Automation of Phase Diagram Recording

J. Rouse[a], S.T. Adamy[a,*], A. Mehreteab[a] and G. Broze[b]
[a]Colgate-Palmolive Co. Technology Center, Piscataway, New Jersey 08855
and [b]Colgate-Palmolive R&D, Inc., B-4041 Milmont (Herstal), Belgium

ABSTRACT: An automated titration system has been developed for generating data to construct phase diagrams, which are extremely useful in the development of personal and household products. In this report, we describe the system and how it can be utilized to perform the technique of dual titration. In the procedure, a clear microemulsion sample is titrated with an oil until the dispersion turns cloudy (defined to be a transmittance below 90%). The mixture is then dosed with a certain quantity of cosurfactant, more than enough to clear the mixture. The sample is again titrated with oil. This process continues until the sample no longer clears upon adding cosurfactant. The resulting measurements of oil uptake can be used to characterize the boundaries of the L1 or oil-in-water microemulsion region of the phase space. Experiments for up to sixteen samples can be performed, each having individual setup and operating instructions. Features include completely automated operation, computer-controlled two-speed mixing, viscosity detection at the end-point condition and the storage of results in a computerized format.

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KEY WORDS: Automatic recording, oil uptake, phase behavior, phase diagram, titration.

Phase diagrams may be regarded as "maps" for product formulation because they describe the states of chemical systems under varying conditions of pressure, temperature and composition. The diagrams are thus extremely useful in the development of personal and household products by giving information on manufacturing pathways, long-term stability, and in some cases, attributes important for consumer acceptance. Of particular importance in surfactant systems are the microemulsion regions. These are macroscopically homogeneous, optically transparent, stable phases that are composed of water (or brine), hydrocarbons and suitable amphiphilic compounds (1). The amphiphiles can be ionic or nonionic surfactants, often with a cosurfactant (typically an alcohol) (2,3). The fact that the mutual solubility between water and oil in microemulsion systems is significantly greater than when no amphiphilic compounds are present makes these dispersions extremely important in research and industry for cleaning (4) and oil recovery (5). The phase boundaries of microemulsion regions in multi-component systems have therefore been well characterized and are described in a number of reviews (1,6–8).

Oil-in-water (o/w) microemulsions, which have been pictured as micelles swollen with oil existing in an aqueous continuous phase (9), are most pertinent to cleaning applications because nearly all consumer-oriented cleaning is done in an aqueous medium. It is therefore extremely important to characterize the boundaries of the o/w microemulsion regions because such information is essentially an indication of oil uptake capacity (i.e., cleaner performance). A typical method of ascertaining the boundaries of the isotropic regions is titration, where a component is incrementally added to a mixture until a clear sample turns cloudy (indicating the boundary between the microemulsion region and the miscibility gap) or *vice versa.* Titration can be represented in the tetrahedral phase space of the water/surfactant/cosurfactant/oil system as shown in Figure 1. Lines within the o/w microemulsion or "L1" region that point toward the oil corner represent the titrations with oil of compositions from clear (one-phase) mixtures to cloudy (two-phase) mixtures, as these lines intersect the "top" surface of the L1 volume. Lines pointing toward the cosurfactant corner represent the dosing of the samples with cosurfactant. Upon dosing, a mixture goes from a two-phase composition to a one-phase composition, as shown by the line entering back into the L1 space of the phase tetrahedron.

The series of oil titrations and cosurfactant dosings described in Figure 1 depicts a "dual titration" method that can

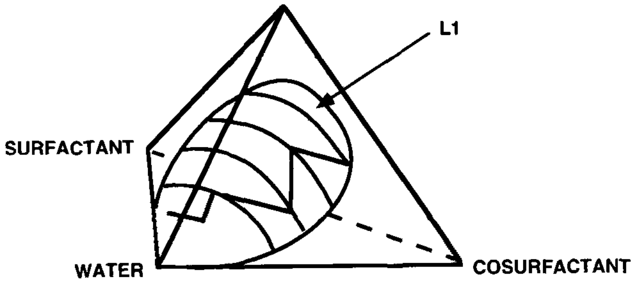

FIG. 1. Tetrahedral representation of the water/surfactant/cosurfactant/oil phase space. Also shown is the dual titration pathway, L1, lines within the oil-in-water microemulsion region. Reprinted with permission from (Ref. 8, p. 729) by courtesy of Marcel Dekker Inc., New York.

