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Alkane-Insoluble Trialkylammonium Double Salts Involving the Dodecamolybdophosphate Anion. II. Effect of Amine Structure on Third-Phase Formation

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ABSTRACT

In this paper, a rational basis is presented for the control of molybdenum "third phase" formation in tertiary amine extraction through appropriate selection of amine structure. The studies have been founded on the observation that third-phase formation in the amine-extraction of molybdenum is mainly caused by the formation of heteropolymolybdates, especially the dodecamolybdophosphate anion $PMo_{12}O_{40}^{3-}$ (DMP). Eight trialkylamine structures with straight and methyl-branched, 8- to 13-carbon chains have been examined with regard to the type of third phase formed and the maximum molarity of the dissolved salt $(R_3NH)_3$[DMP] that can be tolerated in the solvent before precipitation occurs (i.e., the DMP "tolerance", a type of solubility measurement). In the experiments, a standard solvent consisting of 0.05 M tertiary amine (primarily as the trialkylammonium sulfate salt) and 0.15 M n-dodecanol in n-nonane was used. For all of the amines tested, third-phase formation first involved co-extraction of Mo(VI) and phosphate from 0.1 M H_2SO_4 giving the dissolved salt $(R_3NH)_3$[DMP] over extended equilibration times (days to weeks). With no NaCl added to the aqueous phase, liquid third phases were obtained except in the case of triisooctylamine (TIOA), which gave solid $(TIOAH)_3$[DMP]. In the systems containing added chloride, third-phase formation involved combination of $(R_3NH)_3$[DMP] with

$(R_3NH)Cl$ to give the solid double salts $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$. The DMP tolerance of the resulting systems generally decreased with decreasing alkyl chain length, with the addition of methyl branches to a given chain, with decreasing amine concentration, and with addition of NaCl to the aqueous phase to give $(R_3NH)Cl$ in the solvent via anion-exchange with $(R_3NH)_2SO_4$. Use of a tridecylalcohol-modified kerosene diluent under conditions more closely approximating process conditions generally led to higher DMP tolerances than obtained with dodecanol-modified nonane, though the effect of amine structure was similar. Amine purification procedures are discussed.

INTRODUCTION

In the design of solvent extraction reagents, the molecular structure of the reagent must be optimized with respect to a variety of essential properties. In addition to possessing the necessary selectivity and extractive strength, the extractant must, for example, exhibit high organophilicity (negligible distribution to the aqueous phase), be soluble in the diluent, resist third-phase and emulsion formation during extraction, promote rapid phase separation, and possess good thermal and/or radiation stability (1). These and other properties determine the feasibility of using a given extractant in a research or process separation system, but too often it is not possible to predict in advance what structural features of the extractant will lead to desirable behavior. We previously showed that even a physical phenomenon as complicated as phase separation is strongly influenced by extractant structure according to certain identifiable structural parameters (2).

An especially nagging problem in amine solvent extraction is the pronounced tendency for the solvents to split into two organic phases, the heavy organic phase being called the "third phase" (3-9). In general, the occurrence of third phases cannot be tolerated in normal applications of solvent extraction because of reagent losses, degradation of dispersion properties, and erratic behavior (1). A "quick fix" that has generally proven successful involves increasing the solvating power of the solvent by increasing diluent aromaticity or adding a diluent modifier, often a long-chain alcohol (1,3-9). However, the strong influence of amine structure on the susceptibility of the solvent to third-phase formation (4-9) suggests that resistance to third-phase formation could be "built-into" the extractant itself.

Much of the study of the effect of amine structure on the susceptibility of the solvent to third-phase formation has centered on the electrostatic and hydrogen-bonding interactions between individual ion-pairs in solution (5-8). An increase in chain length is thought to increase the masking of the electrostatic field of the monomeric alkylammonium salt and thereby decrease the extent of aggregation in solution and ultimately the tendency to form a third phase. Most alkylammonium-salt solubility (10) and third-phase phenomena (2,5-9,11-13) qualitatively reflect this expectation at least up to a certain number of carbons (10). The effect of branching and other modifications of the tertiary amine structure have not been well characterized experimentally, though some of the possible effects have been considered (4-9). It was noted that the methyl-branched "iso" alkylamines seem worse generally than the straight-chain amines (5,8). On the other hand, long branches seem to minimize third-phase formation (4,9).

One of the most notable third-phase problems yet encountered in using amines as extractants has been associated with the extraction of molybdenum, which is all the more frustrating because of the desirability of recovering this metal (11-23). Early in the development of the Amex (amine-extraction) processes (4,9,24-26), it was observed that extraction of molybdenum from phosphate-containing sulfuric acid solutions led to the precipitation of "green, gummy solids" at the interface (11-17). Ironically, the most severe molybdenum precipitation in the Amex development tests was obtained with conditions that have now become commonly used for uranium recovery: use of tertiary amines with 8- and 10-carbon normal alkyl chains, aliphatic rather than aromatic diluents, and chloride-type stripping (18,19,26). The usual alcohol-modifier remedy for eliminating third-phase problems has proven ineffective and even detrimental beyond a certain point for alleviating molybdenum precipitation (11,15,16,22). Not surprisingly, molybdenum third-phase problems are still being encountered in amine-extraction processing (19,20,27).

Although the nature of the chemistry was not understood at the time, Amex process-development data earlier indicated that amine structure strongly influenced the susceptibility of the solvent to molybdenum precipitation (11-13). Qualitatively, it was shown that both branched- and straight-chain tertiary amines were highly susceptible to molybdenum third-phase formation, with improvement occurring with increasing chain length among the straight-chain amines (11-13,15). Highly branched secondary amines where the branches were usually much longer than methyl groups exhibited good molybdenum tolerance in the development tests, but these amines do not appear to have gained the popularity of the tertiary amines in the extraction of uranium and molybdenum (26).

Recently, the underlying chemistry of the molybdenum third-phase problem has been clarified both through the analysis of uranium-mill interfacial precipitates (20,27) and through studying molybdenum precipitation in a model solvent containing 0.05 M tri-n-octylamine (TOA) in n-nonane modified with 0.05 M n-dodecanol

(3,22,27). The origin of the third-phase problem in these systems can be linked to the co-extraction of molybdate and phosphate from sulfuric acid solution with subsequent formation of the dodecamolybdophosphate (abbreviated DMP) anion $PMo_{12}O_{40}^{3-}$ in the solvent as the dissolved trialkylammonium salt $(R_3NH)_3[DMP]$. When the R group is normal octyl or decyl, the solvent lacks the ability to dissolve or "tolerate" much more than approximately 10^{-4} M of this salt. Amounts of the salt that exceed the solvent tolerance precipitate as a liquid or solid third phase additionally containing other trialkylammonium salts that are normally present in the solvent, including trialkylammonium sulfate, bisulfate, and chloride. In chloride containing systems, the double-salt

$$(R_3NH)_3[PMo_{12}O_{40}]\cdot 3(R_3NH)Cl \qquad (I)$$

crystallizes out of the solvent and collects at the interface, explaining interfacial "crud" problems at a large U.S. uranium mill (27).

A wider significance to the double salt (I) may be recognized in that it demonstrates the formation of a compound between two alkylammonium salts containing different anions. Evidence is accumulating from solution studies that dissolved mixed-salt species occur frequently in amine solvent extraction, playing a key role in third-phase formation and influencing the distribution behavior of metals (3,5-8,22,27-31). Key questions concerning (I) and other mixed salts include whether a preferred, predictable stoichiometry occurs, why the different salts interact in the first place, and how the mixed-salt interaction influences third-phase behavior.

