

Alcohol propoxyethoxylates and alcohol ethoxypropoxylates are referred to by the acronyms A XY-WP-ZE and A XY-ZE-WP, respectively. A refers to the substrate alcohol used to synthesize the surfactant. XY again represents the range of hydrophobe carbon atoms. W refers to the average number of propoxylate groups with P standing for propoxylate. Z again represents the average number of ethoxylate units with E representing ethoxylate. The order of addition of ethylene oxide and propylene oxide to the alcohol/potassium hydroxide-catalyst reaction mixture is given by the order of the E and P terms in the surfactant acronym. Thus A 45-6P-9E contains 14 to 15 carbons in the hydrophobe and an average of six propoxylate units and nine ethoxylate units. One mole of 14-15 carbon alcohol is reacted first with six moles propylene oxide. After complete consumption of propylene oxide, nine moles of ethylene oxide are added to the autoclave and reacted to produce AE 45-6P-9E.

RESULTS

Representative interfacial tension studies are the TIA described below. By substituting an air bubble for the nonaqueous phase, the same test procedures can be used to determine equilibrium surface tension and dynamic surface tension.

Precision of interfacial tension measurement. Two series of equilibrium interfacial tension determinations demonstrate the lower level of experimental uncertainty for the TIA. The first series consisted of nine equilibrium IFT measurements performed in an unmodified spinning-drop tensiometer. The second series consisted of seven equilibrium IFT determinations performed in the TIA. Equilibrium oil droplet widths were similar in both series of experiments, 700–1400 microns.

Test conditions were the same in both sets of experiments and are described in the Experimental Procedures section. Test temperature was 75°C. The oil phase was a California high-viscosity crude oil. The pH 8.0–9.5 aqueous phase contained 3–4% sodium chloride. Surfactant concentration was 0.5% by weight. The surfactants used were a series of α-olefin sulfonates that varied in carbon number and mono/disulfonate ratio. Both series of experiments were performed with pre-equilibrated phases. These phases were then equilibrated to constant drop width in the tensiometer tube.

With the unmodified tensiometer, the mean standard deviation of the equilibrium droplet width was 0.74%. For the TIA, the mean standard deviation was less than half as much, 0.36%. From these data, it is clear that the TIA produces an improvement in IFT precision.

Dynamic interfacial tension. The system studied was 0.5% wt AE 1215-9 against cetane at 25°C. Phases were not pre-equilibrated. The oil drop was injected into a nonrotating tube. The VCR was recording while the oil was injected. The limiting factor, for the minimum elapsed time for which an IFT value can be calculated, is how fast the droplet comes into view of the camera. Within 45 s after injection, the oil drop was in the field of view of the camera. The course of each entire experiment was recorded by the VCR. Figure 2 is the plot of IFT *vs.* elapsed time for this experiment.

In the AE 1215-9 experiment, the length/width ratio was less than 4 for the first 15 min of the experiment. In the unmodified tensiometer this posed problems; it was not possible to determine droplet width and length when both these dimensions were changing during the measurement. However, the TIA was easily able to capture an image of the entire droplet at a precisely known interfacial age. The necessary length and width measurements can then be made in a careful, unrushed manner. Figure 2 shows a smooth decline in IFT with time to a stable value within approximately one hour.

Surfactant structure — dynamic IFT studies. Figures 3 and 4 represent results obtained when comparing the IFT behavior of alcohol ethoxylates and alcohol propoxyethoxylates. Comparisons are between surfactants having the same hydrophobe and containing the same total number of moles of alkylene oxide. Surfactant concentration was 0.5% by weight. Cetane was the oil phase. Phases were not pre-equilibrated.

For these relatively low propylene oxide contents (2 moles propylene oxide per mole of surfactant), equilibrium IFT values for the two surfactant types were almost equal. However, at contact times less than ten minutes, the alcohol ethoxylate actually provided a significantly lower interfacial tension value than did the corresponding alcohol propoxyethoxylate.

The effect of propylene oxide position in the chemical structure of alcohol alkoxylates on IFT was then studied.

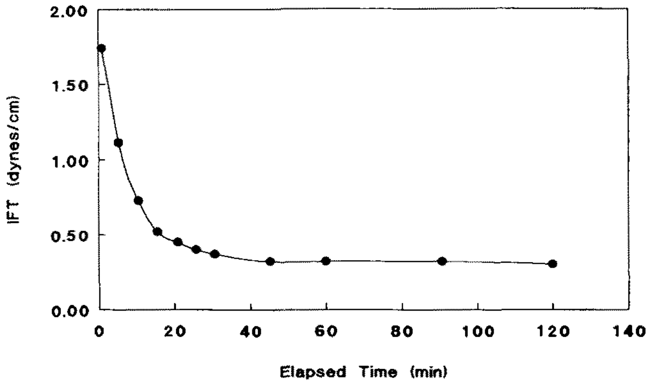

FIG. 2. 25°C Dynamic interfacial tension of 0.5% (by weight) AE 1215-9 against cetane.

