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2005 PUBLICATIONS AND COMMUNICATIONS BY LAB. FIRP ASSOCIATES

SALAGER J. L., BRICEÑO M. I., MARFISI S., ALVAREZ G.

Emulsionation de bruts extra-lourds: un cas typique de génie de la formulation (French)

In "Energie et Formulation", Canselier J. P., Ed., *Cahiers de Formulation*, vol. **13**, 5-25. EDP Sciences Paris (2005).

ABSTRACT: A la fin des années 70 et au début des années 80, l'exploration à l'est du Vénézuéla de la ceinture bitumineuse de l'Orénoque, gigantesque gisement de pétrole biodégradable s'étendant sur 700 km d'est en ouest et sur 150 km du nord au sud, a indiqué l'existence de réserves considérables d'hydrocarbures (40 milliards de tonnes soit à peu près un tiers des réserves connues de bruts conventionnels). Ces bruts sont à 300 m de profondeur et sont relativement faciles à produire, mais ils sont trop visqueux pour être transportables par oléoduc jusqu'à la côte (300 km) par des méthodes conventionnelles. A la fin des années 70, ces pétroles de densité voisine de celle de l'eau étaient devenus une matière première attractive pour produire des bruts synthétiques par cokéfaction, et, en ce qui concerne leur acheminement vers la côte de la Mer des Caraïbes, le transport sous forme d'une émulsion H/E s'est révélée l'alternative la plus prometteuse.

La chute du prix des bruts conventionnels dans les années 80 changea la donne, et la Compagnie nationale *Petróleos de Venezuela* décida d'utiliser l'expertise acquise en matière d'émulsions de bitume pour développer un combustible émulsifié capable de concurrencer le charbon comme source d'énergie pour les centrales thermoélectriques. Ainsi naquit l'Orimulsion® (ou émulsion de brut de l'Orénoque), dont la combustion fut testée pour la première fois en 1985. La première formulation commercialisée à la fin des années 80 comportait 70% de brut sous forme de gouttes d'environ 15 µm dispersées dans de l'eau contenant des sels de magnésium, l'émulsion étant stabilisée par un surfactif nonionique polyéthoxylé. Les recherches universitaires et industrielles qui suivirent dans les années 90 réussirent à produire les connaissances fondamentales et le savoir-faire pratique nécessaire pour faire évoluer la formulation et la fabrication en fonction de contraintes croissantes, tant du point de vue de la performance comme combustible que des spécifications plus exigeantes du point de vue de la stabilité du produit et des risques de pollution.

On retrace pas à pas comment l'adaptation de la formulation physico-chimique combinée à de nouveaux procédés d'émulsification en régime transitoire a permis l'évolution jusqu'à la quatrième génération d'Orimulsion®, plus stable, moins coûteuse, plus calorifique et à la fois moins visqueuse. On peut dire que cet effort de recherche, justifié par une production projetée pour 2004 de 10 millions de tonnes par an, probablement le record mondial actuel en matière d'émulsion, avec un potentiel considérablement plus élevé, a jeté les bases du génie de la formulation des émulsions, et bénéficiera de nombreuses autres applications,

des émulsions alimentaires aux peintures, en passant par les produits cosmétiques et pharmaceutiques.

TYRODE E., ALLOUCHE J., CHOPLIN L., SALAGER J. L.

Emulsion Catastrophic Inversion from Abnormal to Normal Morphology. 4. Following the Emulsion Viscosity during three Inversion Protocol and Extending the Critical Dispersed Phase Concept.

Industrial & Engineering Chemistry Research **44** (1) 67-74 (2005)

ABSTRACT: Three protocols are tested to invert an abnormal emulsion into a normal one. A dynamic process with continuous addition of internal phase, a continuous stirring of a given emulsion with no addition of internal phase, and the combination of the previous ones, i.e., a standstill dynamic process in which the addition of internal phase is interrupted at some time and then followed by a continued stirring. In-situ follow-up of both conductivity and viscosity data in a rheomixer vessel provides complementary information to corroborate the critical dispersed phase concept as a condition for the inversion to take place in all cases. Some applications are discussed.

