Property–Performance Relationships of Commercial Diluents in Sub-Saharan Africa Copper Solvent-Extraction Conditions

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A study of five commercially available solvent-extraction diluents in combination with three commercially available extractants under sub-Saharan African copper solvent-extraction conditions yielded intriguing results. A variety of physical and chemical property analyses showed that the diluents have some property differences, but overall the properties are similar and provide comparable solvent-extraction performance. Although each physical chemical property technique provides useful information, no individual test result suffices for prediction of diluent performance. Furthermore, a diluent should be evaluated within the conditions for which it is targeted to determine a true measure of performance. Overall, the diluents studied possess appropriate physicochemical properties for sub-Sahara Africa copper solvent-extraction conditions and can be utilized to achieve efficient, safe and reliable operations.

INTRODUCTION

Background

Today, commercial SX diluents are available globally from a limited number of manufacturers. Production quality and consistency of these diluents have improved tremendously over the past 20 years. For example, diluent flash points have been increased incrementally to improve transport and handling while reducing fire hazards. In addition, properties have been successfully modified to minimize evaporative losses, ultimately reducing SX plant raw material costs. Diluent manufacturers have also focused on meeting performance requirements of SX plants, including eliminating components detrimental to SX operations, such as olefinic groups that can react with various species resulting in changing phase-disengagement properties over time, as well as ensuring that proper hydrocarbon components are present within diluent mixtures to maintain good reagent–metal complex solubility. These challenges have been met in the midst of ever-increasing stringent environmental regulations.

Sub-Saharan Africa copper SX operations pose a unique set of conditions for diluents due to inherent ore compositions and the associated high reagent concentrations required for complete copper extraction. Chevron Phillips Chemical Company, LP has been manufacturing hydrocarbons and hydrocarbon-based diluents since the mid-80s, applying this experience to identify the physical properties considered crucial for proper performance in SX operations. This paper documents the findings of a study utilizing commercially available diluents in combination with extraction reagents commonly utilized in African SX operations to evaluate the relative performance of the diluents under sub-Saharan Africa copper SX conditions.

Scope

This study evaluated physical/chemical properties of a several commercial diluents, including flash point, density, pour point, aromatics content, and viscosity as a function of diluent source. Physical properties of 80% of maximum copper-loaded organic solution were also studied as a function of diluent source and extraction reagent. Finally, SX performance, including phase-disengagement time (PDT), copper extraction kinetics and extraction reagent–copper complex solubility was evaluated as a function of diluent source, reagent type and temperature.

For all SX experiments the reagent concentration was made up to 38% (v/v) in the desired diluent. This reagent concentration was selected to represent about the highest concentration in use in sub-Saharan Africa, and that if the diluent/reagent blend performed well at this concentration, it should do so at lower reagent concentrations.

EXPERIMENTAL

Materials

Reagents

The organic reagents comprised Orfom® SX80, Orfom® SX12, Orfom® SX11 (Chevron Phillips Chemical Company, LP Mining Chemicals); BP Mining Solvent and Shellsol® 2325; Acorga® OPT 5510 and Acorga® OPT 5540 (Cytec Industries Inc., Mining Chemicals); and LIX® 984N (BASF Mining Solutions). The other chemicals comprised cupric sulfate pentahydrate, ferric sulfate pentahydrate and ammonium sulfate (all reagent-grade from Fisher Scientific), concentrated ammonia (30 %) and concentrated sulfuric acid (95-98%) (Fisher Scientific) and nitrogen (N_2, high purity, cylinder) obtained from Airgas, Inc.). All reagents were utilized as received.

Procedures

Physical Properties of Neat Diluent Samples

All neat diluent physical property measurements, including evaporative loss, were performed by SGS Laboratories (Deer Park, Texas, USA) according to the specifications set for the corresponding ASTM analyses. The analyses were performed in triplicate and the results reported are the average of the three measurement results. ASTM procedures performed on all diluent samples are listed along with the corresponding results in the tables within the results section.

Phase-Disengagement Performance

All phase disengagement tests were performed at room temperature (25 °C) in triplicate. All of the results of the phase-disengagement tests, including PDT, metals analyses, and resulting loaded organic phase viscosity are reported as the average of the three measurements.

Synthetic pregnant leach solution (PLS) for the phase separation and copper extraction kinetics set of tests was prepared using copper sulfate pentahydrate, ferric sulfate pentahydrate, distilled water and sulfuric acid. The PLS contained 16.0 g/L Cu, 2.0 g/L Fe iron and had a pH of 2.0. One lot of PLS solution was prepared and used for all phase-disengagement tests to eliminate batch-to-batch variability.

The method utilized for this test is a Chevron Phillips Chemical Co., LP (CPChem) internal method, which includes kinetics measurements for desired metals. For details regarding the method, please contact CPChem or the author. Analyses for these samples were performed by SGS Laboratories (Tucson, AZ) for Cu content by AA spectroscopy.

Samples of the organic phase were also analyzed for viscosity according to ASTM D445 at 22, 30, 38, and 45 °C and reported in mPas.