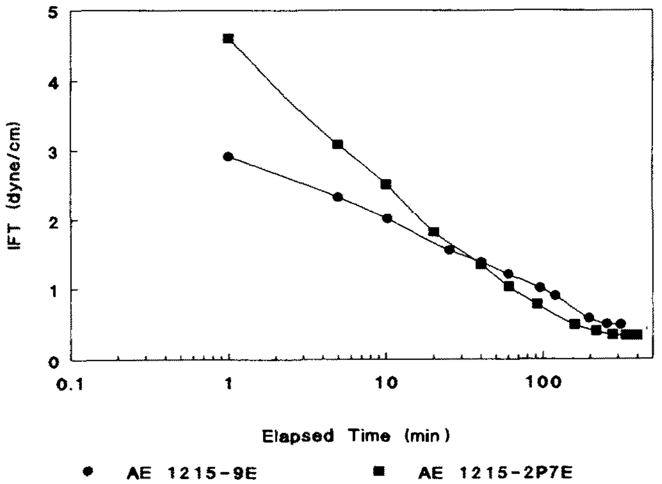

FIG. 3. 25°C Dynamic interfacial tension for 9-mole alkoxylates against cetane.

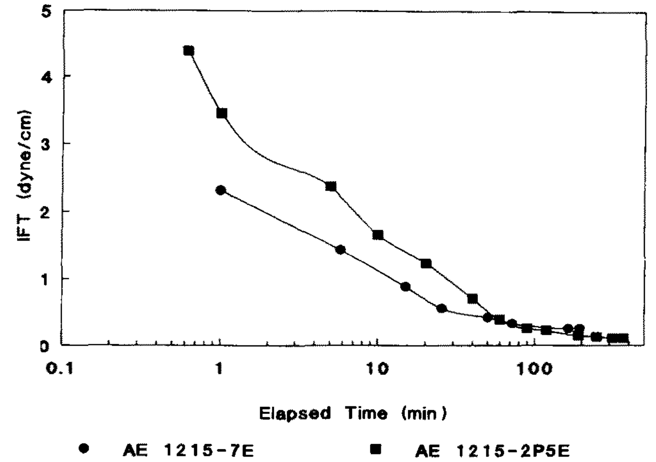

FIG. 4. 25°C Dynamic interfacial tension of 7-mole alkoxylates against cetane.

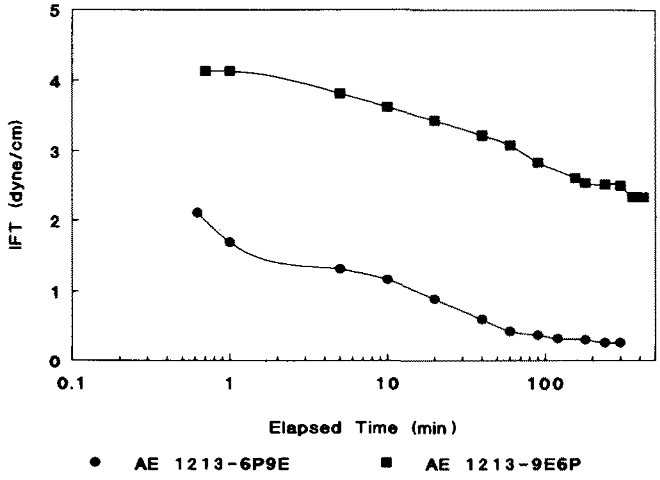

FIG. 5. 25°C Dynamic interfacial tension against cetane—effect of position of the propoxy groups in alcohol alkoxylates.

TABLE 2

Formulation Model of Wood Resins

Component	% by Weight
Oleic acid	70
Abietic acid	20
α-Terpinene	5
α-Terpineol	5

The IFT behavior of A 1213-6P-9E and A 1213-9E-6P were compared under the same test conditions. Results are summarized in Figure 5. Equilibrium and dynamic IFT values exhibited the same trend. The ethylene oxide-terminated surfactant provided significantly lower IFT values thoughout the 300-min experiment.

Applications — removal of wood resins from pulp. Wood resins are complex mixtures of resin acids; fatty acids, esters of fatty acids with glycerol, sterol and other alcohols; fatty alcohols; terpenes; diterpenes; and other chemicals. The resin acids include abietic, dehydroabietic, isopimaric, levopimaric, neoabietic, and palustric acids (3,4). The formulation in Table 2 was chosen as a reasonable model of wood resins.

Earlier deresination studies performed in our laboratory indicated that an alcohol ethoxylate was a more effective deresination agent than a nonylphenol ethoxylate of a similar HLB value. This was consistent with dynamic IFT results. At times less than sixty minutes, the IFT of the alcohol ethoxylate against the model resin was much less than that of the nonylphenol ethoxylate (Fig. 6). The deresination process time in a paper mill normally lasts 20–60 min. Therefore, the dynamic IFT results are probably relevant to real paper mill situations.

The correlation of dynamic interfacial tension values with ink removal from old newspapers is described elsewhere (5).

