Influence of 2-Phenyl Alkane and Tetralin Content on Solubility and Viscosity of Linear Alkylbenzene Sulfonate

L. Cohen*, R. Vergara, A. Moreno and J.L. Berna

Petroquímica Española, S.A., San Roque (Cadiz), Spain

ABSTRACT: Cloud and clear points and viscosities of linear alkylbenzene sulfonates (LAS) have been determined as a function of 2-phenyl alkane and/or tetralin content over a wide interval. While the 2-phenyl content significantly affects the solubility, tetralins have a marked depressive effect on viscosity. The investigation has established that LAS solubility can be explained by assuming eutectic types of isomer and homolog mixtures, which are dependent on internal to external isomer ratios. *JAOCS 72,* 115–122 (1995).

KEY WORDS: Eutectic, LAS, 2-phenyl alkane, solubility, viscosity.

As is already known in the detergent industry, linear alkylbenzene sulfonates (LAS) with high 2-phenyl and tetralin content (chloroparaffins–$AlCl_3$ process) is easier to formulate into liquid detergents than that with a lower content in those components (HF process). The reason is the higher solubility and lower viscosity for LAS produced in the $AlCl_3$ process. A third type of LAS, produced by the $AlCl_3$ process with olefins, can be found on the market. Finally, LAS produced by the DETAL process will be in the market next year. These two products have high 2-phenyl content and low tetralin content. Their solubility is comparable to LAS from the classical $AlCl_3$ process, while their viscosity is within the range of the product from the HF process.

The literature is rife with seemingly contradictory statements: (i) 2-Phenyl alkane LAS products have a higher Krafft point than internal isomers (1); (ii) The cloud point of 1% 2-phenyl C_{12} LAS solution = 67°F; the cloud point of 1% internal C_{12} LAS solution = 32°F (internal communication from CONOCO, 1973); (iii) The 2-phenyl C_{10} Krafft point = 22°C; the 5-phenyl C_{10} Krafft point = <1°C (2); (iv) Phenyl C_{10} LAS solubility increases with the 2-phenyl isomer increase, until reaching a maximum, and then it dramatically decreases (3); (v) Phenyl C_{11} doped with 2-phenyl gives lower cloud and clear points than the nondoped C_{11} (technical report from CONOCO, 1982).

The conclusion is that, in spite of 2-phenyl being the less-soluble isomer, in commercial LAS, solubility increases with an increase in 2-phenyl content. The aim of the present study is to establish whether all these apparent contradictions can be brought into line by assuming that a 2-phenyl content interval exists where the solubility of LAS solutions reaches a maximum.

MATERIALS AND METHODS

Cloud point. The cloud point of the different sulfonate solutions was determined by measuring the temperature at which a transparent sulfonate solution becomes cloudy on cooling.

Clear point. The clear point was determined by measuring the temperature at which a cloudy sulfonate solution becomes transparent on heating.

Viscosity. Viscosity determinations were made at 20°C in a HAAKE RV 100 viscosimeter with NV equipment (HAAKE Co., Karlsruhe, Germany).

Commercial LAS mixtures. Four commercial linear alkylbenzene (LAB) samples, whose compositions are presented in Table 1, were sulfonated on a laboratory scale. Their sodium sulfonates, LAS, were blended in different proportions to obtain mixtures with a wide spectrum of 2-phenyl alkane and tetralin contents (Table 2). Cloud and clear point results as well as viscosity values for 25% active ingredient are also given in Table 2.

TABLE 1
Commercial LAB Compositions[a]

Composition (%)	LAB 1	LAB 2	LAB 3	LAB 4
Paraffins	0.1	0.0	0.1	0.3
$<\phi C_{10}$	1.0	0.0	0.2	0.2
ϕC_{10}	6.2	10.0	15.5	8.4
ϕC_{11}	33.0	40.9	32.2	31.4
ϕC_{12}	31.6	31.7	25.6	32.8
ϕC_{13}	21.5	16.6	15.8	13.5
ϕC_{14}	1.9	0.4	1.2	0.1
Branched alk	4.8	0.3	0.9	0.4
Tetralins	0.0	0.1	8.6	13.2
2-ϕ alkane	15.9	30.6	27.3	26.2
Molecular weight	242.4	239.0	240.1	242.2

[a]ϕ = Phenyl; LAB, linear alkylbenzene.

*To whom correspondence should be addressed at Petroquímica Española, S.A., P.O. Box 40, San Roque (Cadiz), Spain.

TABLE 2
Compositions and Properties of LAS Mixtures Prepared from Commercial LAB Products[a]

Mixture	Tetra	2-ϕ	Cloud point (25%)	Clear point (25%)	Viscosity (20°C)
1	0	15.6	15	20	1200
2	0	19.8	13	19	1460
3	0	23.6	9	14	1254
4	0	26.9	4	8	930
5	0	30.6	2	7	1053
6	0.4	16.5	14	21	1205
7	0.4	19.3	13	18	1258
8	0.4	22.1	10	15	1104
9	0.4	25.5	6	11	1024
10	0.4	30.4	2	4	860
11	1.4	17.4	12	17	1085
12	1.4	21.8	8	14	940
13	1.4	25.7	5	10	816
14	1.4	30.1	2	4	651
15	2.2	18.8	12	18	689
16	2.2	22.2	10	15	721
17	2.2	25.5	6	10	643
18	2.2	30.0	1	4	542
19	2.2	30.0	0	4	388
20	3.0	25.3	2	8	253
21	3.0	29.6	−1	2	190
22	4.4	19.1	9	16	195
23	4.4	21.9	7	12	314
24	4.4	25.5	5	10	404
25	4.4	29.1	1	7	297
26	5.6	23.2	4	11	270
27	5.6	28.5	1	6	212
28	8.6	27.3	0	5	115
29	13.2	26.2	−4	3	11

[a]Tetra = Tetraline; LAB, linear alkylbenzene sulfonates; see Table 1 for other abbreviations.