Copper Complex Solubility Performance

A solution containing about 20 g/L Cu, 27 g/L free ammonia and 100 g/L ammonium sulfate was made up from copper sulfate pentahydrate, concentrated ammonia and ammonium sulfate. The respective reagent diluent pair was vigorously contacted for about 2 minutes with the ammonia copper solution at an O/A ratio needed to achieve 80% of copper maximum loading. This was to ensure quantitative copper transfer into the respective organic phase. Samples of the respective organic phases were placed in glass vials and stored in a refrigerator (7 °C) and at room temperature (25 °C). These samples were inspected visually for a total of seven days to determine any precipitation (crystallization) of the extraction reagent-copper complex from the solution.

RESULTS

The study results are divided into two major sections below: physical and performance properties of "neat" diluent and physical and performance properties of 38 volume % reagent/diluent blends. The property section discusses the physical/chemical property measurements of each diluent as well as evaporative loss measurements on select diluents (for comparison). The "properties of diluent/reagent blends" section discusses phase disengagement time (and behavior) as well as resulting loaded organic physical properties, including viscosity and extractant reagent–copper complex solubility.

Diluent "Neat" Physical and Chemical Properties

The diluent properties measured in this study are summarized in Tables I and II. All of the results reported are the average of three measurements and all measured values were within the acceptable variance as reported for each ASTM procedure. Table I summarizes typical physical/chemical properties including flash point, density, pour point and viscosity at varying temperature. Table II records details on hydrocarbon types present within each diluent, such as aromatics, paraffins and naphthenes (FIA, ASTM D1319). Furthermore, the hydrocarbon types are classified by aromatic hydrocarbon type (as per ASTM D2425) in Table II.

Table I. SX diluent typical physical properties.

Analysis	ASTM method	Orfom SX12	Orfom SX80	Orfom SX11	BP Mining Solvent	Shellsol 2325
Flash point (°C)	D93	81	82	114	83	85
API gravity (15.5 °C)	D1298	40.3	39.4	43.0	40.6	39.2
Specific gravity (15.5 °C)	D1298	0.8236	0.8280	0.8109	0.8222	0.8289
Density (Kg/L)		0.824	0.828	0.811	0.822	0.829
KB value	D1133	33.5	30	24.5	35	36.5
Pour point (°C)	D97	–40	–34	–57	–50	–47
Total sulfur (ppm)	D2622	<3.0	<3.0	<3.0	154	144
Bromine No. (g Br/100 g)	D1159	<0.5	<0.5	<0.5	0.5	0.5
Viscosity at 0 °C (mPas)	D445	4.55	5.84	23.42	3.79	3.91
Viscosity at 10 °C (mPas)		3.44	4.32	14.07	2.93	3.01
Viscosity of 25 °C (mPas)		2.45	3.00	7.69	2.13	2.18
Viscosity at 40 °C (mPas)		1.71	2.03	4.25	1.53	1.56

The diluent typical properties were measured independently by a single laboratory to provide a good comparison; the resulting data compare adequately with the published data for the products from various sources. This consistency with known values provided confidence in the measured data and a reasonable comparison of the diluent properties.

Several interesting observations can be made when comparing the typical property data. First, all of the measured flash points of the diluents are quite similar (near 82 °C), except for Orfom SX11 (114 °C) (see Table I). This difference in flash point for Orfom SX11 is expected since this product is manufactured by tailored processing to achieve specific, desired physical properties including flash point. Its properties make it suitable for higher temperature operations. The range for all other diluents evaluated in this study is 81 °C (Orfom SX 12) to 85 °C (Shellsol 2325).

Another similarity arises in the specific gravity of these diluents. The range is also relatively small from 0.8236 (Orfom SX12) to 0.8289 (Shellsol 2325), resulting in an overall difference of up to approximately 0.6%.

Bromine numbers measured for all of the diluents were relatively low as well (Table I). BP Mining Solvent and Shellsol 2325 samples were measured to have a bromine number of 0.5 g Br/100 g sample compared with a bromine number of <0.5 g Br/100 g sample for the Orfom SX diluents (<0.5 value is reported as being below the detection limits of the method). Although 0.5 g Br/100 g sample is slightly higher than a <0.5 g Br/100 g sample measurement, all of the bromine number values were very low. These data suggest that all of the diluents evaluated in this study have a very low concentration of reactive olefinic groups, especially primary olefins. Therefore, the diluents should all exhibit a low susceptibility to chemical reactions that produce species detrimental to phase disengagement properties (such as sulfonation).

The range of pour point values measured for the diluents (Table I) is somewhat broader than that for some of the other basic physical properties. The pour points measured ranged from the highest at –34 °C (Orfom SX80) to the lowest at –57 °C (Orfom SX11). Again, Orfom SX11 has a tailored structure due to the manufacturing process, producing a primarily branched aliphatic hydrocarbon character (isoparaffins) compared with the other diluents, which results in a lower pour point. Comparing the pour point of the other diluents (excluding Orfom SX11) shows a range of –34 °C (Orfom SX80) to –50 °C (BP Mining Solvent). While this is a significant difference as far as the measurement is concerned, the pour points reported would have little impact on practical plant operation. All of the pour points were significantly lower than temperatures SX plant operations would encounter.