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*To whom correspondence should be addressed at Colgate-Palmolive Co. Technology Center, 909 River Rd., Piscataway, NJ 08855.

effectively outline the shape of the one-phase region. Unfortunately, titration is an extremely tedious procedure requiring a great deal of time to complete. This report describes a system for automation of the process. The system is composed of a Brinkman 702 Titrino unit (Brinkman Instruments, Westbury, NY) and a Brinkman 665 Dosimat interfaced to a personal computer. Solubilization capacities are determined by measurement of sample transmittance by a Brinkman PC901 colorimeter. The automatic system additionally incorporates a computer-controlled two-speed stirring motor, a sample changer able to accommodate up to sixteen samples, and a sensor to measure torque (exerted by the stirring motor) to detect changes in sample viscosity. We additionally report comparisons of titration experiments performed by hand and by the automatic titrating instrument.

EXPERIMENTAL PROCEDURES

Component description. Figure 2 shows a simplified block diagram of the autotitrator apparatus. The major components of the system are described below with numbers corresponding to those in Figure 2: **(1)** Motor control unit (custom built): This unit is designed to provide a two-speed capability to the mixing system. The speed of the mixing motor is selected by the IBM-compatible computer through the digital interface (digital I/O cable). The fast speed is calibrated to mix the sample as quickly as possible without creating bubbles. The slow speed is set to keep the mixing turbulence at a minimum to permit a stable transmittance measurement. An integral part of this unit is a current-to-voltage or "I/V" converter. The I/V converter produces a voltage output that relates to the encountered torque or stress during slow-speed mixing. This voltage is termed "Vs" to differentiate it from other signals. **(2)** PC 900 Colorimeter unit (Brinkman Instruments): The colorimeter is the primary feedback element to the titration system. This detector provides values of transmittance or "Tm," which will drop below 90% when the sample becomes saturated with oil. Light is brought to the sample probe through a fiber-optics cable. The probe assembly has a reflecting mirror and a return fiber cable that brings the light back into the instrument for comparison to the reference intensity. The wavelength of the light can be adjusted with special filters. Tm is expressed as a percentage of incident light with 100% corresponding to an output voltage of 1V dc. **(3)** 702 Titrino unit (Brinkman Instruments): The 702 performs the titration function. The 702 adds titrant in user-defined increments, and then acquires Tm from the analog output of the PC 900 Colorimeter. After each acquisition of Tm, the 702 decides if the end-point condition has been reached. We have defined the end point as occurring when Tm either drops below 90% (or 900 mV from the colorimeter output) or when the Tm jumps above 90%, as would happen if we titrate a cloudy sample until it reaches a clear condition. The 702 therefore only looks for the transition point and does not care whether we titrate a clear or cloudy sample. The unit has an on-board microprocessor unit, a memory and a serial communications interface. It is controlled from the IBM computer via the serial link. **(4)** 665 Dosimat Dispenser (Brinkman Instruments): The 665 is a dispensing unit that has a serial communications interface for remote control. It adds cosurfactant in user-defined increments as instructed from the IBM computer. The 665 has no inputs for feedback but can be queried for status information. **(5)** 673 Lift Station and 674 Sample Changer Unit (Brinkman Instruments): The 673 Lift Station lifts the sample container up from the 674 turntable unit into the titration position. It is controlled from a digital I/O card in the IBM computer through software. The lift station has limit switches for disabling the lift motor travel when the container is fully mounted or dismounted. These limit switches also signal to the computer the position of the sample container and if a container is actually present in the lift station when in the mounted position. The 674 sample changer unit consists of the sample turntable and conveyer system. It positions samples on the 673 lift station for mounting into titration position. The 674 is controlled from the IBM computer through the digital I/O card. 6. 677.2 Controller Unit (Brinkman Instruments): This unit provides the digital hardware interface to the 673 sample lift station and the 674 sample changer unit. The 677.2 unit also has six auxiliary outputs (120 V ac 60 Hz) for any external appliances requiring discreet control from a remote computer. Auxiliary outputs 1 and 2 are fed into the solid-state relay (SSR) interface unit to select the speed of the mixing motor. **(7)** SSR interface unit (custom-built): The SSR unit is composed of several solid-state relay modules that interface the signals from the 677.2 controller unit to the motor control unit. It converts the high-voltage (120 V ac) signals into TTL-compatible (0-5 V dc) logic, thus enabling the computer to select the speed of the mixing motor. **(8)** Computer (IBM-compatible): The computer controls the automation and stores the calculated results of the experiments. It has two serial ports for query and control of the dispensers and a digital I/O card installed in a spare expansion slot to monitor and control the sample changer and motor control unit. The computer runs the software that controls the automation.