Commercial LAS/2-phenyl C_{12} LAS. A commercial LAB (LAB 5) was doped with different amounts of 2-phenyl C_{12}. The mixture compositions are given in Table 3. Cloud points were measured at 25% active ingredient concentration.

TABLE 3
Composition of LAB 5/2-ϕ C_{12} Mixtures[a]

Composition (%)	LAB 5	2ϕC_{12}	S1	S2	S3	S4	S5
<ϕC_{10}	1.0	0.0	1.0	0.9	0.8	0.7	0.6
ϕC_{10}	6.6	0.0	5.7	5.5	5.0	4.4	3.4
ϕC_{11}	34.8	0.4	30.3	28.9	26.1	23.0	18.1
6-ϕC_{12}		0.8					
5-ϕC_{12}		0.9					
4-ϕC_{12}	32.4	1.3	40.5	42.9	47.9	53.5	62.2
3-ϕC_{12}		6.5					
2-ϕC_{12}		84.9					
ϕC_{13}	22.7	5.2	20.5	19.8	18.4	16.8	14.4
ϕC_{14}	2.4	0.0	2.0	2.0	1.8	1.6	1.3
2-Phenyl	15.9	84.9	24.0	27.4	33.0	39.0	48.0
Molecular weight	242.4	247.6	243.0	243.3	243.7	244.2	244.9

[a]See Table 1 for abbreviations.

TABLE 4
Composition of ϕ C_{12} Mixtures[a]

Composition (%)	F1	F2	F3	F4	F5	F6	F7
6-ϕC_{12}	21.5	19.0	16.8	14.6	13.0	9.4	2.2
5-ϕC_{12}	18.5	15.0	14.4	14.8	12.0	9.0	2.4
4-ϕC_{12}	18.5	16.0	14.6	13.9	11.8	9.0	2.7
3-ϕC_{12}	22.5	20.0	18.8	17.8	16.2	14.0	8.3
2-ϕC_{12}	19.0	29.0	35.4	38.9	47.0	58.6	84.4

[a]See Table 1 for abbreviation.

TABLE 5
Composition of ϕ C_{10} Mixtures[a]

Composition (%)	M1	M2	M3	M4	M5	M6	M7	M8
5-ϕC_{10}	49.7	40.0	33.5	29.9	25.1	20.2	12.0	—
4-ϕC_{10}	32.7	27.0	22.4	19.7	16.6	13.5	7.8	—
3-ϕC_{10}	17.3	16.7	16.2	16.2	16.1	15.9	14.7	16.4
2-ϕC_{10}	0.3	16.3	27.9	34.2	42.2	50.4	62.7	83.6

[a]See Table 1 for abbreviation.

Phenyl C_{12} LAS/2-phenyl C_{12} LAS. Phenyl C_{12} LAB doped with 2-phenyl C_{12} isomer mixtures were prepared (Table 4), and cloud points of the sulfonated mixtures were measured at 20% active ingredient concentration.

Phenyl C_{10} LAS. Phenyl C_{10} LAB with various isomers distributions, as given in Table 5, were obtained by distillation, and the cloud points of their sodium salt sulfonates were measured at 25% active ingredient.

RESULTS AND DISCUSSION

Concerning the commercial LAS mixtures, the experimental results as well as the main conclusions depicted here are in perfect agreement with those found in the literature.

Solubility vs. *2-phenyl content.* The experimental results are plotted in Figures 1 and 2. It is concluded that for a given tetralin content, cloud and clear points decrease dramatically with increasing 2-phenyl isomer within the range studied.

Solubility vs. *tetralin content.* As can be concluded from Figures 3 and 4, for a given 2-phenyl content, solubility increases slightly as the tetralin content increases.

Solubility vs. *branched alkylbenzene.* Solubility is slightly affected by branched alkylbenzene content within the range studied (Figs. 5 and 6).

Viscosity vs. *2-phenyl and tetralin contents.* As can be observed in Figure 7, the 2-phenyl content has no significant influence on viscosity, while tetralins have a marked depressing effect on that property.

From these observations it can be concluded that 2-phenyl content has a rather strong influence on solubility and no significant effect on viscosity; while the effect of tetralins on solubility is not nearly as drastic as on viscosity. The latter can be explained by taking into account the tetralin sulfonate structure, with its shortened aliphatic tail, which makes it be-

