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EMULSION STABILIZATION BY SILICIC ACID

K. A. Allen
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Erratum to ORNL-2771

Please change the caption on the right hand figure, p. 12, to read: "Aqueous continuous, cross-linking possible."

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section C

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ABSTRACT

With a given amine (vs. an aqueous phase containing silicic acid) the stability of the emulsion formed was dependent on the anion present in the order $SO_4^{=}$ (most stable) > Cl^- > ClO_4^- (least stable). Emulsion stability increased with silicon concentration and with the age of the silicic acid solution. Other organic solutes that also had electron-donating tendencies (e.g., oxygen atoms) showed smaller but real emulsion-forming abilities when contacted with silicic acid liquors. Organic additives with active hydrogen atoms decreased phase separation times of a typical silica liquor—amine sulfate solution dispersion by factors of 2 or more, presumably by competing with the silicic acid hydrogen atoms for bonding sites on the amine sulfate oxygens. It is suggested that silicic acid stabilizes oil-in-water type emulsions by hydrogen bonding to electron-donating groups adsorbed on the surfaces of the organic droplets and by forming typical silicic acid networks in the aqueous phase.

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1.0 INTRODUCTION

The work described in this report was done in order to elucidate the effects of silicic acid on emulsion formation in the Amex processes for uranium, with a view toward the prediction and testing of specific remedies. While the Amex and Dapex processes have generally operated smoothly in the mills in which they are used,[1] in a few cases there have been phase separation difficulties. Further understanding of the role of silicic acid in causing these troubles could lead to more efficient operation. The variables examined include the effects of different anions, silicon concentration and age, the behavior of silicic acid with organic solutes other than the amine extractants, and the effects of various additives to the organic phase.

Previous observations[2-4] of importance in this work include the following: (a) the offending liquors usually contain silicic acid, (b) synthetic liquors can be made to form emulsions by adding silicic acid, (c) the stable emulsion bands formed contain more silicon per unit volume than either clear phase, and (d) emulsions demonstrably due to silicic acid occur only on aqueous-continuous mixing; water-in-oil type dispersions generally separate well regardless of the presence of silicic acid. These facts suggest that silicic acid may stabilize oil-in-water type emulsions by forming links between the organic droplets through the intervening aqueous phase.

The authors are indebted to A. D. Ryon for background material and references to prior work.

2.0 EXPERIMENTAL

The organic phases studied were benzene, n-nonane, and kerosene solutions of various extractants and additives. A mixed branched secondary amine, Rohm and Haas 9D-178 (mol. wt. 376, 92% secondary, 2% primary, and 6% tertiary), was used for most of the tests in kerosene because of previous experience with this amine-diluent combination. The trilauryl amine used for the tests in benzene was of industrial grade (mol. wt. 552, 93% tertiary, 3% primary, and 4% secondary). The other compounds were generally of Eastman White Label grade or equivalent.

Aqueous solutions containing the highest silicic acid concentration used (5 g of silicon per liter) were prepared by adding weighed quantities of sodium metasilicate to sodium salt solutions of such concentration that the resulting sodium concentrations were 2 M in sulfate solution and 1 M in chloride and perchlorate solutions. These were

adjusted to pH 1 with 1 M acid, giving final concentrations of 0.75 M Na_2SO_4—0.25 M H_2SO_4, 0.919 M NaCl—0.081 M HCl, 0.942 M $NaClO_4$—0.058 M $HClO_4$. Solutions containing less silica were prepared by diluting the stock solutions with the corresponding 1 M, pH 1, acidic salt mixture.* These 1 M, pH 1, solutions without silica were also used to pre-equilibrate the organic phases under study, a precaution of special importance for the amines, which at pH 1 extract appreciable mineral acid.[5] The pertinent analytical methods have been described elsewhere.[5,6]

The phase separation tests were run at constant (25.00 ± 0.01°C) temperature in the cell shown in Fig. 1. This cell excluded air from the mixture** and allowed startup with either phase continuous by moving the paddle temporarily into the desired phase, starting it, and then returning it to the central position. The paddle was run at 600 rpm by a synchronous motor.