Algorithm description. A flow diagram illustrating the algorithm that controls the automatic titrating system is shown in Figure 3. At the top of the diagram, set-up conditions for each sample are entered into the computer and are then passed to the 702 unit through the serial link. The operator is queried for all conditions that are intrinsic to the running of the 702 unit, such as the size of titration aliquot, the endpoint condition and the dispensing rate. Other parameters, such as component densities, number of samples and stirring times, are held in the computer for direct control of components (such as the stirring motor) or for use in calculations (such as converting volume dispensed to weights).

Once the program is run, the computer instructs the sample changer to load the first sample into the titration position. After letting the colorimeter signal stabilize, the computer sends the configuration (inputted by the user) to the 702 unit. During the titration, the 702 runs independently of the computer. Each time a Tm value is acquired by the 702 (i.e., the

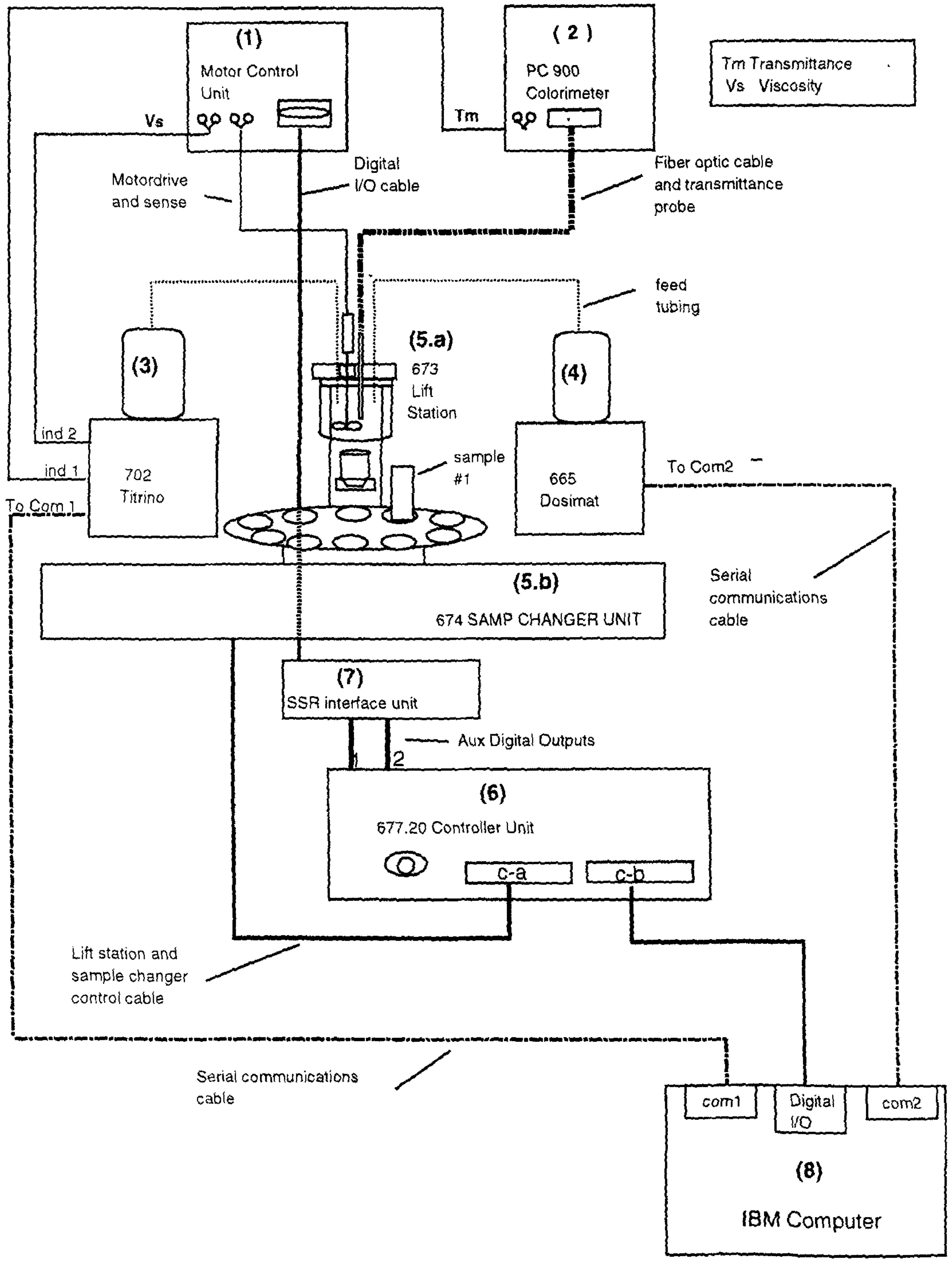

