Correlation Between Spray Cleaning Detergency and Dynamic Surface Tension of Nonionic Surfactants[1]

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ABSTRACT: The role of temperature and dynamic surface tension (DST) in spray-cleaning processes in industrial applications was investigated with nonionic surfactants. Relative performance data for various ethoxylates (derived from primary alcohols or nonylphenol) were obtained by a spray-cleaning method. The spray-cleaning method was developed to screen and identify optimum surfactants, formulations, and conditions for spray-cleaning applications. It is introduced here as a means to mimic spray-cleaning processes by (timed) spraying of a cleaner solution under pressure onto a soiled substrate. Results of this investigation indicated that temperature and DST play major roles in the soil-removal process. Observed temperature trends are typical of nonionic surfactants' clouding phenomena. Optimum cleaning was observed at specific temperatures. Also, nonionics with shorter hydrophobes exhibited the best detergency. Spray-cleaning detergency was compared to the DST because spray cleaning involves a dynamic interfacial process. New interfaces are constantly being created. Results showed that the surfactants with the lowest DST exhibited the best soil removal. This correlation can allow for a fast, cost-effective means for screening potential candidates and reducing development time for industrial spray-cleaning applications.
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KEY WORDS: Brushless cleaning, detergency, hard-surface cleaning, nonionic, spray cleaning, surface tension, surfactant.

Spray cleaning involves the removal of soil from a substrate, e.g., metal, under dynamic conditions. Many industries utilize such procedures to prepare surfaces prior to further treatment (1,2). There is no standard published method for evaluating spray-cleaning performance, however. Thus the first objective of this work was to develop a test method to screen and identify optimum surfactants, formulations, and conditions for spray-cleaning applications. The method involves the use of a spray cabinet and provides a way to mimic spray-cleaning processes by timed spraying of a cleaning solution under pressure onto a soiled substrate (e.g., metal, ceramic, plastic, or glass, soiled with grease, oil, fat, and so forth). Differences in soil removal are determined gravimetrically and allow for discrimination between a wide range of surfactants. The method was used to investigate the cleaning efficacy of various nonionic surfactants at various temperatures to identify optimum conditions for soil removal under a given set of conditions. The effect of temperature was studied because it facilitates the removal of soils with high melting points (1–4) during spray cleaning and plays a major role in soil removal by nonionics.

Spray cleaning involves a dynamic interfacial process. New interfaces are constantly being created. The rate at which the surface tension is reduced on these surfaces will play a role in the cleaning process. Those surfactants (or detergents) that exhibit the quickest surface tension reduction should show the best cleaning efficiency (5). Thus we proceeded to measure dynamic surface tension (DST) with the objective of verifying if those surfactants that show the fastest surface-tension reduction show the best soil removal. The maximum bubble pressure tensiometer was used to obtain DST because it correlates surface-tension reduction with time (6–8). DST results were then compared to the spray-cleaning results to identify any correlation. Results of this investigation indicated that the DST plays a major role in the soil-removal process during spray cleaning. Optimum cleaning was observed to correlate directly with DST.

EXPERIMENTAL PROCEDURES

All surfactants used, alcohol ethoxylates (AE; Shell Chemical Co., Houston, TX) and nonylphenol ethoxylates (NPE, Olin Chemical, Stamford, CT; or Rhone Poulenc, Cranberry, NJ) were of commercial grade and used as received. Their physical properties are listed in Table 1. Deionized (DI) water was used throughout this work. Spray-cleaning tests were conducted in a spray cabinet designed and built in our laboratory. A diagram of the spray cabinet is shown in Figure 1. Steel metal panels (smooth finish, type QD, 0.02 in.; The Q-Panel Co., Cleveland, OH) were coated with a soil composed of vegetable oil (Crisco, 8 g), mineral oil (8 g), hydraulic oil (8 g), metallic brown oxides (40 g), jet turbine fuel (Jet A kerosene, 24 g), and aliphatic hydrocarbon solvent (mineral spirits, 24 g). The soil is similar to that described in section A3 of American Society for Testing and Materials

