CONF-810520--7

FACTORS INFLUENCING PHASE-DISENGAGEMENT RATES IN SOLVENT-EXTRACTION SYSTEMS EMPLOYING TERTIARY AMINE EXTRACTANTS*

B. A. Moyer and W. J. McDowell

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

CONF-810520--7

DE82 017413

Presented at the Second Symposium on Separation Science and Technology, Gatlinburg, Tennessee, May 5-8, 1981.

NOTICE

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

By acceptance of this article, the publisher or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering the article.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

---

*Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

FACTORS INFLUENCING PHASE DISENGAGEMENT RATES IN SOLVENT EXTRACTION SYSTEMS EMPLOYING TERTIARY AMINE EXTRACTANTS

B. A. Moyer and W. J. McDowell
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

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 disengagement 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 solutions, 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 applications of solvent extraction technology in hydrometallurgy and is still used in much the same form today (2). In recent years, however, 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 solution 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 availability. 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 shortcoming 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 performance 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 processes (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 associated 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 titration-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 solution" 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 temperature 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 $\approx$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_2SO_4/Na_2SO_4 solutions ($\sim$0.5 pH units per equilibration) 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 microscope slides and the previously equilibrated system, pH 1 Na_2SO_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_2O for 3 hrs (to ensure complete surface hydration), fresh pH 1 Na_2SO_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-disengagement 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 disengagement 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 synthetic Na_2SO_4 solutions containing silica were used, the break times were very long and ill-defined due to the apparent stabilization 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 approximately 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 appropriate 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 molecular 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 values provided by the vendors, the as-received commercial amines titrated in the range 93-98% tertiary. The balance of the titratable amines is mostly secondary with a minor amount of primary. Since these impurities are known to cause phase disengagement problems (16), they were removed by silica adsorption prior to the phase-disengagement tests.

Third Phase Formation

Table 2 gives the approximate H_2SO_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 ($(R_3NH)HSO_4$) rather than the normal sulfate salts ($(R_3NH)_2SO_4$) (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_2SO_4 solution at 25°C, using 0.1 N amine sulfate in 1 vol % tridecanol-modified kerosene. Under these conditions, all of the amines

TABLE 1

Tertiary Amine Extractants

			As-Received		Purified			Chain Distribution[e]					
Amine[a]	Abb.	Trade Name[b]	Neutral Equiv.[c]	%3°[d]	Neutral Equiv.[c]	Total Carbons per Alkyl[f]	Backbone Chainlength[g]	$\%C_6$	$\%C_8$	$\%C_{10}$	$\%C_{12}$	$\%C_{13}$	$\%C_{14}$
Commercial amines:													
Triisooctylamine	TIOA	Adogen 381	370	98.1	360	8.2	6		99				
Triisooctylamine	TIOA	AZamine T8B	356	97.4	358	8.1	6		99				
Triisodecylamine	TIDA	Adogen 382	448	93.3	441	10.1	7			99			
Triisodecylamine	TIDA	AZamine T10B	447	98.0	443	10.1	7			99			
Triisotridecylamine	TITA	Adogen 383	570	95[e]	568	13.1	8					99	
Tri-C_8,C_{10}-amine	T810A	Adogen 364	397	93.7	393	8.9	8.9	5	60	33	2		
Tri-C_8,C_{10}-amine	T810A	Alamine 336	396	94.1	392	8.9	8.9						
Tri-C_8,C_{10}-amine	T810A	AZamine T810	410	97.7	388	8.8	8.8	5	60	33	2		
Tri-C_8,C_{10},C_{12}-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	TOA	—			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.

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 (Alamine 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.

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 variability 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 interference 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

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, $[UO_2^{2+}]_{org} = 1.34 \times 10^{-4}$ M.

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

notable exceptions of samples of TIOA (AZamine T8B) and TIDA (AZamine T10B) with respective ratios of 5.7 and 3.4.

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 solution 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 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, undergoing an increase in break time of well over four orders of magnitude (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. (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 sulfate 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 therefore 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 disengagement becomes worse as amine is added. They also found that the effect of amine structure may be swamped out by the addition of enough modifier (5 to 10 vol %). There is incentive to go to less modifier, however, 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 overlooked 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 commercial 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 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 predominant 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 (typically 1.0 g/ℓ as SiO_2), and it is well known that synthetic silica solutions 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 preparation 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 interfacial 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 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 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:

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

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 obstruction to droplet coalescence due to particulate matter is expected when the particles coat the <u>outside</u> 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 attachment 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 observations, 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 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 material 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 presence 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 systems 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 generally 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 experiments. 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

This work was sponsored by the Division of Chemical Sciences, U.S. Department of Energy under Contract W-7405-eng-26 with the Union Carbide Corporation.

REFERENCES AND NOTES

1. C. F. Coleman, K. B. Brown, J. G. Moore, and D. J. Crouse, Ind. Eng. Chem. 50, 1756 (1958).

2. G. M. Ritcey and A. W. Ashbrook, *Solvent Extraction/Principles and Applications to Process Metallurgy*, Part II, Elsevier, New York, 1980.

3. K. B. Brown, C. F. Coleman, D. J. Crouse, C. A. Blake, and A. D. Ryon, in *Proceedings of the Second United Nations*

International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. 3, United Nations Publications, New York, 1958.

4. A. D. Ryon and R. S. Lowrie, *Experimental Basis for the Design of Mixer Settlers for the Amex Solvent Extraction Process*, Report ORNL-3381, Oak Ridge National Laboratory, April 19, 1963.

5. V. S. Schmidt, *Amine Extraction*, translated from Russian by J. Schmorak, Israel Program for Scientific Translations Ltd., Jerusalem, Israel, 1971.

6. J. M. P. J. Verstegen, J. Inorg. Nucl. Chem. 27, 201 (1965); A. S. Kertes, J. Inorg. Nucl. Chem. 27, 209 (1965); A. S. Kertes and Y. E. Habousha, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy*, Geneva, 1964, Vol. 10, United Nations Publication, New York, 1965.

