Factors Influencing Phase Disengagement Rates in Solvent Extraction Systems Employing Tertiary Amine Extractants

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ABSTRACT

Phase disengagement rate is a critical property in determining the usefulness of a particular solvent extraction system in hydrometallurgy. A survey of a number of commercial tertiary amine extractants of the type used in uranium extraction hydrometallurgy has been carried out to suggest whether structural factors influence phase disengagement behavior and to provide a useful comparison of different amines with regard to phase disengagement and uranium extraction. The amines $((C_nH_{2n+1})_3N)$ were chosen to cover a range of alkyl chain lengths including straight-chain and branched-chain compositions, and the chemical makeup of the liquid-liquid systems closely paralleled that of the systems used in the Amex uranium extraction process. Batch phase disengagement tests showed significant trends with respect to amine structure and composition using acid sulfate solutions with or without added colloidal silica and actual ore leach solutions as the aqueous phase. In general, organic continuous (OC) phase disengagement became slower with increasing n (number of carbons per chain) whether branched or linear chain, but for any given n, the branched chain amines had much faster OC phase disengagement than the linear chain amines. A key structural factor affecting OC phase disengagement was found

to be the backbone chain length (longest chain in each alkyl group)
since the OC phase disengagement measurements could be correlated
vs backbone chain length on a single curve regardless of whether the
amine was branched or linear. Aqueous continuous (AC) phase disen-
gagement rate was rapid for the acid sulfate solution but decreased
greatly with decreasing n when colloidal silica was added or when
leach solution was used. With both leach and colloidal silica solu-
tions, AC phase disengagement was correlated with wetting behavior
of the amine systems on a glass (silicate) surface. A model based
on silica attachment to the liquid/liquid interface was suggested
to explain the stabilization of AC dispersions by silica and the
related problem of interfacial crud formation.   In addition to
faster AC phase disengagement and less emulsion (crud) stabilization,
the larger molecular weight amines ($n \geq 10$) were found to have higher
uranium extraction coefficients and lower tendencies to form third
phases. Presumably, solubility losses to the aqueous phase are also
lower. The results suggest that the performance of some Amex systems
may be improved by using branched chain tertiary amine extractants
of higher molecular weight than are now normally used.

INTRODUCTION

    The Amex uranium extraction process (1) which evolved in the
mid 1950's represents one of the first successful large-scale appli-
cations of solvent extraction technology in hydrometallurgy and is
still used in much the same form today (2).   In recent years, how-
ever, declining ore grades and rising production costs are creating
incentives for refinements in the existing technology. Outstanding
problems include crud formation, slow phase disengagement, and
solvent loss to the aqueous phase. Together with the need for better
loading and selectivity, these are the familiar challenges facing
solvent extraction technology in general (2).

    In the Amex uranium extraction process (1-4), sulfuric acid
(pH $\sim$1) leach solutions with uranium concentrations in the range of
about 0.2-2 g/ℓ are contacted in a series of countercurrent mixer/
settlers (organic continuous mixing usually) with a kerosene solu-
tion containing 3-5 vol % amine and 2-3 vol % diluent modifier such
as isodecanol. High molecular weight tertiary amines (formula
$(C_nH_{2n+1})_3N$) are the reagents of choice because of their superior
extraction and selectivity characteristics and commercial availabil-
ity. The most popular reagent has been a blend of tertiary amines
containing 8- and 10-carbon straight alkyl chains. Amines of this
structure are not completely compatible with aliphatic diluents such
as kerosene in that their salts tend to separate out of homogeneous

solution as a heavy, viscous third phase in acidic solvent extraction systems (5-7). Use of alcohol diluent modifier eliminates this short-coming and secondarily serves to enhance phase disengagement and decrease crud formation.

Advances in engineering design of mixer/settlers, filters, and decantation equipment continue to improve processing perform-ance in Amex-type processes, but a balanced approach must also include improvements in the solvent system. In the past, a large number of amines were surveyed for possible use in the Amex proc-esses (7), and much was learned about amine extraction of uranium at the same time. However, few laboratory studies have been devoted to elucidating the interfacial chemistry of amines asso-ciated with the problems of phase disengagement and crud formation.

The primary purpose of the present investigation was to examine the effects of amine size and structure on phase disengagement. Nine commercial tertiary amines were tested together with four laboratory-quality amines for uranium extraction and both organic-continuous (OC) and aqueous-continuous (AC) phase disengagement under Amex-type conditions. Synthetic acid sulfate solutions with and without added colloidal silica and actual ore leach solutions were used as the aqueous phases. Phase disengagement results were correlated with amine size and branching and solution wetting behavior on a silicate (glass) surface.

EXPERIMENTAL

Reagents and Solutions

The amines were obtained as follows: trilaurylamine (G. Scibona, C.S.N., Casaccia, Italy), tri-n-octylamine (Aldrich Chemical Co.), tri-2-ethylhexylamine (Eastman), tri-n-decylamine (Eastman), Alamine 336 (Henkel Corp.), Adogens (Sherex Chemical Co.), and AZamines (Mars Chemical Corp.). Tri-n-octylamine was purified by recrystallization as the HCl salt followed by passing the free amine through activated silica (J. T. Baker Chemical Co., 80-200 mesh, heated at 300°C for 72 hrs). In general, activated silica strongly adsorbs polar substances (8), and it was found to remove most or all of the yellow color that is present in some amines. It was further

shown by deliberately contaminating pure tri-n-octylamine with 3%
each of n-octylamine, di-n-octylamine, and dodecyl alcohol that titra-
tion-detectable amounts of these impurities could be completely
removed by passing through activated silica (2 g amine per g silica).
Except as noted in the Results and Discussion section, the other
amines were also purified by silica adsorption and were found by
titration to be in the range 99 ± 1% tertiary amine (based on % of
the neutral equivalent). Since further silica treatment did not
increase the % tertiary amine content, the remaining impurity is
probably not primary or secondary amine. Neutral equivalents were
little affected (±2%).

The amines were diluted to 0.1 N based on measured neutral
equivalent using Kermac 470B kerosene (Kerr McGee Corp.; contains
approximately 17% aromatics) modified with 0, 1, or 1.5 vol %
tridecanol (Enjay Chemical Co.; branched alkyl chains). Before
use, the amine solutions were preequilibrated several times with
pH 1 Na_2SO_4 solution (0.3125 M Na_2SO_4 + 0.1875 M H_2SO_4) to give
primarily the amine sulfate salt. (Throughout, "pH 1 Na_2SO_4 solu-
tion" refers to this composition.) Water was distilled and
deionized, and all other reagents were of reagent quality. UO_2SO_4
and $^{233}UO_2SO_4$ stock solutions were standardized by potentiometric
titration (Oak Ridge National Laboratory Analytical Chemistry
Division) or alpha liquid scintillation counting.

