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# Multivariate Curve Resolution Alternating Least-Squares As a Tool for Analyzing Crude Oil Extracted Asphaltene Samples

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## Supporting Information

**ABSTRACT:** Asphaltene deposition in the early stage of the oil reservoir life and later during any stimulation process emerges critical problems to the petroleum industry. Deposition of asphaltene aggregates raises strict problems in industries and demands markedly a practical and scientific knowledge of the mechanisms of aggregation and precipitation. Fluorescence emission spectroscopy has been widely used to illuminate the fundamental properties of crude oils and asphaltenes. It proposes analysis of some details of equilibrium, dynamic behavior, and aggregation composition of crude oil under specific condition. In this work, the fluorescence spectra of crude-oil extracted asphaltene samples were studied and analyzed by the application of multivariate curve resolution alternating least-squares (MCR-ALS). The asphaltene samples were extracted from crude oil of three different regions of Iran (Kuh-e-Mond, Bangestan, and Gachsaran). The excitation–emission fluorescence spectra of asphaltene solutions of variable concentrations (1.0–60.0  $\mu\text{g/mL}$ ) in toluene were recorded. The application of MCR-ALS analysis on the row-wise augmented matrices allows the identification of major components at different asphaltene solution concentration in each sample. The emission spectra, excitation spectra, and concentration profile of these components were deconvoluted to demonstrating structural features characteristic of each sample.

## 1. INTRODUCTION

The asphaltene fraction, like the resins, is defined as a solubility class, namely the fraction of the crude oil precipitating in light alkanes such as pentane, hexane, or heptane. Aromatic solvents such as benzene and toluene dissolve this precipitate. The asphaltene fraction contains the largest percentage of heteroatoms (O, S, N) and organometallic constituents (Ni, V, Fe) in the crude oil. The structure of asphaltenes has been the subject of several investigations, but it is now believed to consist of polycyclic aromatic clusters, substituted with varying alkyl side chains.<sup>1</sup>

Asphaltenes are known to be suspended as a nanoaggregate in the crude oil, consisting of particles of about 3 nm. Each asphaltene monomer consists of one or more sheets made of fused aromatic rings, with adsorbed resins acting as surfactants to stabilize the colloidal suspension.<sup>2</sup> The pronounced tendency of asphaltenes to self-aggregation is one of their most characteristic traits and is responsible for a large proportion of the problems encountered during crude oil processing and refining.<sup>3</sup>

Problems encountered because of the deposition of asphaltene aggregates in industries demand importantly a practical and scientific knowledge of mechanisms of aggregation and precipitation. Techniques such as light absorption and fluorescence emission have also been widely used to elucidate the fundamental properties of crude oils and asphaltenes.<sup>4–9</sup> The first publication on primary aggregation of asphaltene was by Yokota et al.,<sup>6</sup> who reported strong concentration dependence of UV/vis spectra of Athabasca asphaltene due to aggregation commencing at concentrations above 5  $\mu\text{g/mL}$ .

Acevedo et al. observed a minimum value of thermo-optical diffusivity at asphaltene concentrations of 50  $\mu\text{g/mL}$ .<sup>10</sup> They attributed this minimum as evidence of the asphaltene molecular association.

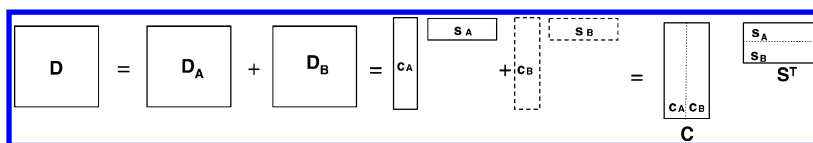
The fluorescence depolarization technique has been used to measure the asphaltene molecular weight<sup>11</sup> and molecular size,<sup>12</sup> where asphaltenes dimer formation was estimated at 60  $\mu\text{g/mL}$  in toluene.<sup>11</sup> It was shown that this technique establish the substantial difference between asphaltene constituents derived petroleum. Also, time-resolved fluorescence depolarization spectroscopy has used to estimate the molecular size, molecular mass,<sup>13–18</sup> and aggregate formation in dilute solution of asphaltene.<sup>19,20</sup> Near-UV/vis absorption spectra reflect the common features of asphaltene aggregation phenomena in toluene solutions of pre-precipitated asphaltenes and in toluene solutions of crude oils.<sup>21</sup> Fluorescence correlation spectroscopy has been used to measure the translational diffusion coefficient of asphaltene molecules in solution.<sup>22</sup>