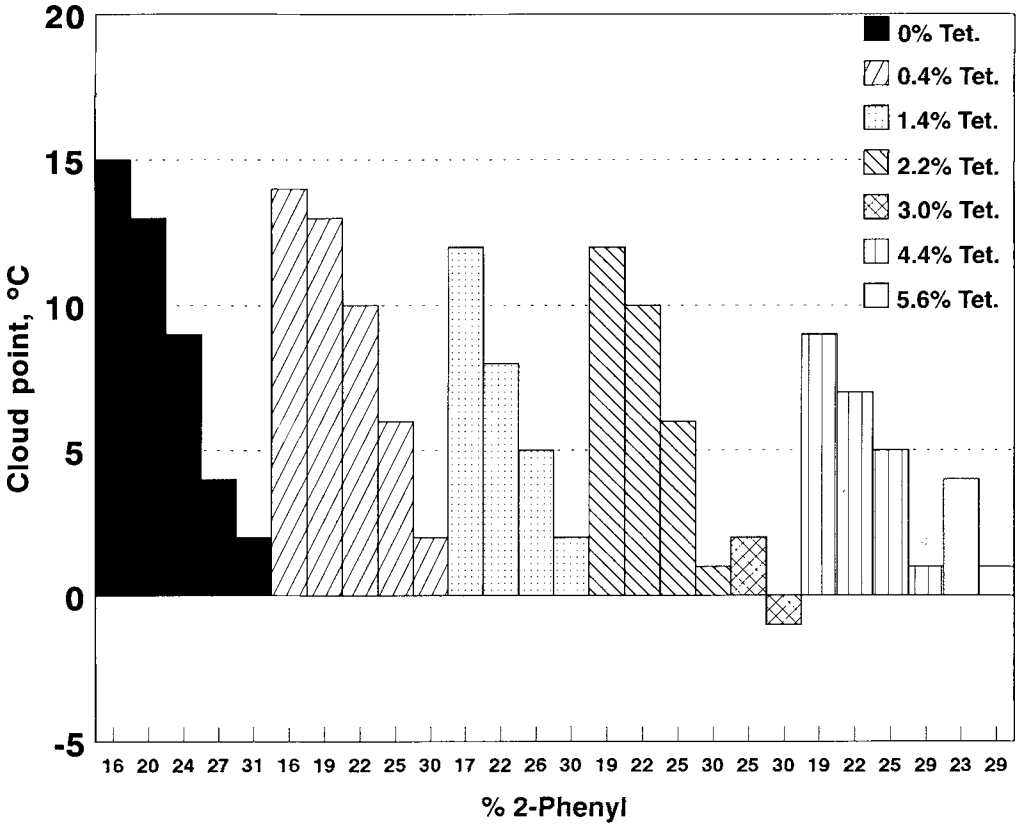

FIG. 1. Solubility vs. 2-phenyl alkane. Cloud point, 25% active ingredient. Tet., tetralin.

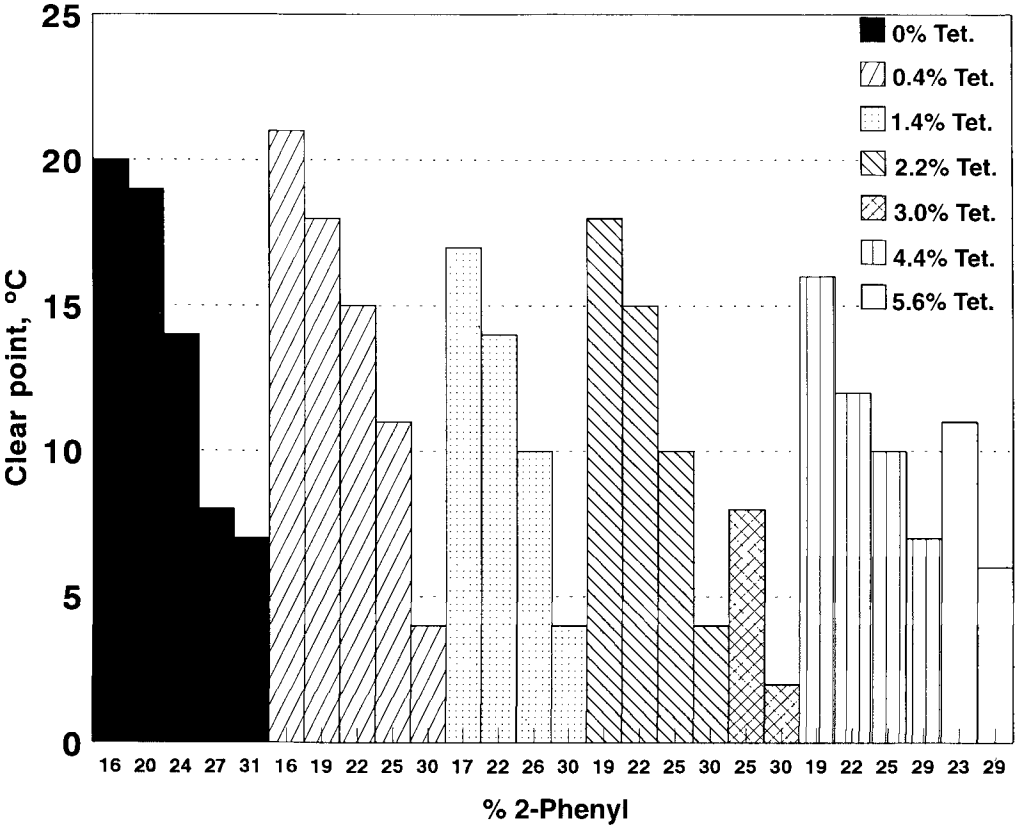

FIG. 2. Solubility vs. 2-phenyl alkane. Clear point, 25% active ingredient. See Figure 1 for abbreviation.