SALAGER J. L., ANTON R. E., SABATINI D. A., HARWELL J. H., ACOSTA E. J., TOLOSA L. I.,

Enhancing Solubilization in Microemulsion – State of the Art and Current Trends.

J. Surfactants and Detergents, **8** (1) 3-21 (2005)

ABSTRACT: Along a formulation scan solubilization is maximum when a bicontinuous microemulsion is in equilibrium with both oil and water excess phases in a so-called Winsor III phase behavior case. The first way to enhance solubilization is to increase the interaction of the surfactant for both oil and water, which is easily attained by increasing the size of both head and tail groups. However this is limited by solubility constraints. Further solubilization enhancement can be attained by introducing some bridging intermediate between the bulk phase and the adsorbed surfactant layer, according to the so-called lipophilic and hydrophilic linker effects, or with block copolymer additives, which are able to modify an extended zone in the oil and water domains close to their boundary. The intramolecular grafting of a linker group in between the hydrophilic and lipophilic moieties, results in a so-called extended surfactant structure, which produces equivalent solubilization as the surfactant/linker combo and even better results since the single molecule structure inhibits selective partitioning. It is concluded that solubilization improvement is directly related to the presence of a smooth and blurred transition across the interfacial region from polar to apolar bulk phases.

LOPEZ-MONTILLA J. C., JAMES M. A., CRISALLE O. D., SHAH D. O.

Surfactants and Protocols to Induce Spontaneous Emulsification and Enhance Detergency.

J. Surfactants and Detergents, **8** (1) 45-53 (2005)

ABSTRACT: In this study the presence of an oil-soluble nonionic surfactant, Brij-30 (polyoxyethylene-4 lauryl ether), in an oil stain, or its addition to the stain through an oil-based solution or water-based mixture is shown to enhance, to a great extent, the spontaneous removal of the stain from a polyester fabric by inducing rollback and spontaneous emulsification phenomena. These findings lead to potential application of Brij-30 as laundry pre-spotter for enhancement of the removal of tough stains. The effect of three key factors, namely, the surfactant type, the surfactant concentration, and the

surfactant application protocol, on the effectiveness of spontaneous detergency was analyzed *via* ultraviolet spectroscopy. The test fabrics were soiled with a stain composed of mineral oil plus orange OT dye [1-(o-tolylazo)-2-naphthol]. The results showed that all three factors were important for effective detergency. Brij-30 removed more than 80% w/w of the stain, whereas sodium dodecyl sulfate removed less than 24% w/w, and Brij-35 (polyoxyethylene-23 lauryl ether) was ineffective, removing less than 1 % w/w. It was also observed that a low threshold concentration of Brij-30, approximately 0.2 mM, was required to spontaneously remove the oil stain, and that higher concentrations did not cause a significant enhancement of the effectiveness of soil removal. Brij-30 completed the detergency effect in less than 1 min, which may have beneficial implications regarding reduced energy consumption. Video microscopy studies revealed that at low Brij 30 surfactant concentrations, the mechanism for spontaneous oil removal proceeded predominantly via a rollback mechanism and that at higher concentrations, a spontaneous emulsification mechanism became progressively more important.

FERNANDEZ A., SCORZZA C., USUBILLAGA A., SALAGER J. L.,

Synthesis of New Extended Surfactants containing Carboxylate or Sulfate Polar Group.

J. Surfactants and Detergents **8** (2) 187-191 (2005)

ABSTRACT: New extended anionic surfactants with carboxylate or sulfate polar head were synthesized from polypropoxylated alcohols and their structures were confirmed by H¹ and C¹³ NMR analysis. The extended surfactant CMC was found to decrease with the length of the polypropylene glycol spacer. Surfactants containing a diethylene glycol link to the head group exhibited a higher CMC than their non-diethoxylated homologs.

FERNANDEZ A., SCORZZA C., USUBILLAGA A., SALAGER J. L.,

Synthesis of New Extended Surfactants derived from a Xylitol Polar Group.

J. Surfactants and Detergents **8** (2) 193-198 (2005)

ABSTRACT: A new class of extended surfactants was prepared, in which the spacer arm between the polar portion and the hydrophobic alkyl chain is a polymer of propylene glycol with average length of six propylene-oxide units. The polar head is a single or double xylitol moiety or a xylitol molecule with a carboxylic acid functionality. Surfactants containing double xylitol polar head showed a much larger CMC value than surfactants with single polar head.