In proceeding to the major topic of this paper, it was our aim to 1) use our previous insights into the formation of DMP-containing third-phases to show that third-phase behavior responds strongly to systematic structural changes in the extractant according to an identifiable pattern, 2) to suggest, if possible, a rational approach to the alleviation of third-phase problems associated with molybdenum and other metals through optimization of amine structure, 3) explain previous empirical observations concerning the effect of amine structure on molybdenum precipitation, and 4) further elucidate the role of mixed-salt phenomena in the formation of third phases and extraction of metal complexes in ion-pairing extraction systems. Toward these goals, eight trialkylamines often used in both laboratory and industrial applications were selected for study. These amines together with their abbreviations, chemical and trade names, major components, and vendors are given in Table I. Three symmetrical, straight-chain amines, TOA, TDA, and TLA, were chosen to determine the effect of chain length in a well-defined, homologous series of amines. T810A represents the most widely used amine reagent in uranium hydrometallurgy and consists of a statistical blend of the various trialkylamines that would be expected from approximately equal starting amounts of n-octyl and n-decyl groups

TABLE I
Trialkylamines Used In Study

Chemical Abbrev.	Chemical Name	Major Alkyl Groups[a]	Commercial Name	Vendor[b]
TOA	tri-n-octylamine	n-octyl	—	Aldrich Chemical Co.
TDA	tri-n-decylamine	n-decyl	—	Eastman Org. Chemicals
TLA	trilaurylamine	n-dodecyl	—	Eastman Org. Chemicals
T810A	tri-C_8,C_{10}-amine	n-octyl, n-decyl	Alamine 336	Henkel Corp.
T812A	tri-C_8,C_{10},C_{12}-amine	n-octyl, n-decyl, n-dodecyl	Adogen 368	Sherex Chemical Co.
TIOA	triisooctylamine	dimethylhexyl, methylheptyl	Adogen 381	Sherex Chemical Co.
TIDA	trisodecylamine	trimethylheptyl	Azamine T10B	Mars Chemical Co.
TITA	triisotridecylamine[c]	tetramethylnonyl	Adogen 383	Sherex Chemical Co.

[a] As given by the product data-sheets (32), previous literature (4,13,24), and/or composition of the starting alcohols (33).

[b] Most of the amines may be obtained in approximately equivalent form from other vendors.

[c] This is usually called simply tritridecylamine though it is branched.

(32). T812A is a similar blend except that the average molecular weight is higher owing to a significant fraction of dodecyl groups (3% C_6, 40% C_8, 25% C_{10}, and 30% C_{12} (32)). These proprietary amines were included in the study to learn whether their behavior could be predicted by interpolation of the patterns observed for the series TOA, TDA, and TLA. To investigate the effect of branching, three branched "iso" amines (derived from "oxo-process" alcohols) were also examined. These extractants consist of narrow molecular-weight distributions of trialkylamines wherein methyl groups are randomly substituted along the chains at all points except at the carbons adjacent to nitrogen (4,13,24,32). Although their purity has improved considerably, T810A, TIOA, TIDA, and TITA appear to be essentially the same products available over 25 years ago (4,13,24).

The experimental approach employed in the present work involved both identifying the various DMP-containing precipitates and measuring the tendency of the DMP-containing systems to form third phases. Dodecanol-modified nonane was deliberately selected as a diluent system likely to promote high instability to third-phase formation. Some of the tests used tridecylalcohol-modified kerosene to assess the behavior of process solvents. As a measure of third-phase tendency, we define the "DMP tolerance" as the maximum molarity of the dissolved salt $(R_3NH)_3[DMP]$ that can be sustained in the solvent without incurring the formation of a third phase. In this case, "solvent" refers to the organic phase containing diluent, modifier, various trialkylammonium salts, and dissolved water. Since $(R_3NH)_3[DMP]$ is hardly soluble at all in dodecanol-modified nonane alone (3,22), the DMP tolerance of an amine solvent represents a measure of the ability of the various other trialkylammonium salts to solubilize the $(R_3NH)_3[DMP]$.

To eliminate experimental and interpretive problems arising from the alcohol, secondary amine and ultraviolet-absorbing impurities usually present in the as-received tertiary amines, purification procedures were undertaken prior to the study. Since comparative data on the effectiveness of commonly used purification techniques for high-molecular-weight amines have rarely, if ever, been reported, the procedures used along with the analytical results will also be presented.

EXPERIMENTAL SECTION

Chemicals and Purification Procedures

Reagents, solvents, and solutions. Water was purified by resin-deionization, charcoal-adsorption, and double distillation (first over $KMnO_4$). The purification of reagent-grade n-dodecanol (Eastman) involved fractional vacuum distillation on a Perkin-Elmer 36-Inch Adiabatic Spinning Band Still, giving at least 99.5% purity as determined by gas chromatography (Dexil 300 column). Spectro-grade (Burdick and Jackson) toluene, xylene, nonane, methanol, acetone, and hexane were used without additional purification. For nonaqueous titrimetry, 1,3-diphenylguanidine (Eastman) and p-dioxane (MC/B spectro-grade) were purified as recommended previously (25,34). The kerosene was Kermac 470B (same as Napoleum 470 from Kerr McGee; 11.7% aromatics, 48.6% paraffins and 39.7% naphthenes (1)) using tridecylalcohol (methyl-branched "oxo-process" alcohol from Enjay Chemical Co.) as modifier. Except for the amines, it may be assumed that reagent-grade chemicals were used in all other instances.

Amine purification, analysis, and characterization. Chloride salts of the straight-chain amines for recrystallization were formed by several contacts of the as-received amines in either xylene or toluene diluent with 1 M HCl, yielding light- to dark-brown waxy solids after rotary evaporation of the solvent. Snow-white crystals were obtained by multiple recrystallizations involving cooling saturated solutions initially at room temperature as follows: (TLAH)Cl: 4 times, toluene, -78°C, 89% yield; (TOAH)Cl: 6 times, acetone-hexane, 6°C, 26% yield; (TDAH)Cl: 4 times, acetone-hexane, 6°C, 48% yield. Free amines were generated by neutralizing solutions of the amine chloride salts in toluene with excess 1 M NaOH followed by several washes with pure water and rotary evaporation of the diluent.

Amine distillation was carried out on a CVC Lab-3 High-Vacuum Centrifugal Molecular Still in 400 to 500 mL batches. A typical run was performed by making 20 passes across the heated, spinning plate at steadily higher temperatures and lower pressures, collecting the middle 70% fraction in the ranges 60 to 140°C and 2 to 20 μ Hg (0.3 to 3 Pa). An optional reductive treatment mainly to remove any remaining yellow color consisted of adding 80 g of previously distilled amine to 0.5 g $LiAlH_4$ (Alpha, 97%) suspended in 150 mL of dry (stored over alumina) diethylether in a 3-neck flask with N_2 purging. Following a 24 h reaction period, the unreacted hydride was destroyed with the addition of 3 mL of methanol and 1 mL of water, evolving hydrogen gas and precipitating a white, waxy solid, which was filtered off and discarded. Although the procedure was not expected to remove such impurities as primary and secondary amines and alcohols (which would react with the $LiAlH_4$ but be liberated again on hydrolysis (35)), additional tests have shown some improvement in the tertiary amine content presumably because some of the impurities get precipitated on hydrolysis (36). Upon rotary-evaporating the ether from the filtrate, the amines were scrubbed repeatedly with 50 mL volumes of methanol, 10 times for TIDA and 20 times for TITA, discarding the methanol layers.

Scrubbing the amines with immiscible methanol served several purposes, including 1) destroying the hydrides, 2) washing out any remaining salts, and 3) removing some of the primary and secondary amines owing to the greater solubility of these impurities in methanol than the tertiary amines of equal chain length (37-39). The final yields after rotary vacuum-drying were 60.5 g (76%) of TIDA and 66.8 g (84%) of TITA.