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TABLE 1
Physical Properties of Nonionics Used

Nonionic[a]	EO/ROH[b]	HLB[c]	Cloud Point[d], °C (°F)
Alcohol ethoxylate			
$C_{9-11}E_{2.5}$	2.7	8.5	Water-insoluble
$C_{9-11}E_4$[e]	4.2	10.5	Water-insoluble
$C_{9-11}E_6$	6.1	12.5	52 (125)
$C_{9-11}E_8$	8.2	13.9	80 (176)
$C_{9-11}E_{9.5}$	9.5	14.6	>80 (>175)
$C_{11}E_5$	5.0	11.2	20 (68)
$C_{11}E_7$	7.0	12.9	61 (142)
$C_{11}E_9$	9.0	13.9	85 (185)
$C_{12-13}E_5$	5.0	10.7	Water-insoluble
$C_{12-13}E_{6.5}$	6.7	12.1	45 (113)
$C_{12-13}E_{7.6}$	7.6	12.6	64 (147)
$C_{12-13}E_{12}$	11.9	14.6	>80 (>176)
$C_{12-15}E_3$	3.0	7.8	Water-insoluble
$C_{12-15}E_7$	7.3	12.3	50 (122)
$C_{12-15}E_9$	8.9	13.1	73 (163)
$C_{12-15}E_{12}$	11.9	14.4	>80 (>176)
$C_{14-15}E_7$	7.1	11.8	44.5 (112)
$C_{14-15}E_{7.6}$	7.9	12.3	55 (131)
Nonylphenol ethoxylate			
NPE-5	5.0	10.0	Water-insoluble
NPE-6	6.0	10.9	<25 (<80)
NPE-9	9.0	13.0	54 (129)

[a]NPE = Nonylphenol ethoxylate, E = average ethylene oxide units content (see footnote *b*).
[b]Average groups of ethylene oxide/alcohol, mole/mole.
[c]HLB = Hydrophile–lipophile balance.
[d]1.0% wt aqueous solution.
[e]$C_{9-11}E_4$ is a 50:50 blend of $C_{9-11}E_{2.5}/C_{9-11}E_6$.

(ASTM) D4488 standard method for hard-surface cleaners (9), but with a higher ratio of oil to pigment. The soil was prepared as described (9).

Before soiling, residual oil on the panel surface is removed by first heating the panel to approximately 65°C and then wiping it clean. The panels are allowed to cool and then weighed on an analytical balance to the nearest milligram before soiling. After the soil is prepared, 0.5 mL is applied to the center of the panel with an automated pipette. The soil is dispersed with a roller, leaving the top portion of the panel unsoiled for attachment in the cabinet. The soiled panels are aged by placing them in a convection oven at 100°C for 4 h. After the panels have been baked, they are allowed to cool and are reweighed. The amount of soil applied is recorded, which is typically about 0.24 ± 0.03 gr.

Spray cleaning was conducted in duplicates (per run) at a spray pressure of 20 psi from full-cone nozzles (Lechler, Inc., St. Charles, IL) with a spray time of 90 s and a panel rotation rate of about 14 rpm. The cleaning solution consisted of 0.25% (wt) surfactant and 0.12% (wt) tetrapotassium pyrophosphate (TKPP) in DI water. Soil removal was evaluated at 26.7, 37.8, 48.9, and 60°C (80, 100, 120, and 140°F, respectively). A 0.12% (wt) TKPP in water-only solution was used as a control. Results are reported as relative soil removal, as obtained by substracting the soil removal by the