CUÉLLAR I., BULLÓN J., FORGARINI A.M., CÁRDENAS A., BRICEÑO M.I.

More efficient Preparation of Parenteral Emulsions or how to improve a Pharmaceutical Recipe by Formulation Engineering. *Chemical Engineering Science* **60**, 2127-2134 (2005)

ABSTRACT: Parenteral emulsions are special O/W emulsions used to feed patients whose medical condition makes them unable to eat normally. Therefore, parenteral emulsions must comply with several specifications. One is that the maximum droplet size must be below 5 µm in order to avoid the risk of a pulmonary embolism. In this work, we describe the step-by-step procedure followed to simplify a current industrial recipe by applying recently developed principles under the name of formulation engineering.

Both hydrodynamic and physicochemical formulation parameters were manipulated to reduce energy input and equipment requirements. The current process consists of two heating steps, three mixing stages and filtering to eliminate droplets larger than 5 µm. The mixing stages require first an agitated tank for the making of a coarse dispersion, then a

high-speed mixer and last a two-stage homogenizer. Despite the intensive mixing the emulsion does not comply with droplet size specifications and filtering is necessary. Our procedure requires heating once and then two mixing stages, the first to produce a coarse dispersion and the second to refine droplet size in a conventional agitated tank. Further, no filtering is necessary since no droplets larger than 3 μm are produced in the mixing tank. The parenteral emulsions resulting of this simplified and less energy intensive process complies with droplet size requirements and are stable over several months.

MARFISI S., RODRIGUEZ M. P., ALVAREZ G., CELIS M. T., FORGIARINI A., SALAGER J. L.,

Complex Emulsion Inversion Pattern Associated with the Partitioning of Nonionic Surfactant Mixtures in presence of Alcohol Cosurfactant.

Langmuir **21** (15) 6712-6716 (2005)

ABSTRACT: Commercial ethoxylated nonionic surfactant mixtures containing alcohol cosurfactant exhibit a three-phase behavior whose formulation strongly varies with the water/oil ratio. As a consequence, a change in water/oil ratio can result in a sequence of up to three different emulsion inversion processes, through a combination of formulation and composition effects.

ESCALANTE M., RODRIGUEZ-MALAVE A. J., ARAUJO E., GONZALEZ A. M., ROJAS O. J., PEÑALOZA N., BULLON J., LARA M. A., DMITRIEVA N., PEREZ-PEREZ E.

Effect of surfactant on Fenton's reagent-mediated degradation of Kraft black liquor.

J. Environmental Biology **26** (2/3) 1-10 (2005)

ABSTRACT: One of the limitations of the biodegradation of hydrophobic material compounds, like lignins, is their low solubility in the aqueous solution where this process takes place. To solve this problem, surfactants have been used to improve the solubility of these compounds. In this investigation, we studied the effect of surfactants (anionic, cationic and nonionic) on the treatment of Kraft black liquor with Fenton's reagent. In the Fenton reaction, H_2O_2 (two different concentrations, 10 mM and 20 mM), FeCl_2 (1 mM) and surfactant solution (10%) were used. Black liquor degradation was determined by UV/Visible spectrometry and by measuring phenolic groups. In the presence of Fenton's reagent, the optimum conditions for the oxidative degradation of black liquor were 10 mM H_2O_2 , 1 μL of 10% solution of anionic surfactant (SDS). The importance of the use of surfactants for preparing black liquor for subsequent Fenton's reagent-mediated degradation was discussed.

ACEVEDO E. J., GONZALEZ A. M., RODRIGUEZ-MALAVAR A. J.

Surface activity of lignin fractions isolated with organic solvents.