Solutions containing colloidal silica were made in one of three
ways. In the first, an aqueous solution of Na_2SiO_4 was added to the
required amount of H_2SO_4 to give pH 1 Na_2SO_4 solution plus 18.8 g/ℓ
SiO_2 in a Waring blender. After six days of storage at room tempera-
ture in a polyethylene bottle, the solution was diluted with pH 1
Na_2SO_4 solution to give 0.80 g/ℓ SiO_2. On first acidifying the
Na_2SiO_3 with violent agitation, a solution of mostly monosilicic acid
$(Si(OH)_4)$ is formed which then undergoes gradual polymerization to
give colloidal SiO_2 (9). In the second method, Cab-O-Sil EH-5 (Cabot
Corp.) fumed silica was simply dispersed in pH 1 Na_2SO_4 solution in a
Waring blender to give a 5% sol. Thirdly, silica gel made by
acidifying a solution of Na_2SiO_3 was washed with H_2O, refluxed
(peptized) 2 days in H_2O, centrifuged, decanted, and evaporated
down to yield a stable 5% sol.

Uranium ore leach solutions were provided by Sohio Western
Mining Company, L-Bar Uranium Project, Albuquerque, NM and Kerr-McGee
Nuclear Corporation, Grants New Mexico Operations, Grants, NM. One
sample was used for most of the work reported here and analyzed as
follows (ORNL Analytical Chemistry Division): 0.4 g/ℓ U, 1.1 g/ℓ
Al, 2.6 g/ℓ Fe, 0.8 g/ℓ Na, 0.08 g/ℓ K, 0.5 g/ℓ Mg, 0.6 g/ℓ Ca,
0.04 g/ℓ Mn, 0.04 g/ℓ V, 0.001 g/ℓ Zr, 0.06 g/ℓ As, 0.08 g/ℓ PO$_4$,
40 g/ℓ SO$_4$ (nominal), 0.4 g/ℓ Cl, 1.0 g/ℓ SiO$_2$, pH $\sim$0.5. These
values are typical of other western ore leach solutions except that
the uranium value is lower (3,4).

Apparatus and Procedures

Determination of neutral equivalent, primary and secondary
amine content, and sulfuric acid extraction was carried out by
nonaqueous titration (7,10) using a combination glass, Ag/AgCl
electrode and an automatic differential titrator. Assessment of
third phase formation in 0.1 N amine solutions in unmodified kerosene
was done by successively equilibrating the organic solutions with
increasingly acidic H$_2$SO$_4$/Na$_2$SO$_4$ solutions ($\sim$0.5 pH units per equili-
bration) until the third phase was clearly seen in the narrow portion
of the separatory funnel. Viscosity was measured by the capillary
flow method in an Ostwald Viscometer (11) and interfacial tension,
by the drop-volume method (12).

Liquid/liquid/solid contact angles were determined by the
Wilhelmy plate method (13) at room temperature using glass micro-
scope slides and the previously equilibrated system, pH 1 Na$_2$SO$_4$
solution/0.1 N amine sulfate in 1.5 vol % tridecanol-modified
kerosene. The microscope slides were treated in conc. HNO$_3$ for
2 hrs, boiling H$_2$O for 3 hrs (to ensure complete surface hydration),
fresh pH 1 Na$_2$SO$_4$ solution for 1 hr, and finally, the actual organic-
equilibrated aqueous phase for 1 hr, taking care to keep the slides
wet during transfers. The receding angles were obtained by slowly
withdrawing the aqueous phase via a syringe pump so that in effect
the plate traveled from the aqueous phase into the organic phase.
The travel was stopped at 3-5 points for weight and cathetometer
readings. Buoyancy corrections were applied to give the contact
angles with a precision of ±2° over a 1 cm length of plate. For

advancing angles, the aqueous phase was returned to the cell in
like manner.

Phase-disengagement tests were carried out at 25.0°C in a 5 cm
dia. glass, paddle mixer. Four vertical baffles placed 90° apart
were pressed to a depth of 0.5 cm each, and the total liquid height
(1:1 phase volume ratio) was 5 cm at the organic/air interface.
Except for the silicic acid experiments, the aqueous and organic
phases were stirred OC for 1 hr before conducting the phase-disen-
gagement measurements. During an experiment, the glass paddle
(1 cm x 3 cm x 1 mm) was initially started in the organic phase to
mix OC and then lowered via a slip joint on the shaft to the mid
position for a 3 min stir time at 600 rpm. For AC mixing, the
paddle could be started at the midpoint. After 3 min, the motor
was stopped, the paddle was withdrawn, and the dispersion band
was monitored visually and with the aid of a cathetometer. Some
dual dispersion (droplets within droplets) was observed in some of
the AC runs, especially with the amine systems with slow OC phase
disengagement (e.g., trilaurylamine). However, a small amount of
dual dispersion did not appear to significantly affect phase disen-
gagement in that if a dual dispersion was deliberately created (by
stirring OC and subsequently stirring AC before the OC dispersion
completely settled), AC break times were about the same as when no
dual dispersion was made. Break times were also unaffected by
stirring speed in the region of 600-1000 rpm in which the system
was completely dispersed yet did not vortex severely. Break time
was defined as the time for the dispersion band to disappear,
leaving about half of the interface clear. Where break times are
reported, they are usually the average of three or more measurements
in one run and were reproducible to ±10% in a given run and ±15%
between separate runs. Some change in break time with repeated
mixing was observed in some of the AC tests, and only the value
for the first mixing is reported since the initial response of the
system is of the most practical value.

In some of the AC dispersions, where leach solutions or syn-
thetic Na_2SO_4 solutions containing silica were used, the break
times were very long and ill-defined due to the apparent stabiliza-
tion of approximately the last 10% of the dispersion. Often the

time for the last 10% of the dispersion to settle greatly exceeded
the time for the first 90%; thus, it was thought that a better
measure of phase disengagement rate would be represented by the
time for 50% of the dispersion band to settle, the "half-volume"
time. Half-volume times were found to give the same relative order
as break times for the various chemical systems when a well defined
break time could be obtained. More detailed analysis of batch
settling including drop size measurements is the subject of current
investigation.

     With the aid of ^{233}U tracer, uranium loading curves were
determined by alpha liquid scintillation counting on a Packard
Tri-Carb Liquid Scintillation Spectrometer, employing an approxi-
mately 10% β-γ background correction. Both organic and aqueous
phases were counted after equilibration, first extracting the
aqueous phase with 0.1 N triisooctylamine sulfate in xylene.
Material balances were excellent (100 ± 1%), and spotchecks by Photon-
Electron Rejecting Alpha Liquid Scintillation (PERALS) spectrometry
(14) agreed to within a few percent. Equilibrations were carried
out at 25.0°C with quiet interface stirring for 10 hrs (2 hrs was
found to be sufficient) in the absence of light (15), though ordinary
room light had no adverse effects. Organic phases were 0.1 N amine
(as received) sulfate in 1 vol % tridecanol-modified kerosene, and
aqueous phases were pH 1 Na_2SO_4 solution to which was added appro-
priate UO_2SO_4 and tracer.