7. K. B. Brown, C. F. Coleman, D. J. Crouse, J. O. Denis, and J. G. Moore, *The Use of Amines as Extractants for Uranium from Acidic Sulfate Liquors: A Preliminary Report*, Report ORNL-1734, Oak Ridge National Laboratory, June 9, 1954; J. G. Moore, K. B. Brown, and C. F. Coleman, *Further Studies of Amines As Extractants for Uranium from Acid Sulfate Solutions*, Report ORNL-1922, Aug. 9, 1955; D. J. Crouse, K. B. Brown, W. D. Arnold, J. G. Moore, and R. S. Lowrie, *Uranium Extraction with Organonitrogen Compounds*, Report ORNL-2099, May 14, 1956; W. D. Arnold and D. J. Crouse, *Further Evaluation of Amines As Extractants for Uranium from Sulfate Liquors*, Report ORNL-3030, Dec. 28, 1960.

8. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley-Interscience, New York, 1972.

9. R. K. Iler, J. Colloid Interface Sci. 75, 138 (1980).

10. J. S. Fritz, *Acid-Base Titrations in Nonaqueous Solvents*, G. F. Smith Chemical Co., Columbus, Ohio, 1952, I. Gyenes, *Titration in Non-aqueous Media*, (D. Cohen and I. T. Millar, eds.), D. Van Nostrand Company, Princeton, N.J., 1967; C. D. Wagner, R. H. Brown, and E. D. Peters, J. Amer. Chem. Soc. 69, 2609 (1947).

11. F. Daniels, R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender, and J. E. Harriman, *Experimental Physical Chemistry*, 7th Ed., McGraw-Hill, New York, 1970.

12. A. E. Alexander and J. B. Hayter, in *Physical Methods of Chemistry*, Vol. 1, Part V, (A. Weissberger and B. W. Rossiter, eds.), Wiley-Interscience, New York, 1971.

13. A. W. Neumann and R. J. Good, in *Surface and Colloid Science,* Vol. 11 (R. J. Good and R. R. Stromberg, eds.), Plenum Press, New York, 1979.

14. W. J. McDowell, in *Liquid Scintillation Counting. Recent Applications and Developments,* Vol. 1, (C. Peng, D. L. Horrocks, and E. L. Aspen, eds.), Academic Press, New York, 1980, pp. 315-332; W. J. McDowell, E. J. Bouwer, J. W. McKlveen, and G. N. Case, ibid., pp. 333-346.

15. C. Deptula and S. Minc., J. Inorg. Nucl. Chem. 29, 221 (1967).

16. D. A. Brown and A. L. Marston, *Curium Process Development. III-6. Characterization of Emulsions Formed in Curium Solvent Extraction,* Report DP-1215, E. I. DuPont de Nemours & Co., Savannah River Lab, Sept. 10, 1970.

17. I. B. Ivanov, R. K. Jain, P. Somasundaran, and T. T. Traykov, in *Solution Chemistry of Surfactants,* Vol. 2, (K. L. Mittal, ed.), Plenum Press, New York, 1978.

18. P. Sherman, in *Emulsion Science,* (P. Sherman, ed.), Academic Press, New York, 1968.

19. M. Cox and D. S. Flett, in *Proceedings of the International Solvent Extraction Conference,* Toronto, Canada, 1977, Vol. 1, Canadian Institute of Mining and Metallurgy, 1979, pp. 63-72.

20. W. J. McDowell and C. F. Coleman, J. Inorg. Nucl. Chem. 29, 1325 (1967); G. F. Vandergrift, S. M. Lewey, F. R. Dyrkacz, and E. P. Horwitz, J. Inorg. Nucl. Chem. 42, 127 (1980).

21. E. Barnea, Hydrometallurgy 5, 15 (1979).

22. K. A. Allen and W. J. McDowell, *Emulsion Stabilization by Silicic Acid,* Report ORNL-2771, Oak Ridge National Laboratory, Aug. 17, 1959.

23. R. K. Iler, *The Chemistry of Silica,* Wiley-Interscience, New York, 1979.

24. Edward Maurer, Mill Manager, L-Bar Uranium Project, Sohio Western Mining Co., Albuquerque, NM, private communication.

25. P. Somasundaran and R. B. Grieves, eds., *Advances in Interfacial Phenomena of Particulate/Solution/Gas Systems; Applications to Flotation Research,* AIChE Symp. Ser., Vol. 71, No. 150, American Institute of Chemical Engineers, New York, 1975. R. Lemlich, ed., *Adsorptive Bubble Separation Techniques,* Academic Press, New York, 1972.

26. A. W. Adamson, *Physical Chemistry of Surfaces,* 3rd ed., Wiley-Interscience, New York, 1976.

27. P. Somasundaran, Trans. AIME 241, 105 (1968); L. Ter-Minassian-Saraga, in *Contact Angles, Wettability, and Adhesion,* Adv. in Chem. Series, Vol. 43, American Chemical Society, Washington, D.C., 1964.

28. To simplify the discussion, spherical particles have been assumed, but owing to aggregation phenomena, *chains* of spherical particles may be more realistic for colloidal silica solutions made from silicic acid (23). For irregular-shaped particles, direct application of these arguments is less certain, though the model presented does, in general, make the correct qualitative predictions of the effect of various solids on droplet coalescence (4,18,29).

29. J. H. Schulman and J. Leja, Trans. Faraday Soc. 50, 598 (1954); E. H. Lucassen-Reynders and M. van der Tempel, J. Phys. Chem. 67, 731 (1963); S. U. Pickering, J. Chem. Soc. 91, 2001 (1907); J. M. Pickett and K. A. Ellway, J. Pharm. Pharmac. 28, 625 (1976).

30. Some solids actually decrease the OC break times in a spectacular way. Colloidal silica made from acidified sodium silicate did not have much effect on OC break time, but fumed silica caused OC break times to decrease to 20 sec or less.

31. D. W. Fuerstanau, Trans. AIME 208, 1365 (1957).

32. G. M. Ritcey, Hydrometallurgy 5, 97 (1980).

33. R. Tolun, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy,* Geneva, 1958, Vol. 3, United Nations Publication, New York, 1958.

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_2SO_4 solution containing UO_2SO_4 and tracer; 25°C; as-received amines.

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.