The procedure followed comprised filling the cell with equal volumes of the two phases, starting the paddle as described, and running it for 5 min. When the motor was turned off, the shaft was hand-braked to reduce slowdown time. The separation time was taken as that elapsed between paddle stoppage and the appearance of a clear phase boundary over ~50% of the interfacial area. With a given aqueous and a given organic solution, tests run the same day were generally reproducible within ± 10%. On different days, or with different solutions, much wider variations often occurred. Consequently, in each series of tests other than that in which age was a measured parameter, the whole series was run within a small enough time interval that the comparative effects observed could be considered reasonably reliable.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Silicon Concentration and Anion

With three different salts of trilauryl amine, the phase separation times of benzene solutions of the amine salts and the corresponding aqueous salt solutions depended strongly on the silicon concentration when the anion was

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*In some cases gelation occurred immediately on dilution; unless this occurred at once, however, no gelation was observed.

**Results with and without air were apparently the same, within experimental error; its exclusion allowed somewhat better observation of the separation process after the stirrer was turned off.

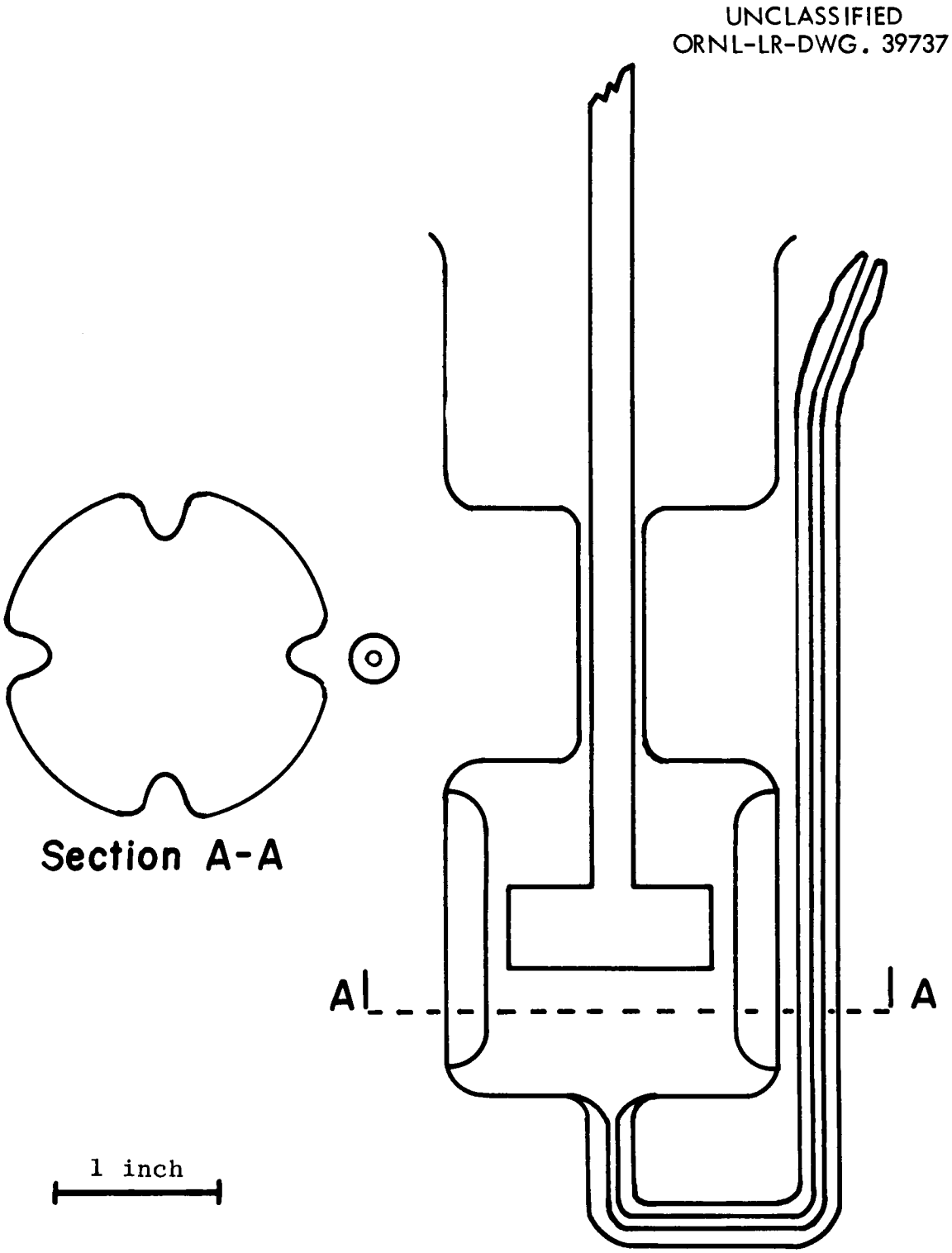