7th International Lignin Institute Forum, Barcelona España, April 27-28, 2005. pp 87-90

ABSTRACT: In this work we studied the surface activity of different lignin fractions isolated with organic solvents. Lignin fractions were obtained from Kraft black liquor by their precipitation at pH 2. After precipitation, the extraction was carried out with organic solvents of different polarities (hexane, dichloromethane, ethyl acetate and methanol). It was found that non-polar solvents showed a very low extraction yield, and do not allow working with these fractions. Spectrophotometric analysis of all the fractions was carried out to confirm the presence of lignin. Conductivity and surface tension of fraction solutions

using 0.01 N and 0.1 N NaOH as aqueous phase were determined. The lignin fraction extracted with dichloromethane exhibited the highest surface activity. In the case of conductivity the most polar fractions exhibited a smaller concentration. Water-oil (60/40) emulsions were prepared using lignin fractions as stabilizer and 0.1 N and 0.01 N NaOH as aqueous phase, and their stability was directly dependent on fraction concentration, and most polar fractions presented a better behavior as emulsifiers. In addition, we studied the rheological properties of emulsions and found that they had low viscosities and Newtonian behavior.

TOLOSA L. I., RODRIGUEZ-MALAVAR A. J., GONZLAEZ A. M., ROJAS O. J.

Fenton reagent effect on black liquor stabilized O/W emulsions.

7th International Lignin Institute Forum, Barcelona España, April 27-28, 2005. Proceedings pp 187-190

ABSTRACT: The effect of Fenton's reagent (FR) on surface and dispersion properties of Kraft lignin from black liquors (BL) was investigated. The properties observed were compared to those of commercial lignin. Indulin C (IC) and also egg lecithin (Le). The FR was applied at two different bulk concentrations of H₂O₂ (160 and 320 mM). At pH 8, a minimum in surface tension for BL with FR treatment was observed. The dispersant ability of BL, IC, and Le in oil-in-water (O/W) emulsions was studied by measuring emulsion stability. It was found that the surface activity and emulsifying capability of BL was higher than that of IC. The emulsifying capability of Le was improved with FR treatment at low H₂O₂ concentration.

MARCANO Y., GONZALEZ A. M., RODRIGUEZ-MALAVAR A. J.

Surface activity of lignin fractions obtained at different pH values.

7th International Lignin Institute Forum, Barcelona España, April 27-28, 2005. Proceedings pp 199-202.

ABSTRACT: In this work, the surface activity of lignin fractions isolated at different pH values (2, 5 and 7) was studied. The samples isolated at pH 2 were obtained directly from the black liquor, whereas those at pH 5 and 7 were obtained from the fraction at pH 2. All the samples were studied spectroscopically and it was observed that their absorbance increased with the increase in precipitation pH value. Conductivity and surface tension of all the fractions were carried out and it was demonstrated that the surface activity of obtained fraction was dependent on the precipitation pH value. Water-in-oil emulsions with a ratio equal to 60/40 were prepared by using edible oil as organic phase and sodium hydroxide solution as aqueous phase. Emulsions were prepared by varying the percentage of lignin content and sodium hydroxide concentration, and their stability was determined. Emulsion stability was evaluated by the measurement of conductivity with respect to the time and drop diameter. The emulsions that showed the highest stability in time were those that had 0.1 N NaOH as aqueous phase and were prepared using the lignin fractions isolated at pH 2 and 5.

LEON M. G., GONZALEZ A. M., RODRIGUEZ-MALAVAR A. J.

Adsorption effects of black liquor lignin compounds.

7th International Lignin Institute Forum, Barcelona España, April 27-28, 2005. Proceedings pp 203-206.

ABSTRACT: In this work we studied the adsorption capacity of black liquor lignins on substances such as clay, sand and activated coal at constant temperature. The capacities of

commercial lignins and lignins isolated from black liquor were compared. Black liquor lignins were characterized by determination of absorbance, pH, conductivity and phenolic concentration. Also, Langmuir isotherms were established. Through the spectrophotometric analysis, the mass and the optimal time of adsorption were determined. The results of this work showed that adsorption properties of black liquor lignins and commercial lignins were very similar, being feasible their substitution.

RONDON-GONZALEZ M., SADTLER V., CHOPLIN L., SALAGER J. L.

Emulsion Inversion from Abnormal to Normal Morphology by Continuous Stirring without Internal Phase Addition,

Formula IV Symposium, King's College, London, July 4-7, 2005.