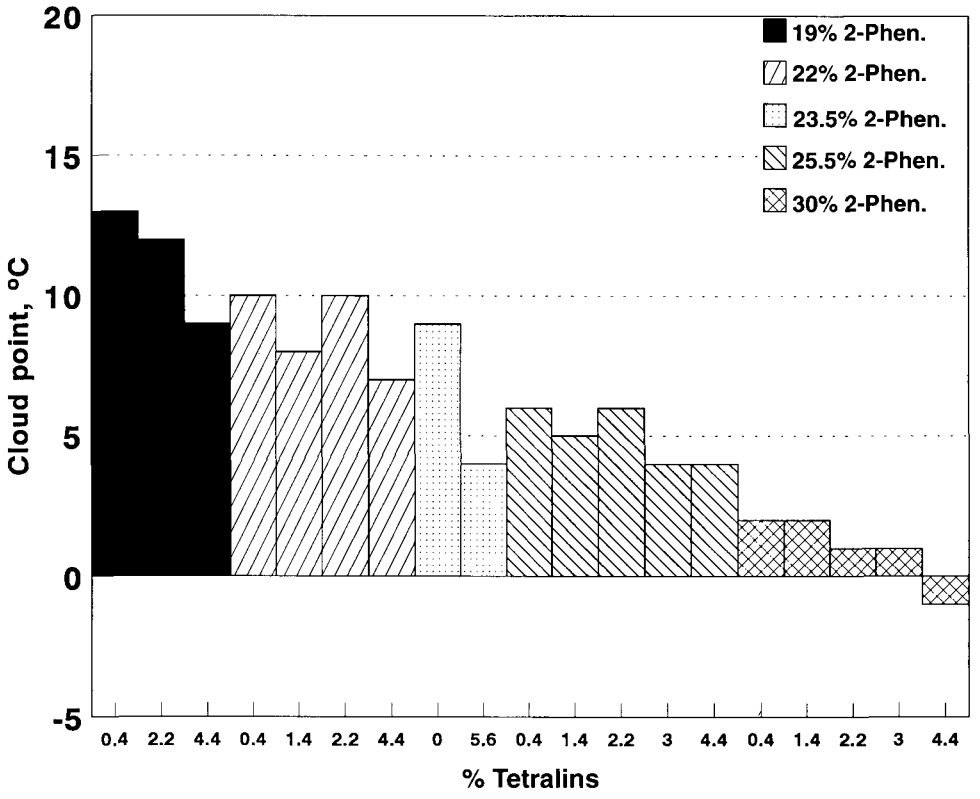

FIG. 3. Solubility vs. tetralins. Cloud point, 25% active ingredient. Phen., phenyl.

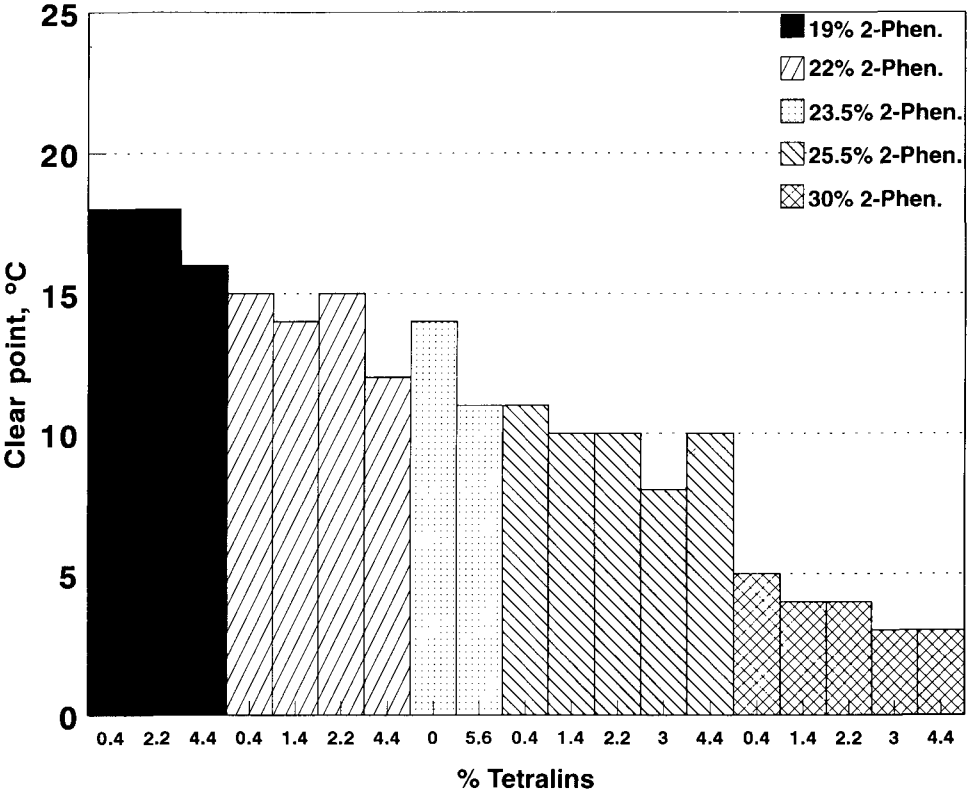

FIG. 4. Solubility vs. tetralins. Clear point, 25% active ingredient. Abbreviation as in Figure 3.