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

FIGURE 4. Effect of Backbone Chain Length on OC Break Time. The data from Fig. 3 are replotted against backbone chain length (Table 1).

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.

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 Na_2SO_4 solution containing 0.8 g/ℓ SiO_2. The organic phases had been preequilibrated with pH 1 Na_2SO_4 solution only.

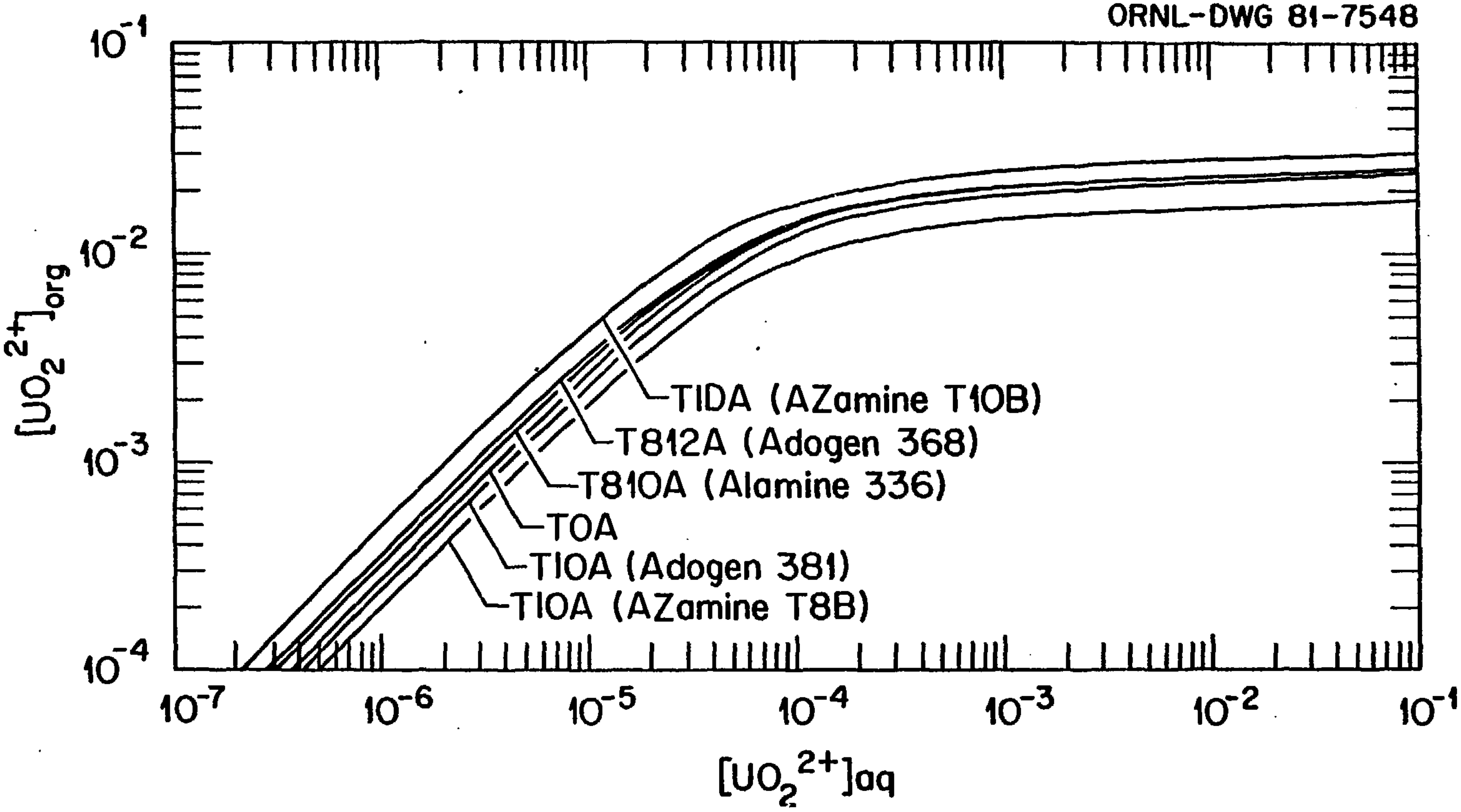
FIGURE 7. Contact Angles by the Wilhelmy Plate Method to Predict Microscopic Particle Attachment to the Liquid/Liquid Interface. The interfacial free energies, γ, are given according to the subscripts ow = oil/water, so = solid/oil, and sw = solid/water. In the lower right, the dashed line is a tangent line at the point of contact between the solid particle and the liquid/liquid interface.

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.