                          RESULTS AND DISCUSSION

Reagents

     Table 1 identifies the amine extractants examined in these
studies. The commercial straight-chain tertiary amines, T810A and
T812A, are blends containing even-numbered alkyl chains of 6 to 14
carbons, and the average molecular weight is equal to the neutral
equivalent. The branched "iso" alkylamines have more narrow molec-
ular weight distributions but can vary with respect to degree and
points of branching. "Iso" branching consists of methyl groups on
an alkyl backbone roughly 6 and 9 carbons long in the cases of TIOA
and TITA, respectively (1). Closely approximating the nominal

TABLE 1

Tertiary Amine Extractants

Amine[a]	Abb.	Trade Name[b]	As-Received Neutral Equiv.[c]	As-Received %3°[d]	Purified Neutral Equiv.[c]	Total Carbons per Alkyl[c]	Backbone Chainlength[f]	%C6	%C8	%C10	%C12	%C13	%C14
Commercial amines:													
Triisooctylamine	TIOA	Adogen 381	370	98.1	360	8.2	6		99				
Triisooctylamine	TIOA	A2amine T8B	356	97.4	358	8.1	6		99				
Triisodecylamine	TIDA	Adogen 382	448	93.3	441	10.1	7			99			
Triisodecylamine	TIDA	A2amine T10B	447	98.0	443	10.1	7			99			
Triisotridecylamine	TITA	Adogen 383	570	95[e]	568	13.1	8					99	
Tri-C8,C10-amine	T810A	Adogen 364	397	93.7	393	8.9	8.9	5	60	33	2		
Tri-C8,C10-amine	T810A	Alamine 336	396	94.1	392	8.9	8.9	5	60	33	2		
Tri-C8,C10-amine	T810A	A2amine T810	410	97.7	388	8.8	8.8						
Tri-C8,C10,C12-amine	T812A	Adogen 368	434	96.6	432	9.9	9.9	3	40	25	30		2
Laboratory amines													
Tri-n-octylamine	TOA	—			355	8	8		100				
Tri-n-decylamine	TDA	—			438[e]	10	10			100			
Trilaurylamine	TLA	—			522[e]	12	12				100		
Tri-2-ethylhexylamine	T2EHA	—			354[e]	8	6		100				

[a] The prefix "iso" denotes branched hydrocarbon chains. TITA is sometimes referred to as tristridecylamine, although it is branched.

[b] Vendors are given in the Experimental Section.

[c] Grams/equivalent as determined by titration.

[d] Given as % of the titratable amine (% of neutral equivalent).

[e] Nominal values provided by vendors or theoretical value.

[f] Computed from the neutral equivalent (NE) of purified amines having the chemical formula, $(C_nH_{2n+1})_3N$, where $n = (\frac{1}{42.1})(NE-17)$.

[g] Defined as $n-n_b$, where n_b is the number of branching carbons. For TIOA and TITA, the values were taken as an estimate from the literature (1), and TIDA was taken as the intermediate value. For T810A and T812A, the average value of n was used.
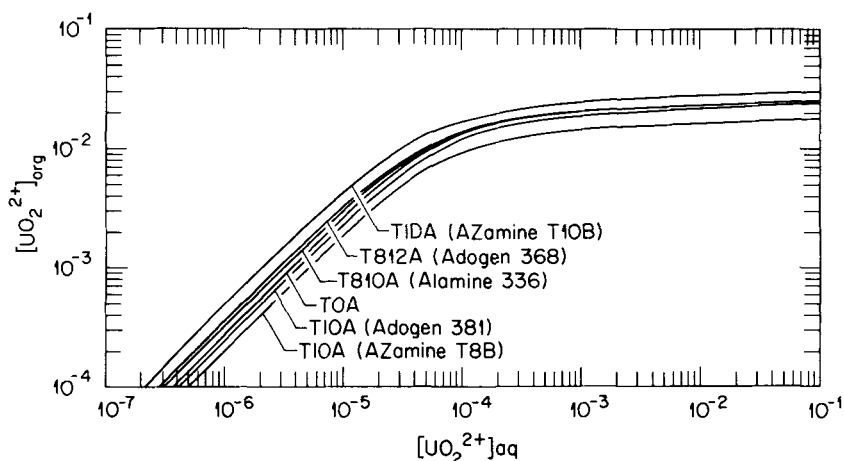
FIGURE 1. Uranium (VI) Extraction Isotherms for a Representative
           Group of Tertiary Amine Extractants. Conditions: 0.1 N
           amine sulfate in 1 vol % tridecanol-modified kerosene vs
           pH 1 Na$_2$SO$_4$ solution containing UO$_2$SO$_4$ and tracer; 25°C;
           as-received amines.

values provided by the vendors, the as-received commercial amines
titrated in the range 93-98% tertiary. The balance of the titrat-
able amines is mostly secondary with a minor amount of primary.
Since these impurities are known to cause phase disengagement prob-
lems (16), they were removed by silica adsorption prior to the phase-
disengagement tests.

Third Phase Formation

    Table 2 gives the approximate H$_2$SO$_4$ acidity at which third-phase
formation begins for the various amines in unmodified kerosene. The
results reflect the formation of the third phase by the bisulfate
salts ((R$_3$NH)HSO$_4$) rather than the normal sulfate salts ((R$_3$NH)$_2$SO$_4$)
(1) and show a trend toward less acid extraction and a lower pH
threshold for third-phase formation as molecular weight and branching
increase.

Uranium Loading Isotherms

    Figure 1 shows the U(VI) extraction isotherms for selected amines
from pH 1 Na$_2$SO$_4$ solution at 25°C, using 0.1 N amine sulfate in 1 vol %

TABLE 2

Selected Properties of Tertiary Amine Solutions[a]

Amine	Third Phase[b]	Acid Extraction[d]	Viscosity (Pa·S)[e]	Interfacial tension (N/m)	Contact angles (deg)[f] receding	advancing
TIOA (Adogen 381)	pH 1.5	1.15	0.00240	0.0099	20	47
TIOA (AZamine T8B)	pH 1.5	1.19	0.00241	0.0097	21	49
TIDA (Adogen 382)	2 N H_2SO_4	1.01	0.00239	0.0132	15	36
TIDA (AZamine T10B)	2 N H_2SO_4	1.10	0.00241	0.0136	17	40
TITA (Adogen 383)	15 N H_2SO_4	1.00	0.00251	0.0165	10	26
T810A (Adogen 364)	pH 1.0	1.27	0.00244	0.0115	21	46
T810A (Alanine 336)	pH 1.0	1.29	0.00246	0.0116	17	45
T810A (AZamine T810)	pH 1.0	1.28	0.00245	0.0112	21	47
T812A (Adogen 368)	pH 0.5	1.26	0.00250	0.0115	19	44
TOA	pH 1.5	1.35	0.00245	0.0106	18	50
TLA	1 N H_2SO_4[c]		0.00261	0.0146	12	27
T2EHA	5 N H_2SO_4		0.00209	0.0090	0	34

[a]Except as noted, 1.5 vol % tridecanol-modified kerosene diluent; preequilibrated with pH 1 Na_2SO_4 solution; purified amines; 25°C. Average density = 0.815 ± 0.001 g/ℓ.

[b]Acidity at which third phase formation occurred. pH values are given for aqueous solutions adjusted to $[SO_4]$total = 0.5 M with Na_2SO_4. Unmodified kerosene; as received amines; room temperature.

[c]The organic phase became a viscous gel.

[d]Acid/amine equivalent ratio in the organic layer equilibrated with pH 1 Na_2SO_4 solution. A ratio of 1.0 corresponds to the amine sulfate form. Room temperature.

[e]Pa·S = 10^{-3} centipoise.

[f]Solid phase = glass microscope slides. The angle is referenced through the aqueous phase.