Fig. 1. Mixing cell (actual size). Section A-A shows the cross section of the mixing compartment with indentations for baffles. The phase boundary was centered in the mixing compartment.

sulfate, less so with chloride, and not at all with perchlorate (Table 1). In other words, the emulsion-stabilizing ability, and therefore probably also the hydrogen bonding ability, of these anions with silicic acid decreases in the order $SO_4^{=} > Cl^- > ClO_4^-$. This is also the generally recognized order of complex-forming tendencies of these ions.

Table 1. Effect of Silicic Acid Concentration on Phase Separation Times for 0.05 N Benzene Solutions of Trilaurylamine from Aqueous Solutions

Aqueous-continuous mixing

Si Conc., g/liter	Separation Time, min
Amine sulfate, 1 M SO_4 at pH 1.00	
None	2.0
0.625	2.5
1.25	7.5
2.50	>30
Amine chloride, 1 M Cl at pH 1.00	
None	2.5
0.625	3.0
1.25	3.0
2.50	2.5
Amine perchlorate, 1 M ClO_4 at pH 1.00	
None	1.0
0.625	1.0
1.25	1.0
2.50	1.0

3.2 Effect of Silicon Concentration and Age of Silicic Acid Solutions

The stability of emulsions formed by solutions of Amine 9D-178 in kerosene and kerosene alone with an aqueous sulfate system containing silicic acid appeared to vary directly with the silicic acid concentration and the age of the silicic acid solution (Fig. 2). In some cases kerosene alone behaved even worse than the amine solution; this is attributed to the known presence of polar impurities in the kerosene. Of three attempts to reproduce these results, two showed much longer break times and in one case the times