Viscosity of the diluents was also measured as a function of temperature ranging from 0 °C to 45 °C (Table I.) These values examine possible handling differences for the diluents, both from simply moving the material (pumping) to mixing with an aqueous PLS. The viscosity of Orfom SX11 can be noted as being significantly higher than the other diluents, which is due to the highly branched aliphatic character of the hydrocarbon components. This re-emphasizes the application of Orfom SX11 for higher temperature operations. The viscosities of the remaining diluents show a reasonable range within the diluents and by temperature. BP Mining solvent and Shellsol 2325 demonstrated a similar viscosity profile over the temperature range studied, with BP Mining Solvent having the lowest viscosities measured. Orfom SX12 was slightly higher than BP Mining Solvent and Shellsol 2325 and Orfom SX80 was measured as having the highest viscosity across the entire temperature range. At 0 °C the viscosities measured ranged from 5.84 mPas (Orfom SX80) down to 3.79 mPas (BP Mining Solvent).

Although there is a measurable difference in the viscosities of the diluents within this study, this difference did not appear to significantly influence the extraction and phase-disengagement performance, as discussed in the following section (PDT and copper extraction kinetics were not vastly different for the various diluents). Furthermore, a systematic study of phase disengagement and/or extraction performance as a function of diluent viscosity has not been found in a search of public literature. Although there may be effects that arise from diluent viscosity at some point, the viscosities measured for the products within this study are within SX operational capabilities (pumping, etc.) and provide desirable performance.

One easily noted difference in physical property measurements for these diluents was total sulfur (Table I). The Orfom SX diluents were all measured to have very low total sulfur content, listed as <3.0 ppm, which is essentially below the detection limit of the method. BP Mining Solvent and Shellsol 2325 were measured as having 154 ppm and 144 ppm, respectively. The total sulfur analysis (ASTM D2622 – X-Ray Fluorescence, XRF) measures every form of sulfur which can include elemental sulfur and organosulfur compounds (such as thioethers, thiols and sulfates). This difference in total sulfur is likely due to regional production regulations that refineries must adhere to for fuels sulfur content. While SX diluents are not classified as "fuels", they are produced by similar conditions as diesel or jet fuels within refinery equipment. Therefore, these products contain the amount of sulfur as stipulated by regional regulations. Orfom SX diluents are all produced in U.S. refineries, and current regulations for U.S. refineries state that diesel/jet fuels produced by these refineries must have <15.0 ppm total sulfur (US EPA, 2000). These limits were imposed for environmental protection to yield cleaner air emissions. However, not all global regions, where the other diluents used in this study may be produced, are currently held to the same total sulfur specification for fuels. For example, fuel-based products produced in South Africa do not currently have the same total sulfur limit for diesel/jet fuels produced in the U.S. Therefore the total sulfur contained in diluents produced within South Africa may be (by way of processing) slightly higher. However, sulfur content does not appear to correlate to diluent performance.

The KB tests were developed as a measurement of product solubility. The test is not directly applicable to diluent solubility, but can provide an interesting comparison of the physical/chemical properties of the diluents analyzed within this study. The measured KB values ranged from 24.50 (Orfom SX11) to 36.50 (Shellsol 2325) (Table I). Orfom SX11 is somewhat different in nature than the other diluents within this study as it is manufactured to have no aromatic content and composed almost entirely of branched (saturated) hydrocarbons. Since aromatic content can increase the KB value in the test and Orfom SX11 has no aromatics content, this may help explain this observed difference. The remaining diluents evaluated have KB values that range from 30.00 to 36.50, which is not a significant difference in terms of SX operation performance. While KB values provide some insight into relative solubility of different diluents, KB values are only a small part of the subject of solubility, and there are many different solubility scales (ACL, 2014).

KB values are measured by determining the amount of a given hydrocarbon that can be added to a solution of Kauri resin in n-butanol. Kauri resin is a fossilized resin derived from the sap of the Kauri pine tree, which grows primarily in New Zealand. This resin dissolves easily in n-butanol but does not dissolve readily in hydrocarbon solvents. The KB value definition is, according to the ASTM (method D1133), the volume given in milliliters of any solvent with which, at 25 °C (77 °F), a standard KB solution is titrated and a certain amount of turbidity is detected. KB values are often misinterpreted and directly related with "universal solvent power". However, there is no such a thing as "universal solvent power". Each solvent (diluent) has its own capacity to dissolve a certain type of substance more or less effectively than others depending on its own physical-chemical properties as well as those of the substance that has to be dissolved. The optimum scenario is to test the desired diluents within the conditions for which they are targeted to determine solubility effectiveness for specific reagent-metal complexes. Therefore, the listed diluents were examined within the operational conditions of sub-Saharan African copper SX conditions to compare solubility of the resulting reagent–copper complex (discussed in the following section).