TABLE 3

Uranium Extraction by Tertiary Amines[a]

Amine	E_a^{o}[b]	Uranium loading[c]	
		$[U]_{org}$	amine/ruanium
TOA	278	0.0242	4.1
TIOA (Adogen 381)	246	0.0234	4.3
TIOA (AZamine T8B)	208	0.0176	5.7
TIDA (Adogen 382)	320	0.0230	4.3
TIDA (AZamine T10B)	494	0.0295	3.4
T810A (Adogen 364)	299	0.0238	4.2
T810A (Alamine 336)	325	0.0247	4.0
T810A (AZamine T810)	333	0.0245	4.1
T812A (Adogen 368)	362	0.0248	4.0

[a] 0.1 N amine sulfate in kerosene modified with
1 vol % tridecanol; as-received amines. Aqueous
phase is pH 1 Na_2SO_4 solution plus added UO_2SO_4;
25°C.

[b] Calculated at low loading, $[UO_2^{2+}]_{org} = 1.34$ x
10^{-4} M.

[c] $[UO_2^{2+}]_{aq} = 0.1$ M; amine/uranium mole ratios based
on amine neutral equivalent.

tridecanol-modified kerosene. Under these conditions, all of the amines
tested are quite good extractants for U(VI), with extraction
coefficients in the range of about 200-500 at low loading (see
Table 3). Conforming to trends in earlier data (1), the extraction
coefficients increase with molecular weight or chain length within
a similar group of amines, though there is some noticeable vari-
ability among samples of similar material from different vendors,
especially among the branched amines. T2EHA is known (1) to be a
relatively poor extractant for U(VI) probably owing to steric inter-
ference with bonding interactions at the nitrogen. At the upper end
of the loading isotherms, the amine/uranium mole ratios (calculated
using the amine neutral equivalents) approach a value of 4.0 with the
notable exceptions of samples of TIOA (AZamine T8B) and TIDA
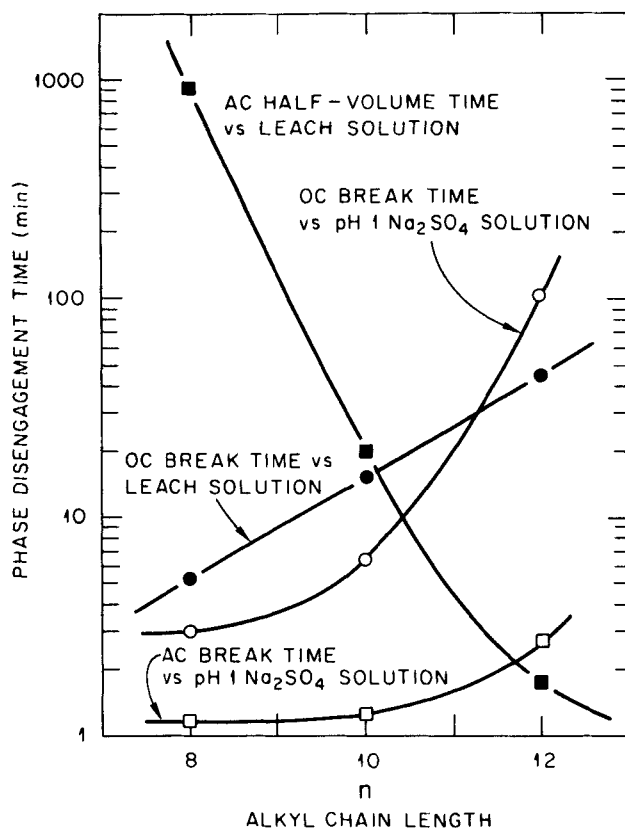(AZamine T10B) with respective ratios of 5.7 and 3.4.

FIGURE 2.   Phase Disengagement Comparison of TOA, TDA, and TLA vs n.
            Conditions: 0.1 N amine sulfate in 1.5 vol % tridecanol-
            modified kerosene vs pH 1 Na_2SO_4 solution or leach solution;
            25°C.

Phase Disengagement

   Laboratory amines. Phase disengagement results for the pure
straight-chain compounds, TOA, TDA, and TLA, are compared in Fig. 2
in which break times (or half-volume times) are plotted vs n, the
total number of carbons per alkyl group. As n increases, OC break
time increases rapidly whether pH 1 Na_2SO_4 solution or leach solu-
tion is used as the aqueous phase, and a small increase in AC break
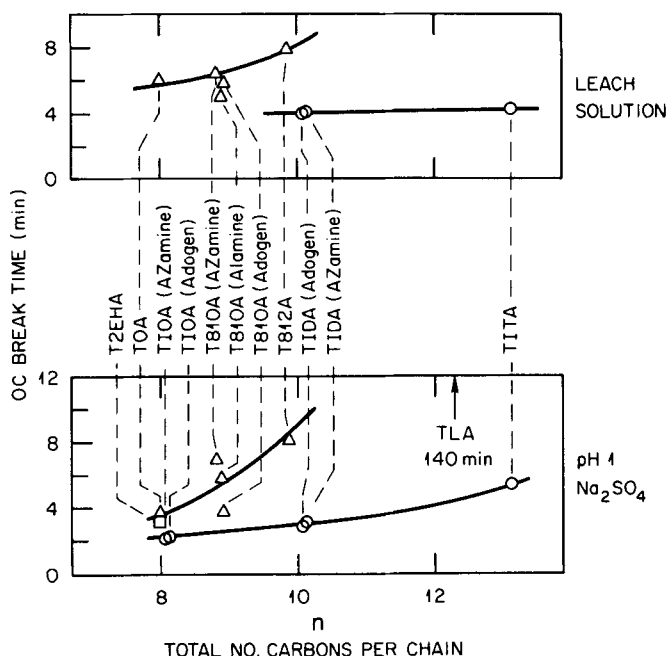time with increasing n also occurs using pH 1 Na_2SO_4 solution. A

FIGURE 3. OC Break Time vs n. Conditions: same as Fig. 2; purified
           amines. Key: △ -straight chain, ◯ -"iso" branched chain,
           ☐ -T2EHA.

dramatic reversal of this pattern is observed when leach solution is
substituted for pH 1 Na_2SO_4 solution (half-volume times are plotted
in this case because full break times were very long and poorly
defined). TOA was especially affected by the substitution, under-
going an increase in break time of well over four orders of magni-
tude (1.2 min to >13 days). On the other hand, TLA was affected very
little by the substitution, jumping from a break time of 2.7 min to
6.7 min. Clearly, there are some remarkable differences in OC and
AC phase disengagement brought about by the addition of only four
carbons to each alkyl chain.