Amine purity criteria included the neutral equivalent (NE), mole-% tertiary-amine content, and "uv cutoff" (Cary 219 Spectrophotometer), defined as the wavelength at which the absorbance exceeds 1.0 in a 1 cm quartz cell containing undiluted amine. Procedures recommended earlier (25,34,40-42) were adapted for differential titration (overall ±0.2% precision) with a Metrohm Herisau Potentiograph E536 and Dosimat E535 equipped with a combination glass, Ag/AgCl electrode. NE values were obtained by titrating 50 to 90 mg of amine in 20 mL glacial acetic acid with 0.05 M $HClO_4$ in p-dioxane standardized against 1,3-diphenylguanidine. To determine the mole-% tertiary-amine content, the amine was first allowed to stand for 1 h at room temperature in 2 mL of an acetylating solution of 10 parts acetic anhydride to 1 part glacial acetic acid. An 18 mL volume of glacial acetic acid was then added and the solution titrated as before to give the tertiary-amine neutral equivalent NE_3 (42) and mole-% tertiary amine (100% x NE/NE_3).

DMP Tolerance Measurements

Except for the experiments involving kerosene diluent described later, solvents (0.05 M amine in dodecanol-modified nonane) were pre-equilibrated several times with 0.1 M H_2SO_4 before use to convert the amine primarily to the sulfate salt (2,3,22,27). A 0.15 M concentration of dodecanol was selected as an approximate minimum level of modifier that would permit all of the amines to be compared without danger of precipitation of third phases attributable just to the trialkylammonium sulfate, bisulfate, and/or chloride salts. The pre-equilibrated solvents were further equilibrated at 25°C using techniques described previously (22,27) with equal volumes of aqueous solutions containing 0.1 M H_2SO_4, 0.001 to 0.12 M Mo(VI), 0.001 to 0.02 M H_3PO_4, and 0 to 1 M NaCl. The Mo(VI) was added to the aqueous solutions initially in the form of $H_3PMo_{12}O_{40}\cdot15H_2O$ in the TLA experiments and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ for the other amines. Equilibration times (9 to 26 d) were such that essentially all of the Mo(VI) in the system would be converted to $(R_3NH)_3$[DMP] (22,27).

In general, the DMP tolerance for a given amine under a given set of conditions was determined by varying the aqueous Mo(VI) concentration by trial and error in a series of equilibrations to produce visible third phases in some of the systems. At equilibrium, the DMP molarity in the bulk solvent phase (not including the third phase, if present) was made by a spectrophotometric measurement of the absorbance of the DMP peak at 310 nm using previously determined values of the molar absorbtivity (ε), 24,800 in amine solvent or 25,700 in $CHCl_3$, isopropanol (22). In Figs. 1A and 1B, the measured DMP molarity is plotted against the total organic Mo(VI) expected if all of the Mo(VI) is extracted but does not form a third phase. The DMP molarity was observed to increase linearly with a least-squares slope of 0.0877 = 1/11.4 regardless of the

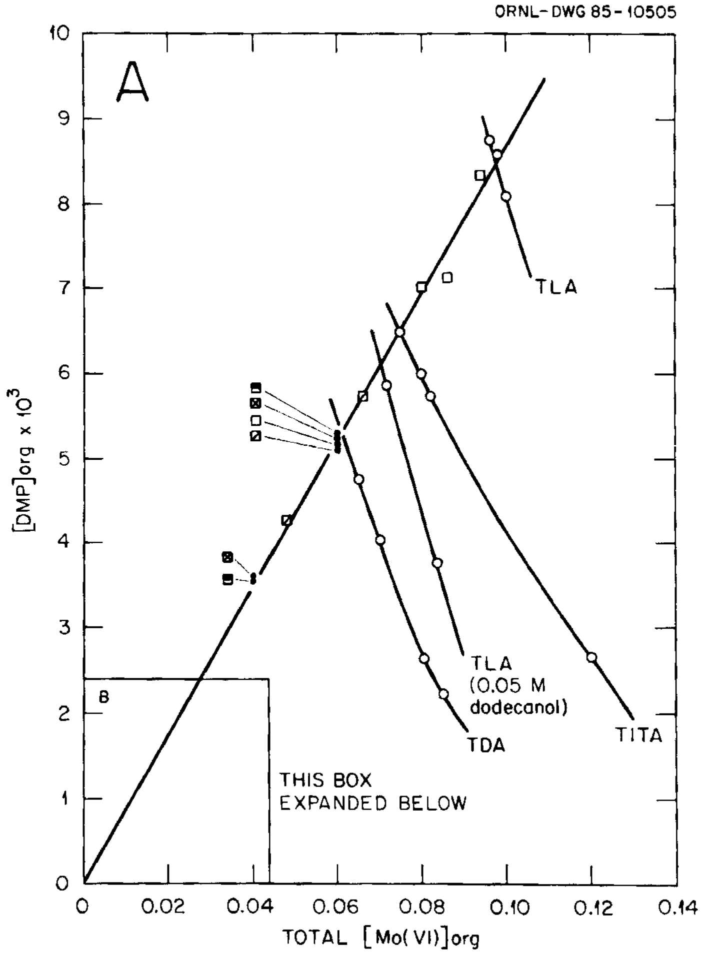

Figure 1A. Measured solvent molarity of dodecamolybdophosphate vs expected Mo(VI) molarity at 25°C. (See Figure 1B for details.)

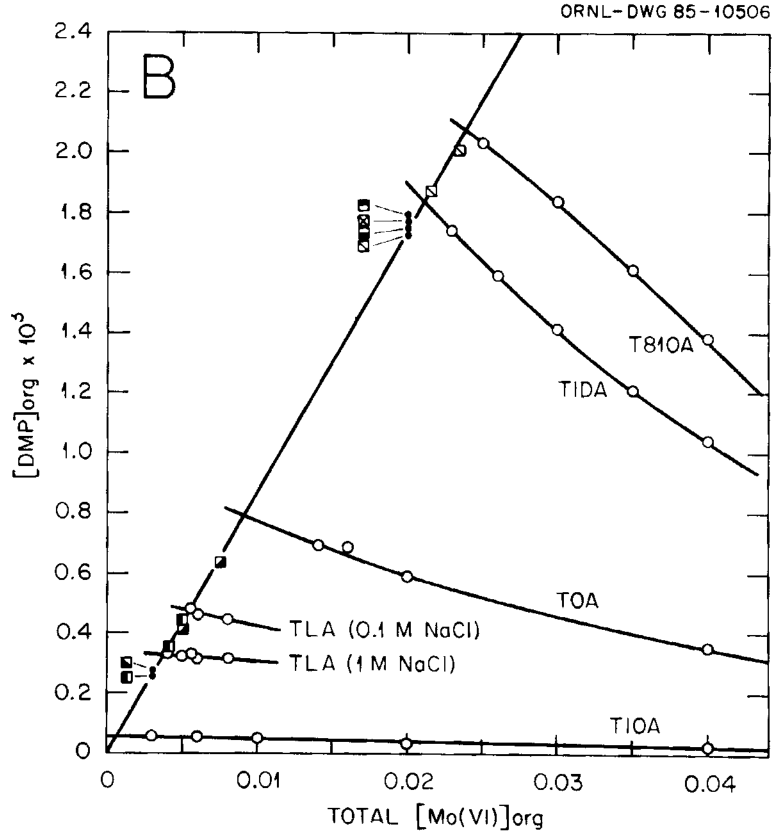

Figure 1B. An expanded portion of Figure 1A. Details for Figs. 1A and 1B: Except as noted in Fig. 1A, the solvents consisted of 0.05 M amine plus 0.15 M dodecanol in nonane and were pre-equilibrated with 0.1 M H_2SO_4. Solvents were then equilibrated for 9 to 26 d at 25°C with equal volumes of aqueous solutions containing 0.1 M H_2SO_4, 0 to 0.12 M Mo(VI), and 0.001 to 0.02 M H_3PO_4, with no NaCl (unless indicated otherwise). Points designated by squares (□) indicate no observation of a third phase while points designated by circles (o) indicate that a third phase was visible. The DMP molarity at the intersection of the straight-line segments was taken as the DMP tolerance. □ – TLA; ▨ – TLA (0.05 M dodecanol); ◧ – TLA (0.1 M NaCl); ◩ – TLA (1 M NaCl); ⊠ – TDA; ⧅ – T810A; ◪ – TOA; ⬒ – TITA; ⬓ – TIDA.

amine used as long as no visible third phase had formed (points given as boxes in the figures). Within the spectrophotometric experimental error of ±7%, this confirms the expected quantitative conversion of Mo(VI) to DMP (theor. slope = 0.0833 or 1/12). Depending on the amine and conditions used, breaks in the plot occurred upon third-phase formation giving the DMP tolerance as the intersection of an extrapolation from the descending curve (points given as circles in Figs. 1A and 1B) back to the common ascending line (estimated ±10% reliability).