ABSTRACT: Emulsion inversion is a process in which an emulsion changes its morphology from oil-in-water (O/W) to water-in-oil (W/O) or *vice versa*. It is an alternative to produce fine emulsions in many industrial processes by one of two different procedures referred to as transitional and catastrophic inversions, whose paths are clearly identified in a formulation- water/oil ratio bidimensional map. The catastrophic inversion is usually triggered by adding (too much) internal phase. However it can be also attained by continuously stirring an abnormal system, i. e. an emulsion whose morphology does not match the one expected from the formulation effect. The emulsion inversion takes place through the formation of a multiple emulsion in which the external phase is continuously included as droplets in the dispersed phase drops. As a consequence, the dispersed phase apparent volume increases until the conditions for inversion are reached. The present study reports the follow-up of emulsion inversion by *in situ* conductivity and viscosity measurements for nonionic systems. The surfactants used were Igepal CO-630 and Span 80 (HLB of the mixture = 6) with different water/oil ratios (from 60 to 90 vol% water). The system exhibited an initial O/W morphology, then a w/O/W multiple one before inverting into a W/O emulsion. The general trend is that the higher the initial water content, the longer it takes to incorporate enough « w » droplets in the « O » drops for those to swell and attain the critical dispersed phase volume to trigger inversion. This trend is found to unexpectedly reverse when the initial water content increases beyond 80%. This apparently anomalous result is attributed to an indirect increase in the lipophilicity of the formulation due to the variation of the interfacial surfactant mixture with the water/oil ratio, an effect which becomes dominant at extreme water/oil ratios.

TYRODE E., SALAGER J. L.,

Controlling Inversion through a Formulation Engineering Protocol.

Formula IV Symposium, King's College, London, July 4-7, 2005.

ABSTRACT: An emulsion can be simply defined as a liquid / liquid dispersion of an oil phase in an aqueous phase or *vice versa*, where its stability is normally guaranteed by the presence of surface active agent. The type and corresponding properties of an emulsion can be understood in terms of three main classes of variables: formulation, composition and emulsification protocol. The formulation variables, related to the physical chemistry of the involved phases, can be all put together around a single variable such as the HLD, which is directly linked to the affinity of the surface active agent towards the oil or water phase. The composition variables, include the water to oil ratio and the surfactant concentration, while the emulsification protocol variables, involve the energy input and procedure followed when preparing the desired emulsion. The effect of the first two main types of variables has

been rationalized in the so-called formulation - composition map (left Fig.), which can be used to predict emulsion properties such as morphology (O/W, W/O or multiple emulsions of the type w/O/W or o/W/O), stability, drop size or viscosity. The different branches of the inversion frontier allow separating the different regions in the map. When crossing any of these border lines an emulsion inversion will occur, which is no less than the exchange of the continuous or external phase by the dispersed phase, with the corresponding dramatic change in the emulsion properties. If the inversion is reached through a change in composition (horizontal displacements) the inversion is referred to as catastrophic, while if is reached by a change of a formulation variable at constant composition (vertical displacement) it is generally referred to as transitional. Extensive recent work has shed light into the complexity of the different inversion mechanisms (right Fig.), which can now be used to control the inversion process and attain the desired emulsion properties. These latest advances will be reviewed and put into the context of the design of engineering processes to manufacture macro to nanoemulsions.

QUESTE S., SALAGER J. L., AUBRY J. M.

Absolute Classification of Surfactants according to the PACN (Preferred Alkane Carbon Number) Scale.

Formula IV Symposium, King's College, London, July 4-7, 2005.