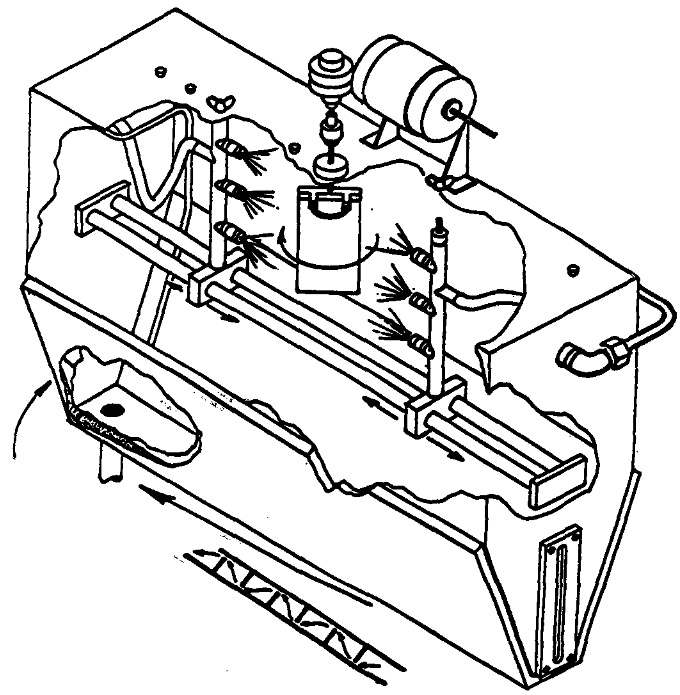

FIG. 1. Diagram of the spray-cleaning cabinet, designed and built at Shell Development Co. (Houston, TX).

control from that of the test solution. This procedure allows for exclusion of any effects by the water and builder on soil removal and provides measurement for soil removal based solely on the cleaning efficacy of the surfactant. After cleaning, the panels were rinsed with DI water and dried in an oven at 40°C for 30 min. The panels were allowed to cool and were weighed, and the amount of soil removed was recorded. Three duplicates (six replicates) were evaluated and averaged. Soil removal can also be determined by other means, such as reflectance, water break, and so forth (1,2).

DST values were measured with a SensaDyne 6000 tensiometer (Chem-Dyne Research Corp., Milwaukee, WI) on 1.0% (wt) surfactant solutions at 26.7, 37.8, 48.9, and 60°C (80, 100, 120, and 140°F, respectively). Nitrogen gas was used to produce bubbles at rates of 1–10 bubbles/s. DI water and ethanol were used as the calibration standards.

RESULTS AND DISCUSSION

The role of temperature in the spray-cleaning process in industrial applications was investigated with AE and NPE. Relative soil removal was obtained at various temperatures. Results are shown in Table 2 and Figures 2 and 3. Statistical analysis for all results indicated a least significant difference at 95% confidence level (LSD_{95}) of 0.01 g. Based on the results, soil-removal trends for the ethoxylate series can be observed. For example, Figure 2 compares temperature vs. soil removal for the C_{9-11} AE series studied here. In general, results show that the higher the ethylene oxide (EO) content, the higher the temperature at which the nonionic exhibits optimum cleaning. Soil removal decreased at temperatures above the optimum. This result is typical of nonionic surfac-

TABLE 2
Relative Spray-Cleaning Performance (soil removal) Results[a]

Nonionic[b]	Temperature 26.7°C	37.8°C	48.9°C	60.0°C
AE $C_{11}E_5$	0.123	0.164	0.192	0.207
AE $C_{11}E_7$	0.135	0.154	0.204	0.201
AE $C_{11}E_9$	0.103	0.161	0.188	0.204
AE $C_{12-13}E_5$	0.089	0.133	0.149	0.132
AE $C_{12-13}E_{6.5}$	0.126	0.150	0.171	0.167
AE $C_{12-13}E_{7.6}$	0.116	0.141	0.160	0.203
AE $C_{12-13}E_{12}$	0.091	0.139	0.182	0.175
AE $C_{14-15}E_7$	0.010	0.019	0.050	0.079
AE $C_{14-15}E_{7.6}$	0.020	0.053	0.096	0.024
NPE-5	0.043	0.077	0.078	0.095
NPE-6	0.053	0.107	0.098	0.135
NPE-9	0.103	0.132	0.138	0.135

[a]LSD_{95} = 0.01 g (LSD_{95} = least significant difference at 95% confidence level). Results were corrected by substracting the soil removal by water/tetrapotassium pyrophosphate only (see Experimental Procedures section), based on the average grams of soil removed of six replicates. Data for AE C_{9-11} and AE C_{12-15} series are shown in Figures 2 and 3.
[b]AE = Alcohol ethoxylate, NPE = nonylphenol ethoxylate, E = average ethylene oxide units content (average groups of ethylene oxide/alcohol, mole/mole.

