

EFFICIENCY OF WETTING AGENTS*

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INTRODUCTION

TEXTILE materials like raw cotton and wool, which are not uniformly and quickly wetted under normal circumstances, can be thoroughly wetted by the action of wetting agents which thus play a prominent part in processes like dyeing, finishing and kier-boiling in the textile industry. Hundreds of wetting agents are now on the market and several new wetting agents are being discovered day to day. The evaluation of a wetting agent has therefore become a matter of considerable practical importance.

Several methods¹ are available for the determination of efficiency of wetting agents in industrial practice. These methods however are semi-quantitative in character and only serve as a rough guide in textile practice. Theoretically, the determination of spreading coefficient of the wetting agent solution on the grey yarn should give a precise idea of the wetting power. But the measurement of this quantity is beset with many difficulties since the system involves solids. Complications due to roughness of the surface⁶ and irreproducible kinetic effects and friction effects at the meniscus, render difficult to get at an accurate determination of the contact angles in such systems. For the evaluation of wetting agents, Cupples⁵ worked out a method based on the fundamental similarity between the mineral oil surface and the hydrophobic portion of the inner surface of the grey yarn. His experimental procedure however is not satisfactory since he has measured surface tension by the ring method without taking necessary precautions.⁷ Rao and Doss⁸ have adopted the free lens technique of Langmuir for the purpose. The latter method is very cumbersome. Rao and Doss have however shown that the surface tension lowering runs parallel to the wetting power. In the present work this fact has been taken advantage of for comparing the efficiencies of some of the common wetting agents (pure and commercial) and for studying the effect of salts on the wetting efficiency. The surface

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tension lowering of five-minute-old surfaces has been determined by the ring method taking adequate precautions. A few measurements have also been made by the maximum bubble pressure method with a view to investigate the suitability of the method for the evaluation of wetting agents.

EXPERIMENTAL

The ring method.—The work was mainly on Nekal BX. Its purification has been described previously⁸. The other wetting agents used were commercial products and were used without purification.

For determining surface tension the ring method was employed. Temperature control was not aimed at, for, very precise measurements were not necessary since the aim of the work was only to classify the order of efficiency of the wetting agents. The solution under investigation was kept in a platinum dish. One advantage in using the dish was that the surface-active impurities in it could be completely removed by heating the dish to red heat before each experiment. In all the measurements the maximum pull for the five-minute-old surface was taken since it was not very convenient to measure the maximum pull more quickly. In every case the average of at least three values was taken as the representative value.

The maximum bubble pressure technique.—The technique introduced by Jæger was modified and used in this laboratory¹⁽²⁾ for the study of variation of surface tension of wetting agent solutions with time. This modified form of apparatus was employed in the present work. Air was pumped to the dropping tip through a constant head blow off, a drying tower, a buffer bottle and a capillary. The air was dried to prevent the condensation of the water vapour in the capillary tube and consequent blocking of the passage. The buffer bottle was used to check the pulsations in air. The dropping tip drawn out of a soft glass tube was washed with chromic acid mixture and distilled water. It was vertically fixed to the stand and could be moved up and down by means of a screw arrangement. The verticality was tested by viewing the tip and its reflection at a mercury surface. The tips used required a pressure of about 15 and 13 cm. of xylene to force a bubble through water. The solution whose surface tension was to be measured was allowed to attain a temperature of $30^{\circ} \pm 0.1^{\circ} \text{C.}$, immersing the bottle containing the solution, in a water thermostat up to its neck and allowing it to remain there at least half an hour before the reading was taken. The bottle was then taken, opened and brought underneath the tip. The tip was then lowered slowly so that it just touched the surface of the liquid. A small length of the tip was then made to immerse under the solution by placing the container on a glass plate of known and uniform thickness. The pressure was adjusted

at the constant head blow off so that every bubble came out at an interval of five seconds. The maximum pressure was read out on the xylene manometer, employing a reading lens. The pressure, corrected for the height of the tip below the liquid, was proportional to the surface tension of the solution. Since the correction factor was practically equal to unity for a capillary of the size employed.³ The correction to be applied for the pressure, shown by xylene manometer, for temperature fluctuations, was negligible and was always less than 0.1 per cent. The apparatus was standardised by taking measurements both for water and toluene. The results are noted in Table I, the surface tension of water being calculated on the basis of the standard value of the surface tension of toluene.