Although the aromatic, polar, and heteroatomic contribution to the asphaltene composition is well-established, the size and nature of aggregation in this fraction is still a polemical discussion. Although asphaltenes are not composed solely of fluorescent aromatic compounds, this technique permits evaluation of the components that do fluoresce, and hence, the results are representative of the behavior of this complex mixture.<sup>19</sup> Due to the molecular-weight (MW)-dependent

Received: March 25, 2012

Revised: July 27, 2012

Published: August 20, 2012



**Figure 1.** Measurement model of a two-component system, described as an additive model of pure signal contributions, as a model of additive dyads of pure concentration profile and spectrum and as a bilinear model of concentration profiles and spectra.

fluorescence of asphaltene discovered over 23 years ago,<sup>23</sup> in this work, we employ fluorescence techniques to study aggregation process in asphaltenes solutions at relatively low concentration regimes. Changes in peak shift in the fluorescence spectra with concentration demonstrate the beginning of aggregation of asphaltene at concentrations as low as 50 mg/L.<sup>24</sup>

Fluorescence spectroscopy offers the possibility of qualitative and quantitative analysis of some details of equilibrium properties, dynamic behavior, and composition of crude oil portions under certain conditions, including aggregation processes.<sup>25</sup> In fluorescence spectroscopy, one is able to acquire three-dimensional fluorescence spectrum by systematically varying the excitation and emission wavelengths and collecting the resulting emission data in a matrix of size  $n_{\text{ex}} \times n_{\text{em}}$ , where  $n_{\text{ex}}$  and  $n_{\text{em}}$  are being the number of excitation and emission wavelengths, respectively. Band overlapping is a problem that may arise, when using the fluorescence spectroscopy for studying chemical reactions and aggregations. In this case, the changes in emission spectra can be attributed to the contribution of almost all species involved in the process, and hence, finding selective emission wavelength is not feasible.

However, since the introduction of chemometrics in chemistry, the problem of band overlapping has been diminished thanks to the resolving power of different chemometrics methods, which can decompose the emission data matrices into the pure spectra of the coexisting species. Multivariate curve resolution alternating least-squares (MCR-ALS),<sup>26–30</sup> which is a constrained interactive alternating least-squares procedure, is one of the well-known and most used chemometrics techniques for the analysis of the multidimensional data matrices. Unlike to other multiway data analysis methods, such as parallel factor analysis (PARAFAC), MCR-ALS does not follow a rigorous multilinear model.<sup>31</sup>

This paper presents the utilization of fluorescence spectroscopy combined with MCR-ALS analysis to study the aggregation of asphaltene samples provided from the different reservoirs in Iran. To the best of our knowledge, this is the first report concerning with the chemometrics analysis of the fluorescence spectra of asphaltene samples.

## 2. THEORETICAL BACKGROUND

Presently, samples are far from simple and often contain many components to be simultaneously analyzed or a few interesting analytes in the presence of many other chemical interferences. More complex instrumentation is needed to cope with these systems in an efficient way, and equally needed are tools to handle and interpret the information obtained. Here, we used the capability of the multivariate data analysis methods to analyze the spectrofluorimetric signals recorded from a multicomponent mixture.

Consider that, at specified excitation and emission wavelengths, the fluorescence intensity ( $d$ ) is proportional to the concentration ( $c$ ) of analyte ( $d = sc$ ), where  $s$  is the proportionality constant. For a mixture of more than one

analyte, considering the additivity of the fluorescent signals, we have  $d = c_1 s_1 + c_2 s_2 + \dots$ , where  $c_i$  and  $s_i$  are the concentration of the  $i$ th analyte in the solution and its respective proportionality constant. Now, consider monitoring of an evolutionary chemical process (e.g., aggregation of an asphaltene sample by increasing in concentration) by spectrofluorimetric method. If the fluorescence spectrum is recorded at different emission wavelengths for a series of solutions of mixtures of analytes, the fluorescence intensity data can be collected in a two-way data set, a matrix  $D$ , with concentration and spectral directions. In this case, the fluorescence additive data can be written in the matrix notation of the form of  $D = C S$ , where  $C$  is the concentration matrix, each column of which represents the concentration profile of one analyte, and  $S$  is the pure spectral data, each row of which represent the pure fluorescence spectra of an analyte.

