Anionic Hydrotropes For Industrial and Institutional Rinse Aids

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The effectiveness of eight commercial hydrotropes having differing structures (sodium xylenesulfonate, sodium-2-ethyl hexysulfate, phosphate ester of oxyethylated phenol, amine alkylaryl sulfonate, linear alkyl naphthalene sulfonate, TEA salt of DDBS, sodium dihexyl sulfosuccinate, and sodium dodecylbenzene sulfonate) was evaluated with seven commercial rinse aid surfactants of the following structural types: block copolymers and alcohol oxyalkylates with high and low levels of ethylene oxide. Two hydrotrope levels (3 and 6 wt %) were evaluated at two surfactant levels (20 and 40 wt %). Dispersibility, compatibility index, and blender foam heights were measured; the test methods are described.

Nonionic surfactants impart two critical properties to rinse aids: the ability to wet tableware, which helps give spotless, easily dried dishes, and the ability to defoam, which allows higher rinse water velocities. Higher rinse water velocities result in better rinsing. Achieving a wetting and defoaming balance represents a challenge to the chemist, because increased wetting can result in increased foaming.

Defoaming is effected by surfactants coming out of solution above their cloud point. Previously, high water temperatures were normally used and this resulted in the surfactants being used above their cloud point. As energy costs increase and water temperatures fall, the surfactants have to be modified to reduce the cloud points. The cloud point reduction can be harmful to the stability of the formulated rinse aid, and separation of the active components can occur. For this reason hydrotropes or solubilizers (1-3) are added to improve the rinse aid stability.

Most hydrotrope information is buried in patent and product literature. Many hydrotrope patents deal with the ability to solubilize anionic surfactants. Matson and Berretz published a series of articles on non-built, heavy-duty laundry liquids, the first of which deals with the effects of ethanolamines, sodium xylene sulfonate, ethanol, and inorganic salts as hydrotropes (4,5). Friberg and Cox have described the hydrotropic action of 5-carboxy-4-hexyl-2-cyclohexene-1-yl octanoic acid (6). More recently, non-patent hydrotrope publications deal with the analytical separation of hydrotrope-surfactant blends (7,8). No reference giving concise information on hydrotropes for rinse aid formulations was found.

A need was identified, the need to determine and report the effect of hydrotropes on nonionics used in rinse aids. Seven nonionics manufactured and sold by BASF Corporation and eight commercial anionic hydrotropes were evaluated. Both block copolymers of ethylene oxide and propylene oxide, as well as alcohol oxyalkylates, were evaluated. Hydrotrope structures ranged from aromatic sulfonates to dialkylsulfosuccinates. These cover the ranges of nonionic surfactants and anionic hydrotropes found in commercial rinse aids.

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EXPERIMENTAL

Dispersibility testing. 100 ml distilled water were heated in a 150-ml beaker to 82 C. 1 ml of the rinse aid was drawn into a 1-ml pipet. With the pipet tip approximately seven in. above the water surface, the bulb was removed from the pipet and the rinse aid was allowed to drip into the water. The dispersibility was rated as follows:

1. Drops disperse as they enter the water, causing an even haze in the water.
2. Drops trail through the water, but dispersion occurs.
3. Drops partially disperse, causing some haze, but some remain as a discrete phase.
4. Some dispersion takes place, but only after the mixture is stirred.
5. Drops do not disperse with stirring.

Compatibility index. Into a 150-ml beaker approximately 100 ml of the rinse aid was poured. A thermometer was suspended in the solution so it was approximately 0.5 in. from the beaker front. The solution was heated slowly while being agitated with a magnetic stirring bar. The compatibility index is the temperature, reported in °C, at which the thermometer bulb was no longer seen.

Blender foam test. Into a 16-oz bottle were weighed 1.25 g detergent, 0.50 g standard soil, 0.10 g rinse aid and 500 ml distilled water. The bottle was capped; it and the blender container were placed into the oven until the solution came to the desired temperature. (Note: Heating the bottle above 82 C may result in an explosion.) The bottle and blender container were removed and immediately shaken well. The contents were poured carefully into the warm blender container, frapped for 30 seconds and allowed to stand 30 seconds. Foam height was measured.