    Commercial and laboratory amines — OC mixing. Figure 3 shows
the results of a separate OC experiment in which the commercial amines
and several laboratory amines were compared under identical conditions.
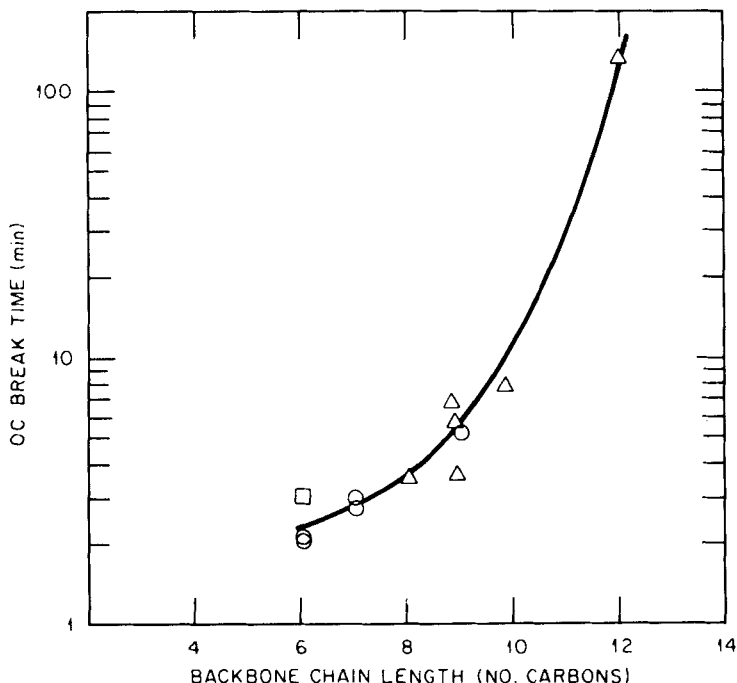
FIGURE 4.   Effect of Backbone Chain Length on OC Break Time.   The
            data from Fig. 3 are replotted against backbone chain
            length (Table 1).

(The results are not directly comparable to Fig. 2 because the leach
solution had been sampled from the bottle and used at an earlier date,
and a similar but not identical mixing vessel was used.)   Essentially
the same trends are observed as seen in Fig. 2, except that for a
given n, the "iso" branched amines perform much better than the
straight-chain amines.   However, if the amines are compared on the
basis of backbone chain length (longest possible chain in an alkyl
group; see Table 1), the OC break times fall about a single curve as
shown in Fig. 4.   The correlation is surprisingly good considering
that the commercial amines contain a distribution of chain lengths,
branching points, etc.   Thus, if one desires to increase the molecular
weight of an amine extractant (e.g., to decrease aqueous solubility),
the addition of carbons as branches to a given backbone chain will

tend to have a minor effect on OC phase disengagement as compared with
adding the carbons to the end of the backbone chain.

Theoretical analysis of droplet coalescence indicates that the
rate of coalescence (breaking) is related to the rate of thinning of
the liquid film between approaching droplets. In agreement with
experiment, the analysis predicts that film thinning and, hence,
breaking will be retarded by the presence of surfactants soluble in
the continuous phase (17,18). By their very design, most solvent
extraction reagents are interface active (19). For example, TOA sul-
fate and related N-methyl quaternary ammonium salts saturate the
interface at low concentrations (20). The results in Figs. 2-4 make
it clear that the presence of the amine sulfate does indeed greatly
influence OC phase disengagement and that the effect is very dependent
on the size and structure of the amine. However, it is not yet known
why the structural trends bring about the observed trends in the phase
disengagement. Presumably, the systematic effects lie in key dynamic
interfacial properties such as interfacial viscosity and elasticity
(17,18) since the differences in bulk organic phase viscosities and
densities are minor (Table 2).

A comparison of Fig. 3 and Table 2 shows that OC break times
increase as interfacial tensions increase. This is opposite to the
effect expected from reasoning that higher interfacial tensions
indicate greater thermodynamic instability toward breaking and there-
fore cause a decrease in break time. As shown by repeated experience
(21), interfacial tension is not by itself a reliable measure for the
prediction of phase disengagement rates, and in fact, just the opposite
trend was noted in earlier work on amine solvent extraction (4). In
general, it is well known that rates of physical processes do not
necessarily correlate with net thermodynamic instability, and it
follows that the effect of interfacial tension on phase disengagement
rate must arise in other ways such as its influence on drop shape in
the dispersion band. Apparently, other variables can be more important
than interfacial tension.

In their studies for the scale-up of the Amex process, Ryon and
Lowrie examined the effects of several variables on phase disengagement,
including amine concentration and modifier concentration (4). Not
surprisingly, at constant modifier concentration, OC phase disengage-
ment becomes worse as amine is added. They also found that the effect

of amine structure may be swamped out by the addition of enough modi-
fier (5 to 10 vol %). There is incentive to go to less modifier, how-
ever, since it represents added expense in the process. Although its
role is not precisely understood, the modifier probably influences
phase disengagement by interacting with the amine sulfate in the bulk
organic phase and also possibly by its own presence at the interface.
Recognizing the role of the modifier in third phase prevention (6),
the bulk phase interaction is important and in effect withdraws amine
from the interface as shown by a rise in interfacial tension (4). The
effect of uranium loading probably operates in this manner also, and
on seven successive contacts with leach solution, OC break time was
observed in these tests to drop from 3.4 to 1.5 min in the system
0.1 N Alamine 336 in 1 vol % tridecanol-modified kerosene.

The effect of impurities in the commercial extractants on OC
phase disengagement was shown to be minor (not true for AC) by
testing an as-received sample of Alamine 336 in the same series of
tests shown in Fig. 3. Within experimental error, the same break
time was observed for both as-received and purified samples. In
actual plant operation, however, there are many other sources of
impurities than just from the amine extractants (e.g. solvent
degradation products and humic acids from the ore), and their
buildup over time can have a marked effect on phase disengagement
rates (16,21).

Commercial and laboratory amines — AC mixing. The Amex process
normally uses OC mixing, but AC phase disengagement should not be over-
looked because (a) it is difficult to avoid some formation of AC
dispersion even when nominally mixing OC, (b) it is advantageous under
some conditions (i.e., little or no suspended solids in the aqueous
phase as is the case in the related Eluex process (2)) to use AC
mixing in some of the mixers, and (c) it may be closely related to
interfacial crud or emulsion formation. The results for the commer-
cial amines shown in Fig. 5 again follow the same general patterns
observed for the laboratory amines in Fig. 2. (Fig. 5 is an extension
of the same experiment shown in Fig. 3 except that the mixing was AC.)
AC phase disengagement was rapid and not very sensitive to amine
structure using pH 1 Na_2SO_4 solution as the aqueous phase. AC break
times with pH 1 Na_2SO_4 solution were, in fact, significantly less than
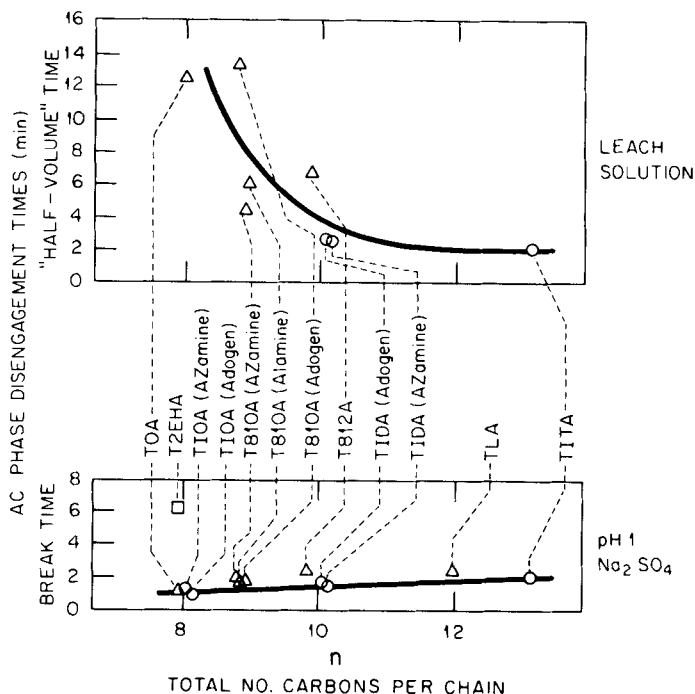
FIGURE 5. AC Phase Disengagement vs n. Conditions: same solutions,
           conditions, and key as used in Fig. 3. Half-volume times
           are plotted for the leach solution experiments because full
           break times were excessively long and indefinite.