To begin with, Figure 1 and eqs 1–3 describe in detail the raw measurements and the underlying model of pure contributions. For simplicity, we give an example of a two-component system.

$$D = D_A + D_B \quad (1)$$

$$D = C_A S_A^T + C_B S_B^T \quad (2)$$

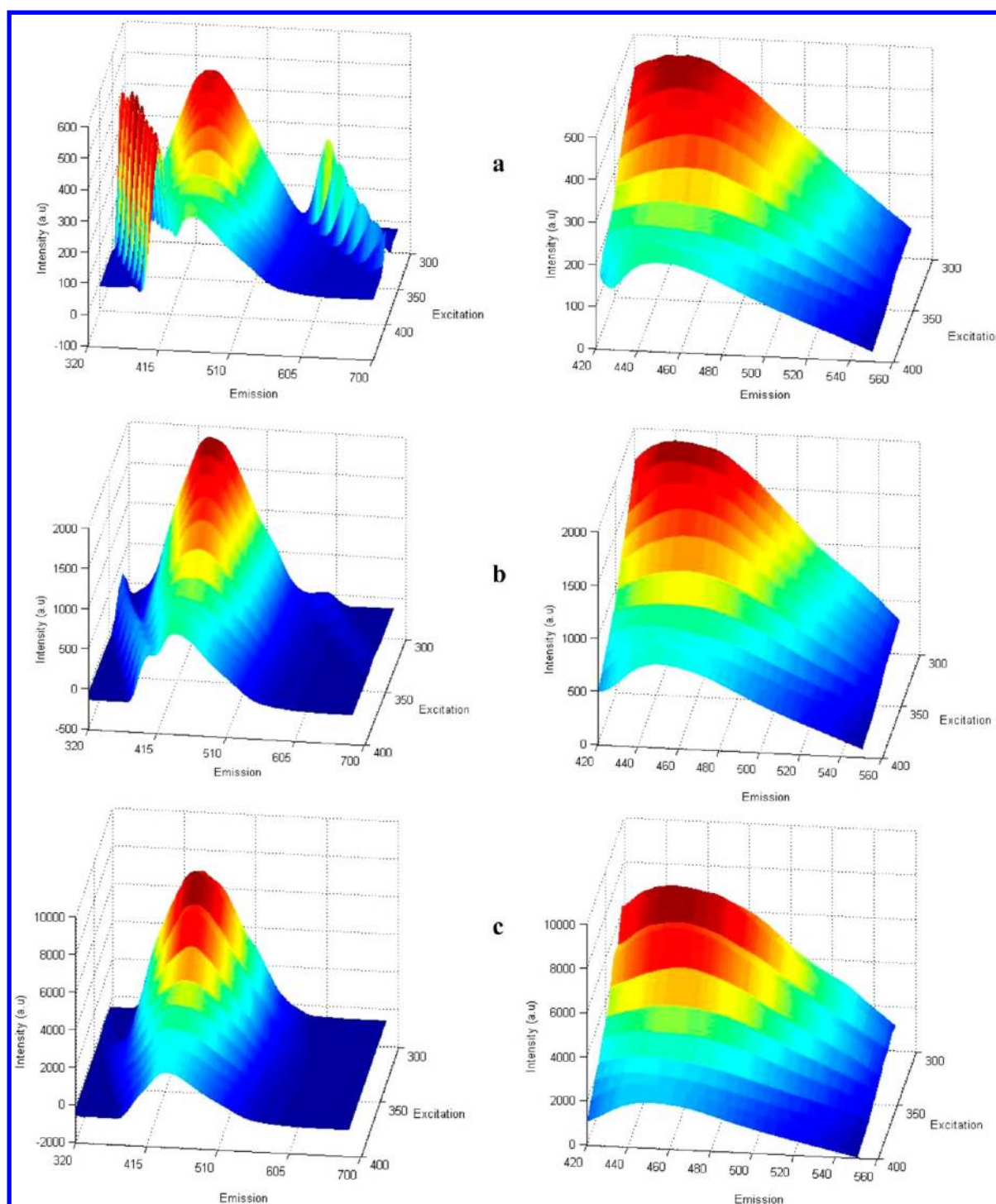
$$D = C S^T \quad (3)$$

Thus, the landscape of raw data can be easily decomposed into  $D_A$  and  $D_B$ .  $D_A$  and  $D_B$  are data matrices from pure signals to A and B. Each one of these landscapes,  $D_i$ , is obtained from a dyad of profiles  $D_i = C_i S_i^T$ , where  $S_i^T$  is a unit pure spectral profile and  $C_i$  is a concentration profile (see Figure 1 and eq 2). Finally, the additive model in eq 2 can be expressed in a more compact way, grouping together all the concentration profiles and all spectra in the  $C$  and  $S^T$  matrices, respectively (Figure 1 and eq 3).