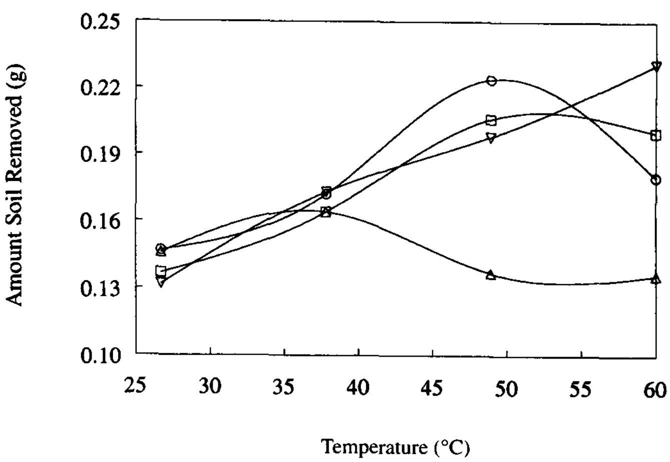

FIG. 2. Effect of temperature on spray-cleaning detergency of alcohol ethoxylate (AE) C_{9-11} series [△, 4 ethylene oxide (EO); ○, 6 EO; □, 8 EO; ▽, 9.5 EO].

tants' clouding phenomena and had been observed in other detergency studies (10–13). Figure 3 shows a similar trend for the C_{12-15} AE series (excluding $C_{12-15}E_3$, which did not exhibit any soil removal).

Detergency of some nonionics in this study (i.e., AE $C_{14-15}E_7$, AE $C_{11}E_5$, NPE-5, and NPE-6) seems to increase with temperature consistently without exhibiting an optimum. Based on previous knowledge in relating soil removal to clouding phenomena, one would expect to see an optimum for these nonionics at or slightly above their cloud points (10–13). This corresponds to an optimum below 50°C. This behavior does not correlate with the trend observed above and is not fully understood at this time. Other forces, such as wetting and DST, may play a stronger role here.

Shorter hydrophobes are preferred for optimum detergency, given a similar hydrophile–lipophile balance (HLB) or EO content. This trend is shown in Figures 4 and 5, and is

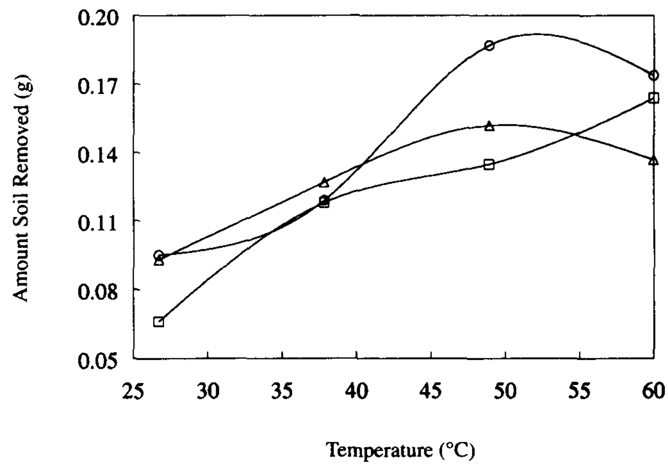

FIG. 3. Effect of temperature on spray-cleaning detergency of AE C_{12-15} series (△, 7 EO; ○, 9 EO; □, 12 EO). See Figure 2 for abbreviations.