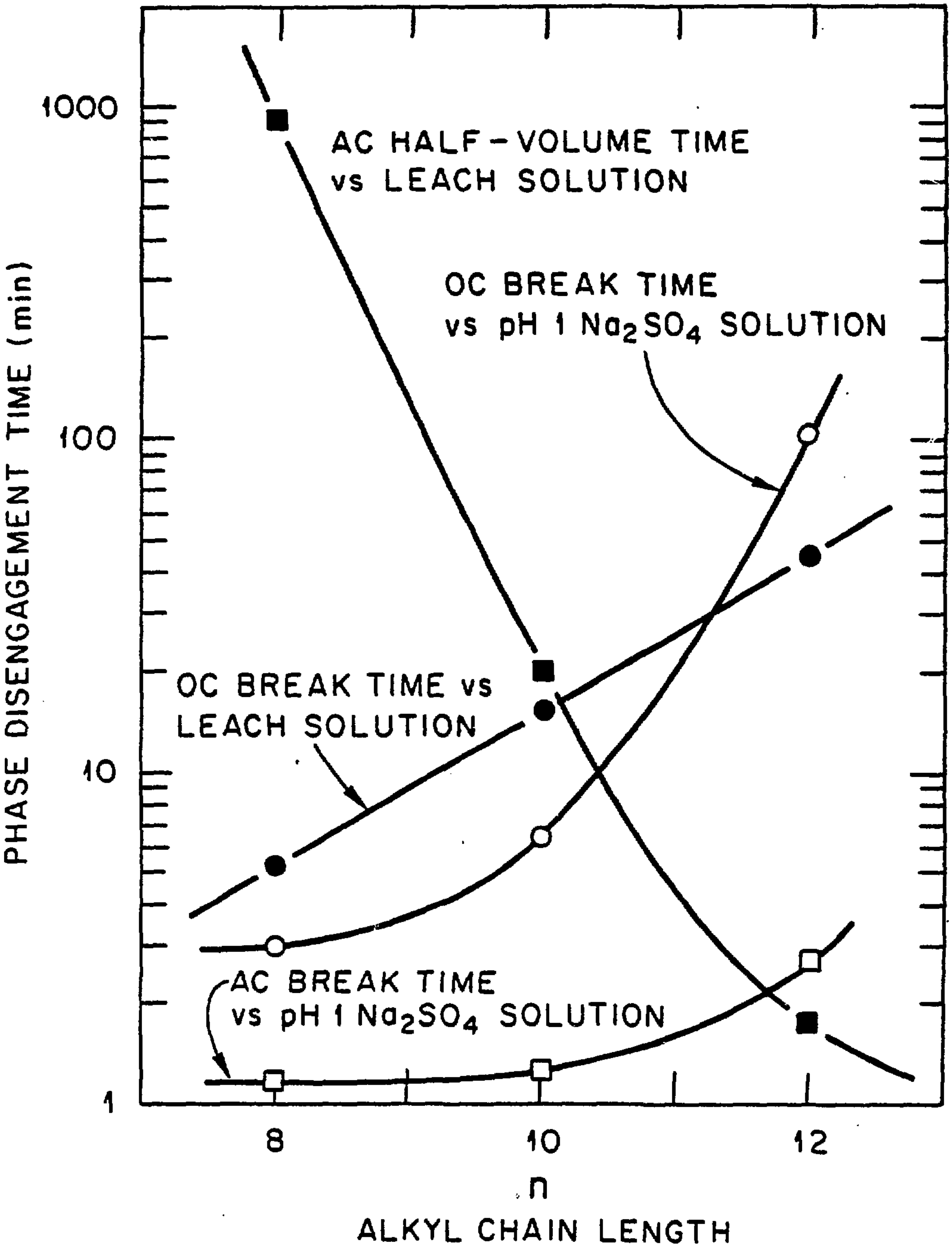
FIGURE 9. "Armoring" of Droplets by Solid Particles. Particles predominantly wetted by the aqueous phase (acute contact angle) will coat the outside of the organic droplets in AC dispersions, obstructing coalescence, but in OC dispersions, the obstruction does not exist.

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 % tridecanol-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 dispersion was formed and allowed to settle for one day.