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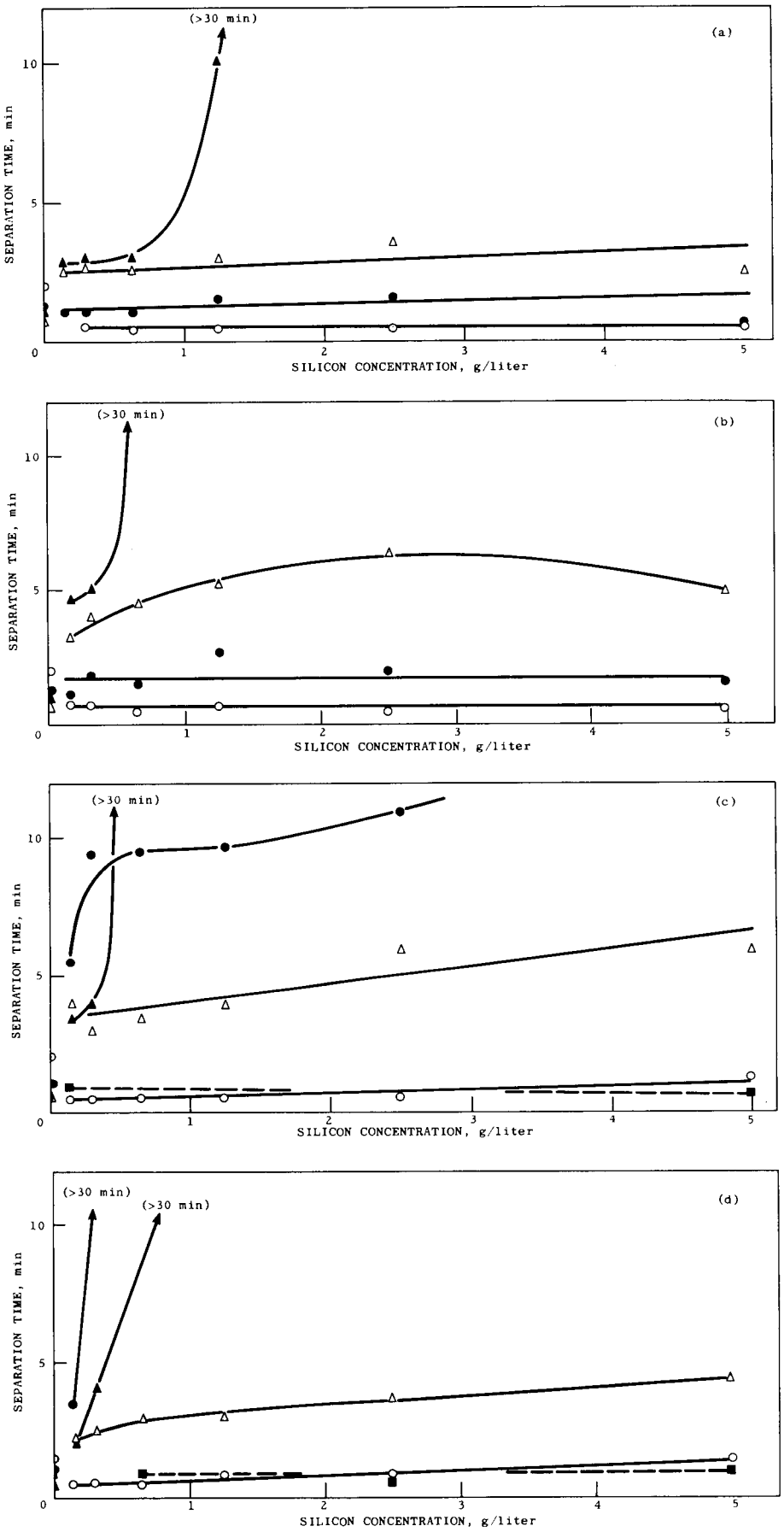


Fig. 2. Phase separation time as a function of silicon concentration. Aqueous phase: 0.75 M Na_2SO_4, 0.25 M H_2SO_4, silicon. Organic phase: ○, kerosene; Δ, sulfate-bisulfate of amine 9D-178 in kerosene; □, n-nonane. Open points indicate organic continuous mixing. Closed points indicate aqueous continuous mixing. Solutions were aged for (a) zero days, (b) 2 days, (c) 24 days, (d) 45 days.

were shorter; in all three cases, however, the relative trends were qualitatively similar to those shown.

3.3 Behavior of Other Solutes

The phase separation times of an aqueous sulfate system contacted with n-nonane solutions of diisobutyl ketone and n-propyl ether increased with increasing silicic acid concentration (Table 2). Both these organic compounds have electron-donating tendencies, and both showed small but reproducible increases in break times over those shown by the solvent alone.