The goal of MCR is, thus, passing from the mixed nonselective information that comes from the instrument ( $D$ ) to the real contributions of the pure components in our system (represented by the profiles in  $C$  and  $S^T$ ) without using any behavior model or a priori information about the system. How to do this in the most efficient and reliable way has been the task of MCR research from early days until present.<sup>32</sup>

Consider that we have a series of  $n$  concentrations of asphaltene samples ( $n_c$ ). If emission spectral profiles of each solution are recorded at  $n_{\text{ex}}$  excitation wavelengths, a data matrix of size of ( $n_{\text{ex}} \times n_{\text{em}}$ ) is obtained for each sample. This matrix is called an excitation–emission fluorescence data matrix. The excitation–emission matrices (EEM) can be augmented to form a bigger data matrix<sup>33</sup> or can be arranged in a cubic array. In the former case, the augmented data matrix ( $D$ ) has  $n_c$  rows and  $n_{\text{em}} \times n_{\text{ex}}$  columns.

Consider that in the system under study,  $n_f$  fluorescent species are coexisting and the global fluorescence intensity corresponds to the sum of the fluorescence of the individual species. In matrix notation, the fluorescence spectra of the



**Figure 2.** Three-dimensional EEM plot for different concentrations of Bangestan sample (a) 2.5 ppm, (b) 15 ppm, (c) 60 ppm, before (left) and after (right) range selection.

samples can be represented as  $\mathbf{D}$  ( $n_o, n_{em} \times n_{ex}$ ) and its bilinear decomposition can be described by the following equation:

$$\mathbf{D} = \mathbf{C}\mathbf{S}^T + \mathbf{E} \quad (4)$$

where  $\mathbf{C}$  ( $n_o, n_f$ ) and  $\mathbf{S}$  ( $n_{em} \times n_{ex}, n_f$ ) are concentration and augmented spectral profiles, respectively,<sup>34</sup> and  $\mathbf{E}$  ( $n_o, n_{em} \times n_{ex}$ ) is the matrix of residuals.

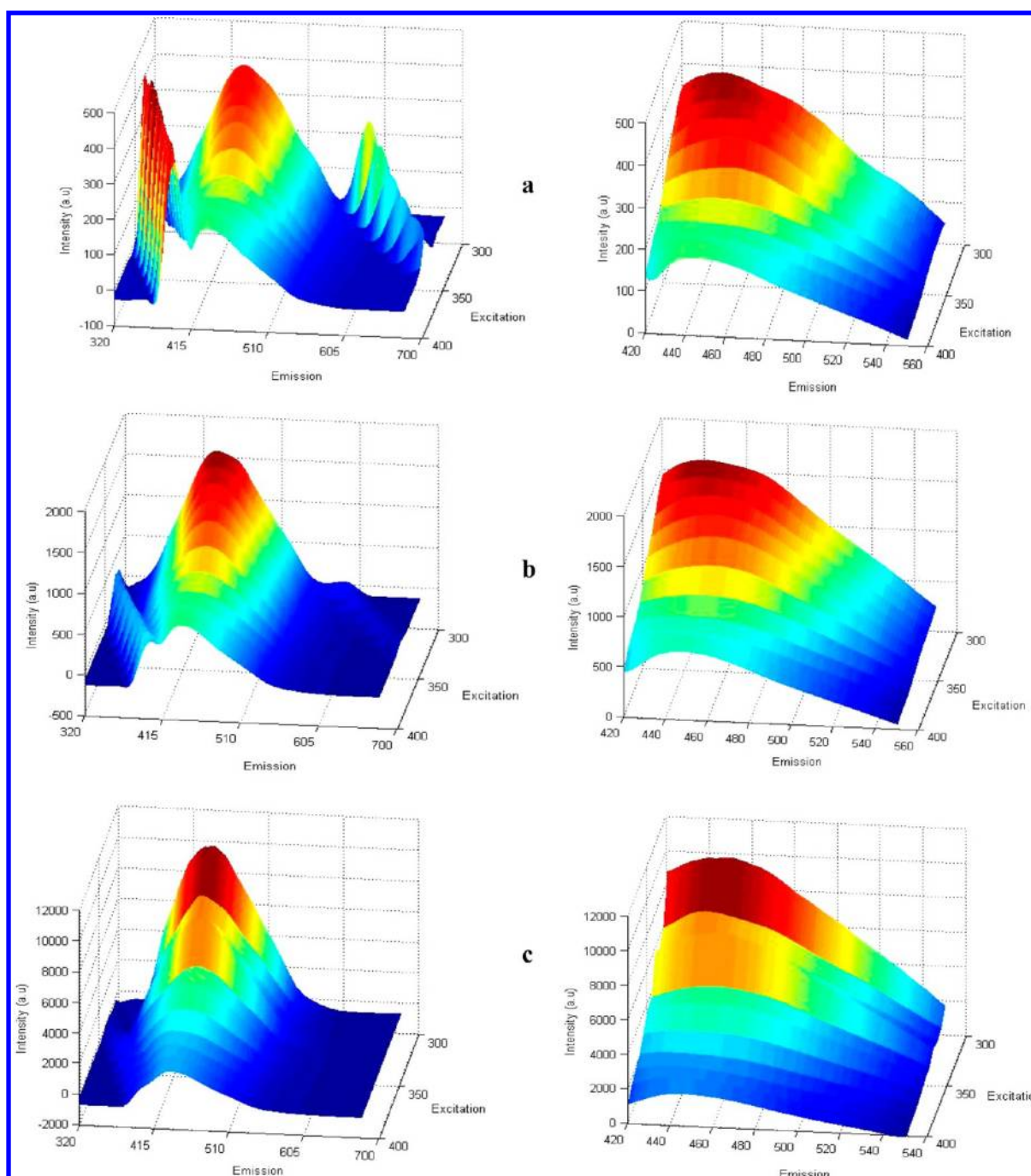
Decomposition of matrix  $\mathbf{D}$  to matrices  $\mathbf{C}$  and  $\mathbf{S}$  can be achieved by utilizing MCR-ALS. It is an iterative method, which requires initialization with system parameters (each one of the