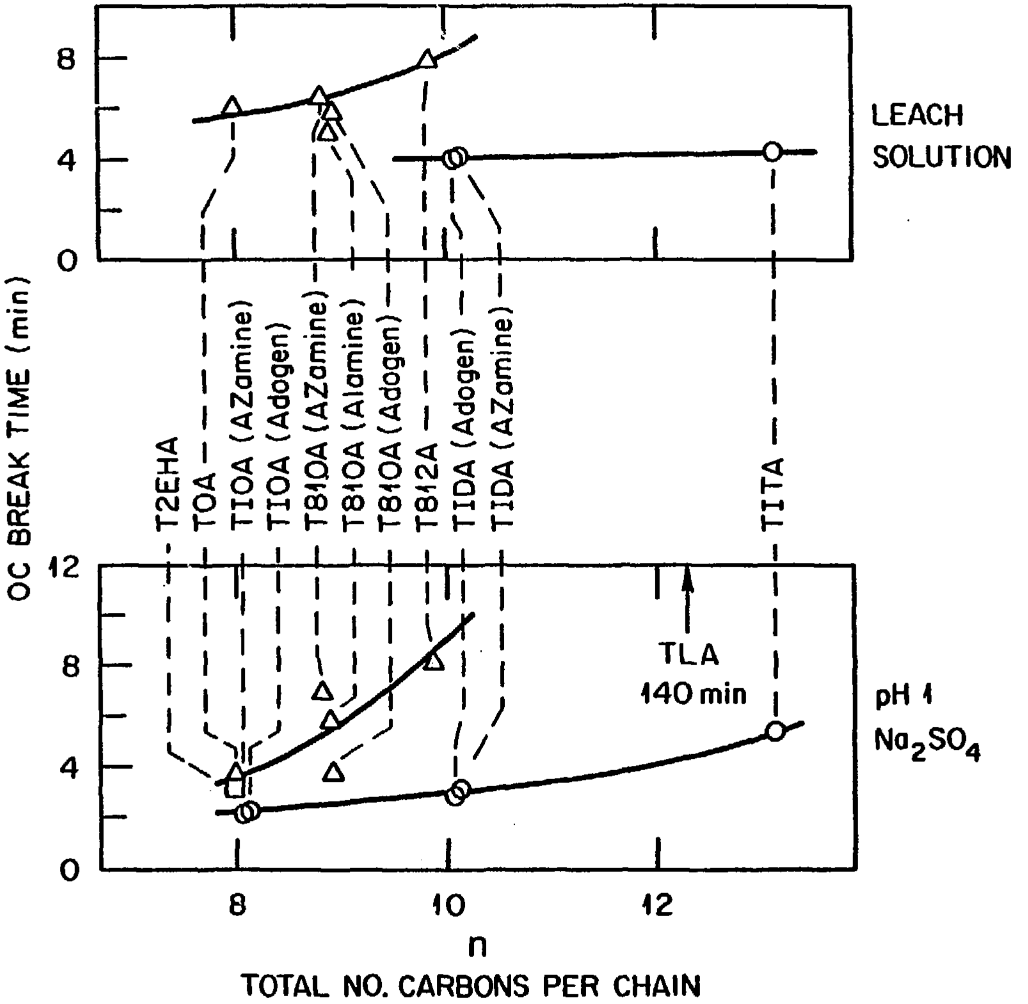
ORNL-DWG 81-7548



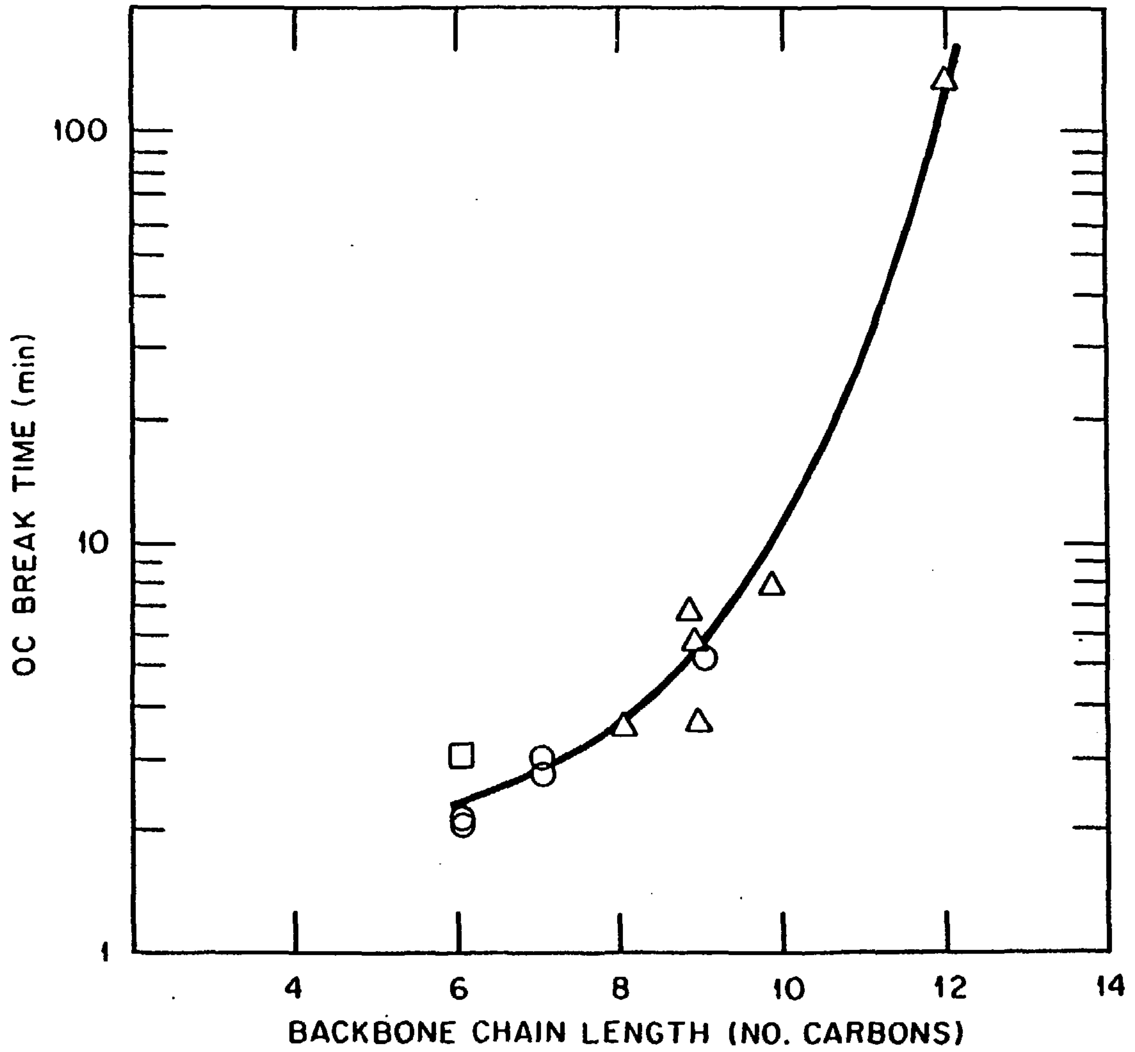
ORNL-DWG 81-12206



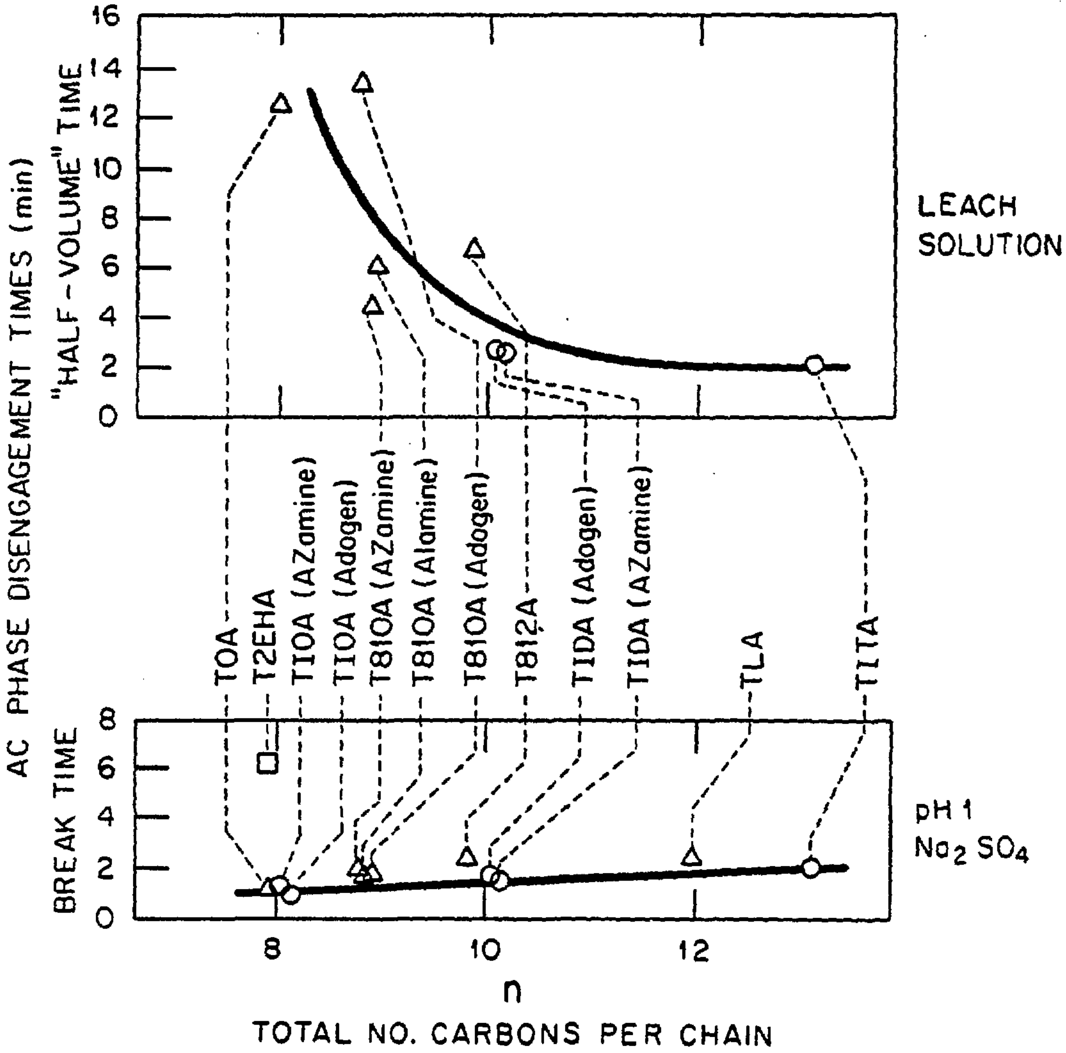
ORNL-DWG 81-7546R