Table 2. Effect of Silicic Acid Concentration on Phase Separation Times for Organic Solutes Containing Hydrogen-Bonding Oxygen Atoms from Aqueous Sulfate Solutions

Si Conc., g/liter	Separation Time, min	
	Org. Cont.	Aq. Cont.
n-Nonane (no organic solute); 1 M SO_4, pH 1		
None	0.5	0.7
0.156	0.5	0.7
0.625	0.5	0.7
2.5	0.5	0.7
5.0	0.5	0.7
0.2 M diisobutyl ketone in n-nonane, 1 M SO_4, pH 1		
None	0.5	0.7
0.156	0.5	0.8
0.625	0.5	1.2
2.5	0.5	1.3
5.0	0.5	1.5
0.2 M n-propyl ether in n-nonane, 1 M SO_4, pH 1		
None	0.5	0.7
0.156	0.5	0.7
0.625	0.5	0.8
2.5	0.5	1.0
5.0	0.5	1.0

With a constant silicic acid concentration, the ability of silicic acid to stabilize organic-aqueous emulsions depended on the presence of electron-donating (hydrogen bonding) sites in the organic phase (Table 3).

Table 3. Comparison of Abilities of Various Organic Compounds, 0.2 M in n-Nonane, to form Emulsions with the Same Silicic Acid Solution

Silica concentration: 2.5 g/liter in 1 M sulfate, pH 1

Compound		Separation Time, min Org. Cont.	Aq. Cont.
n-Nonane (no solute)	Electron donors	0.5	1.0
Acetyl acetone		<1.0	5.0
Tri-n-octylphosphine oxide		0.5	6.0
8-Hydroxyquinoline[a]		0.5	4.0
2-Bromo-4-tert-butylphenol	Electron acceptors	0.5	0.3
Butyric acid		0.5	0.2

[a]This material is appreciably soluble in the aqueous phase.

3.4 Effect of Additives

Several organic materials were tested for their effect in preventing emulsions. Compounds containing active hydrogens decreased phase separation times markedly (Table 4), presumably by competing with the silicic acid hydrogen atoms for bonding locations on the amine sulfate oxygen atoms.

3.5 Postulated Mechanism

In view of the results of these experiments and the previous observations mentioned in the introduction, it seems reasonable to postulate that silicic acid stabilizes oil-in-water type emulsions by forming links between the organic droplets through the intervening aqueous phase (see Fig. 3). The silicic acid hydrogen atoms apparently bond to electron-donor groups (e.g., the amine sulfate oxygen atoms) absorbed from the organic phase at the organic-aqueous interface of one droplet, and connect it with others by forming networks in the aqueous phase.

Recent physicochemical studies rule out the likelihood of amine salt cross-linking in the organic phase[7] (otherwise water-in-oil type emulsions would form also), whereas this type of behavior on the part of silicic acid is well known.[8] It is important to note that viscosity measurements showed no correlation with emulsion formation; either the solutions showed the same viscosities both with and without silica, or, as pointed out above, in some cases the silicic acid solutions jelled completely.