TABLE I

Liquid	Corrected maximum pressure	Calculated surface tension	Standard value of surface tension
Water ..	15.03 cm.	71.11 dynes/cm.	71.18 dynes/cm.
Toluene ..	5.77 cm.	..	27.30 dynes/cm.

Preparation of the solutions.—The stock solution was prepared by adding a calculated weight of the substance, and was stored in well cleaned jena bottles. Less concentrated solutions were obtained by progressive dilution on volume basis. The surface tension was measured soon after the solution was prepared. The solutions of commercial wetting agents were all prepared in 0.01 N acetate buffer of pH 3.7, so as to avoid the influence of varying pH on wetting efficiency. Measurements were made with purified Nokal BX solutions with and without salts. The results obtained by the ring method are given in Tables II and III. The results obtained by the maximum bubble pressure method are given in Tables IV and V.

TABLE II

Surface tension of wetting agent solutions by the ring method

Age of the surface = 5'; pH 3.7; Temperature 23 ± 2° C.

Percentage of wetting agent	Nokal BX	Cardinol C. A.	Ultrawon WX.	Diazopon A	Igepon T	Surfax	Silvatol I	Turkey red oil	Triethanol amine
0.4	30.8	30.9	31.8	41.1	30.8	29.7	40.7	38.1	71.6
0.2	34.9	31.3	32.0	41.6	31.3	29.7	40.5	39.7	..
0.1	39.9	32.3	32.3	41.9	32.0	29.3	40.7	41.0	..
0.05	45.1	33.4	33.4	42.7	33.2	30.3	42.0	42.3	..
0.025	50.3	35.9	35.9	43.3	34.8	35.6	50.1	43.5	..
0.01	39.1	45.5	..	45.3	..
0.005	45.0	47.2	..

TABLE III

Surface tension of purified Nekal BX solutions in water, acid and salt solutions Ring method

Age of surface = 5'. Temperature = 23° C. ± 2° C.

Percentage of Nekal BX	In Water	In 0.01 N HCl	In 0.01 N NaCl	In 0.1 N NaCl	In 0.01 N BaCl ₂	In 0.01 N BaCl ₂ + 1.25% Calgon	In 1.25% Calgon	Commercial Nekal BX solution in water
0.8	31.9	30.7
0.4	32.4	30.5	31.4	29.4	..	29.7	29.9	31.2
0.2	37.2	32.4	34.1	29.3	..	29.6	29.7	36.9
0.1	42.4	36.1	38.5	29.9	..	30.6	31.2	42.9
0.05	48.5	40.4	43.3	33.6	..	34.5	35.1	49.1
0.025	52.5	44.7	48.3	37.9	32.9	38.6	39.5	..
0.01	61.3	49.9	54.3	43.9	38.8	44.6	45.5	..
0.005	66.0	54.4	58.6	48.4	43.7	49.0	49.7	..
0.0025	69.8	59.2	63.3	53.1	47.5	54.1	54.4	..
0.001	..	68.0	69.5	62.4	50.2	63.3	62.8	..
0.0005	70.0	..	69.7	69.7	..

TABLE IV

Surface tension of five-seconds'-old surface of Nekal BX solutions in 0.01 N hydrochloric acid by maximum bubble pressure method at 30° C.

Percentage concentration of Nekal BX	Surface tension in dynes per cm.	
	Tip ₁	Tip ₂
0.8000	31.4	31.6
0.4000	31.7	33.0
0.2000	33.6	37.9
0.1000	38.9	45.5
0.0500	45.7	54.1
0.0250	54.7	63.6
0.0100	64.2	68.0
0.0050	68.6	69.7
0.0025	69.9	70.1
0.0010	70.7	70.7

TABLE V

Surface tension of five-seconds'-old surface of commercial wetting agents of 1.0 per cent. solutions in water by maximum bubble pressure method at 30° C.