ABSTRACT: Surfactants are ubiquitous in formulation issues thanks to their extraordinary versatility. However, in spite of considerable improvement of their scientific knowledge, formulators often rely on questionable (HLB) or limited (PIT) scales when they have to choose a suitable surfactant for a given application. In the past decade, the “fish” diagram and the HLD concept were proposed to characterize in a reliable way Surfactant/Oil/Water true ternary systems (SOW). Both are based on the attainment of “optimal formulation” which corresponds to a perfectly balanced system, where the surfactant has the same affinity for the aqueous and the oil phases. Under these conditions (i) the interfacial tension $\sigma_{O/W}$ is minimal, (ii) the amount of surfactant required to co-solubilize an iso-massic O/W mixture is also minimal, and (iii) the ternary mixture often exhibits a triphasic behaviour (Winsor III). The application of the “optimal formulation” concept provide a thermodynamics-based method to compare and classify surfactants and oils. In a first step a series of aliphatic, aromatic, and ester oils were ranked according to their EACN (Equivalent Alkane Carbon Number) by comparing the temperatures at which an optimal formulation is obtained with C₁₀E₄/O/W systems. Linear alkanes from pentane to octadecane were used as standards to set this EACN scale. In a second step various ionic and non-ionic surfactants were classified according to the so-called PACN (Preferred Alkane Carbon Number). The PACN value of a given surfactant is defined as the EACN of the oil that results in an optimal formulation at 25°C with a true ternary SOW system free of any other additive (alcohol, electrolyte,...). This scale constitutes a powerful tool to help formulators in preparing of micro/macro-emulsions.

ZERPA L., QUEIPO N. V., PINTOS S., SALAGER J. L.

An optimization methodology of alkaline-surfactant-polymer flooding process using field scale numerical simulation and multiple surrogates

J. Petroleum Science Engineering, 47, 197-208 (2005)

ABSTRACT: After conventional waterflood processes the residual oil in the reservoir remains as a discontinuous phase in the form of oil drops trapped by capillary forces and is

likely to be around 70% of the original oil in place (OOIP). The EOR method so-called alkaline-surfactant-polymer (ASP) flooding has proved to be effective in reducing the oil residual saturation in laboratory experiments and field projects through the reduction of interfacial tension and mobility ratio between oil and water phases. A critical step to make ASP floodings more effective is to find the optimal values of design variables that will maximize a given performance measure (e.g., net present value, cumulative oil recovery) considering a heterogeneous and multiphase petroleum reservoir. Previously reported work using reservoir numerical simulation have been limited to sensitivity analyses at core and field scale levels because the formal optimization problem includes computationally expensive objective function evaluations (field scale numerical simulations). This work presents a surrogate-based optimization methodology to overcome this shortcoming. The proposed approach estimates the optimal values for a set of design variables (e.g., slug size and concentration of the chemical agent) to maximize the cumulative oil recovery from a heterogeneous and multiphase petroleum reservoir subject to an ASP flooding. The surrogate-based optimization approach has been shown to be useful in the optimization of computationally expensive simulation-based models in the aerospace, automotive, and oil industries. In this work, we improve upon this approach in two directions: (i) using multiple surrogates for optimization, and (ii) incorporating an adaptive weighted average model of the individual surrogate. The cited approach involves the coupled execution of a global optimization algorithm and fast surrogates (i.e., based on Polynomial Regression, Kriging, Radial Basis Functions and a Weighted Average Model) constructed from field scale numerical simulation data. The global optimization program implements the DIRECT algorithm and the reservoir numerical simulations are conducted using the UTCHEM program from the University of Texas at Austin. The effectiveness and efficiency of the proposed methodology is demonstrated using a field scale case study.

CELIS M. T., GARCIA-RUBIO L. H.

Emulsifier distribution in liquid-liquid systems

International Symposium on the Role of Adsorbed Films and Particulate Systems in Nano and Biotechnologies, Gainesville, FL USA, August 24-26, 2005

ABSTRACT: Emulsification processes result in the generation of droplet populations determined primarily by the nature and amount of emulsifier, mixing characteristics and emulsion preparation. Analysis of the emulsion droplet size distribution gives valuable information on the properties of the dispersed phase. This paper reports on a spectroscopy technique for the measurements of droplet size distribution, the chemical composition of the emulsions, and the emulsifier distribution. The particle characterization methodology is based on a spectroscopy technique that yields reliable estimates of the droplet size as function of the oil phase and the emulsifier concentrations.

ESCALANTE M., RODRIGUEZ-MALAVAR A. J., ARAUJO E., GONZALEZ A. M., ROJAS O. J., PEÑALOZA N., BULLON J., LARA M. A., DMITRIEVA N., PEREZ-PEREZ E.

Effect of surfactants on Fenton's reagent-mediated degradation of Kraft black liquor.