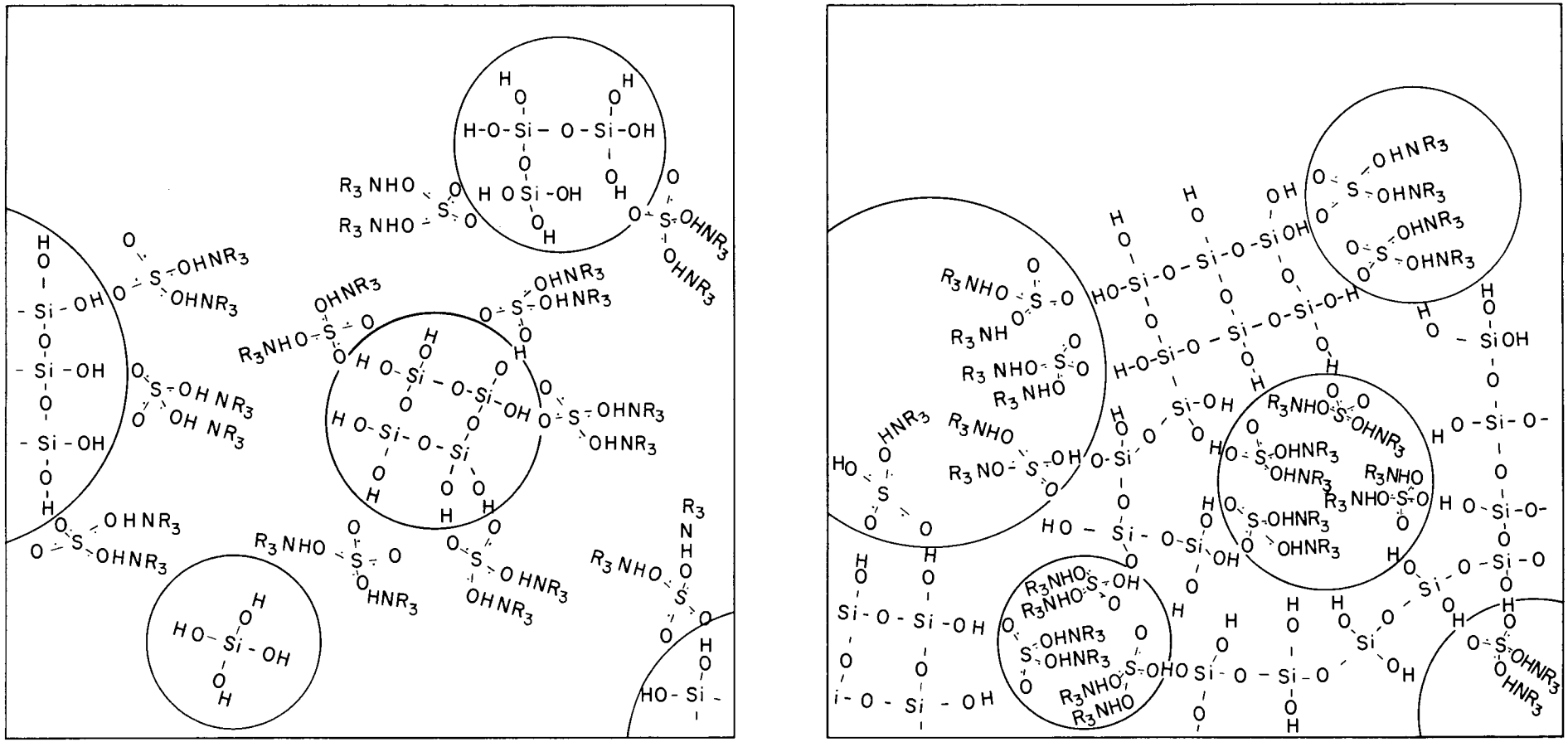
Table 4. Effect of Organic Additives on Phase Separation Time

Aqueous phase: 0.625 g of silicon per liter as silicic acid in 1 M sulfate, pH 1
Organic phase: 0.1 N amine 9D-178 sulfate in kerosene
1 mole of additive used for each equivalent of amine

Additive	Phase Separation Time, min	
	Org. Cont.	Aq. Cont.
None	3.0	>30
Chloroform	3.5	11
Triethyleneglycol dichloride[a]	3.0	7
α,β-dichloroethyl ether[a]	1.7	9
8-Hydroxyquinoline[b]	2.5	7
2-Bromo-4-tert-butylphenol	2.0	20
2,6-ditert-butyl-4-methylphenol	2.7	8
m-Cresol[a]	1.1	7
Butyric acid[b]	2.0	7
Lauric acid	2.0	10

[a]Compounds soluble to the extent of 0.5 to 1 wt % in water. Their distributions from kerosene solutions were not measured but were probably less.

[b]Compounds very soluble in water.



Organic continuous, no possibility of cross linkage

Aqueous continuous, ~~no possibility of cross linkage~~ Cross-linking possible *

Fig. 3. Highly pictorial representation of suggested method of emulsion stabilization by silicic acid.

* See erratum

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