OC break times (Fig. 3), though T2EHA was an exception. These results
are consistent with the theoretical analysis of droplet coalescence
which predicts that surface active substances will have their predomi-
nant effect on coalescence only when soluble in the continuous phase
(17).

    When leach solution was used as the aqueous phase, however, full
AC break times increased greatly for the amines with low n (e.g., TOA,
break time >30 min) but again not much for the amines with high n
(TIDA-AZamine, break time 3.6 min; TIDA-Adogen, 4.1 min; TITA, 3.6 min).
This trend is reflected in the half-volume times plotted in Fig. 5.
With the available data, there did not appear to be a correlation with
backbone chainlength, as there was with OC mixing.

    The extremely slow AC phase disengagement observed for some amines
vs leach solution has been attributed to the presence of silica (typi-
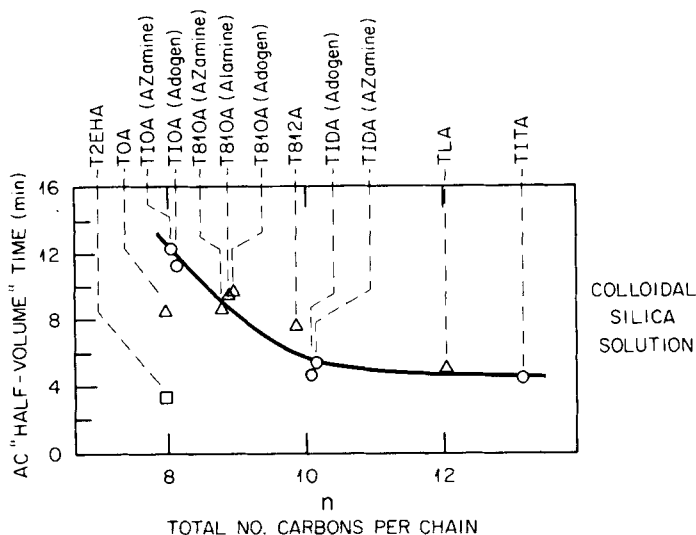
FIGURE 6.   AC Phase Disengagement vs n Using Colloidal Silica Solution
            as the Aqueous Phase. The AC experiment in Fig. 5 was
            repeated except that the aqueous phase was pH 1 Na₂SO₄ solu-
            tion containing 0.8 g/ℓ SiO₂. The organic phases had been
            preequilibrated with pH 1 Na₂SO₄ solution only.

cally 1.0 g/ℓ as SiO_2), and it is well known that synthetic silica solu-
tions can cause severe emulsion problems in amine systems (4,16,22).
It is therefore entirely consistent to find that when a pH 1 Na_2SO_4
solution containing 0.8 g/ℓ SiO_2 is used as the aqueous phase, the
same general trend in AC half-volume times (Fig. 6) is observed as when
leach solution was the aqueous phase (Fig. 5). The low-n amines (TOA
and TIOA) produced dispersions with silica-containing aqueous phases
that were so stable that a layer of emulsion remained at the interface
even after 2 months. The high-n amines, TITA, TLA, and TIDA, had full
break times of 13, 19, and 26 min, respectively.

     Figure 6 illustrates the effect of amine structure on the amine
sulfate/silica interaction. The exceptionally low break time of T2EHA
of 4.3 min may be due to steric interference with that interaction.
Some preliminary experimentation has shown that the effect of silica on
AC phase disengagement is extremely sensitive to the method of prepara-
tion of the silica solution (sol). The effect appears to be related to

the extent of polymerization (23) of silicic acid ($Si(OH)_4$) because
fresh solutions of silicic acid made from the careful acidification of
Na_2SiO_3 solutions slow down AC phase disengagement significantly only
after aging (22). Further, silica sols made by dispersing fumed silica
or silica gel have an enormous retarding effect, even at only 20 ppm
SiO_2. Leach solutions contain about 1 g/ℓ SiO_2, nearly 10 times the
solubility of monosilicic acid (23), and polymerization and aggregation
phenomena are probably responsible for the observed worsening of AC
phase disengagement with age (4). This may explain the intensified
phase-disengagement and emulsion problems that occur when recycling
solutions from a tailings pond back into the solvent-extraction circuit
in actual mill operation (24). It is not clear what chemical species
are polymerizing in leach solution, however, because silicic acid may
polymerize in the presence of metal ions as silicates (23). In any
case, the results suggest that the interaction of the amine sulfate
with synthetic colloidal silica is similar to the interaction with
colloidal silica or silicates in leach solution.

Whereas purity of the amines did not appear to be a predominant
factor in the OC tests, it did prove important in the AC tests in
which leach solution was used as the aqueous phase. Thus, in the
side-by-side comparison of the phase disengagement of purified vs
as-received Alamine 336 described in the previous section, AC half-
volume times of 4.3 min vs 8.2 min and break times of 12 min vs
>14 hr were obtained, respectively. These results suggest that an
impurity in the amines has an even stronger interaction with inter-
facial silica than does the major amine compound.

Effect of solids at liquid-liquid interfaces. Results of
the AC phase-disengagement experiments with added silica suggest
that the behavior of particulate matter at the aqueous/organic
interface is an important factor in phase disengagement. An obvious
analogy with froth (air/liquid) and oil (liquid/liquid) flotation (25)
of suspended solids suggests that the mechanism by which colloidal
silica impedes AC phase disengagement involves particle attachment at
the liquid/liquid interface. As shown in Fig. 7, particle attachment
becomes thermodynamically possible when the liquid/liquid/solid contact
angle, θ, is nonzero (i.e., $0° < \theta < 180°$) (26). This is, particle
attachment can occur if the organic phase partially wets the solid
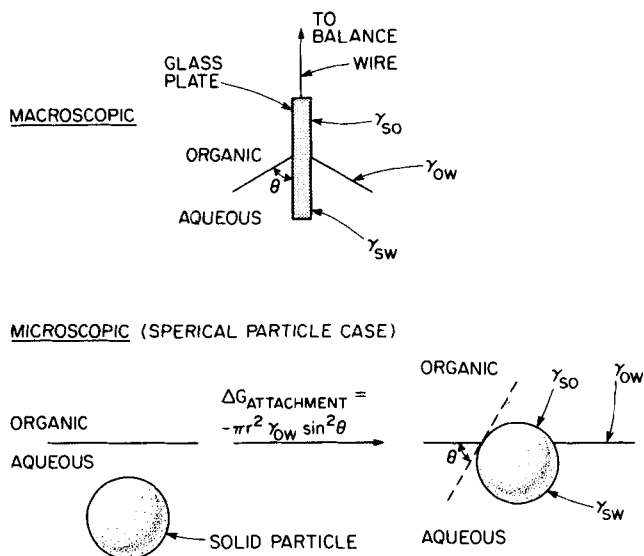
FIGURE 7.   Contact Angles by the Wilhelmy Plate Method to Predict
            Microscopic Particle Attachment to the Liquid/Liquid Inter-
            face.   The interfacial free energies, γ, are given according
            to the subscripts ow = oil/water, so = solid/oil, and sw =
            solid/water.   In the lower right, the dashed line is a tan-
            gent line at the point of contact between the solid particle
            and the liquid/liquid interface.

surface. Contact angles of a particular liquid/liquid system at the
surface of a solid substance are, of course, directly measurable only
on the macroscopic scale, but such measurements can be successfully
used to predict the attachment of particulate forms of that solid at
that liquid/liquid interface, even for solids of colloidal size (25).