Equipment and conditions for the test were: blender, Osterizer Galaxie or Pulse-matic 16; standard soil, 80 wt % Blue Bonnet margarine, 20 wt % Carnation non-fat dry milk; detergent, U.S. Chemicals Stalwart detergent, and temperatures, 49 C and 82 C. The nonionic surfactants evaluated and their relative ethylene oxide contents are:

Block Copolymer Surfactant	% EO
Pluronic® L-10 polyol	Decreasing ↓
Industrol® N-3 polyol	
Pluronic® L-62D polyol	
Pluronic® 25R2 polyol	
Alcohol Oxyalkylates	**% EO**
Plurafac® RA-20 surfactant	Decreasing ↓
Industrol® DW-5 surfactant	
Plurafac® RA-40 surfactant	

The hydrotropes are: Petro® ULF, linear alkylnaphthalene sulfonate (LANS); Conoco AAS-45S, sodium dodecylbenzene sulfonate (SDDBS); Calsoft T-60, triethanolamine salt of DDBS; Ninate® 411, amine alkylaryl sulfonate; Stepanate® X, sodium xylene sulfonate (SXS); phosphate, ester of oxyethylated phenolic; Witcolate® D510, sodium-2-ethylhexyl sulfate (SEHS); Monawet® MM80, sodium dihexyl sulfosuccinate (SDHS).

RESULTS AND DISCUSSION

A typical industrial rinse aid consists of four components. The nonionic surfactant provides the sheeting and defoaming action. The hydrotrope solubilizes surfactants that are insoluble in the formulated system; it can also facilitate dispersion of the rinse aid. Perfumes and dyes add to the aesthetics of the final product. Water reduces viscosity and overall cost. Table 1 shows typical concentration ranges of each component.

We chose economically acceptable hydrotrope levels (3 and 6 wt %) and water temperatures (49 C and 82 C) for the study. Rinse aid formulators identified three important properties to measure: dispersibility, or how quickly the rinse aid goes into solution; compatibility index, (CI) the temperature at which the formulated rinse aid becomes cloudy, and blender foam, an indication of whether the hydrotrope increases foaming.

Dispersibility is perceived by some formulators as an indication of how readily a rinse aid can be introduced into the rinse cycle. This is true from a qualitative sense. However, experience has shown that poor laboratory dispersibility does not preclude a rinse aid from being commercially successful.

The compatibility index is the temperature at which the rinse aid begins to turn cloudy; it is the onset of separation of the surfactant from the aqueous phases. In industrial establishments the container which dispenses the rinse aid is often exposed to high temperatures (49–54 C). If the temperatures are high enough to cause creaming or flocculation of the rinse aid, it is possible that erratic rinsing will occur as a result of variable rinse aid concentration. The CI gives the formulator an indication of those temperatures that may cause field problems.

Blender foam is used to determine rapidly whether a given formulation has the potential to increase foaming. At the 6% hydrotrope level, less than one ml of foam is considered passing. If increased foaming is observed at this level, it may be possible to reduce foaming by a further reduction in hydrotrope. Because this is a screening test, it is recommended that large scale laboratory testing on a commercial or semi-commercial machine be used to corroborate the blender tests. Furthermore, the corroboration of the blender tests in laboratory machines will not guarantee success of a formulation under all field conditions.

Surfactants alone. It is beneficial to look at how rinse aids perform without hydrotropes.

In general, dispersiblity is poor, CI's are low to marginal (≤ 56 C), defoaming characteristics are good when used above recommended use temperatures, and higher EO levels give higher CIs.

TABLE 1

Typical Industrial and Institutional Rinse Aid

Component	Wt %	Function
Nonionic surfactant	10-50	Sheeting action Defoaming
Hydrotrope	0-10	Solubilizing nonionic Dispersing agent
Perfume-dye	0-2	Aesthetics
Water	balance	Profit enhancer Viscosity improver

HYDROTROPE EVALUATION

Linear alkyl naphthalene sulfonate (LANS). The hydrotrope with the largest aromatic moiety improves the dispersibility of one of the block and most of the alcohol oxyalkylate formulations (Table 3). As might be expected, the 20% surfactant formulation is more readily dispersed than the 40% formulation, and this trend is reasonably consistent for all the hydrotropes evaluated. The CI increases average 14 C at 3% hydrotrope and 20 C at 6% hydrotrope. A second trend that emerges is that the CI's increase with increasing hydrotrope concentration. This is not predictable a priori if one considers that a number of these hydrotropes are insoluble in water at the 3 and 6% levels. This hydrotrope produces negligible increases in the blender foam tests; of the 14 formulations tested, 12 pass at 82 C and 6 at 49 C. Furthermore, the rinse aids that pass in the presence of LANS are the same that pass without a hydrotrope.