One common misconception is that the presence of relatively higher molecular weight hydrocarbons within a given mixture always explains a higher relative viscosity. Indeed higher molecular weight hydrocarbon content can result in increasing viscosity to some extent. However, molecular weight is not the only factor that affects viscosity. This can be noted by reviewing the data for Orfom SX11, which has a much higher viscosity than any of the other diluents evaluated. Through various internal analyses and production processes with Chevron Phillips Chemical, Co. it is known that Orfom SX11 has a hydrocarbon content predominantly in the range of C_{13}–C_{16} chains. Orfom SX80 also has a hydrocarbon predominant chain length content in this range of C_{13}–C_{16} but also does contain some hydrocarbon chains slightly higher than C_{16}. If viscosity were strictly a function of hydrocarbon molecular weight then Orfom SX11 should have a lower viscosity than Orfom SX80 due to the relative difference in hydrocarbon chain lengths (molecular weights) within the two products, but it does not. The significantly higher viscosity measured for Orfom SX11 is most probably a function of the higher branched hydrocarbon content relative to the other diluents. Although there are some differences in physical properties of the various diluents studied, all appeared to perform similarly and adequately throughout the tests.

Evaluation of the hydrocarbon types present within each of the targeted diluents was also an objective for this study. Two methods were selected for this comparison: FIA (ASTM D1319) and hydrocarbon types (ASTM D2425). Data from these analyses are summarized in Table II. FIA data recorded included the amount (volume %) of aromatics, olefins, and paraffins. ASTM D2425 was employed as a second measurement of hydrocarbon types and recorded the weight content of aromatics, naphthenes and paraffins. Furthermore, ASTM D2425 provided a breakdown of the aromatic types within each diluent, including mono-, di-, tri-, tetra-, penta-, thiophenes and "unidentified". Two methods were used to obtain a reasonable understanding of the hydrocarbon types and content. Both methods provide some detail about hydrocarbon mixture compositions with physical properties in the range of the SX diluents within this study, but neither provides all of the information desired. There is a variety of techniques beyond the two employed in this study that are known for analyzing mixtures for hydrocarbon types and all have advantages and disadvantages. These two were selected due to their familiarity for analysis of these types of products, their practicality and the reasonable reliability of the data produced.

By comparing the FIA aromatics content (Table II), it can be seen that Orfom SX12, BP Mining Solvent and Shellsol 2325 have similar concentrations of alkyl-aromatic hydrocarbons, approximately 20%. These values agree well with reported data for these products. One difference to be noted in aromatics content is in comparing Orfom SX80 with Orfom SX12 and BP Mining Solvent and Shellsol 2325. Orfom SX80 was measured to have 5% aromatics (by both FIA and ASTM D2425). Although Orfom SX80 does have significantly less aromatic content than these other three diluents mentioned, the data measured also agrees well with known/reported data for Orfom SX80 diluent.

The aromatics values measured by both FIA (ASTM D1319) and hydrocarbon types (ASTM D2425) agree reasonably well also for all of the diluents analyzed (all of the aromatics values from the two methods measured within approximately 3%). In addition, the paraffins content measured by FIA compares reasonably with the total of naphthenes and paraffins obtained by hydrocarbon types (Table II). For example, FIA analysis for Orfom SX12 resulted in a total of 77.6 vol.% and hydrocarbon types analysis measured a total of 76.6 wt.% of naphthenes plus paraffins (45.12 + 31.46). The slight difference is likely due to the difference in techniques and units of measure. In addition, FIA analysis provides a "total" paraffin content while ASTM D2425 (hydrocarbon types) provides further detail of the paraffin hydrocarbon types – saturated cyclic rings (naphthenes) and paraffins. This trend of FIA paraffin content being consistent with the total of naphthenes and paraffins measured by ASTM D2425 appeared to be consistent throughout the series of diluents. All of the results comparing paraffin content by FIA to naphthenes plus paraffin content by ASTM D2425 are within approximately 4% units of each other. These results provide more confidence in the data measured and suggest that these two analyses are complimentary to one another.

Another noteworthy observation can be made by evaluating the aromatic hydrocarbon types (Table II). ASTM D2425 provides this additional level of detail to understand a little more about the aromatic hydrocarbon character within a given sample. Of all the aromatics measured within all of the diluents analyzed (excluding Orfom SX11), the composition is predominantly due to mono-aromatic structures. The remaining aromatic content for all the diluents is then composed of di-aromatic compounds. This suggests that most of the aromatic content of all of the diluents analyzed is alkylated benzene structures (mono-aromatic ring) followed by a small content (<2%) of alkylated naphthalene (di-aromatic ring) compounds. However, this does not mean that these mono- or di-aromatic compounds are structures of hazardous concern, such as benzene, toluene, xylene or naphthalene. Rather, the mono- and di-aromatic structures have various carbon length chain substitutions on a single or di-aromatic ring. A more sophisticated analysis technique must be utilized to arrive at concentrations of specific compounds.

Table II. SX diluent hydrocarbon types.