The branched-chain amines exhibited such low tolerances in the chloride-containing systems that the DMP in the solvent could not be easily measured spectrophotometrically. On the hypothesis that polymolybdate intermediates were interfering, the DMP was not formed in situ but rather was added directly by dissolving small amounts of the pure compounds $(TIOAH)_3[DMP]$, $(TIDAH)_3[DMP]\cdot 3(TIDAH)Cl$, and $(TITAH)_3[DMP]\cdot 3(TITAH)Cl$ (see preparations below) in their respective amine-sulfate solvents. Contact of these DMP-containing solvents with 0.1 M H_2SO_4 containing 0.01 M H_3PO_4 and 0.1 or 1 M NaCl then gave solid precipitates without interference due to intermediates. Measurement of the $(R_3NH)_3[DMP]$ remaining in the solvent provided tolerance values for TIOA in this way, but only upper limits could be set for TIDA and TITA.

In some experiments, the solvent was 0.06 M amine in kerosene modified with 0.06 M tridecylalcohol and was pre-equilibrated with pH 1 Na_2SO_4 (0.3125 M Na_2SO_4 + 0.1875 M H_2SO_4). The amines used in these experiments were purified by passing them undiluted through activated silica; the procedures and analytical data have been described previously (2). Room temperature equilibrations were made by slow rocking using pH 1 Na_2SO_4 containing Mo(VI), 0.02 M NaCl, and 0.002 M H_3PO_4. By varying the Mo(VI) concentrations, the DMP tolerance (assumed to be 1/12 the molybdenum tolerance) could be bracketed between two valves by visual inspection of the systems for third phases. No visual changes occurred in the systems after 23 days of contact.

Preparation and Analysis of Solids

Unless otherwise stated, all of the solvents used in the preparations of solid compounds employed 0.05 M amine in nonane modified with 0.15 M dodecanol. Equilibrations involving Mo(VI) were made at room temperature in the absence of light by quiescent stirring (unbroken interface) or gentle rocking. Generally, the Mo(VI) was the limiting reagent with the amine, NaCl, and H_3PO_4 being far in excess of the stoichiometrically required amounts. As summarized in Table II, the precipitates were analyzed by spectrophotometric, titrimetric, and powder x-ray diffraction procedures described previously (22,27) and/or by elemental analysis (Galbraith Laboratories, Knoxville, TN).

Table II
Analytical Summary of Amine-DMP Compounds[a]

Sample		%C	%H	%N	%Cl	$\%PMo_{12}O_{40}$[b]	Note on Preparation[d]
$(TDAH)_3[DMP]\cdot 3(TDAH)Cl$	exper.	47.79	8.36	1.85	2.24	39.9	Mo(VI), PO_4^{3-}, + Cl^- extracted together
	theor.	47.40	8.48	1.84	2.33	36.5	
$(TLAH)_3[DMP]\cdot 3(TLAH)Cl$	exper.	51.24	9.27	1.66	2.06	36.0	Mo(VI), PO_4^{3-}, + Cl^- extracted together
	theor.	51.21	9.07	1.66	2.10	36.0	
$(TIOAH)_3[DMP]\cdot 3(TIOAH)Cl$	exper.	—	—	—	—	43.2	Mo(VI) + PO_4^{3-} extracted; Cl^- added later
	theor.	—	—	—	—	44.9	
$(TIOAH)_3[DMP]$	exper.	30.16	5.45	1.46		59.9	3TIOA + $H_3PMo_{12}O_{40}\cdot 15H_2O$
	theor.	29.98	5.45	1.46		63.1	
$(TIDAH)_3[DMP]\cdot 3(TIDAH)Cl$	exper.	47.68	8.53	1.69,1.94[c]	2.44	40.4	Mo(VI) + PO_4^{3-} extracted; Cl^- added later
	theor.	47.51	8.50	1.84	2.32	39.8	
$(TITAH)_3[DMP]\cdot 3(TITAH)Cl$	exper.	52.51	9.28	1.58	2.12	31.9	Mo(VI) + PO_4^{3-} extracted; Cl^- added later
	theor.	52.35	9.25	1.60	2.03	34.8	
Uncertainty		±0.3	±0.3	±0.2,±0.1[c]	±0.2	±~3	

[a] Elemental-analysis results unless otherwise indicated.

[b] Spectrophotometric method; ±7% uncertainty (3,27).

[c] From titration of the free amine released by base (3,27).

[d] Full details given in the Experimental Section.

$(TLAH)_3[DMP]\cdot3(TLAH)Cl$. 10 mL of TLA solvent were contacted for 3 d with 45 mL of an aqueous solution containing 0.1 M H_2SO_4, 0.5 M NaCl, 0.02 M Mo(VI) (as ammonium molybdate), and 0.05 M H_3PO_4. The bright yellow precipitate that had formed loosely on top of the liquid/liquid interface was filtered onto a Millipore FHLP filter, washed with hexane, and dried in vacuo.

$(TDAH)_3[DMP]\cdot3(TDAH)Cl$. The same general procedure was followed as given in the previous preparation.

$(TIDAH)_3[DMP]\cdot3(TIDAH)Cl$. 20 mL of TIDA solvent were contacted for 5 d with 14.6 mL of an aqueous solution containing 0.1 M H_2SO_4, 0.0328 M Mo(VI) (as ammonium molybdate), and 0.017 M H_3PO_4. The liquid third phase was eliminated (or nearly so) by diluting with 15 mL more TIDA solvent. 20 mL of the resulting solution was then placed over 10 mL of an aqueous phase containing 0.1 M H_2SO_4, 1 M NaCL, and 0.01 M H_3PO_4. After 1 d, the yellow solid precipitate was collected as described above.

$(TITAH)_3[DMP]\cdot3(TITAH)Cl$. The same general procedure was followed as given in the previous preparation.

$(TIOAH)_3[DMP]\cdot3(TIOAH)Cl$. The same general procedure was followed as given in the previous two preparations except that the diluent was unmodified toluene to prevent crystalline $(TIOAH)_3[DMP]$ from precipitating before the NaCl could be added. In the preparation, a liquid third phase formed before the NaCl was added, requiring the addition of fresh solvent to homogenize the solvent.

$(TIOAH)_3[DMP]$. A solution containing 0.103 g $H_3[DMP]\cdot15H_2O$ (0.049 mmole) dissolved in 2 mL isopropanol (some white undissolved solid was centrifuged out) was added dropwise to 0.0549 g (0.155 mmole) TIOA dissolved in 1 mL isopropanol immediately forming a fine, yellow precipitate. After 1 h of stirring, the precipitate was filtered onto a Millipore FHLP filter, washed with isopropanol and hexane, and dried in vacuo. The identical product was alternatively prepared in an extraction system by contacting 5 mL of TIOA solvent overnight with 0.7 mL of 0.083 M $H_3[DMP]\cdot15H_2O$, filtering the precipitate, and washing with isopropanol and hexane.