Alkylaryl sulfonates. Sodium dodecyl benzene sulfon-

TABLE 2

Rinse Aid Properties Without Hydrotropes[a]

	Block Copolymer Concentration, wt %								Alcohol Oxyethylates Concentration, wt %					
	L-10		N-3		L-62D		25R2		RA-20		DW-5		RA-40	
	20	40	20	40	20	40	20	40	20	40	20	40	20	40
Dispersibility	5	5	5	5	5	5	2	5	5	5	5	5	5	5
CI, °C	51	56	16	33	24	50	20	28	46	47	25	26	27	29
Foam height, mm														
49 C	4	6	0	0	6	9	0	0	4	6	<1	0	6	5
82 C	<1	0	0	0	1	0	<1	0	1	1	<1	0	4	3

[a]Formulations are 20 and 40 wt % nonionic with the balance of water.

TABLE 3

Rinse Aid Properties With Linear Alkyl Naphthalene Sulfonate[a]

	Block Copolymer Concentration, wt %								Alcohol Oxyethylates Concentration, wt %					
	L-10		N-3		L62-D		25R2		RA-20		DW-5		RA-40	
	20	40	20	40	20	40	20	40	20	40	20	40	20	40
Dispersibility, 3%	2	4	5	5	5	5	5	5	1	2	2	5	2	2
Dispersibility, 6%	3	3	5	5	5	5	5	5	1	2	3	5	2	2
CI, °C, 3%	66	68	44	44	61	53	39	37	62	60	36	34	34	34
CI, °C, 6%	78	77	51	47	73	61	46	40	68	70	43	41	38	38
Foam height, mm														
49 C	5	6	0	0	6	8	0	0	4	5	<1	0	6	5
82 C	<1	0	0	0	1	0	<1	0	1	1	<1	0	4	3

[a]Formulations are 20 and 40 wt % nonionic, 3 and 6 wt % hydrotrope with the balance water. Dispersibilities and CI are listed for rinse aids made with both 3 and 6 wt % hydrotrope. Foam heights at 49 and 82 C are listed for the 6 wt % hydrotrope formulations only.

TABLE 4

Rinse Aid Properties With Alkyl Benzene Sulfonates [a,b]

	Block Copolymer Concentration, wt %								Alcohol Oxyethylates Concentration, wt %					
	L-10		N-3		L-62D		25R2		RA-20		DW-5		RA-40	
	20	40	20	40	20	40	20	40	20	40	20	40	20	40
Dispersibility, 3%	1-2	2-4	3-4	2	2	4-5	2	4-5	1	2	2	5	1	2-3
Dispersibility, 6%	1-2	1-2	2	3	2	4	2-3	3-4	1	1-2	2	3-4	1-2	2
CI, °C, 3%	82±5	65±2	52±3	37±2	64±2	51±1	51±4	32±1	66±2	52±2	41±1	28±1	38±3	39±3
CI, °C, 6%	88±5	63±6	83±1	36±2	79±4	64±1	64±6	30±2	76±4	57±3	52±2	29±2	50±8	47±6
Foam height, mm														
49 C	5	7	2-4	0	6	7-8	1-3	0-<1	5-6	5-7	4-5	<1-6	4-5	5
82 C	1-3	1-5	<1-1	0	3-4	2-4	2	<1-1	4	2-3	1	0-3	4-6	3-4

[a]Formulations are 20 and 40 wt% nonionic, 3 and 6 wt % hydrotrope with the balance water. Dispersibilities and CI are listed for rinse aids made with both 3 and 6 wt % hydrotrope. Foam heights at 49 and 82 C are listed for the 6 wt % hydrotrope formulations only.
[b]The data represent the averages or ranges found with sodium dodecyl benzene sulfonate, triethanolamine dodecylbenzene sulfonate, and amine alkarylsulfonate.