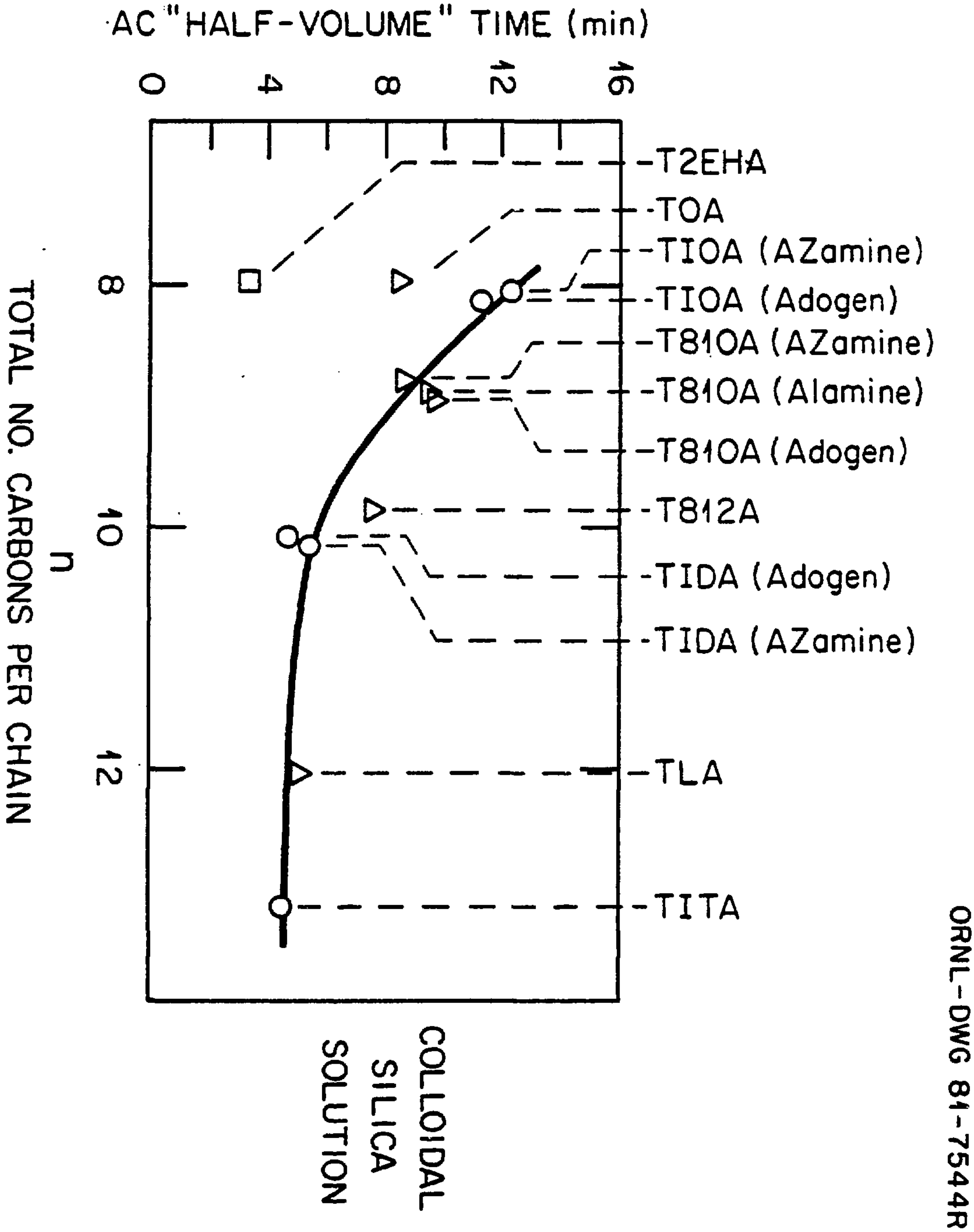


ORNL-DWG 81-7551R

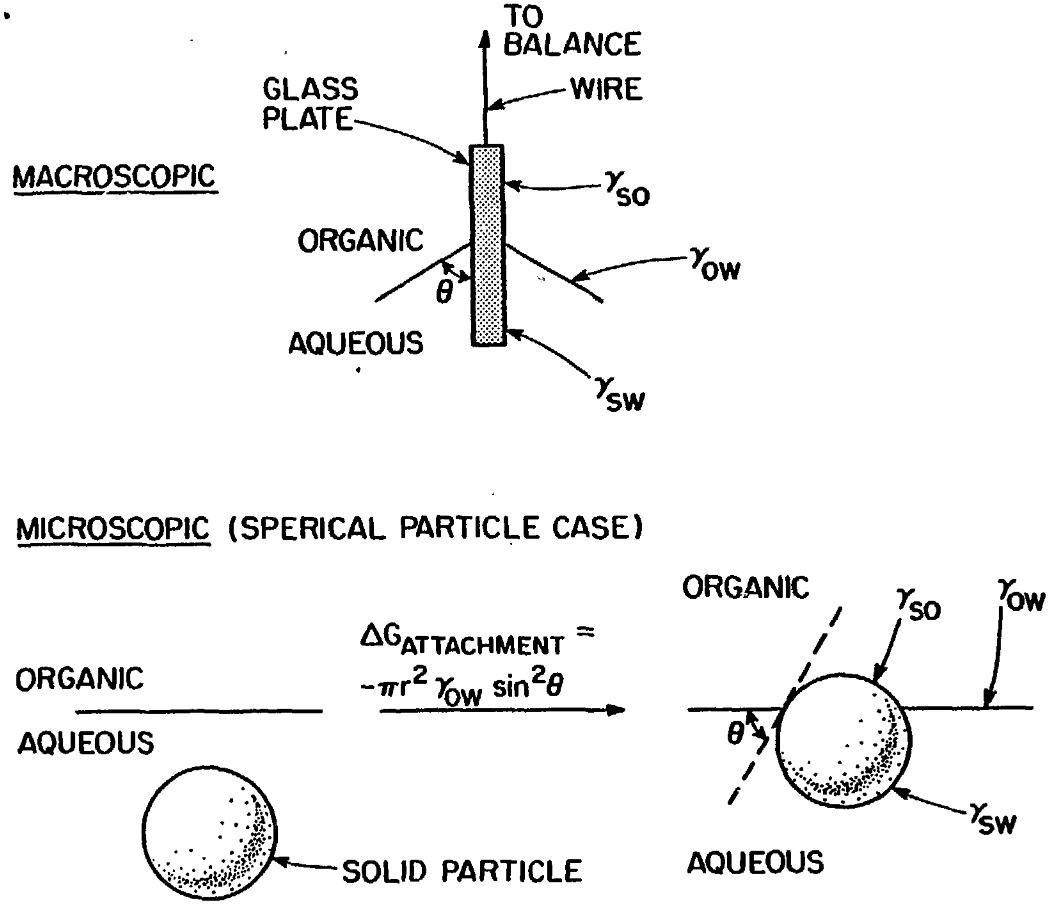


ORNL–DWG 81–7547R

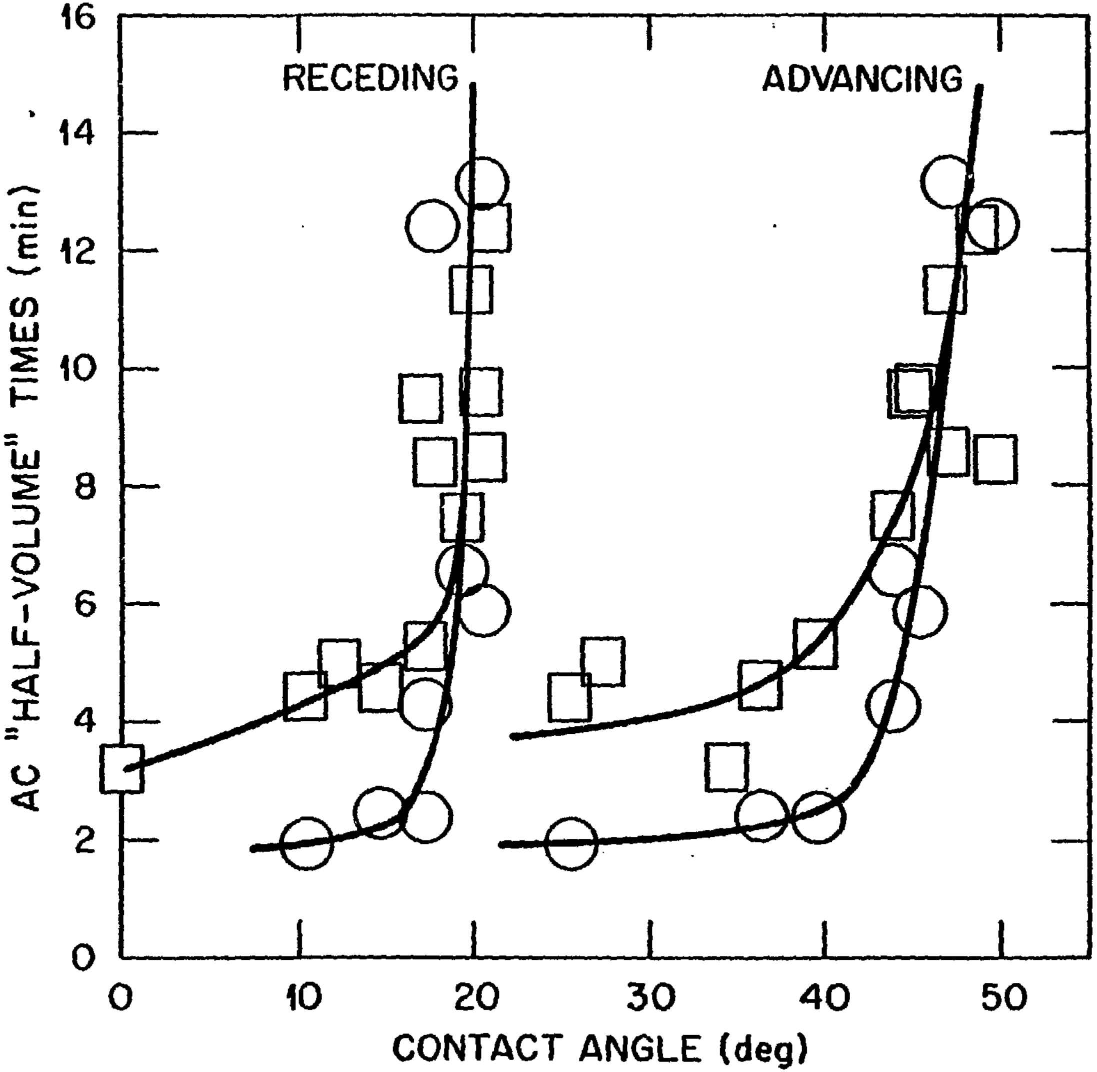



AC "HALF-VOLUME" TIME (min)
0
4
8
12
16
TOTAL NO. CARBONS PER CHAIN
n
8
10
12
T2EHA
TOA
TIOA (AZamine)
TIOA (Adogen)
T810A (AZamine)
T810A (Alamine)
T810A (Adogen)
T812A
TIDA (Adogen)
TIDA (AZamine)
TLA
TITA
COLLOIDAL
SILICA
SOLUTION
ORNL-DWG 81-7544R

