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Separation and identification of polymeric dispersants in detergents by two-dimensional liquid chromatography

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ABSTRACT

Polymeric dispersants are an important ingredient in many consumer products. Their separations and identifications in final product formulation can be very challenging due to the presence of multiple polymeric dispersants at different levels and the presence of other polymeric and small-molecule components. In this study, using nearly comprehensive two-dimensional liquid chromatography (2D-LC), various water-soluble polymer and co-polymer dispersants were separated with aqueous size exclusion chromatography (SEC) in the first dimension (^{1}D) and gradient elution reversed-phase liquid chromatography (RPLC) in the second dimension (^{2}D). Detection of the polymeric dispersants was accomplished by evaporative light scattering detector (ELSD). A large ID (8.0 mm) SEC column used in common one-dimensional SEC practices was directly adopted in the 2D setup for rapid method development. A close representation of fully comprehensive 2D separation was achieved even with 60% of ^{1}D eluent diverted to waste, demonstrating the flexibility and versatility of having SEC in ^{1}D for two dimensional separation of polymers. Important method parameters, such as ^{2}D column dimensions and flow rate, gradient conditions, and buffer pH were studied. Practical aspects of routine industrial applications such as solvent consumption and analysis time were also considered. This method was exploited for quick identification of polymeric dispersants in commercial detergent samples. Nine detergent samples were screened and polymeric dispersants and additional polymer features were detected in the samples.

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1. Introduction

Polymeric dispersants are an important component in many consumer products such as paints, detergents, cosmetic formulations, etc. Water soluble polyacrylate based dispersants can act as crystal growth modifiers and inhibit scale formation/deposition on hard and soft surfaces while promoting particulate dispersancy [1]. Very frequently, homopolymers and statistical copolymers of various acrylates are used to generate desired properties. These copolymers exhibit complex distributions in molar mass and chemical composition, making the characterization very challenging and hence the structure-property relationships difficult to establish. To take the complexity to another level, many consumer products contain more than one polymeric dispersant along with many other components including surfactants, chelants, silicates, inorganic and

organic salts, etc. making the identification of individual polymeric dispersant extremely difficult [2]. Spectroscopic techniques such as infrared spectroscopy (IR), nuclear magnetic resonance (NMR) spectroscopy, and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) are only able to provide information on average chemical composition of the material and cannot differentiate individual polymers in a polymer mixture especially when the polymers have similar compositions [3].

Two-dimensional liquid chromatography (2D-LC) is an attractive technique for polymer analysis as most polymer materials exhibit two or more distributions simultaneously such as molecular weight distribution (MWD), chemical composition distribution (CCD), functionality-type distribution (FTD) and branching distribution (BD), etc [4–7]. Several different separation mechanisms can be exploited in the first and second dimension of comprehensive 2D-LC separation. Size-exclusion chromatography (SEC) is the most commonly used technique for the characterization of MWD. Interaction chromatography (IC) or liquid adsorption chromatography (LAC) for polymers have been widely used to separate polymers based on chemical composition or functional groups [8–12]. LC at

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critical conditions (LCCC) allows separation of polymers by chemical composition of functional groups or end-groups without the impact of MWD [9,13,14].

Among the many different combinations of separation mechanisms, different formats of LC (IC, LAC or LCCC) in the first dimension ([1]D) and SEC in the second dimension ([2]D) are the most commonly used configuration in 2D-LC separation of polymers [4,10,15–21]. This combination can provide excellent orthogonality at reasonable peak capacity for polymers [22]. However, there are a few challenges with this approach. When LCCC is performed in [1]D the critical conditions are hard to achieve experimentally and are sensitive to chain architectures and end group variations [23,24]. Also, for copolymers it can only be exploited for block copolymers with distinct composition of the blocks and is limited to polymers containing no more than two components [4]. Additionally, LCCC is very sensitive to method conditions, making it very difficult to develop a robust method [23,25]. When gradient LC is used in [1]D, the LC separation is convoluted with MWD and thus the orthogonality of the 2D separation is compromised [20]. Another challenge is [1]D under-sampling (recombination of already separated compounds) due to the relatively long [2]D run time and relatively narrow [1]D peaks [5]. Additionally, the choice of the SEC column is limited for fast SEC separations in [2]D [5].

Comprehensive 2D-LC in SEC × LC mode with SEC in [1]D and gradient LC in [2]D is another mode of operation which is less frequently practiced. SEC × LC has some advantages especially for water soluble polymers which can be separated by aqueous SEC conditions. Refocusing of [1]D effluent on top of the [2]D column can be easily achieved leading to improved [2]D separation and peak intensity [26]. Also with SEC in [1]D, fractions with relatively narrow MWD are transferred to [2]D, leading to better decoupling of MWD and CCD without obtaining the critical conditions [20]. Other benefits include minimized [1]D under-sampling due to broad SEC peaks and more choices of [1]D and [2]D columns with different phases and dimensions. In spite of these advantages, separation in SEC × LC mode also brings several challenges including higher demand on instrumentation when [2]D requires very fast gradient elution, potential risk of breakthrough if [2]D injection solvent is strong, and limited choices of detectors compatible with gradient LC [5].