J. Environmental Biology **26**, 709-718 (2005)

ABSTRACT: One of the limitations of the biodegradation of hydrophobic chemical compounds, like lignins, is their low solubility in the aqueous solution where this process takes place. To resolve this problem, surfactants have been used to improve the solubility of

these hydrophobic compounds. In this investigation, we studied the effect of surfactants (anionic, cationic and nonionic) on the treatment of Kraft liquor with Fenton's reagent. In the Fenton reaction, H₂O₂ (two different concentrations, 10 mM and 20 mM), FeCl₂ (1 mM) and surfactant solution (10%) were used. Black liquor degradation was determined by UV/Visible spectroscopy and by measuring phenolic groups. In the presence of Fenton's reagent, the optimum conditions for the oxidative degradation of black liquor were 10 mM H₂O₂, 1 µL of 10% solution of anionic surfactant (SDS). The importance of the use of surfactants for preparing black liquor for subsequent Fenton's reagent-mediated degradation was discussed.

BURGUERA J. L., BURGUERA M., ANTON R. E., SALAGER J. L., ARANDIA M. A., RONDON C., CARRERO P., PETIT de PEÑA Y., BRUNETTO R., GALLIGNANI M.

Determination of Aluminum by Electrothermal Atomic Absorption Spectroscopy in Emulsified Lubricating Oils in a Sequential Injection Analysis System.

Talanta **68**, 179-186 (2005)

ABSTRACT: The sequential injection (SIA) technique was applied for the on-line preparation of an "oil-in-water" microemulsion and for the determination of aluminum in new and used lubricating oils by electrothermal atomic absorption spectrometry (ET AAS) with Zeeman-effect background correction. Respectively 1.0, 0.5 and 1.0 ml of surfactant mixture, sample and co-surfactant (sec-butanol) solutions were sequentially aspirated to a holding coil. The sonication and repetitive change of the flowing direction improved the stability of the different emulsion types (oil in water, water in oil and microemulsion). The emulsified zone was pumped to fill the sampling arm of the spectrometer with a sub-sample of 200 µl. Then, 10 µl of this sample solution were introduced by means of air displacement in the graphite tube atomizer. This sequence was timed to synchronize with the previous introduction of 15 µg of Mg(NO₃)₂ (in a 10 µl) by the spectrometer autosampler. The entire SIA system was controlled by a computer, independently of the spectrometer. The furnace program was carried out by employing a heating cycle in four steps: drying (two steps at 110 and 130 °C), pyrolysis (at 1500 °C), atomization (at 2400 °C) and cleaning (at 2400 °C). The calibration graph was linear from 7.7 to 120 µg Al l⁻¹. The characteristic mass (m₀) was 33.2 pg/0.0044 s and the detection limit was 2.3 µg Al l⁻¹. The relative standard (RSD) of the method, evaluated by replicate analyses of different lubricating oil samples varied in all cases between 1.5 and 1.7 %, and the recovery values found in the analysis of spiked samples ranged from 97.2 to 100.4 %. The agreement between the observed and reference values obtained from two NIST Standard Certified Materials was good. The method was simple and satisfactory for determining aluminum in new and used lubricating oils.

MEDINA H., BULLON J., ONTIVEROS F., CHACON T., CARDENAS A.

Zinc separation of aqueous solutions using emulsion liquid membranes. The pH Influence.

Revista Facultad Ingeniería UCV **20** (3) 57-62 (2005)

ABSTRACT: Zinc ions can be separated from aqueous streams by multiple emulsion membranes. This method can be applied in industrial effluent treatment. In this study, multiple emulsions were prepared by two step process and used to extract zinc ions from he continuous external aqueous phase. For the extraction, kerosene was the membrane phase,

DEHPA the carrier, SPAN 20 the surfactant, and a solution of sulfuric acid the inner phase that received the zinc ions. A study of the effect of protons (pH) in the extraction of zinc was made. The results show that below a pH of 3, there is no zinc extraction and that the extraction can be enhanced by neutralizing continuously with NaOH. A model of the kinetics of extraction is proposed. It shows that the extraction is proportional to the concentration of zinc ions and inversely proportional to the concentration of protons.

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