Name of the wetting agent	Surface tension in dynes per cm.	
	Tip ₁	Tip ₂
Surfax ..	29.80	30.1
Nekal BX ..	31.30	31.0
Gardinol C.A. ..	36.30	36.0
Igepon T ..	36.30	38.8
Turkey red oil ..	38.30	39.4
Silvatol I ..	40.00	39.8
Diazopon A ..	42.80	43.8
Ultrawon WX ..	47.60	49.8
Triethanolamine ..	71.30	71.1

DISCUSSION

1. *Relative efficiencies of some of the common wetting agents.*—A study of the variation of wetting efficiency of commercial Nekal BX solution with concentration by the apparent density method¹⁽⁴⁾ has revealed that solutions

having concentrations higher than 0.2 per cent. have a high wetting power, while the wetting efficiency falls off quickly at lower concentrations. 0.2 per cent. solution of commercial Nekal BX in water was found to have a surface tension of about 36.9 dynes per cm. (*vide* Table III). It may therefore be assumed that the surface tension of any good wetting solution should be of the order of 37 dynes per cm. or less. Judged from this standard Diazopon A and Silvatol I are not sufficiently good wetting agents even at a concentration of 0.4 per cent. It may be pointed out in this connection that the former product is used mainly as an emulsifier and the latter is used as a detergent; thus, good detergent and emulsifying properties are not necessarily associated with good wetting action. Turkey red oil also has a low wetting efficiency in acid medium. Triethanolamine has no wetting properties at all in acid medium. Gardinol C.A., Ultrawon WX, Igepon T and Surfax are found to be very good wetting agents and indeed they are much better than Nekal BX. Igepon T is particularly good in that considerable wetting property persists even at low concentrations. These conclusions refer to media having a pH of 3.7.

2. *Effect of salts.*—The influence of salts on the five-minute values of surface tension is interesting. An examination of Table III shows that barium chloride is much more effective than sodium chloride in reducing the surface tension. This may be due to the Ba^{++} ions attaching themselves to the mono-layer reducing the electrical charge and consequently lowering the electrical potential barrier. Hydrochloric acid itself is more effective than sodium chloride. This can be correlated with the higher absorbability of hydrogen ions.² It is of interest to note that by the addition of sodium hexametaphosphate to the Nekal BX solution containing barium chloride, the influence of latter is largely annulled. This is evidently due to the removal of Ba^{++} ions by the hexametaphosphate (Calgon) with the formation of soluble complex. Salts considerably increase the efficiency of wetting agents, though a salt by itself has no wetting power. In fact, the commercial sample (which contains sodium sulphate) has a higher efficiency than the pure sample itself at equivalent concentrations. As has been already pointed out, divalent cations are much more effective than univalent ions in increasing the wetting power. This fact is of special interest from the point of view of commercial practice. It is usual in the textile industry to soften the water before use. But our results show that a small degree of hardness is highly beneficial to the action of the wetting agent. A similar effect has been observed by Kalinor.³ It is important however not to have too high a concentration of the divalent cations since they may partially precipitate out the wetting agent and thereby reduce the wetting power.

3. *Maximum bubble pressure method.*—Though the maximum bubble pressure method has been used by Adam⁴ for studying the variation of surface tension with time, it has been shown by S. V. Venkatachala¹⁽⁴⁾ that the method cannot be adopted for such studies since reproducible values cannot be obtained. The irreproducibility is due to the fact that during the process of formation of the bubble large irregular changes in the area of the surface take place. Venkatachala however observed that if the age of the surface was less than 5 seconds the values were fairly reproducible. The results got in the present work (Tables IV and V) show that with different tips the values of surface tension may sometimes differ by over 8 dynes per cm. even when the age of the surface is 5 seconds. This shows that the maximum bubble pressure method cannot be used for the measurement of surface tension of systems which exhibit a variation with time. A rough idea of the order of wetting efficiency of different solutions can however be obtained by this method.

SUMMARY

The relative efficiencies of some of the common wetting agents have been determined by measuring the surface tension of five-minute-old surfaces of the solutions using the ring method in a modified form. Aqueous solutions giving a surface tension of 37 dynes per cm. may be considered to have good wetting properties. It is found that wetting power is not necessarily associated with detergent and emulsifying properties.

Salts greatly increase wetting power. Bivalent cations are more effective than univalent cations in increasing wetting power. A moderate degree of hardness in water employed in preparing solutions of wetting agents may be of advantage in the textile industry.

The maximum bubble pressure method is shown to be unsuitable for the measurement of surface tension of solutions which show a variation with time. A rough idea of the order of wetting efficiencies of wetting agents can however be obtained by measuring the surface tension of a five-second-old surface by this method.

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