Analysis	ASTM method	Orfom SX12	Orfom SX80	Orfom SX11	BP Mining Solvent	Shellsol 2325
FIA (vol.%)	D1319					
Aromatics		20.5	5.0	<5	18.3	18.4
Olefins		1.9	2.9	3.3	0.8	0.8
Paraffins		77.6	92.1	94.4	80.9	80.8
Hydrocarbon type (wt.%)	D2425					
Aromatics		23.42	5.53	1.43	21.69	18.84
Naphthenes		45.12	66.57	51.76	46.46	53.02
Paraffins		31.46	27.9	46.81	31.85	28.14
Aromatic type (wt.%)	D2425					
Mono		21.76	5.06	0.00	20.43	17.87
Di		1.62	0.41	0.46	1.24	0.94
Tri		0.00	0.00	0.96	0.00	0.00
Tetra		0.02	0.02	0.01	0.00	0.01
Penta		0.00	0.00	0.00	0.00	0.00
Thiophenes		0.00	0.01	0.00	0.01	0.02
Unidentified		0.02	0.02	0.00	0.00	0.00

Limitations in both methods can be noted when evaluating Table II data for Orfom SX11. Orfom SX11 is specially manufactured to have no aromatic content, no olefin content and a high concentration (>99%) of saturated, branched paraffins. The FIA data for Orfom SX11 do not agree. For example, the olefin content measured by FIA for Orfom SX11 was 3.3% (Table II). Although FIA has been utilized for many years to perform hydrocarbon type analysis, the results are not necessarily accurate and lab-to-lab reproducibility is poor. Lubeck and Cook (1992) state regarding FIA ASTM D1319 that it "is questionable for a number of reasons, including poor inter-laboratory reproducibility, erroneous results (particularly at low olefin levels), and inappropriate units of measurement".

FIA analysis is performed by introducing a hydrocarbon sample onto an activated silica gel column packed in a small glass column with uniform bore size. Before sample introduction the top of the column is treated with fluorescent dyes. Once the sample is introduced, isopropyl alcohol is added as an eluent to desorb the hydrocarbons and move them down the column at different rates according to their affinity for the silica gel – saturates have the least affinity and move first/faster and then progressively slower rates (higher affinity) are observed with olefins and finally aromatics. The hydrocarbon types carry the fluorescent dyes into separate "zones" and the dyes are detected under UV light, each type of hydrocarbon showing up as a different color. These colors mark the zone "boundaries" of the hydrocarbons, saturates, olefins and aromatics. The volume % of each hydrocarbon type is then calculated from the length of each zone on the column. One source of error in this technique is due to the difficulty in determining the position of the zone "boundaries" of the hydrocarbon layers, which is performed visually. In addition, the isopropyl eluent is applied under pressure, which can vary somewhat depending on the operator and thus influence the speed at which hydrocarbon components travel down the silica gel column and the efficiency of separation. Furthermore, individual hydrocarbon compounds can be somewhat complex, having for example aromatic character and paraffin character (having a long carbon chain substituted aromatic ring).

Such compounds may lie in a "boundary layer" within the analysis, obscuring the results slightly sand making the distinction between zones more difficult.

Aromatics types analysis (from ASTM D2425) for Orfom SX11 suggests that the product contains di- and tri-aromatic ring structures. Based on knowledge of the product and production methods these cannot be present. This data points to some limitations in the ASTM D2425 analysis also. First, the method is a gas chromatography (GC)–mass spectrometry technique for identifying compounds. As such, it also requires separation of hydrocarbon components by a silica gel column before introduction into a mass spectrometer to measure component masses. Because these products can contain complex hydrocarbon structures, the individual components are not always completely resolved and separated which can lead to misleading data. Once the separated hydrocarbon components enter the mass spectrometer a mass spectrum is obtained for each. The parent molecular ion (mass) is referenced to known compounds to identify type and calculate mass fractions. Again, because diluent products can contain complex hydrocarbon compounds, some may be misidentified as being an aromatic compound when it may be an aliphatic compound, or vice versa. Because Orfom SX11 is composed of entirely branched, isoparaffin-type compounds, many of the components are not in the reference compounds used for the method, and thus some components were misidentified.

FIA (ASTM D1319) and hydrocarbon types (ASTM D2425) analyses provide useful information for interpreting the nature of SX diluents, but it should be understood there are limitations associated with these methods. All of this information underscores the need to utilize multiple analysis techniques to determine structural information about complex hydrocarbon mixtures. Because every analysis technique has limitations, no individual analysis should be used to determine application performance of SX diluents.

Performance Properties of 38 volume % Reagent/Diluent Blends

The performance properties of 38 volume % reagent/diluent blends evaluated in this study are summarized in Table IV. Note from Table IV that both neat diluents and also 80/20 and 60/40 blends of BP Mining Solvent with Orfom SX80 and 80/20 and 60/40 blends of Shellsol 2325 with Orfom SX80 were tested. Table VI lists phase disengagement and copper extraction kinetics data for each of the topic diluents when combined with three different extractant reagents (Cytec Acorga OPT 5510, Acorga OPT 5540 and BASF LIX 984N). PDT utilizing both organic continuous and aqueous continuous modes are recorded along with observation comments for both. Table VI also records the kinematic viscosity measured for each of the respective organic phases from the kinetics/phase-separation tests at the 5 minute point of the organic continuous mixing mode over temperatures ranging from 22 °C up to 45 °C. All data reported are the average of three tests for each combination/condition. PDT within a test series varied generally <3%, viscosity measurements varied <5% and copper extraction kinetics ranged <2%.