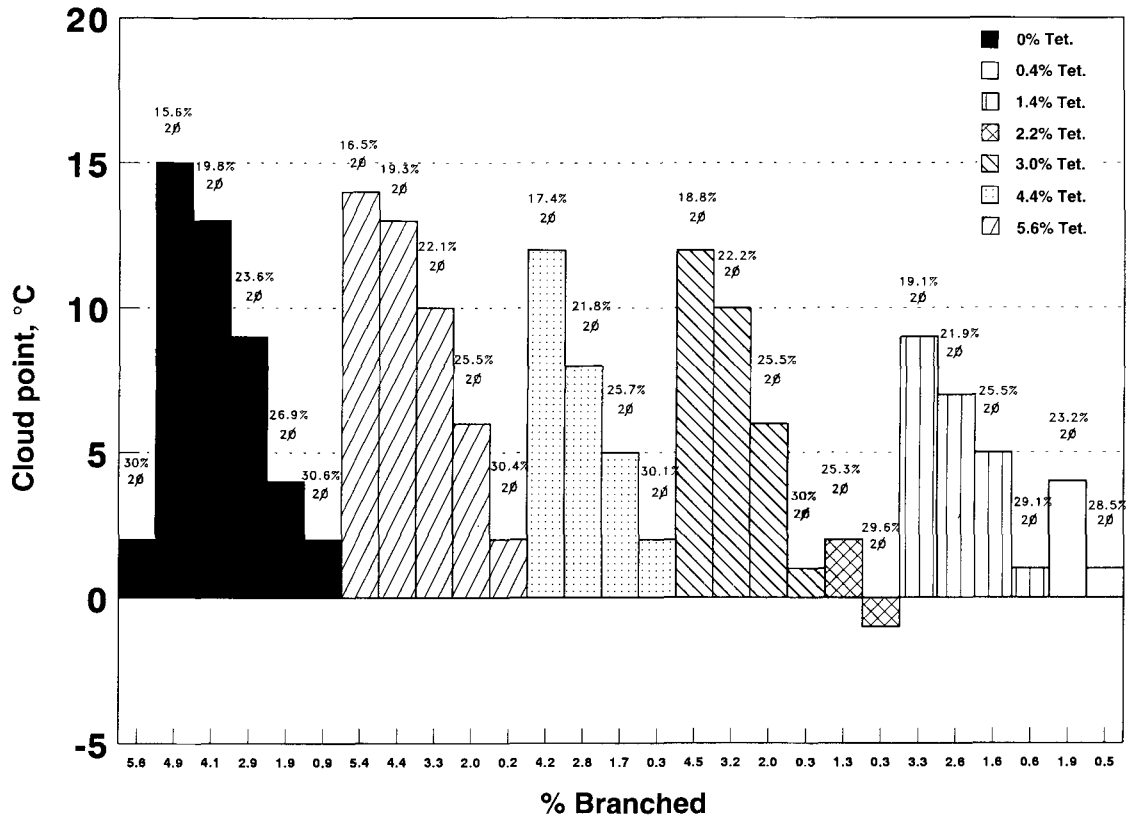

FIG. 5. Solubility vs. branched alkylbenzene. Cloud point, 25% active ingredient; ϕ = phenyl. See Figure 1 for abbreviation.

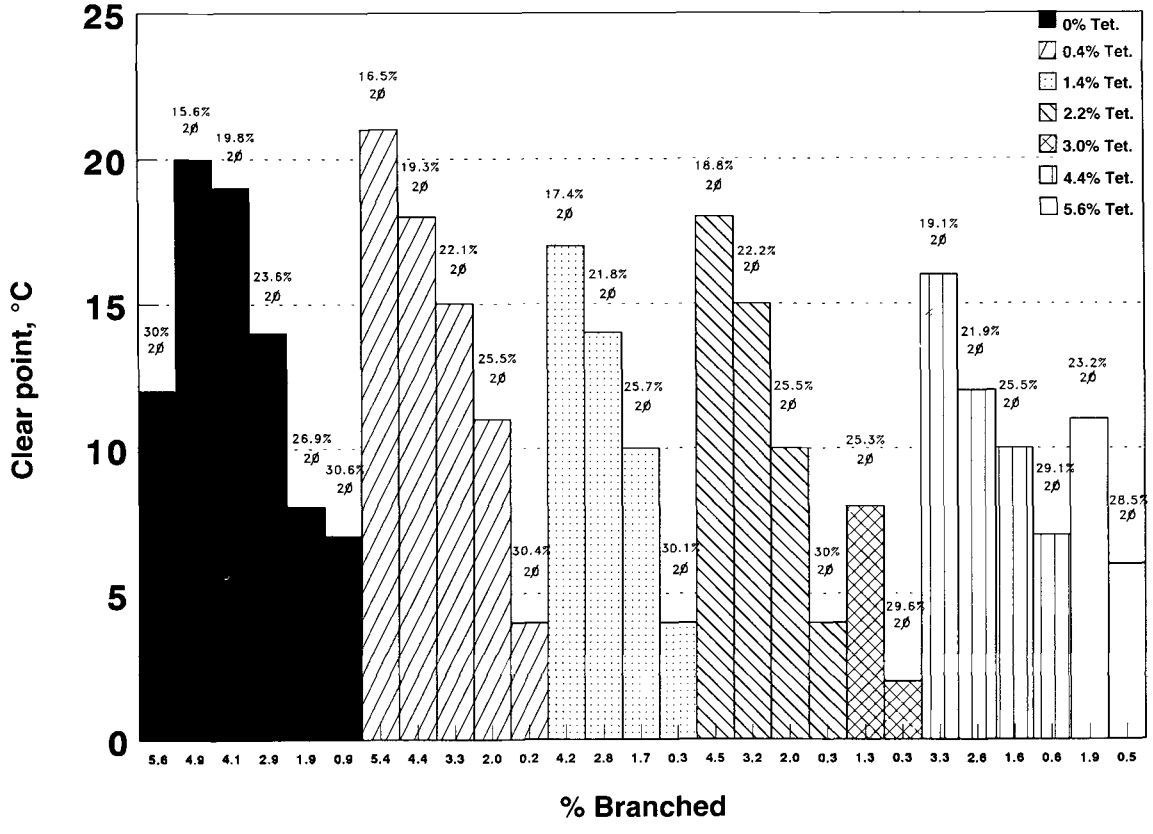

FIG. 6. Solubility vs. branched alkylbenzene. Clear point, 25% active ingredient. See Figures 1 and 5 for abbreviations.