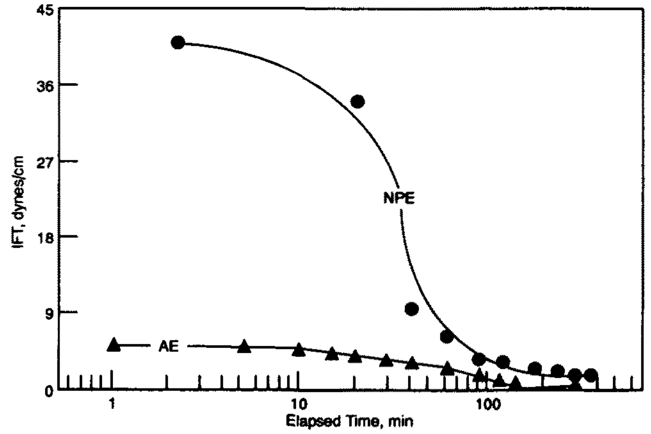

FIG. 6. 75°C Dynamic interfacial tension of surfactants against a model wood resin.

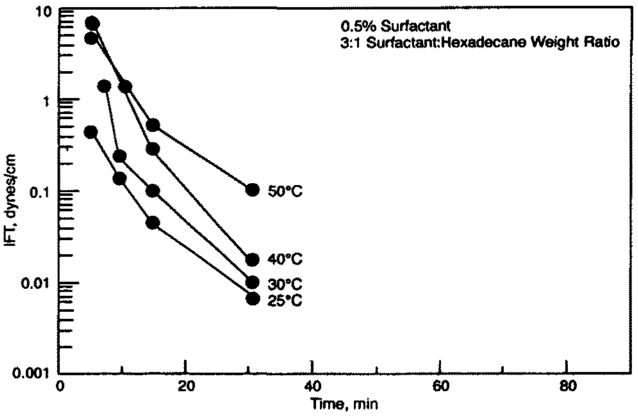

FIG. 7. Effect of temperature on interfacial tension of a 78:22 (by weight) mixture of AE 12-3 and AES 1213-3 against cetane (taken from reference 6).

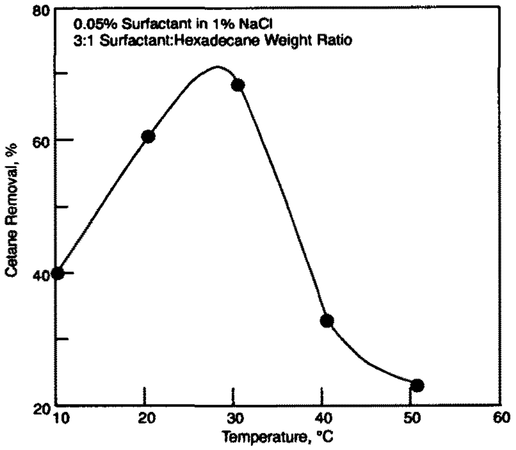

FIG. 8. Effect of temperature on cetane detergency of a 78:22 (by weight) mixture of AE 12-3 and AES 1213-3 (taken from reference 6).

Applications—detergency. Previously published results illustrate the use of this instrumentation in optimizing the nonionic:anionic surfactant ratio in surfactant blends and thereby increasing nonpolar oily soil removal from fabrics (6). The lowest dynamic interfacial tensions were found at approximately 25–30°C (Fig. 7). Detergency results (Fig. 8) indicated this correlated closely with the temperature at which maximum cetane solubilization was observed in the same system (6,7).

DISCUSSION

Overcoming limitations of the spinning-drop technique. The main experimental difficulties of the conventional spinning-drop tensiometer to determine dynamic IFT (8) are: (i) poor temperature control—increasing test temperature with time; (ii) imprecise interfacial age determination. It takes so long to measure drop dimensions that the elapsed time value is significantly different for each drop dimension measurement. This is particularly the case when both drop length and width must be determined; (iii) imprecise drop measurements—before reaching equilibrium, the drop can move, expand and contract quickly. This causes significant changes in drop dimensions during measurement. (A single drop width measurement is insufficient to calculate a meaningful IFT value. An average drop width based on several measurements is preferred.)

With the TIA apparatus we have been able to maintain a constant test temperature, thereby overcoming objection (i). This is done by passing air through a long coil placed in a constant temperature bath. This hot air then passes over the spinning sample tube. However, we have experienced difficulty at times in maintaining lower test temperatures, *ca.* 25°C. A refrigerated bath solves this problem.

By capturing an image, droplet measurements can be made at exact intervals; the droplet does not age while it is being measured. This overcomes difficulty (ii). It is most convenient to do this on images previously recorded with a VCR. Analyzing a frozen image obtained at an accurately measured time also overcomes difficulty (iii). The static image does not change dimensions while those dimensions are being measured.

In addition to determining interfacial tension, the VCR permits oil solubilization phenomena to be recorded for later study. With a stronger incident light source, a cross-polarized filter could be introduced between the light source and the tensiometer sample tube. Liquid crystal formation and behavior could then be recorded.

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