To investigate the relationship of such a wetting mechanism to
AC phase disengagement in these amine sulfate systems in the presence
of silica, contact-angle experiments were carried out on the system,
glass/pH 1 Na_2SO_4 solution/0.1 N amine sulfate in 1.5 vol % tridecanol-
modified kerosene. Glass microscope slides were used as a convenient
approximation of the silica surface (27). No attempt was made to avoid
the large hysteresis effect (difference between advancing and receding
angles), and both advancing and receding angles are given in Table 2.
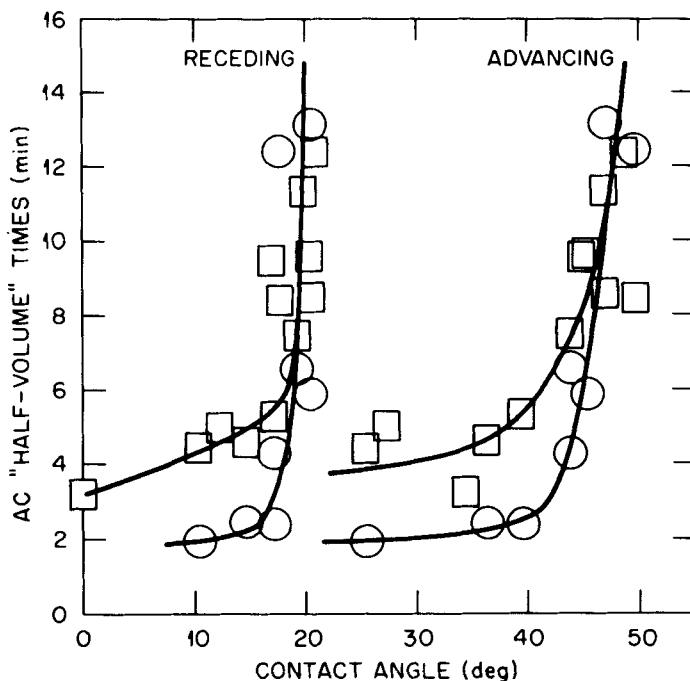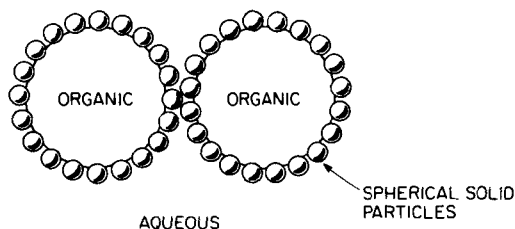In all but one case (T2EHA), nonzero angles acute to the aqueous phase

FIGURE 8.   AC Phase Disengagement vs Contact Angle.   AC half-volume
            times from Figs. 5 and 6 are plotted vs the organic/aqueous/
            glass contact angles from Table 2.   Key: ☐ - colloidal
            silica solution and ◯ -leach solution.

were obtained. Despite the hysteresis effect, a significant pattern

developed when AC phase-disengagement times were plotted vs contact

angle (Fig. 8). Those amine systems that broke the fastest, with

either leach solution or silica solution as the aqueous phase, had the

lowest angles whether advancing or receding.

    The hysteresis effect precludes any quantitative interpretation

of the contact-angle data, but assuming that the glass surface is a

reasonably valid approximation to the silica surface, some qualitative

statements can be made. First, there are indeed differences in wetting

of the glass (silicate) surface among the various amine systems. Through

the Young equation (eq. 1) (26), these differences in contact angle

indicate differences in chemical interactions at the glass surface and

imply differences in silica particle attachment:

AQUEOUS CONTINUOUS (PARTICLES ON OUTSIDE OF DROPLETS)
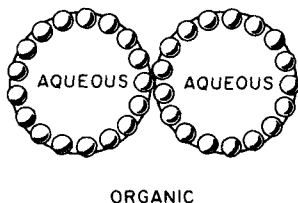
ORGANIC CONTINUOUS (PARTICLES ON INSIDE OF DROPLETS)

FIGURE 9. "Armoring" of Droplets by Solid Particles. Particles
predominantly wetted by the aqueous phase (acute contact angle)
will coat the outside of the organic droplets in AC disper-
sions, obstructing coalescence, but in OC dispersions, the
obstruction does not exist.

$$\gamma_{ow}\cos\,\theta = \gamma_{so}-\gamma_{sw} \tag{1}$$

where γ is the interfacial free energy, and the subscripts, ow, so,
and sw, denote the oil/water, solid/oil, and solid/water interfaces.
Inspection of Table 2 reveals that γ_{ow} and cos θ both increase together
over the series of amines and that the term $\gamma_{so}-\gamma_{sw}$ therefore varies
by about 0.010–0.015 J/m^2. Second, the nonzero angles imply that silica
particles can indeed become attached or wetted at the liquid/liquid
interface since the free energy of attachment is negative (spherical
particles case) (26):

$$\Delta G = -\pi r^2 \gamma_{ow}\sin^2\,\theta \tag{2}$$

Third, since the measured angles are all acute, it can be inferred

from Fig. 7 that the bulk of a single silica particle attached to the
interface will lie on the aqueous side of the interface (28). Thus, in
an AC dispersion, the organic droplets can become encapsulated in a
"suit of armor" that mechanically obstructs coalescence as shown in
Fig. 9 (29).

    In previous studies, it has been shown that suspended solids
only stabilize dispersions when a nonzero macroscopic contact angle
is observed and also only when the continuous phase has the acute
angle (4,18,29). As shown in Fig. 9, significant mechanical obstruc-
tion to droplet coalescence due to particulate matter is expected when
the particles coat the outside of the droplets, and this is consistent
with past (22) and present observations on amine systems: AC phase
disengagement is greatly hindered by silica, but OC phase disengagement
is not (30). It is apparent from eq. 2 that the free energy of attach-
ment will diminish rapidly as θ approaches zero, eventually reaching a
point where viscous and/or thermal effects can cause detachment. In
mineral flotation, this point appears to be in the domain of 10 - 20° (31).
Therefore, it is possible to understand how the amine systems with the
lowest contact angles could show improved AC phase disengagement in
the presence of silica even though all the systems had some tendency
to wet the glass.