TABLE 5

Rinse Aid Properties With Sodium-2-Ethylhexyl Sulfate[a]

	Block Copolymer Concentration, wt %								Alcohol Oxyethylates Concentration, wt %					
	L-10		N-3		L-62D		25R2		RA-20		DW-5		RA-40	
	20	40	20	40	20	40	20	40	20	40	20	40	20	40
Dispersibility, 3%	5	5	5	5	5	5	5	5	2	5	5	5	2	2
Dispersibility, 6%	5	5	5	5	5	5	5	5	1	4	5	5	2	2
CI, °C, 3%	66	62	39	36	62	54	36	31	62	53	36	28	34	38
CI, °C, 6%	73	63	43	37	77	63	39	32	70	58	41	28	47	43
Foam height, mm														
49 C	4	5	0	0	6	9	0	0	4	5	<1	0	7	4
82 C	<1	0	0	0	<1	0	<1	0	1	1	<1	0	4	4

[a]Formulations are 20 and 40 wt % nonionic, 3 and 6 wt % hydrotrope with the balance water. Dispersibilities and CI are listed for rinse aids made with both 3 and 6 wt % hydrotrope. Foam heights at 49 C and 82 C are listed for the 6 wt % hydrotrope formulations only.

TABLE 6

Rinse Aid Properties With Sodium Dihexyl Sulfosuccinate[a]

	Block Copolymer Concentration, wt %								Alcohol Oxyethylates Concentration, wt %					
	L-10		N-3		L-62D		25R2		RA-20		DW-5		RA-40	
	20	40	20	40	20	40	20	40	20	40	20	40	20	40
Dispersibility, 3%	2	2	5	5	2	5	5	5	1	1	3	5	1	2
Dispersibility, 6%	2	2	5	5	1	2	5	5	1	1	2	5	2	2
CI, °C 3%	87	75	62	47	76	54	57	41	68	67	42	33	40	41
CI, °C, 6%	>96	>82	>82	49	>82	70	74	48	81	80	53	38	51	51
Foam height, mm														
49 C	4	5	0	0	6	7	0	0	4	6	3	0	6	2
82 C	0	0	0	0	<1	0	<1	0	1	1	<1	0	4	1

[a]Formulations are 20 and 40 wt % nonionic, 3 and 6 wt % hydrotrope with the balance water. Dispersibilities and CI are listed for rinse aids made with both 3 and 6 wt % hydrotrope. Foam heights at 49 and 82 C are listed for the 6 wt % hydrotrope formulations only.

ate, triethanolamine dodecylbenzene sulfonate and an amine alkylaryl sulfonate give very similar results. On the average they give the best improvement in dispersibility, increase the CI's 14 to 29 C and increase foaming characteristics of the rinse aid.

It should be emphasized that rinse aids formulated with Pluronic® polyols L-10, 25R2 and Industrol® surfactants N-3 and DW-5 give acceptable foaming characteristics (Table 4).

Sodium xylene sulfonate (SXS) and the phosphate ester (PE). With one exception, formulations based on Plurafac® RA-40 surfactant, these hydrotropes give little improvement in dispersibility. Average increases in CI are modest and range from 6 to 11 C. These hydrotropes do not hurt the defoaming characteristics of the surfactants. With SXS, only those formulations based on the high EO containing surfactants (Pluronic® L-10, L-62D and Plurafac® RA-40) are worth consideration. Only the Pluronic® polyol L-62D formulation is worth consideration with the PE. Data for these hydrotropes will be supplied upon request.

Sodium-2-ethylhexyl sulfate. This hydrotrope is more effective at dispersing alcohol oxyalkylates than the block copolymers. Good average increases, 12 to 17 C in CI, are observed with little increased foaming tendencies (Table 5).

Sodium dihexyl sulfosuccinate. Improves the dispersibility almost as much as the alkyl benzene sulfonates. It gives the highest CI's of the evaluated hydrotropes. Furthermore, it maintains the excellent defoaming characteristics of the rinse aids at their recommended use temperatures (Table 6).

The sulfosuccinate, formulation for formulation, is superior to the other hydrotropes tested in this study, regardless of the fact that in some formulations the dispersibilities are slightly lower than with the alkylarylsulfonate. This would be the first anionic hydrotrope recommended for screening studies.

Unfortunately, no outstanding universal rinse aid is identified clearly by the data. Rather, each formulation represents a balance of desired properties. It is up to the formulators to decide which best suits their individual needs. We believe, however, that this work gives the information needed by the formulators to rapidly choose hydrotrope-surfactant combinations best suited for their requirements.

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