FIG. 2. Block diagram of the autotitrating system SSR, solid-state relay; Tm, transmittance; Vs, viscosity. PC 900 Colorimeter, 702 Titrum Unit, 665 Dosimat, 673 Lift Station, 674 Sample Changer Unit, 677.2 Controller Unit: company source is Brinkman Instruments (Westbury, NY).

signal is stable within a user-defined tolerance), the unit begins dispensing the next volume increment and informs the computer that an acquisition has occurred. The computer then queries the 702 for the value of Tm as well as Vs and instructs the 702 to stand by in a hold mode. While in the hold mode, the sample (to which titrant has just been added) is first stirred fast and then slowly. The computer then releases the 702 from the stand by mode, and the unit continues to look for the endpoint condition. Once the endpoint condition is detected, the 702 signals the computer and transmits the final data string to the computer.

A dosing of cosurfactant is required to bring Tm back to the original (clear) condition. The software now commands the 665 Dosimat to dispense the defined quantity of cosurfac-

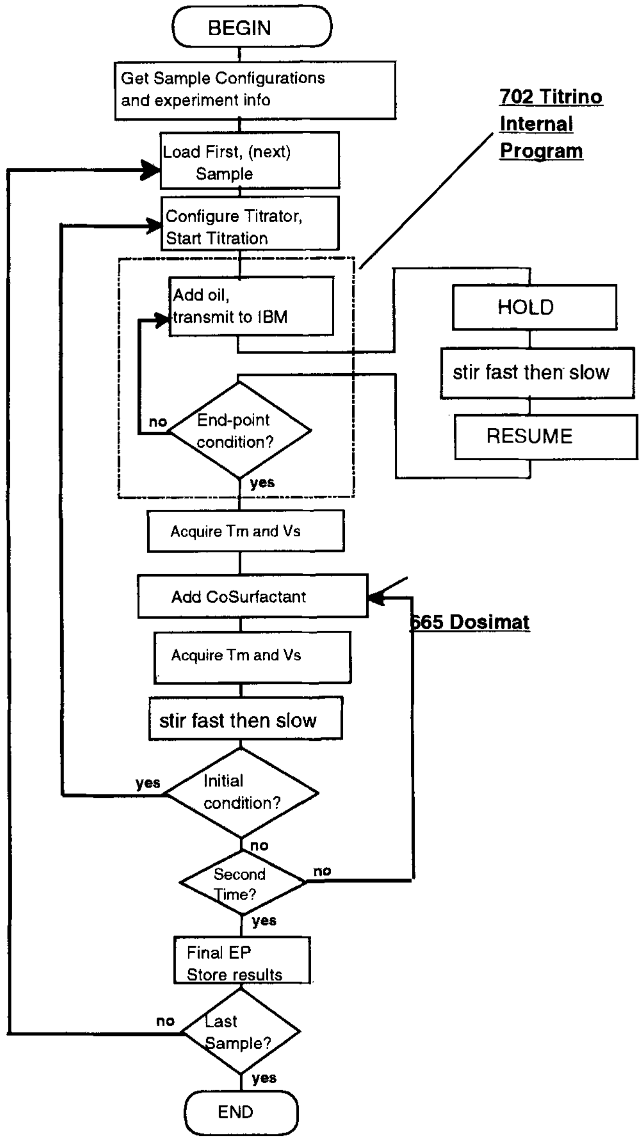

FIG. 3. Flow chart describing the autotitrating system algorithm. See Figure 2 for abbreviations and company source.