RESULTS

Amine Purification and Analysis

Analytical data for the purified trialkylamines are given in Table III. In general, the purification procedures become less effective as the molecular weight (equivalent to the NE for pure amine) increases, and all of the methods used have the disadvantage of being time-consuming. Recrystallization of the amines as mineral-acid salts produces good results for the straight-chain com-

TABLE III
Analytical Summary of Purified Trialkylamines

Amine	Nominal NE[a]	Titrated NE[b]	Titrated mole-% 3[c]	Average No. carbons per alkyl[d]	Average backbone chain length[e]	uv cutoff[f]	Purification method[g]
TOA	353.69	353.7	99.9+%	8.0	8.0	269 nm	Recryst. HCl salt
TDA	437.85	433.2	98.6%	9.9	9.9	275 nm	Recryst. HCl salt
TLA	522.02	515.0	97.7%	11.9	11.9	273 nm	Recryst. HCl salt
T810A	396	382.1	99.4%	8.7	8.7	330 nm	Distillation
TIOA	370	354.0	99.5%	8.0	6.8	353 nm	Distillation
TIDA	447	440.1	99.3%	10.1	8.0	303 nm	Dist. + LAlH$_4$ + MeOH
TITA	570	551.0	98.7%	12.7	10.1	314 nm	Dist. + LAlH$_4$ + MeOH

[a] Theoretical neutral equivalent in grams/equivalent for TOA, TDA, and TLA and for the remaining amines, nominal NE values supplied by vendor (32).

[b] Represents total contribution due to primary + secondary + tertiary amines.

[c] Equal to 100% × (moles tertiary)/(moles primary + moles secondary + moles tertiary) or experimentally, 100% × (NE/NE$_3$); see Experimental Section.

[d] Calculated from the NE values, making allowance for the titrated impurity assumed to be secondary amine.

[e] Estimated (±10%) by pmr for the branched amines assuming all methyl branches (no ethyls) and no branching at the alpha carbon.

[f] Lowest wavelength for which a 1 cm-pathlength sample of neat amine gives an absorbance $\leq$ 1.00.

[g] See Experimental Section for details on purification.

pounds, giving effective removal of primary and secondary amine impurities and especially ultraviolet-absorbing decomposition products that build up over time. In the case of TDA, the purification was substantial owing to the poor starting condition of the amine after more than a decade of storage at room temperature, i.e., NE = 495.1, mole-% tertiary = 94.1%, and uv cutoff = 475 nm (brown color).

Vacuum distillation was chosen as the most appropriate purification method for the branched-chain amines because of the large number of isomers. The starting amines were found to have 95 to 98 mole-% 3° amine content (close to the vendors' specifications as were the NE's) with uv-cutoffs of 329 nm to 383 nm (yellow color). For molecular weights less than 400, these values were improved acceptably (Table III), but the higher commercial amines retained some of their original yellow color and primary + secondary amine content: 98.7 mole-% tertiary and 319 nm uv cutoff for TIDA and 96.6 mole-% tertiary and 371 nm uv cutoff for TITA. On the assumption that the yellow-colored impurities were air-oxidation products, TIDA and TITA were further subjected to a reduction procedure (see Experimental Section) with $LiAlH_4$ followed by methanol scrubbing to give the improved values listed in the table.

Backbone chain lengths (the maximum number of consecutive carbons in the alkyl group) were estimated (±10%) by integration of the pmr spectra of the branched amines (Table III). These values represent an average over the various isomers present and follow a reasonable correspondence with the values that would be expected from the nominal alkyl groups listed in Table I. No alpha-methine protons were detected, confirming that branching does not occur at the alpha carbons.

DMP Third-Phase Behavior

Isolation of $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$. For TOA and T810A solvents, extraction of sulfuric acid solutions containing Mo(VI), H_3PO_4, and NaCl was shown previously (22,27) to give solid precipitates having the double-salt composition $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$ (I). As part of the present investigation, an attempt was made to show whether the other amines in Table I also give these double-salt compounds in extraction systems. Solvents containing 0.05 M amine and 0.15 M dodecanol in nonane were pre-equilibrated with 0.1 M H_2SO_4 and then contacted for several days with aqueous solutions containing 0.1 M H_2SO_4 plus Mo(VI), H_3PO_4, and NaCl together. As described in detail in the Experimental Section, the expected double salts were obtained in this manner for TDA and TLA (Table II).

Analogous procedures for the branched-chain amines TIOA, TIDA, and TITA gave yellow solids with slightly less than the expected wt.-% DMP as shown in Table IV. To obtain the double salts in pure

TABLE IV
Analysis of DMP-Containing Solids Obtained with Branched-Chain Amines[a]

Amine	% DMP found	% DMP theor.[b]
TIOA	35.6	44.9
TIDA	33.5	39.8
TITA	31.9	34.8

[a] The solvents contained 0.05 M amine plus 0.15 M dodecanol in nonane and were initially equilibrated with 0.1 M H_2SO_4. A 10 ml volume of each solvent was then contacted for 3 d with 25 to 45 ml of an aqueous phase containing 0.1 M H_2SO_4, 0.5 M NaCl, 0.01 to 0.05 M H_3PO_4, and 0.02 M Mo(VI) (as ammonium molybdate). The yellow precipitates were filtered, washed with hexane, vacuum dried, and analyzed for DMP spectrophotometrically in 1:1 chloroform:isopropanol (22).

[b] Based on $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$.

form for these three amines (Table II), it was necessary to delay adding the NaCl to the aqueous phase until after the DMP anion had time to form in the solvent.

Compositions of other precipitates. As we found with TOA (22,27), contact of most of the amine solvents with 0.1 M H_2SO_4 solutions containing Mo(VI) and H_3PO_4 but no NaCl generally led to the appearance of dense, yellow-green, liquid third phases at the interface when the solvent tolerance for $(R_3NH)_3[DMP]$ was exceeded (Figs. 1A and 1B). These liquid third phases were also noticed in the preparations of the solid double salts of the branched amines (Experimental Section) before NaCl was added to the aqueous phases. Assuming the behavior to be similar to that found for TOA (22,36), these liquid third phases probably contain a variable mixture of trialkylammonium DMP, sulfate, and bisulfate salts with a small amount of diluent and possibly water (but no modifier).

The single surprise in the chloride-free systems was the appearance of a solid precipitate on contacting the TIOA solvent (dodecanol-modified nonane system) with 0.1 M H_2SO_4 containing Mo(VI) and H_3PO_4. Comparison of the x-ray diffraction powder patterns of this extraction precipitate and a sample of $(TIOAH)_3[DMP]$ prepared by reaction of TIOA with $H_3[DMP]\cdot 15H_2O$ in isopropanol confirmed the equivalence of the two substances (see Experimental Section and Table II). By contrast, we note that a liquid third phase formed when toluene was used as the diluent (see preparation of $(TIOAH)_3[DMP]\cdot 3(TIOAH)Cl$, Exper. Section).

DMP tolerance. As shown above, the third-phase behavior of solvents containing dissolved $(R_3NH)_3[DMP]$ involves several types of precipitates depending on the amine structure, diluent type, and the availability of chloride ion needed to form $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$. To be able to discuss the third-phase tendency of solvents containing dissolved $(R_3NH)_3[DMP]$ in general terms, we have been using the word "tolerance" defined here as the maximum concentration of dissolved $(R_3NH)_3[DMP]$ that can exist in the solvent without formation of a DMP-containing third phase. Thus, the term equally applies to situations involving well-defined solid precipitates or variable-composition liquid third phases. The more restrictive term "solubility" is a property only of the solid precipitates.