    Microscopic observations. Using silica particles in the range
of 10-100 μm, particle attachment at the interface can be shown
directly by ordinary light microscopy. Figure 10 is a photograph of
the interface in the system 0.1 M TOA in 1.5 vol % tridecanol-modified
kerosene vs pH 1 Na_2SO_4 solution with about 0.2 mg/mℓ silica particles,
and the round structures are organic droplets resting just under the
interface. The experiment was carried out as a sequence of observa-
tions, and Fig. 10 was the last step. Initially, the silica particles
were briefly dispersed in the aqueous phase by gentle stirring without
disrupting the interface. The interface developed a thin, rigid skin
which microscopy showed to be linked "rafts" of silica particles as
can be seen in Fig. 10. After rapid stirring for several minutes to
create an AC dispersion, the system was allowed to settle to a discrete
interface. Microscopy showed many small organic droplets rising to
the interface and coalescing in the clear patches devoid of silica
particles. The droplets that rose underneath the rafts of silica
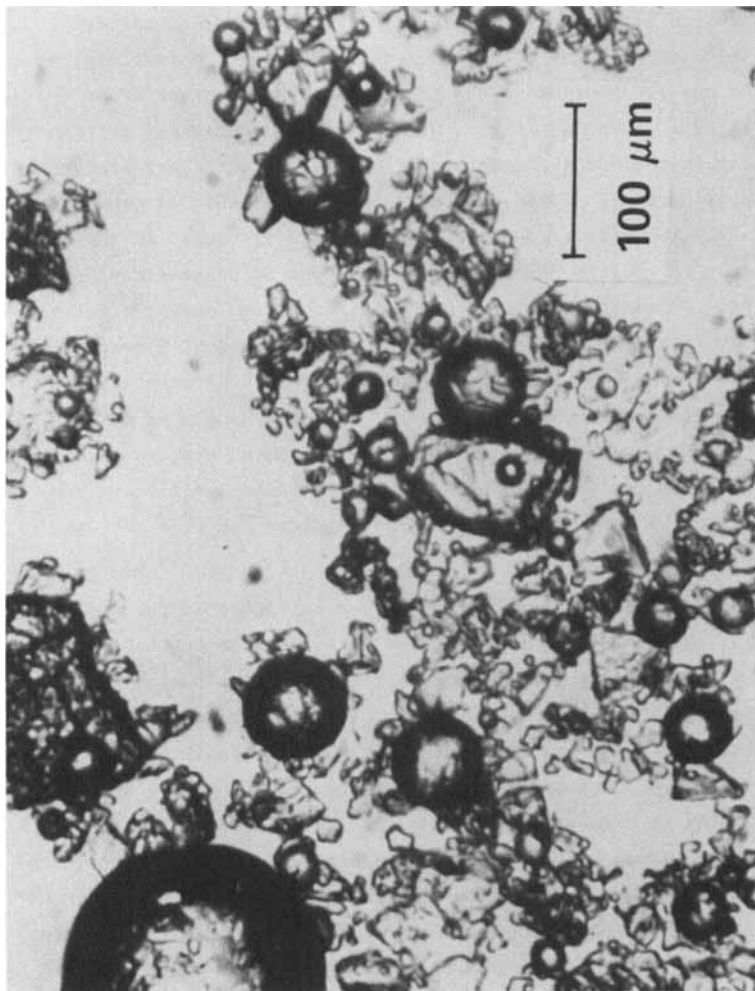
FIGURE 10. Photomicrograph of the Organic/Aqueous Interface in the Presence of 10-100 μm Silica Particles. Using the system, 0.1 N TOA sulfate in 1.5 vol% tri-decanol-modified kerosene/pH 1 Na_2SO_4 solution containing 0.2 mg/mℓ silica (Aldrich, 99.9999% SiO_2 sized to 10-100 μm by sedimentation), an AC disper-sion was formed and allowed to settle for one day.

particles did not coalesce and remained at the interface after one
day as shown in Fig. 10. The experiment is a vivid demonstration
of silica particle attachment at the interface and inhibition of
coalescence in agreement with the predictions of the contact angle
work.

    Interfacial crud formation. Interfacial crud has been described
as the buildup of particulate solid matter at the interface in solvent
extraction systems, a problem that becomes severe when the suspended solids
content of the aqueous phase is high (32,33). Figure 10 may actually
represent the initial stages of crud formation. A layer of particulate
matter covering the interface stabilizes organic droplets with respect to
coalescence, thus forming more interfacial area for the further
collection of solids. Eventually, a large band of loose solid mate-
rial can form, trapping significant quantities of solvent. This model
suggests that crud may be decreased by using a well-designed mixer
that produces little entrainment or AC dispersion when nominally mixing
OC, and this is known to be the case (32). Further, it follows that
amine systems which exhibit rapid AC phase disengagement in the pres-
ence of silica should also tend to have reduced crud and emulsion
problems since interfacial crud and AC phase disengagement both
appear to be sensitive to silica or silicate particle attachment.

CONCLUSIONS AND RECOMMENDATIONS

    The major importance of this work is that it demonstrates a
positive relationship between phase disengagement and amine structure.
The amine-structure effect may be totally different according to
whether the mixing is carried out OC or AC and depending on the aqueous-
phase composition. Phase disengagement is more rapid for amines with
shorter backbone chain lengths when OC mixing is used. This may be due
to systematic changes in the dynamic interfacial properties. As
expected from theoretical considerations, AC phase disengagement is
relatively insensitive to amine structure when the aqueous phase is
pH 1 Na_2SO_4 solution. When solutions containing colloidal silica
(leach solutions or synthetic silica solutions) are used as the aqueous
phase, AC phase disengagement is severely retarded if amines with
low n or low molecular weight are used. This effect appears to be
related to differences in interaction between the amines and silica or

silicate particles in the aqueous phase. The interaction manifests
itself in silica particle attachment to the interface which becomes
"armored" and stable to coalescence. This phenomenon provides a
reasonable explanation for interfacial crud formation even in sys-
tems using nominal OC mixing.

The data presented above show that the higher molecular weight
amines (n $\geq$10) may offer some advantages in Amex processing. The
advantages include faster AC phase disengagement, decreased crud and
emulsion formation, higher uranium extraction coefficients (for the
some molar concentrations), decreased third phase formation, lower
acid extraction, and possibly lower solubility losses. Thus, the same
process performance might be achievable under relaxed conditions such
as lower modifier concentration, higher suspended solids content, and
less alkaline scrubbing. Further, such improved reagents may make it
possible to process aqueous feed solutions that are normally difficult
to treat (such as tailings-pond liquors) or even to use AC mixing under
some conditions.

Since OC phase disengagement worsens as *backbone* chain length
increases, an increase in molecular weight of the amine extractant
must be accomplished by branching the alkyl chains, but not so as to
produce steric crowding of the nitrogen as in T2EHA. High purity is
also desirable. The results suggest that with this approach, a gener-
ally improved tertiary amine extractant may be designed for use in the
Amex uranium extraction process. The branched amines, TIDA, and TITA,
appear to be a good step in this direction on the basis of these experi-
ments. Selectivity needs to be considered, however, and continuous
countercurrent mixer/settler tests are needed. In addition, the
rational design of such improved extractants requires a more detailed
knowledge of the effect of branching.

Acknowledgments

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