tant. After dosing, the mixer is set to "fast stir" for a defined time period to assist in solubilization. At completion of the interval, the slow stirring speed is re-engaged, and Tm and Vs are acquired (through the 702 Titrino). The dosing cycle is repeated, if necessary, to determine if Tm can be brought back to the original condition. If the addition of cosurfactant is successful in bringing Tm back to the original condition, the sample is titrated again; otherwise, dual titration for this sample is finished and the software performs the actions necessary to begin experimenting on the next sample.

Data and calculations. The data from the autotitrating instrument are accessible through output files written to the computer's hard disk. The file contains the values of Tm and Vs at each volume increment of titrant added as well as the original set-up parameters. Also created is a summary file, which lists only the endpoint values for each sample. The computer also calculates the weight percentages of each component and includes these values in each file. It is typical to calculate the amount of each component as a percentage of the total weight of water, surfactant, cosurfactant and oil. For analyzing oil uptake, we have found it useful to describe the amounts of the components as percentages of water, surfactant and cosurfactant only:

$$\%\ \text{component} = \frac{\text{weight component}}{\text{weight sum of water, surfactant and cosurfactant}} \times 100\% \qquad [1]$$

We will discuss the reasoning behind this calculation in the Results and Discussion section.

Materials. The water used was filtered and deionized. Sodium chloride (99.9% pure) was purchased from Baker, Inc. (Phillipsburg, NJ); A 0.15 M NaCl (aq) stock solution was prepared and used in all experiments. 1-Butanol was purchased from Baker, Inc. and was estimated to have a purity of 99.8%. Ethylene glycol monohexyl ether (C_6E_1) was obtained from Union Carbide Chemicals and Plastics Co., Inc. (Danbury, CT) under the trade name Hexyl Cellosolve and was estimated to have a purity of at least 97%. Sodium dodecyl sulfate (SDS) was obtained from Sigma Chemical Co., Inc. (St. Louis, MO) and was at least 99% pure. *n*-Dodecane was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI), and was estimated to be 99% pure. All viscosity standards were obtained from Brookfield Engineering Laboratories, Inc. (Stoughton, MA).

RESULTS AND DISCUSSION

To ascertain the accuracy of the autotitrating system, data taken by the instrument were compared with data from experiments performed by hand. A comparison of dodecane uptake measurements in the 0.15 M NaCl (aq)/SDS/1-butanol system, which has a relatively low degree of uptake, is shown in Figure 4. The experiments were done at an SLS/brine (wt/wt) ratio of 0.20. Figure 4 shows that the agreement between the data points acquired by hand and those acquired by the autotitrator is exceptionally good.

A comparison of dodecane uptake measurements taken by hand and by the autotitrator was also made using system of 0.15 M NaCl (aq), SDS and C_6E_1, which is able to solubilize a high amount of dodecane. Shown in Figure 5 is a comparison of data taken at an SLS/brine (wt/wt) ratio of 0.18. As in the butanol system, the agreement between the two data sets is exceptional. The accurate reproduction of manually derived data by the automatic system in both the butanol and C_6E_1 systems shows that the autotitrator can accurately measure oil uptake over wide ranges of magnitudes.