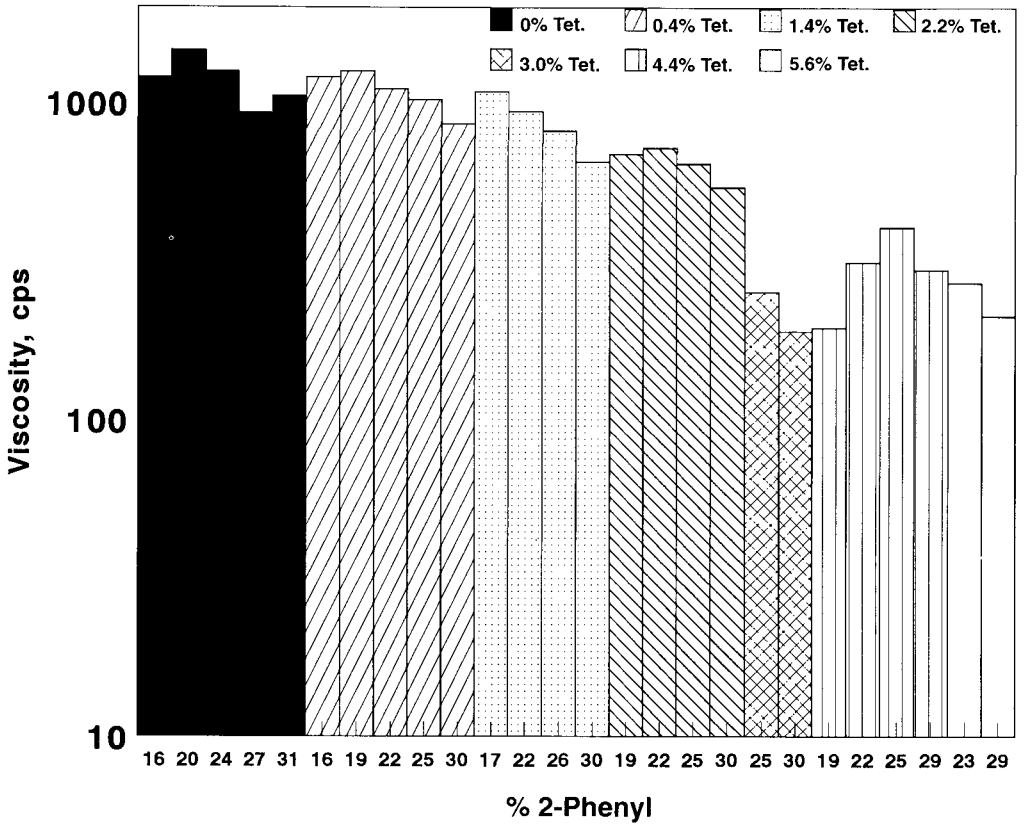

FIG. 7. Viscosity vs. 2-phenyl alkane and tetralins (Tet.) 20°C, 25% active ingredient.

have like a hydrotrope (e.g., a xylene or a toluene sulfonate). In an attempt to give an explanation to the observed solubility/2-phenyl content relationship, three different mixtures have been prepared and studied.

(i) Commercial LAS/2-phenyl C_{12} LAS. A commercial LAS with 16% 2-phenyl content was mixed in different proportions with a 2-phenyl C_{12} LAS (84.9% 2-phenyl content). The cloud point variation is shown in Figure 8. Two main conclusions can be drawn: solubility increases with 2-phenyl increase, reaches a maximum and then decreases dramatically; and the curve shape can be explained by a eutectic behavior, where the eutectic blend, corresponding to the minimum of the curve, occurs within the 30 to 35% 2-phenyl content interval.

There is a synergism when LAS 5 (Table 3) and 2-phenyl C_{12} are mixed, so that a significant depression, with regard to cloud points of the original components, is observed. This synergism can be explained on the basis of mixture–heterogenity, i.e., the different contributions of each isomer to mixed micelles and to precipitate. The theory given in Reference 4 considers that, when the cloud point is reached, monomers, micelles and precipitate are together in equilibrium. Whereas micelles are composed by all components of the mixture, the initial precipitate is solely formed by that component whose solubility product has first been attained.