concentration or spectral profiles). In our case (i.e., row-wise augmentation mode), the initial estimates of concentration profiles were obtained from the analysis of the spectra based on the evolving factor analysis (EFA).<sup>35</sup>

### 3. EXPERIMENTAL SECTION

**3.1. Asphaltene Extraction.** Asphaltene samples were extracted from crude oil according to the existing procedure.<sup>36</sup> Each crude oil was treated by an excess amount of *n*-heptane (40:1 volume ratio), equilibrated for two days at ambient conditions, and then filtered by a





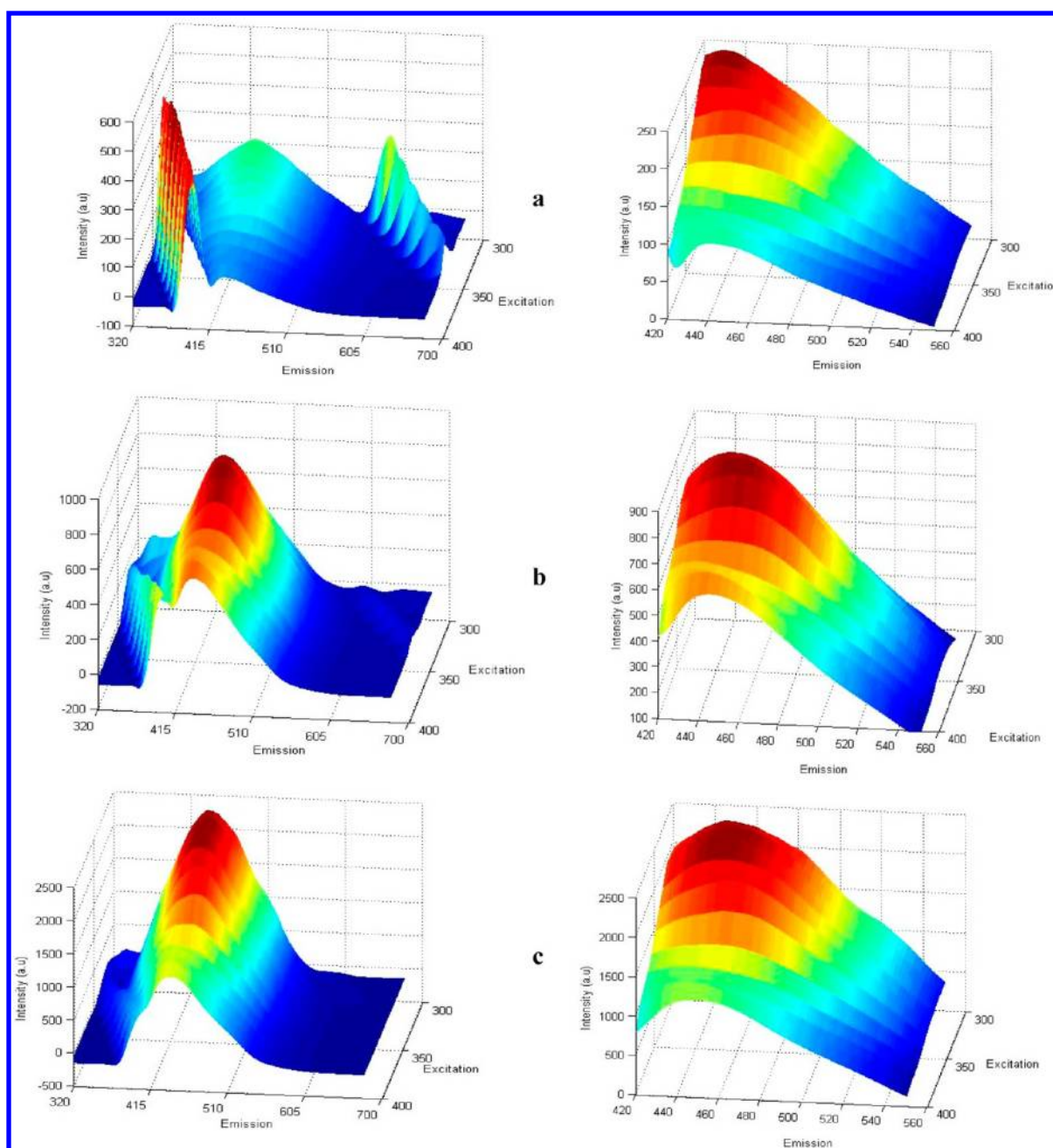
**Figure 3.** Three-dimensional EEM plot for different concentrations of Kuh-e-Mond sample (a) 2.5 ppm, (b) 15 ppm, (c) 60 ppm, before (left) and after (right) range selection.

grade 589/2 Whatmann filter paper. The filtered solid was rinsed with several aliquots of *n*-heptane. Then, by adding toluene to the filtered solid (e.g., asphaltene), the toluene soluble asphaltene were collected. Finally, the solid asphaltene was obtained by vaporization of the collected filtrate at ambient condition. Toluene (Merck) and *n*-heptane (Merck) were used as received.

**3.2. Apparatus and Software.** All fluorescence spectra were recorded on a Perkin-Elmer spectrofluorometer (LS50B) equipped with 1.0 cm quartz cell. The FL WinLab Software (Perkin-Elmer) was used to collect the measured data. UV-vis spectra were recorded using HP diode array spectrophotometer employing a quartz cuvette with 10 mm path length. The fluorescence signal was corrected for inner filter effect (IFE) at high concentration of asphaltene.