As previously mentioned, we have found it useful to describe oil uptake as a percentage of the aqueous component, surfactant and cosurfactant only (see Equation 1). This means that the water/surfactant/cosurfactant/oil phase space is a prism, as shown in Figure 6. Figure 6 displays a dual titration

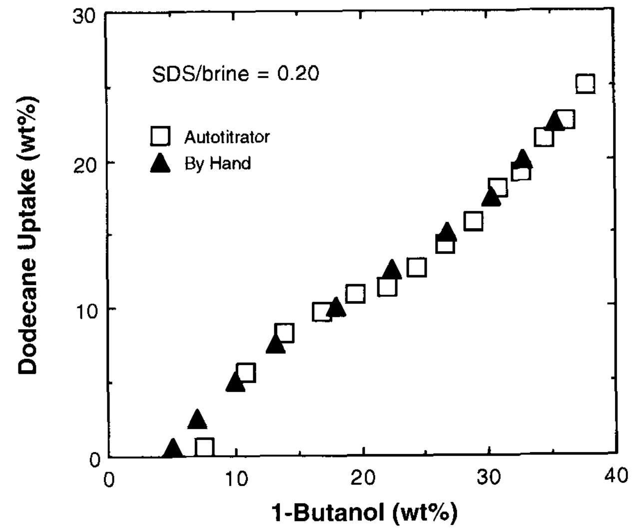

FIG. 4. Comparison of dodecane uptake in the brine/SDS/1-butanol system as measured by hand and by the autotitrating system. SDS, sodium dodecyl sulfate.

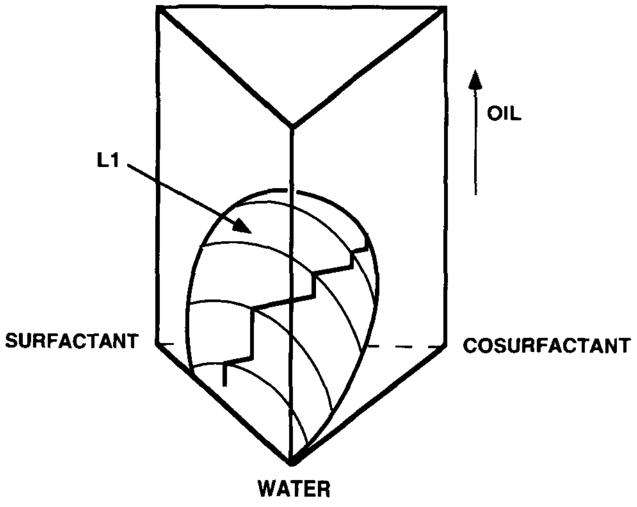

FIG. 6. Representation of the water/surfactant/cosurfactant/oil phase space as a prism, where each component is shown as a percentage of water, surfactant and cosurfactant only. The dual titration path is also shown. See Figure 1 for abbreviation. [Reprinted with permission from Ref. 8, p. 729, by courtesy of Marcel Dekker Inc., New York].

experiment as would be implemented by the autotitrator. The vertical lines in Figure 6 represent titrations with oil and those oriented toward the cosurfactant corner represent dosing increments of cosurfactant. When many of these titration-dosing cycles are performed, the shape of the upper surface of the L1 volume can be determined and represented in the form of a contour map plotted on the water/surfactant/cosurfactant basal plane.

An example of such a contour plot is shown in Figure 7 for a system composed of 0.15 M NaCl (aq), SDS and 1-butanol, with *n*-dodecane as the oil. Figure 7 represents a partial phase diagram, with the top corner and the lower right corner representing 50% SDS and 50% 1-butanol, respectively. The line k_x represents an example path that the autotitrator would take across the contour diagram. If a number of these paths are done, then the contours can be constructed by connecting the points of equal oil uptake.

The autotitrator has limited ability to detect the changes in the viscosity of a sample based on the voltage requirement of the stirring motor when exerting varying degrees of torque. Figure 8 relates the voltage to viscosity from 1 to 10,000 cP. All calibrations were performed with viscosity standards that display Newtonian behavior. The empirical expression,

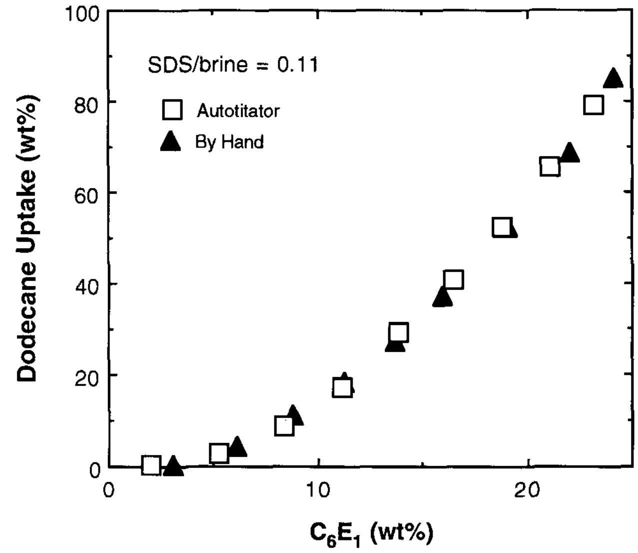

FIG. 5. Comparison of dodecane uptake in the brine/SDS/C6E system as measured by hand and by the autotitrating system.