The PDT for organic-continuous mode is plotted as Figure 1. First, it can be seen that Orfom SX11 diluent resulted in the highest PDT. This observation was true regardless of the extractant reagent utilized. All of the extractant reagents in combination with Orfom SX11 provided very similar PDT. Orfom SX11 PDT from organic-continuous mode ranged from 188 to 182 s and from 179 to 176 s from aqueous-continuous mode. These higher PDT may have been due, in part, to the higher viscosities of the neat diluent as well as the loaded organic relative to the other diluents (see Tables I and IV). However, the Cu extraction kinetics observed for Orfom SX 11 were quite good (all ≥91%), regardless of the reagent used (see Table IV). Furthermore, the quality of all phase-disengagement tests with Orfom SX11 was observed as being "clean with a clear break". Because all of the phase-disengagement tests with Orfom SX11 were observed as being "clean with a clear break", it could be that the tests intended to be aqueous continuous actually "flipped" to organic-continuous mode while stirring. It is not clear why this would occur with Orfom SX11, but it is an interesting observation and one worthy of note.

Table IV. SX diluent phase disengagement performance

	Phase Disengagement Time (sec)				Viscosity (mPas) at temp (°C)				Cu extraction kinetics (%) at time (s)		
Product and extractant[1]	Org. cont.	Aq. cont.	Comments org. cont.	Comments aq. cont.	22	30	38	45	30	60	90
SX12-OPT 5510	86	91	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.57	5.13	3.97	3.54	94	96	97
SX12-OPT 5540	84	89	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.49	5.10	3.93	3.50	93	94	98
SX12-LIX 984N	153	137	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.15	4.01	3.21	2.80	97	97	99
SX80-OPT 5510	109	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase	7.70	5.91	4.66	3.99	95	96	97
SX80-OPT 5540	102	91	Clean, Clear	Cloudy, small droplet of org. within aq. phase	8.15	6.25	4.62	4.22	91	93	94
SX80-LIX 984N	153	149	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.30	4.81	3.83	3.26	90	91	93
SX11-OPT 5510	184	177	Clean, Clear	Clean & clear break	17.10	12.35	9.46	7.34	96	98	98
SX11-OPT 5540	188	179	Clean, Clear	Clean & clear break	18.39	13.34	10.09	7.81	96	96	98
SX11-LIX 984N	182	176	Clean, Clear	Clean & clear break	13.17	9.62	7.44	4.80	91	99	100
Shellsol 2325-OPT 5510	114	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.04	3.98	3.29	2.88	94	94	99
Shellsol 2325-OPT 5540	106	92	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.82	4.67	3.86	3.37	93	96	98
Shellsol 2325-LIX 984N	136	125	Clean, Clear	Cloudy, small droplet of org. within aq. phase	4.92	3.89	3.32	2.86	91	96	98
BP Mining Solvent-OPT 5510	112	101	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.46	4.57	3.73	3.22	94	98	99
BP Mining Solvent-OPT 5540	105	97	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.46	4.57	3.73	3.22	95	96	97
BP Mining Solvent-LIX 984N	132	124	Clean, Clear	Cloudy, small droplet of org. within aq. phase	4.69	3.89	3.21	2.81	84	90	92
BP Mining Solvent/SX80 (80/20)-OPT 5510	111	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.04	5.32	4.31	3.62	91	94	94
BP Mining Solvent/SX80 (80/20)-OPT 5540	104	101	Clean, Clear	Cloudy	6.08	4.92	3.92	3.31	98	98	100
BP Mining Solvent/SX80 (80/20)-LIX 984N	132	124	Clean, Clear	Cloudy, small droplet of org. within aq. phase	4.58	4.12	3.44	2.86	92	96	98
BP Mining Solvent/SX80 (60/40)-OPT 5510	114	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.50	4.81	3.89	3.32	94	96	98
BP Mining Solvent/SX80 (60/40)-OPT 5540	101	98	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.15	5.32	4.23	3.57	98	98	98
BP Mining Solvent/SX80 (60/40)-LIX 984N	139	122	Clean, Clear	Cloudy, small droplet of org. within aq. phase	4.87	4.25	3.45	2.95	93	95	96
Shellsol 2325/SX80 (80/20)-OPT 5510	113	99	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.07	5.29	4.34	3.63	98	99	99
Shellsol 2325/SX80 (80/20)-38% OPT 5540	105	101	Clean, Clear	Cloudy	6.37	5.14	4.10	3.53	97	99	100
Shellsol 2325/SX80 (80/20)-38% LIX 984N	142	129	Clean, Clear	Cloudy, small droplet of org. within aq. phase	4.98	4.19	3.30	2.93	95	99	99
Shellsol 2325/SX80 (60/40)-38% OPT 5510	110	102	Clean, Clear	Cloudy, small droplet of org. within aq. phase	6.76	5.95	4.47	4.01	93	94	97
Shellsol 2325/SX80 (60/40)-38% OPT 5540	102	97	Clean, Clear	Cloudy	6.98	5.61	4.35	3.66	97	97	98
Shellsol 2325/SX80 (60/40)-38% LIX 984N	149	136	Clean, Clear	Cloudy, small droplet of org. within aq. phase	5.42	4.53	3.54	3.12	92	94	98