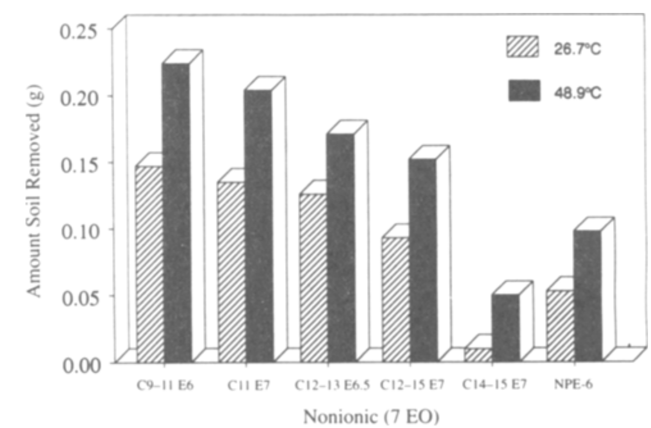

FIG. 4. Effect of hydrophobe length on spray-cleaning detergency of nonionics containing approximately 7 EO. See Figure 2 for abbreviation.

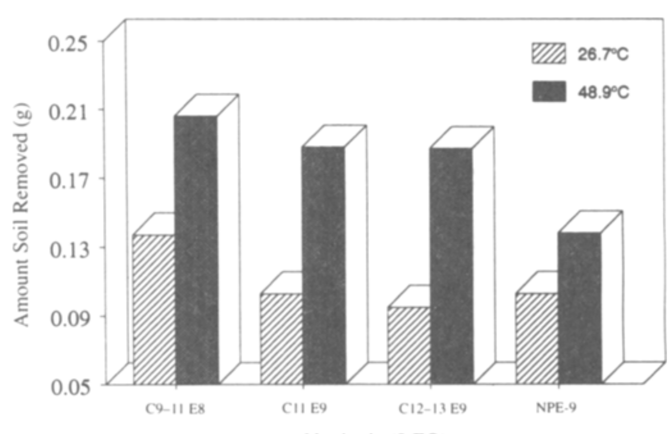

FIG. 5. Effect of hydrophobe length on spray-cleaning detergency of nonionics containing approximately 9 EO. See Figure 2 for abbreviation.

TABLE 3
Dynamic Surface Tension of Nonionic Surfactants (1.0% wt)

Nonionic[a]	Surface tension (dynes/cm) at varied temperatures and bubble rates (bubbles/s)															
	26.7°C				37.8°C				48.9°C				60.0°C			
	1	3	5	10	1	3	5	10	1	3	5	10	1	3	5	10
AE $C_{9-11}E_6$	28.1	29.7	31.3	29.2	26.7	27.8	29.2	27.2	26.9	27.6	28.9	26.8	26.5	26.7	28.2	28.0
AE $C_{9-11}E_8$	32.8	33.9	34.8	36.1	31.2	31.9	32.6	27.7	29.6	30.3	30.3	27.6	28.5	28.5	29.1	25.9
AE $C_{9-11}E_{9.5}$	35.4	36.6	39.6	38.0	33.4	34.0	35.1	37.2	31.3	32.1	32.9	32.8	29.3	30.0	30.7	26.6
AE $C_{11}E_5$	26.2	27.9	29.9	37.3	25.7	27.2	28.3	37.5	26.7	29.1	35.2	42.2	26.4	29.1	31.9	38.2
AE $C_{11}E_7$	29.6	31.0	29.9	35.1	28.4	29.5	30.5	27.4	27.8	28.1	28.9	26.9	26.5	26.9	27.3	25.2
AE $C_{11}E_9$	31.4	33.1	32.5	36.7	29.6	30.8	31.8	28.3	28.3	28.8	29.5	27.0	26.5	27.2	27.4	24.8
AE $C_{12-13}E_5$	37.5	49.0	57.4	58.8	34.2	47.7	55.8	59.5	31.8	41.1	51.2	51.7	27.4	34.7	41.0	45.6
AE $C_{12-13}E_{6.5}$	30.5	35.0	38.9	46.2	28.8	31.8	35.8	45.4	28.4	32.7	37.7	43.6	30.5	39.9	48.4	47.5
AE $C_{12-13}E_{7.6}$	31.4	34.7	37.6	43.0	29.6	31.7	34.2	42.6	28.1	29.5	31.0	35.8	27.1	28.4	29.6	35.5
AE $C_{12-13}E_{12}$	37.4	40.3	44.1	42.5	35.1	37.2	38.8	43.5	33.0	34.3	35.5	40.7	30.7	31.6	32.3	30.6
AE $C_{12-15}E_3$	51.9	66.4	69.8	71.4	41.7	57.6	63.3	60.5	43.2	56.8	63.7	61.5	31.5	45.3	53.8	52.2
AE $C_{12-15}E_7$	33.3	40.1	46.8	47.5	30.3	37.4	43.6	47.0	30.3	35.3	43.0	45.4	28.0	31.2	35.6	40.7
AE $C_{12-15}E_9$	35.6	41.0	46.4	45.5	32.7	36.7	41.3	44.8	29.8	32.7	35.4	42.4	28.1	30.1	32.2	31.7
AE $C_{12-15}E_{12}$	39.2	43.5	48.3	52.6	36.4	39.5	43.8	45.2	33.5	35.6	37.3	40.7	31.1	32.7	34.5	36.7
AE $C_{14-15}E_7$	41.3	52.2	58.5	62.4	39.6	49.6	57.8	55.7	35.5	47.6	53.8	48.9	31.5	43.9	49.6	50.3
AE $C_{14-15}E_{7.6}$	38.6	49.3	55.5	50.7	37.1	47.6	54.5	55.7	34.3	46.6	54.2	49.3	35.7	49.0	52.5	47.6
NPE-9	31.9	37.6	40.1	43.8	—	—	—	—	—	—	—	—	—	—	—	—