The DMP tolerance experiments are summarized in Table V for three starting aqueous NaCl concentrations and a range of dodecanol modifier concentrations. Except for one system using 0.05 M TIOA in unmodified toluene diluent, the solvent consisted of 0.05 M amine in dodecanol-modified nonane and was pre-equilibrated with 0.1 M H_2SO_4 to convert the amine to primarily $(R_3NH)_2SO_4$ with minor formation of $(R_3NH)HSO_4$ (2,22). As discussed fully in the Experimental Section, the procedures for determining the tolerances ensured that all of the Mo(VI) in the system was in the form of DMP, essentially replacing some of the sulfate and/or bisulfate in the solvent to give $(R_3NH)_3[DMP]$. Previous measurements using 0.05 M TOA in nonane modified with 0.05 M dodecanol showed that some of the sulfate and bisulfate in the solvent could also be replaced by chloride by adding NaCl to the aqueous 0.1 M H_2SO_4 (22). From these and earlier (2) results, the following general conclusions may be made concerning the proportion of the trialkylammonium chloride, sulfate, and bisulfate salts in the present systems. First, with no NaCl added to the 0.1 M H_2SO_4, the amine not in the form of $(R_3NH)_3[DMP]$ can be expected to be proportioned mainly as the sulfate salt $(R_3NH)_2SO_4$, with minor amounts of $(R_3NH)HSO_4$ increasing in the order TITA < TIDA < TIOA < T810A < TOA. Equilibrated with 0.1 M H_2SO_4 + 1 M NaCl (initially), practically all of the amine not in the form of $(R_3NH)_3[DMP]$ can be expected to be in the form of $(R_3NH)Cl$. With 0.1 M H_2SO_4 + 0.1 M NaCl (initially), an intermediate situation involving significant amounts of the chloride, sulfate, and bisulfate salts is expected; approximately half of the amine not in the form of $(TOAH)_3[DMP]$ was in the form of the chloride salt using TOA (22). Although 0.001 to 0.01 M aqueous H_3PO_4 was present in the experiments for reaction with Mo(VI) to give DMP, it does not get significantly extracted by itself (D = 0.0130) (22).

Since all of the Mo(VI) appears to eventually end up as DMP in the systems examined, the DMP tolerances represent 1/12 of the overall molybdenum tolerance that would be observed on extended equilibration of the solvents with sulfuric acid solutions containing Mo(VI), phosphate, and chloride. During the approach to equilibrium, however, the effective molybdenum tolerance is always greater at first since it may be some time after all of the Mo(VI) gets extracted that any precipitate appears (22,27). As suggested by the data of Table IV, DMP is probably not the only polymolybdate anion capable of causing precipitation, though DMP does appear to be the most stable one.

A limited amount of data listed in Table V shows that the concentration of the dodecanol modifier has a mild effect on the observed tolerance. In the chloride-free systems, an increase in the modifier concentration produces an increase in the DMP tolerance while the chloride-containing systems are characterized by a shallow minimum in DMP tolerance as a function of modifier concentration.

Although the effect of amine concentration on the DMP tolerance was not the major concern of this study, some information regarding this effect may be extracted from Figs. 1A and 1B. The figures show that once the solvent tolerance for DMP is reached, the molarity of dissolved $(R_3NH)_3[DMP]$ in the bulk solvent does not level off but instead decreases as the unprecipitated amine in the solvent is gradually depleted. As work described elsewhere shows, wet nonane containing only dodecanol exhibits little tendency to dissolve $(R_3NH)_3[DMP]$ (3,22). Together with the data of Fig. 1, this fact supports the conclusion that much of the solvation of $(R_3NH)_3[DMP]$ in the extraction solvent appears to come from the other trialkylammonium salts present. The solubilization of low-solubility alkylammonium salts by dissolved alkylammonium salts is characteristic of amine-extraction solvents (6,7).

The dramatic increase in resistance to third-phase formation on replacing an alkane diluent by an aromatic one (4-7,9,11-15) was observed during in the preparation of $(TIOAH)_3[DMP]\cdot 3(TIOAH)Cl$ (see Experimental Section) using toluene as the diluent rather than dodecanol-modified nonane. As shown in Table V, the use of toluene diluent gives a 50-fold increase in DMP tolerance for 0.05 M TIOA over the value for dodecanol-modified nonane.

Effect of amine structure and aqueous chloride concentration. Selected data from Table V are plotted in Fig. 2 to illustrate the dependence of DMP tolerance on amine structure. The highest tolerance values are obtained in the chloride-free systems wherein liquid third phases form; TIOA is an exception, giving instead solid $(TIOAH)_3[DMP]$. At the upper end of the scale, the TLA solvent achieves approximately half of the theoretical maximum loading of 0.0167 M before forming a third phase. The tolerance drops approximately an order of magnitude as the chain length is decreased in the family of straight-chain amines. A similar, yet separate, curve is

TABLE V
Dodecamolybdophosphate Tolerances at 25°C[a]

Amine	Dodecanol molarity	Tolerance (No NaCl)	Tolerance (0.1 M NaCl)	Tolerance (1 M NaCl)
TOA	0.05[b]	1.3×10^{-4} (L)	2.2×10^{-5} (s)	2.9×10^{-5} (s)
	0.10[b]		1.7×10^{-5} (s)	
	0.15	7.9×10^{-4} (L)	1.3×10^{-5} (s)[c]	1.7×10^{-5} (s)
	0.20[b]		1.4×10^{-5} (s)	
	0.30[b]		1.7×10^{-5} (s)	
	0.50[b]		2.8×10^{-5} (s)	
TDA	0.15	5.4×10^{-3} (L)	3.0×10^{-5} (s)	2.5×10^{-5} (s)
TLA	0.05	6.1×10^{-3} (L)		
	0.15	8.7×10^{-3} (L)	4.8×10^{-4} (s)	3.3×10^{-4} (s)
T81OA	0.15	2.1×10^{-3} (L)	1.5×10^{-5} (s)	1.7×10^{-5} (s)
TIOA	0.15	5.6×10^{-5} (s)	6.5×10^{-7} (s)	2.3×10^{-6} (s)
	0[d]	2.8×10^{-3} (L)		
TIDA	0.15	1.8×10^{-3} (L)	$<6.7 \times 10^{-7}$ (s)	$<1.7 \times 10^{-7}$ (s)
TITA	0.15	6.6×10^{-3} (L)	$<2.2 \times 10^{-7}$ (s)	$<3.8 \times 10^{-7}$ (s)

[a] DMP tolerance is the maximum molarity of $(R_3NH)_3[DMP]$ that can exist in the solvent without the formation of a DMP-containing third phase. The solvents consisted of 0.05M amine in dodecanol-modified nonane (except as noted) and were pre-equilibrated with 0.1M H_2SO_4 to give primarily $(R_3NH)_2SO_4$ in the organic phase. In the experiment, part of the sulfate in the organic phase was effectively replaced by DMP to give $(R_3NH)_3[DMP]$. The three starting aqueous NaCl concentrations 0, 0.1, and 1M (in addition to 0.1M H_2SO_4 and 0.001 to 0.01M H_3PO_4) respectively permitted none, part, or practically all of the remaining sulfate in the organic phase to be replaced by chloride to give $(R_3NH)Cl$. Whether the third phases were solid (s) or liquid (L) is indicated in parenthesis. Accuracy in the tolerance values is ±10%.

[b] Values taken from Ref. 22.

[c] The value 1.5×10^{-5} was previously reported in Ref. 22.

[d] Unmodified toluene was used as the diluent; room-temperature measurement based on the concentration of Mo(VI) in the solvent that produced a visible third phase.