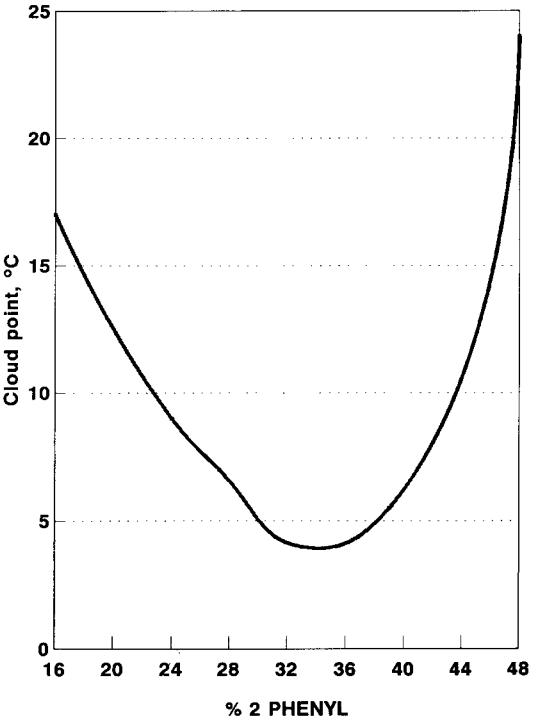

FIG. 8. Commercial linear alkylbenzene sulfonates (LAS)/2-phenyl C_{12} LAS mixtures. Cloud point, 25% active ingredient.

Due to its contribution to mixed micelles, each monomer concentration will be lower than the one corresponding to the pure monomer; thus, the saturation temperature of the solution will be lower in mixtures.

(ii) Phenyl C_{12} LAS mixtures. The experimental results represented in Figure 9 cover an interval ranging from 19 to 84.4% 2-phenyl content. These results confirm the theory given above; however, the eutectic blend in this case is reached at 30% 2-phenyl content.

(iii) Phenyl C_{10} LAS. The work has been completed by studying phenyl C_{10} homolog behavior. From Figure 10 it can be concluded that this homolog has the same behavior as phenyl C_{12}, but the eutectic mixture is reached at 28% 2-phenyl content.

Therefore, the eutectic behavior is a general trend for all LAS homologs and isomer blends.

These results led us to suggest that the eutectic blend corresponds to an optimal isomer distribution. To show this, an internal to external isomer ratio was calculated by assuming the external isomers to be the 2- plus the 3-phenyl, and the internal to be the sum of the remaining 4-, 5-, 6- and 7-phenyl isomers.

In Figures 11 and 12, the relationship between the cloud point and the mentioned ratio has been plotted for phenyl C_{10} and for phenyl C_{12} as well. Besides this, Figure 13 shows the same relationship for three commercial LAS with different 2-phenyl alkane content.

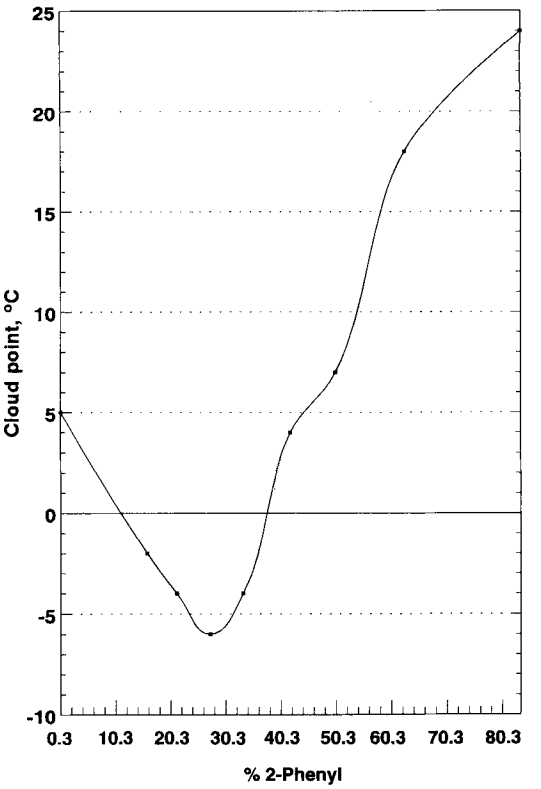

FIG. 10. Phenyl C_{10} linear alkylbenzene sulfonates. Cloud point, 25% active ingredient.

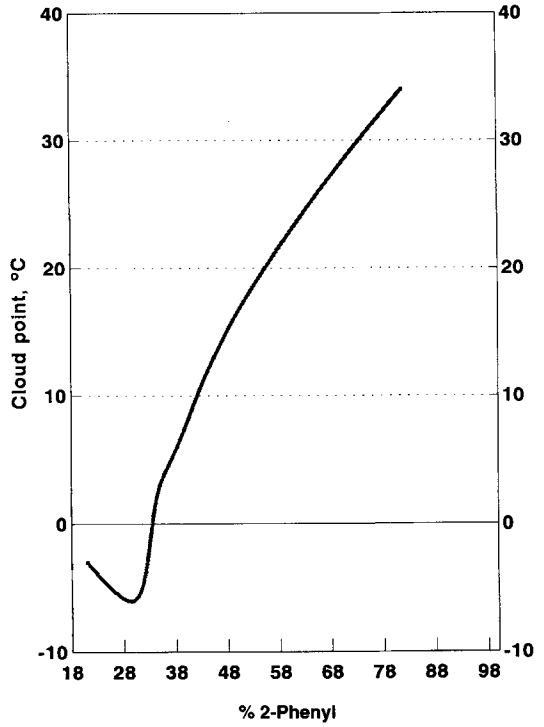

FIG. 9. Phenyl C_{12} LAS/2-phenyl C_{12} LAS mixtures. Cloud point, 20% active ingredient. See Figure 8 for abbreviation.