ORNL-DWG 81-7545

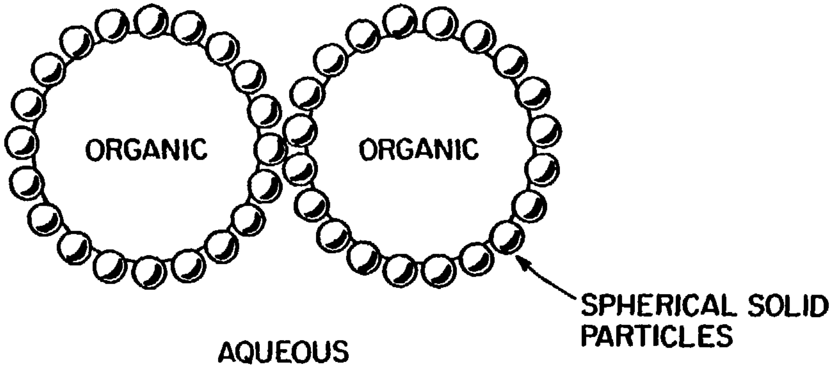


ORNL-DWG 81-7550

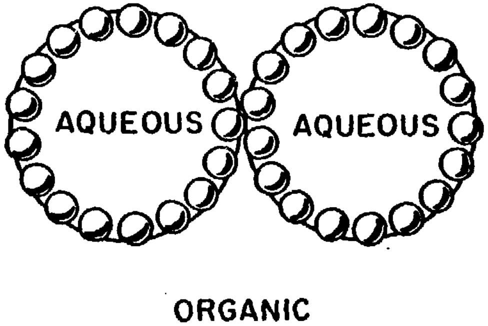


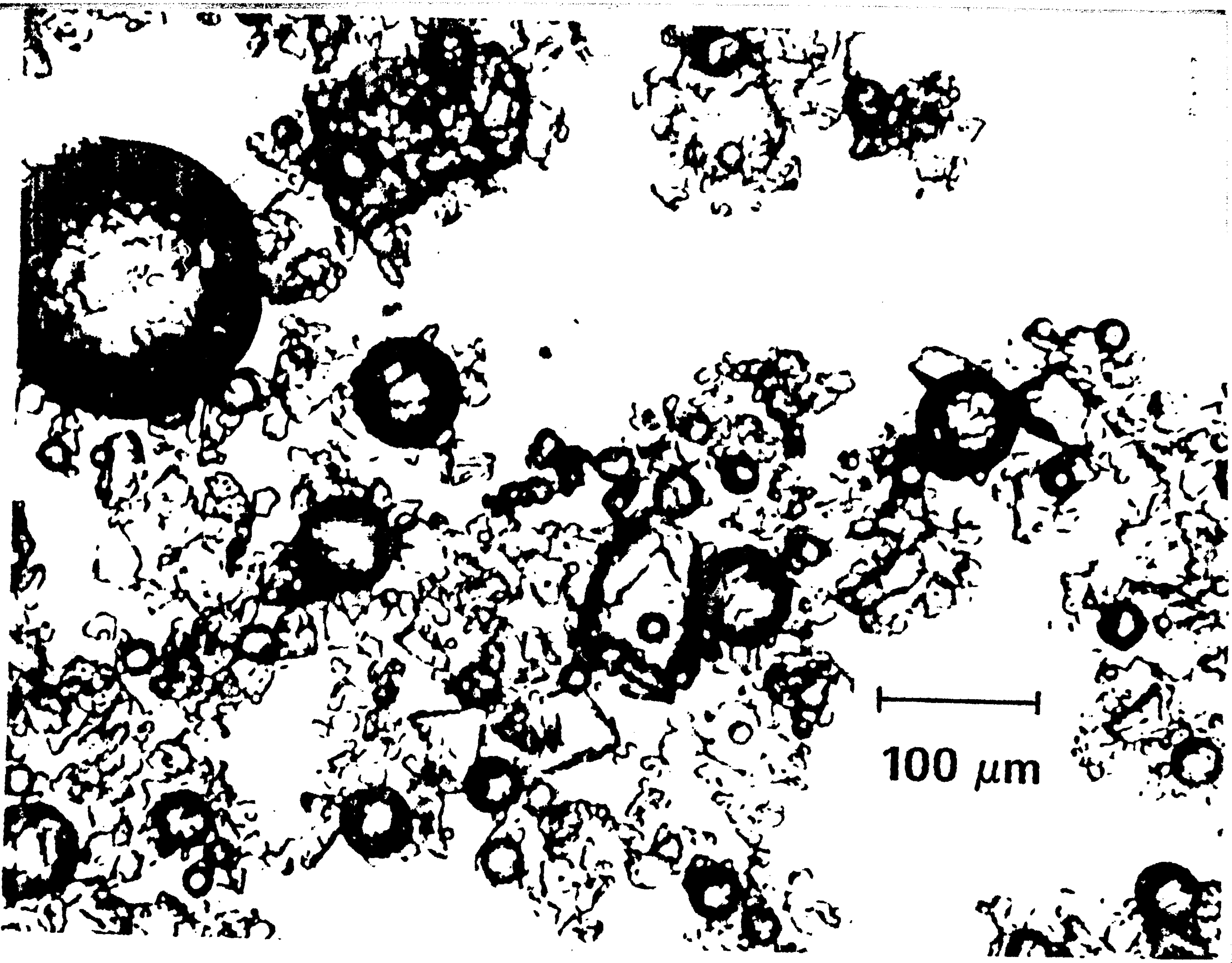
ORNL-DWG 81-7549R

AQUEOUS CONTINUOUS (PARTICLES ON OUTSIDE OF DROPLETS)



ORGANIC CONTINUOUS (PARTICLES ON INSIDE OF DROPLETS)




100 μm