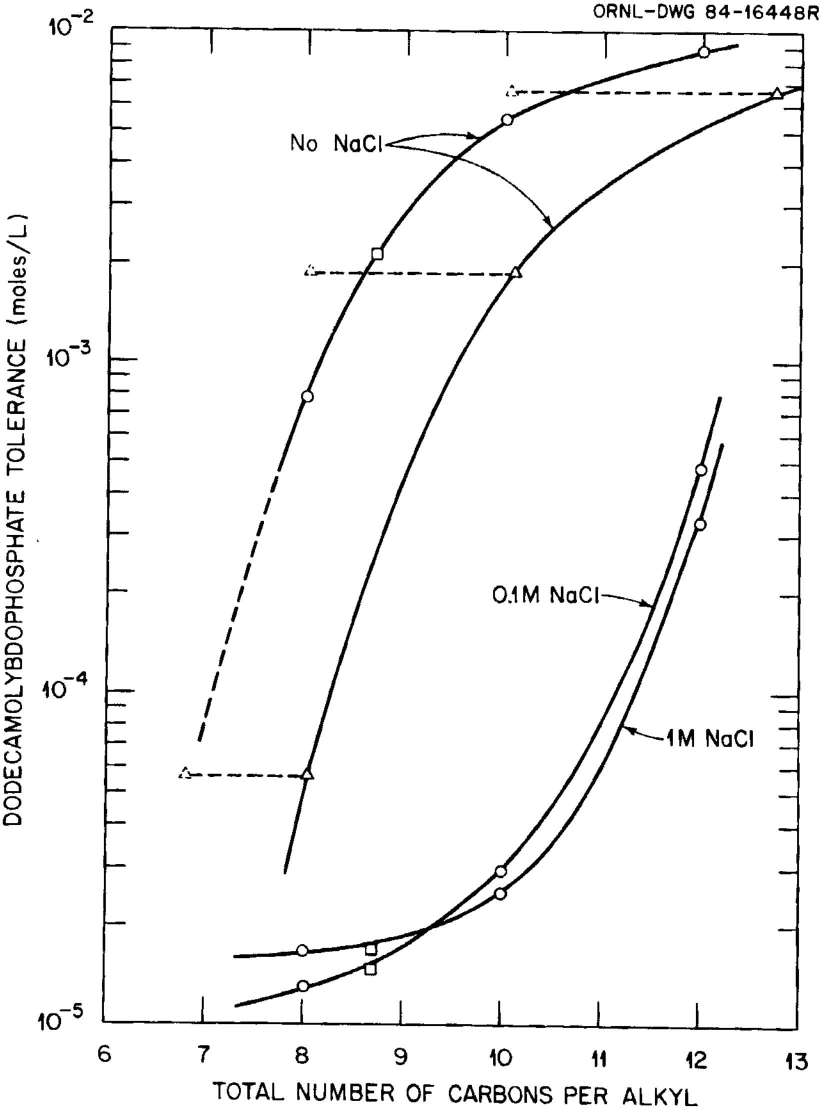

Figure 2. Maximum solvent molarity of DMP that can be tolerated without formation of a third phase at 25°C vs the total number of carbons per alkyl. □ — T810A; o — straight-chain laboratory amines; Δ — branched amines; ∆ — branched amines replotted vs backbone chain length. The data is taken from Table V.

obtained for the methyl-branched family of amines when plotting against the total number of carbons per alkyl. On this basis, the branched-chain amines appear to be worse than the straight-chain amines, but the behavior is more nearly equivalent to the straight-chain family when plotting against the backbone chain-length. Thus, for chloride-free systems, the DMP tolerance appears to be governed primarily by the physical length of the alkyl chains rather than their "fatness." A similar effect was observed previously when comparing phase-disengagement rates (2).

Significant differences in solubility trends may be noted between the branched-chain family of double salts and the straight-chain family of double salts in the chloride-containing systems. Solubility increases rapidly with the length of the straight alkyl chains, and the T810A blend behaves again approximately according to the average chain length. The tendency of the T810A values to fall just below the solid curve based on the series TOA, TDA, and TLA may be some reflection of the lower solubilities of some of the shorter-chain components of the T810A blend. The solubilities of the branched-chain double salts fall much below the solubilities of the straight-chain double salts. Further, it is clear that the differences between the solubilities of the straight- and branched-chain families of double salts cannot be correlated simply on the basis of the differences between backbone chain length and the total number of carbons per alkyl group.

In general, adding chloride to the system causes the DMP tolerance to drop sharply, corresponding to a phase change from a liquid third phase to crystalline $(R_3NH)_3[DMP]\cdot3(R_3NH)Cl$ (I). As was observed with more extensive measurements using TOA (22), the DMP tolerance, i.e. solubility of (I), subsequently tends to level off or even increase slightly.

Behavior in process solvent. To compare the above results to a more practical system, the experiment summarized in Fig. 3 was performed (see also Exper. Section). Aqueous concentrations that could reasonably be expected in process feed (2,14,27,45,46) were used. In each case, the precipitate was a yellow-green particulate interfacial solid, presumably $(R_3NH)_3[DMP]\cdot3(R_3NH)Cl$. It is evident from Fig. 3, that the variation in DMP tolerance with amine structure follows similar trends in process solvent as were obtained in dodecanol-modified nonane (Fig. 2). Although T812A has an average chain length comparable to that of TDA, the DMP tolerance for T812A is worse, undoubtedly because the solubility of the T812A precipitate is determined by the short-chain components of T812A. A similar, but less noticeable, effect can be seen for T810A in Figs. 2 and 3. (This suggests that the molybdenum tolerance of these blends could be increased somewhat by preferentially precipitating the low molecular-weight amine components with DMP and recovering the high molecular-weight fraction for reuse.) Lastly, it may be remarked that the absolute values for the DMP tolerances in Fig. 3 are substantially larger (factor of 15 to 30) than the values given in

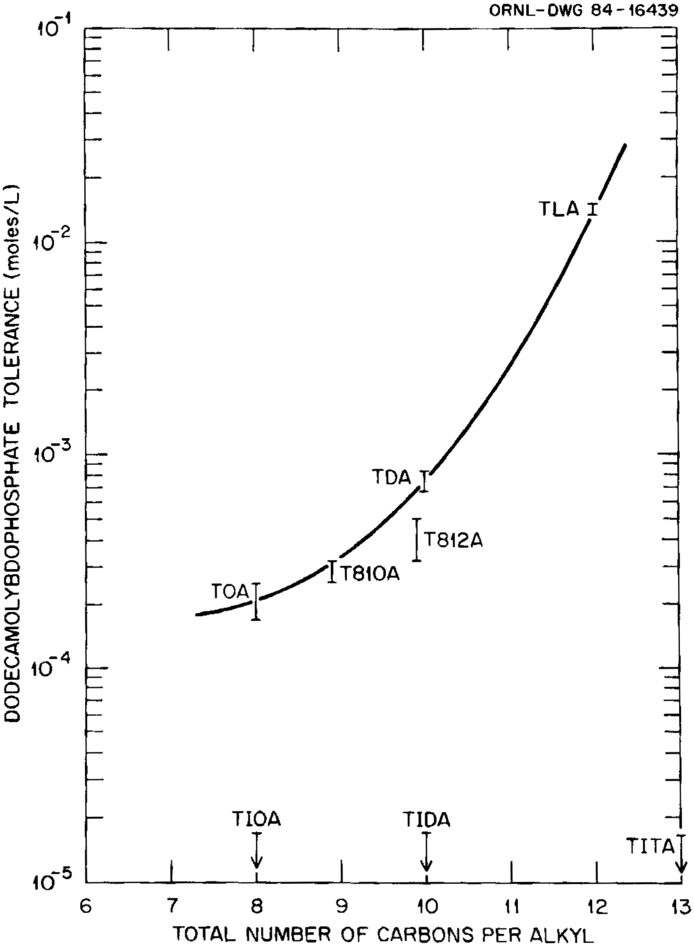

Figure 3. DMP tolerances for 0.06 M amines in Kermac 470B kerosene modified with 0.06 M tridecylalcohol at room temperature (23-25°C). Solvents pre-equilibrated with pH 1 Na_2SO_4 (0.3125 M Na_2SO_4 + 0.1875 M H_2SO_4) were contacted for 1 to 2 months with pH 1 Na_2SO_4 containing 0.02 M NaCl, 0.002 M H_3PO_4, and Mo(VI) (as ammonium molybdate). The aqueous Mo(VI) concentration was increased until a precipitate formed, bracketing the DMP tolerance between two values, giving the indicated uncertainties. Complete conversion of Mo(VI) to DMP was assumed. Only upper limits could be obtained for the branched amines.