[1] All extractants were added to diluents and diluent blends at 38 volume percent

Comparing the phase disengagement times of the other diluent-reagent combinations (excluding Orfom SX11) reveals additional trends. All of the diluent combinations with Acorga reagents resulted in lower PDT relative to those using LIX 984N. Use of the Acorga reagents in organic-continuous mode resulted in PDT that ranged from approximately 101 to 114 s, with Acorga OPT 5510 producing the higher of these of the Acorga reagents (see Figure 1). An exception to this trend was with the use of Orfom SX12. Orfom SX12 in combination with the Acorga reagents resulted in PDT of 86 and 84 s, which is measurably lower than the other diluent–reagent combinations.

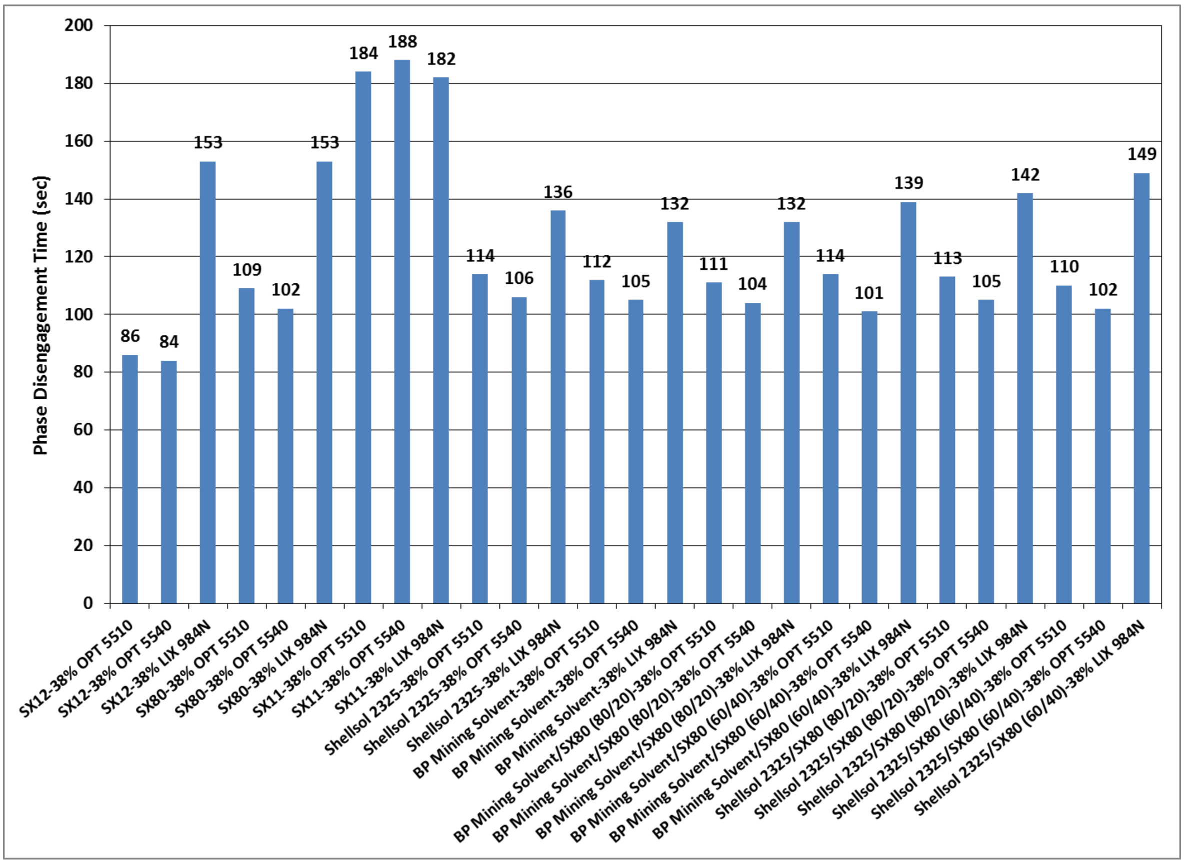

Figure 1. Phase-disengagement time with varying diluent/extract reagent (organic-continuous).