[a]Abbreviations as in Table 2.

similar to that observed for hard-surface cleaning applications that involve abrasion (14,15). The shorter hydrophobe chain also gives the nonionic some solvent-like properties that help increase soil removal. In addition, nonionics with shorter or branched hydrophobes are more effective surface-active agents (5). They reduce surface tension and wetting times faster than nonionics with longer hydrophobes. This is preferred for the dynamic conditions found in spray cleaning.

Within the spray-cleaning environment, we have dynamic forces that must act quickly to invade the soil surface. Once the surfactant has penetrated the initial soil layer, greater soil removal will occur. By identifying a nonionic that shows fast-surface tension reduction, and by comparing it to the results obtained from the spray cleaning, we can perhaps correlate these properties and identify a faster way to screen the spray-cleaning detergency of surfactants. We proceeded to measure DST to identify if those surfactants that show the fastest surface-tension reduction show also the best soil removal.

DST results are shown in Table 3. Expected trends are observed in the data. Optimum cleaning was observed at specific temperatures and correlated directly with DST. Surfactants with the lowest DST exhibit the best soil removal. Two examples are shown in Figures 6 and 7 for the AE C_{9-11} and AE C_{12-15} series, respectively. Similar trends are observed for

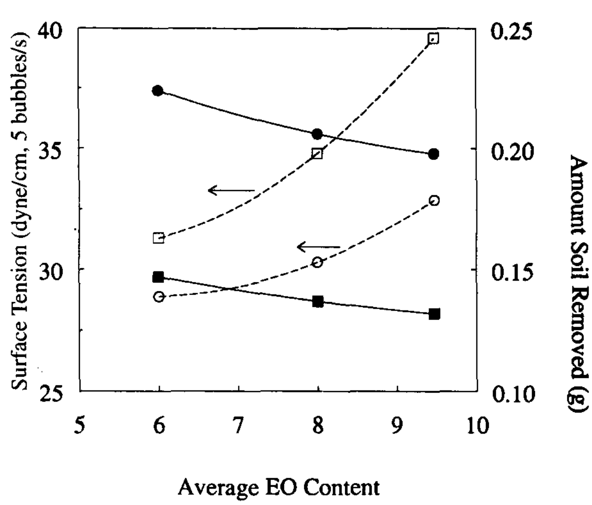

FIG. 6. Comparison of dynamic surface tension with spray-cleaning detergency results for AE C_{9-11} series (□ and ■, 26.7°C; ● and ○, 48.9°C). See Figure 2 for abbreviation.