Table V for the chloride-containing systems. The increase may be attributed to several factors, including higher diluent aromaticity (i.e., 11.7% (1)), lower aqueous chloride concentration, higher amine concentration, and lower modifier concentration.

DISCUSSION AND CONCLUSIONS

Chemical Implications

As a general observation, most of the qualitative features of DMP-caused third-phase formation reported for TOA (22,27) are preserved among the various other tertiary amines examined above: T81OA, TDA, TLA, TIOA, TIDA, and TITA. It may be generalized that the co-extraction of Mo(VI) and phosphate from 0.1 M H_2SO_4 leads to formation of the dissolved salts $(R_3NH)_3[DMP]$, which may partially precipitate in either liquid or solid third phases. When part of the amine is in the form of $(R_3NH)Cl$ as a result of the exchange of aqueous chloride for trialkylammonium sulfate, a solid compound precipitates with the fixed stoichiometry $(R_3NH)_3[DMP]\cdot3(R_3NH)Cl$ (I) as shown for each of the trialkylamines tested (Table II). The overall average N/Cl ratio in the various double salts shown in Table II plus the double salts of TOA and T81OA (22,27) is 1.93 ± 0.12. Although it seems probable that other trialkylammonium salts could also combine with $(R_3NH)_3[DMP]$ to give other crystalline double-salt compounds, $(R_3NH)_3[DMP]$ tends to precipitate together with $(R_3NH)_2SO_4$ and $(R_3NH)HSO_4$ as liquid third phases with variable, rather than fixed, mixed-salt ratios (3,22), at least under the conditions examined here. However, the isolation of crystalline $(TIOAH)_3[DMP]$ shows that the single DMP salt may be the stable precipitate under some conditions.

A central issue in the understanding of amine-extraction chemistry is the tendency of alkylammonium salts to aggregate in nonpolar diluents (5,6) to form entities that could be described as small inverted micelles. Although self-aggregation of pure trialkylammonium salts in organic solvents has often been investigated, the results have limited applicability to the more common, yet less understood, situation involving solvents containing more than one trialkylammonium salt. A growing number of papers indicate that mixed-salt interactions strongly influence both the extractive properties and third-phase behavior of alkylammonium extraction systems (5-8,22,27-31). In solution, a number of mixed-salt aggregates given by $(R_3NH)Y\cdot(R_3NH)X$ have been hypothesized (5,29-31) where X^- and Y^- are univalent anions. The isolation of $(R_3NH)_3[DMP]\cdot3(R_3NH)Cl$ here suggests a broader categorization in terms of the stoichiometry

$$(R_3NH)_qX\cdot q(R_3NH)Y \quad (II)$$

where X^{q-} may be a multiply charged anion and Y^- is restricted (for the time being) to a single charge.

That there should be any physical basis for proposing that a special stability may, under certain conditions, be associated with stoichiometry (II) as opposed to less restricted salt combinations is not yet clear. Undoubtedly, other combinations occur, though few well-characterized systems exist. However, it may be noted that in the cases so far exhibiting the stoichiometry (II), X^{q-} is significantly larger in size than Y^- and consequently (44) possesses a weaker ability to accept the hydrogen bond from the proton of the trialkylammonium cation. If X^{q-} weakly accepts the hydrogen bond, an instability in the monomeric single salt $(R_3NH)_qX$ arises in that the proton of the cation then potentially becomes available to hydrogen bond with other acceptors including Y^-. Infrared evidence, in fact, suggests that the hydrogen bond does shift from X^{q-} to the better hydrogen-bond acceptor Y^- (29-31) as has also been found (36) for (I). If Y^- is limited for steric and/or electronic reasons to just two hydrogen bonds, the stoichiometry of (II) arises.

That crystalline solid compounds, rather than viscous liquid third phases, precipitate is an unusual feature of the amine-DMP chemistry, especially since some of the trialkylammonium cations are branched. Features of the DMP anion that contribute to stabilizing the solid phases probably include its large size, high charge, and high symmetry (T_d).

Among the straight-chain amines, the resistance of the solvent to DMP-caused third-phase formation increases with amine chain length, following the generally observed pattern in amine extraction (2,5-9). Extrapolation of the trend to higher chain lengths, however, may be misleading because of the tendency of the chain-length effect to maximize in some cases (10). Based on the length of the main alkyl backbone, the methyl-branched "iso" amines exhibit a similar chain-length effect and correlate favorably with the straight-chain amines in the chloride-free systems. Blends of various normal alkyl chain lengths are inefficient because the short chain lengths dominate the DMP tolerance.

The effect of branching on third-phase tendency cannot be as easily generalized as the effect of chain length. Although little change in the DMP tolerance associated with the chloride-free liquid third phases occurs with adding methyl branches onto a given backbone, such branching leads to a strong precipitation tendency in the presence of chloride.

Process Implications

The available evidence (11-15,20,22,27) indicates that formation of heteropolymolybdates, especially dodecamolybdophosphate (DMP), lies at the heart of the molybdenum third-phase problem in amine-extraction hydrometallurgy. Indeed, since phosphate is usually a constituent of ore leach solutions (2,14,27,45,46), the times when the possibility of DMP formation can be ruled out are relatively few. The kinetics of DMP formation in the solvent tend to be slow (22,27), however, and the systems most vulnerable to precipitation problems are consequently those which permit long Mo(VI) residence times in the solvent. Thus, the advantage of chloride stripping as a selective U(VI) strip (leaving the Mo(VI) behind in the solvent) has been offset by increased molybdenum third-phase formation, mainly because the Mo(VI) is not immediately stripped and has more time to polymerize. Chloride stripping may also exacerbate the problem by making it possible for $(R_3NH)_3[DMP]\cdot 3(R_3NH)Cl$ to crystallize, but ore leach solutions typically contain sufficient chloride (22) for this to happen anyway.

As summarized in Table V and Figs. 2 and 3, the solvent tolerance for $(R_3NH)_3[DMP]$ exhibits high sensitivity to amine structure, providing a rational basis for selecting an optimum tertiary-amine reagent for extraction of molybdenum from acidic sulfate and/or chloride media. The results agree with qualitative observations concerning the effect of amine structure on molybdenum tolerance in process-development studies (11-15). Namely, the longest normal alkyl chains available (in TLA) give the greatest resistance to molybdenum third-phase formation (as well as the greatest resistance to silica-caused emulsion formation (2)). At least one solvent-extraction plant has processed high-molybdenum sulfuric-acid leach solutions successfully with TLA in a largely aliphatic diluent (Kermac 470B kerosene) without any sign of molybdenum third-phase formation (47).

Despite the nuisance value of molybdenum third-phase formation, the precipitation of molybdenum compounds from the solvent could conceivably be exploited, in itself, as a selective separation of molybdenum from other extracted metals such as uranium. In this case, the data presented above could be optimized for, rather than against, third-phase formation, perhaps using branched-chain amines to ensure low solubilities. The slow molybdenum-polymerization kinetics could be accelerated by loading the solvent to higher molybdenum concentrations and by deliberately adding phosphoric acid to the aqueous feed. Advantages might include good selectivity and efficiency.

In conclusion, the most important lesson of the present work is that criteria in the design and selection of extraction reagents must include not only selectivity considerations but such practical criteria as good solubility of extraction complexes in the solvent.

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