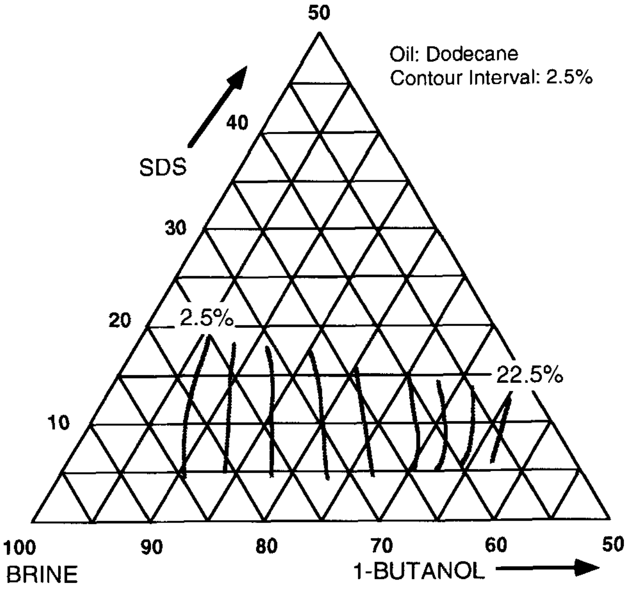

FIG. 7. Contour plot of dodecane uptake in the brine/SDS/1-butanol system. See Figure 4 for abbreviation. [Reprinted with permission from Ref. 8, p. 731, by courtesy of Marcel Dekker Inc., New York].

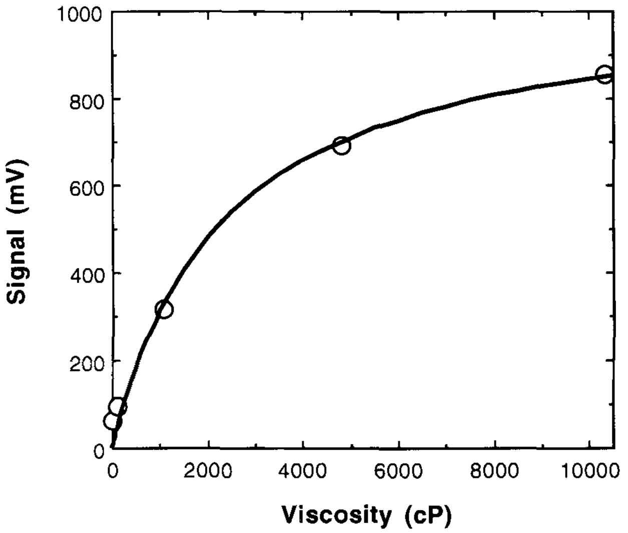

FIG. 8. Calibration curve between stirring motor voltage and sample viscosity.

$$V = \frac{A\eta}{\eta + B} \qquad [2]$$

where the voltage V is in mV, the viscosity η is in cP, $A = 1.045 \times 10^3$ (mV) and $B = 2.363 \times 10^3$ (cP), relates the voltage and viscosity quite adequately, and the corresponding plot of this function is shown in Figure 8. The instrument is not sensitive to small changes (on the order of 10 cP) in viscosity, but is able to adequately detect changes that would accompany a transition from an L1 or L2 isotropic phase to a liquid crystal phase because the viscosity would increase by many hundredfold (10).

We finally note that we have only cited the example where we titrate a water/surfactant/alcohol mixture with oil. The autotitrator can titrate with other components, such as water, to find the boundary of an L2 region. Similarly, a liquid surfactant or surfactant solution could be employed as the titrant. We are investigating these options and will continue to update the system.

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