Regardless of the many applications reported in literature, 2D-LC is still considered an academic research tool with very limited practical industrial applications in polymer separations. 2D-LC methods apparently are more sophisticated and more demanding in terms of operation and maintenance. Not every polymer related problem requires a 2D separation. In many cases a simple one dimensional SEC separation is sufficient and should always be used as a starting point when trying to solve a complex polymer problem. When a desired separation cannot be achieved by a simple SEC separation, adding a gradient LC separation as the second dimension can be a practical and effective way to achieve improvement in peak capacity without having to re-optimize the existing SEC separation [27].

To minimize sample overloading and solvent effect on the [2]D column, typically a smaller inner diameter (ID) column with low flow rate is used in [1]D and a larger ID column with shorter column length and higher flow rate is used in [2]D. However, choices of small ID SEC columns are very limited especially for aqueous SEC separations when pH compatibility and secondary interactions place restrictions on column selection [28]. In addition, SEC columns are significantly more costly than reversed-phase LC columns, hence re-optimizing the SEC separation for the 2D separation is impractical for many labs. In this report, we described a practical and effective 2D-LC method development approach for the separation

and identification of water-soluble acrylate based polymeric dispersants in complex detergent samples.

2. Experimental

2.1. Materials and reagents

Acetonitrile (HPLC grade), ammonium acetate (99.0%), and formic acid (88%) were purchased from Fisher Scientific (Pittsburgh, PA). Ammonium formate (99.0%), acetic acid (99.99%) and ammonium hydroxide (5.0 N) were all obtained from Sigma-Aldrich (St Louis, MO). Water was purified by an ultra-pure milli-Q water system (EMD Millipore, Billerica, MA). The 20 mM ammonium acetate buffer was prepared in milli-Q water and adjusted to pH 9 with ammonium hydroxide (5.0 N). The 100 mM ammonium formate buffer was prepared in milli-Q water and adjusted to pH 3 with formic acid (88%). Poly acrylic acid (PAA) standard was obtained from American Polymer Standards Corporation (Mentor, OH). Polymeric dispersant reference materials were available at Dow internally.

2.2. Instrumentation and chromatographic conditions

2.2.1. SEC-MALS

For one-dimensional SEC analysis, a Waters Alliance 2690 system (degasser, pump, autosampler, column oven) from Waters (Milford, MA) with a Wyatt (Santa Barbra, CA) HELEOS II multi-angle light scattering detector (MALS), and a Wyatt T-rEX refractive index detector were used. Empower[TM] 3 software from Waters was used for 2690 system control, and ASTRA® software version 6.1.1.17 from Wyatt Technology was used for data acquisition and process.

The injection volume was set to 100 μL for all of the analyses. The temperature was ambient and the flow rate was 1.0 mL/min. The column was Shodex OH pak® SB-804HQ column (8.0 mm ID × 300 mm, 10 μm polymer based particles) from Amuza Inc. (San Diego, CA) and the mobile phase was 20 mM ammonium acetate at pH 9.

The 90-degree MALS detector was calibrated using HPLC grade toluene (Fisher Scientific). The detectors at other angles were normalized using a polystyrene narrow molecular weight standard with weight average molecular weight of 30 kDa from Wyatt Technology. The dn/dc values of the dispersant standards were calculated based on sample injection mass, flow rate, refractometer calibration constant and RI peak area with the assumption of 100% mass recovery. The determined dn/dc values of these five standards were in the range of 0.175-0.195 mL/g. Light scattering signals from twelve angles (from 29.6° to 130.4°) were used to fit first order Zimm formulism in combination with the RI signal for absolute molecular weight calculation at each elution moment. The average molecular weights were obtained using the fitted linear line of the measured absolute molecular weight versus retention time of the main peak region and the RI chromatogram of each sample.

2.2.2. SEC × RPLC

The SEC × RPLC analysis was performed on an Agilent 1290 Infinity II system with a 1290 Infinity II multi-sampler, 1290 flex pump for the first dimension, 1290 binary pump for the second dimension, a thermal column compartment, a 1290 Infinity II evaporative light scattering detector (ELSD), a 2 position / 4 port duo valve with 40 μL loop size. The ELSD signal was acquired with a sampling rate of 80 Hz. The ELSD evaporator and nebulizer temperatures were both 80 °C and the drying gas flow rate was 1.0 L/min. The column thermal compartment was set at 30 °C.

The [1]D column was the same column used in the one dimensional SEC analysis and the [2]D column was an Agilent Zorbax Eclipse C18 column (3.0 mm ID × 50 mm, 1.8 μm particles). The [1]D mobile