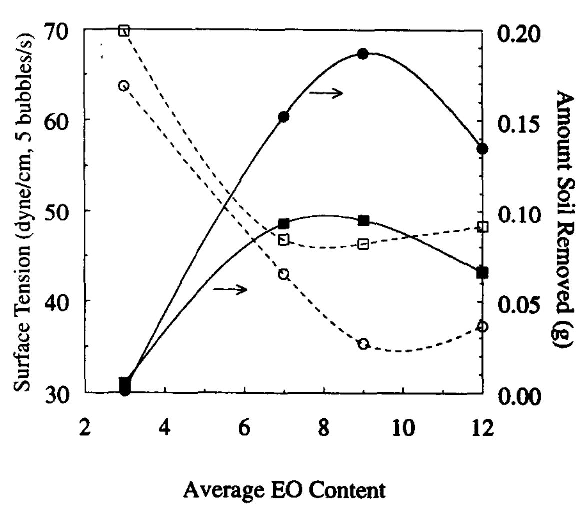

FIG. 7. Comparison of dynamic surface tension with spray-cleaning detergency results for AE C_{12-15} series (□ and ■, 26.7°C; ● and ○, 48.9°C). See Figure 2 for abbreviation.

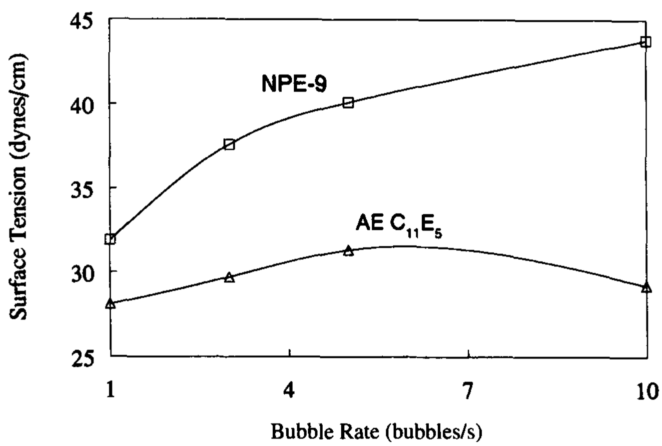

FIG. 8. Dynamic surface tension comparison for nonylphenol ethoxylate (NPE)-9 (□) and AE $C_{11}E_5$ (△) at 25°C. See Figure 2 for other abbreviation.

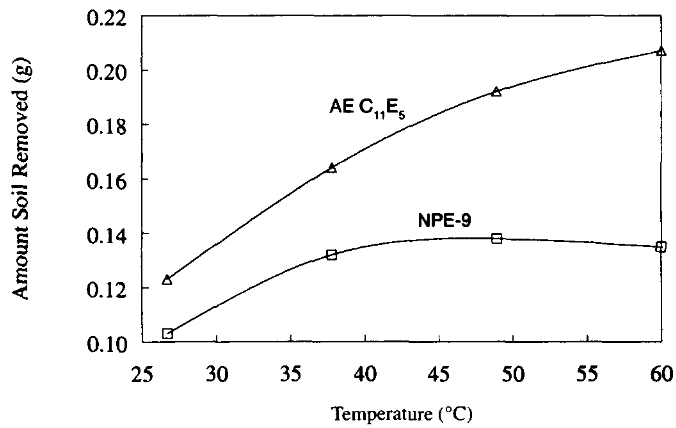

FIG. 9. Spray-cleaning detergency comparison for NPE-9 (□) and AE $C_{11}E_5$ (△) as a function of temperature. See Figures 2 and 8 for abbreviations.

the various series at the different temperatures studied. Surfactants with different structures can also be compared by this approach. For example, if one was to select between two structurally different nonionics, such as NPE-9 and AE $C_{11}E_5$, one can predict the better performer by measuring the DST (compare Figures 8 and 9). Thus this correlation provides a fast, cost-effective means for screening potential candidates and reducing development time for industrial spray-cleaning applications.

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