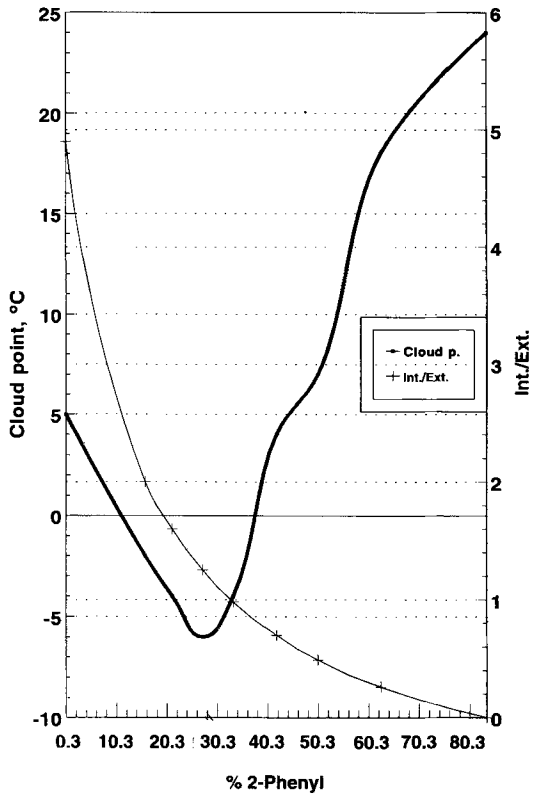

FIG. 11. Relationship between phenyl C_{10} cloud point (Cloud p.) and internal/external (Int./Ext.) isomer ratio; 25% active ingredient.

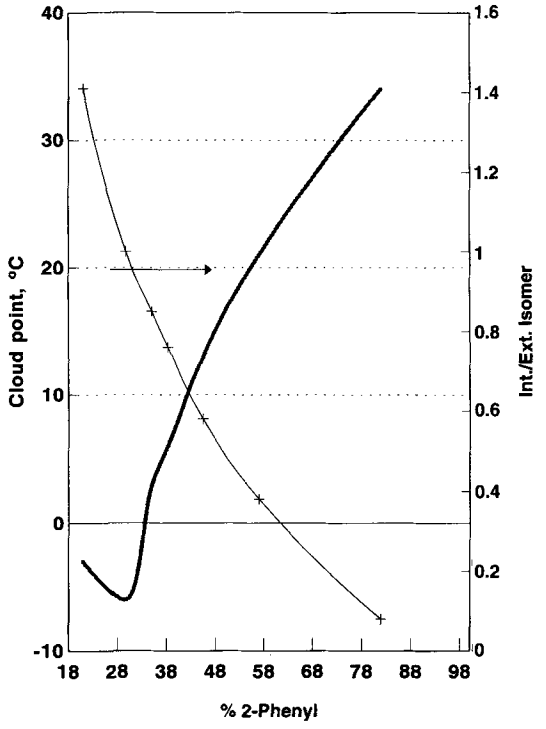

FIG. 12. Relationship between phenyl C_{12} cloud point and Int./Ext. isomer ratio; 20% active ingredient. See Figure 11 for abbreviations.

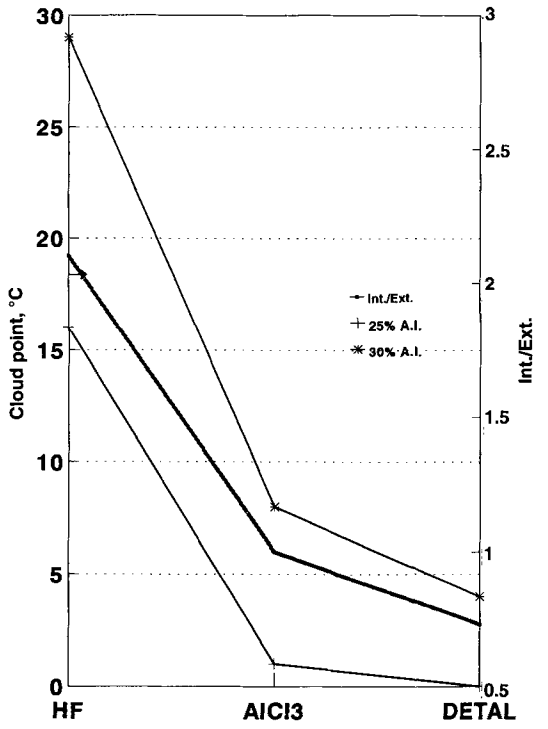

FIG. 13. Relationship between commercial linear alkylbenzene sulfonates (LAS) cloud point and Int./Ext. isomer ratio; 25 and 30% active ingredient (A.I.). HF, AlC13, DETAL: three commercial LAS.

It shows that there is an optimal ratio value, which depends on each homolog and on each type of blend. For phenyl C_{10}, the optimal value is 1.2, and for phenyl C_{12} it is 1. For the three commercial LAS studied with the same molecular weight, the best ratio is 0.75, which corresponds to that for the DETAL process. For the HF process, the ratio is 2.1, and for the $AlCl_3$ process it is 1.0.

REFERENCES

1. Smith, F.D., *J. Am. Oil Chem. Soc. 43*:501 (1966).
2. van Os, N.M., *Tenside 29*:175 (1992).
3. Moreno, A., and L. Cohen, *Ibid. 25*:216 (1988).
4. Scamehorn, J.F., *Phenomena in Mixed Surfactant Systems,* 311 ACS Symposium Series, 1986.

[Received February 28, 1994; accepted July 18, 1994]