The use of LIX 984N resulted in higher PDT with all diluents relative to the Acorga reagents evaluated within this study. Generally, the phase disengagement times were 20–30 s higher when using LIX 984N relative to the Acorga reagents, except when in combination with Orfom SX12 or Orfom SX80 (see Figure 1). For example, the use of LIX 984N with Orfom SX80 under organic-continuous conditions resulted in a PDT of 153 s compared with 102 s observed using Orfom SX80/Acorga OPT 5540 (a difference of more than 50 s). An initial consideration to explain this difference might be viscosity. For example, if the viscosity of the loaded organic of Orfom SX80/Acorga OPT 5540 is significantly lower than that of Orfom SX80/LIX 984N. then one may expect such a large PDT difference, with the Orfom SX80/Acorga OPT 5540 having a lower PDT. However, upon examination of the viscosities of the 80% of maximum loaded organic samples (Table IV), it can be seen that the viscosity of the Orfom SX80/Acorga OPT 5540 sample is actually higher than that of the Orfom SX80/LIX 984N (a viscosity difference of approximately 1.85 mPas at 22 °C). A measurably higher viscosity loaded organic sample resulted in a significantly lower PDT. This characteristic is also observed when comparing the PDT of Orfom SX12 with those of the Acorga reagents in organic-continuous mode. The viscosities of the two loaded organic samples were higher than that of any of the other single diluents in combination with the Acorga reagents (Table IV), but the resulting PDT were lower by comparison.

The 80% of maximum loaded organic phase resulting viscosities of all reagent/diluent blends have relatively similar viscosity profiles, except Orfom SX11 (Table IV). Excluding Orfom SX11, the various diluent–reagent loaded organic phases ranged in viscosities of approximately 4.58–8.15 mPas at 22 °C down to 2.81 – 4.22 mPas at 45 °C.

It seems reasonable that viscosity of the loaded organic phase would have an effect on PDT at some point as viscosity increases. As materials become more viscous, it is more difficult to mix them, and once mixed, more viscous materials should require a longer time to phase separate. Perhaps this is the reason Orfom SX11 demonstrated higher PDT. The loaded organic phase when using Orfom SX11 may have achieved a "critical point" in viscosity, above which the PDT starts to increase rapidly. Such a study as a function of loaded organic phase viscosity has not been identified (just as a study of neat diluent viscosity has not), although it would be very interesting.

From the data gathered within this study, it appears that the diluent–reagent combinations evaluated would have acceptable performance within sub-Saharan African copper SX conditions, most certainly those not utilizing Orfom SX11. The Cu extraction kinetics data (Table IV) was also consistent throughout the various combinations studied. However, from review of the data here, it is quite clear that there was not a direct correlation between phase-disengagement characteristics and diluent viscosity or loaded organic phase viscosity. Viscosity is only one of many variable properties within SX operations that should be evaluated for desired performance.

Mixtures of Orfom SX80 and BP Mining Solvent or Shellsol 2325 were also evaluated for phase-disengagement performance and the resulting data are summarized along with the individual diluent data. Mixtures of 20% and 40% by volume Orfom SX80 were prepared with BP Mining Solvent and Shellsol 2325 independently. These mixtures were evaluated through the same set of phase-disengagement and solubility tests as the neat diluent–reagent combinations. As can be noted from reviewing Table IV and Figure 1, these diluent mixtures performed very similarly to the stand-alone diluents. All of the phase-disengagement properties were quite comparable with those of the other diluent–reagent combinations within the study.

Another performance property that was of interest for this study was the final loaded organic phase stability. The solubility of the reagent–copper complex within the given diluents of interest was examined to observe any performance differences. This comparison was accomplished by placing aliquots of the final 80% of maximum loaded organic phase from the organic-continuous mode tests in glass test tubes and subjecting them to room (25 °C) and cooled (7 °C) temperatures for one week. None of the diluent–reagent combinations demonstrated any precipitation after one week of storage at room temperature or under refrigeration, including the diluent mixtures of Orfom SX80 with BP Mining Solvent or Shellsol 2325. Although these results are not dramatic, they do suggest a couple of interesting considerations.

Solubility is a complex phenomenon involving a variety of factors and therefore there is no single analytical technique that may be used to predict diluent solubility performance. These data suggest that the KB values measured for the diluents within this study (Table I) are not significantly different as to predict solubility performance for sub-Saharan African copper SX conditions. While KB values may provide a comparison of solubility at very large KB value differences, the solubility performance is for a specified resin and set conditions.

The data also suggest that aromatics content does not provide an individual measure for diluent solubility performance. Aromatics content does provide some contribution to solubility properties, but it is apparent from the data that the diluents evaluated within this study contain the appropriate molecular structures to successfully maintain solubility of the reagent–copper complex under sub-

Saharan African copper SX conditions. These observations serve to re-emphasize the thought that any diluent (or solvent for that matter) should be evaluated by multiple techniques, including subjection to the conditions for which it is targeted, to obtain a true measure of performance.

CONCLUSION

Various techniques exist for analyzing SX diluents and all provide useful insight into the properties and composition of such complex hydrocarbon mixtures. However, no individual analytical method provides sufficient data to predict diluent performance in practical operation. While some analyses provide a quick and consistent measurement for reference, other methods yield data that must be utilized cautiously or complemented by another analyses.

The data compiled in this study suggest that all of the diluents evaluated in this study possess sufficient properties to perform similarly and successfully for sub-Saharan African copper SX conditions (except perhaps Orfom SX11). Although the diluents differ slightly in physical properties and composition, diluent suppliers provide diluents with needed physicochemical properties for successful SX plant operation. SX plants should be able to utilize these diluents to achieve efficient, safe, and reliable operation.

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