<sup>37</sup>

All calculations were performed in the MATLAB (Mathwork, Inc.) environment. The corrected emission data were processed using MCR-ALS programs developed by Tauler et al. (<http://www.ub.edu/gesq/mcr/mcr.htm>).

**3.3. Experimental Procedure.** A stock solution of 500  $\mu\text{g/mL}$  of asphaltene was prepared in toluene. Serial dilutions of this stock solution were done for recording the fluorescence spectra. For eliminating the quenching effect of dissolved  $\text{O}_2$ , each sample was deoxygenated by purging with Ar gas for a few minutes before recording the fluorescence spectra. The fluorescence spectra were collected at excitation wavelengths of 300 to 400 (in 10 nm intervals) and emission wavelengths from 320 to 700 (2 nm interval) for concentrations of 1.0, 2.5, 5.0, 10.0, 15.0, 20.0, 30.0, 40.0, 50.0, and 60.0  $\mu\text{g/mL}$ . As the concentration increases, an inner filtering effect



**Figure 4.** Three-dimensional EEM plot for different concentrations of Gachsaran sample (a) 2.5 ppm, (b) 15 ppm, (c) 60 ppm, before (left) and after (right) range selection.

would be caused by fluorescence quenching such that an inappreciable signal could be acquired at concentrations higher than 60.0  $\mu\text{g/mL}$ , hence the limiting concentration.

**3.4. Data Set and Data Analysis.** Although the fluorescence spectra was recorded at 320–700 nm, the emission wavelengths of 420–550 nm were selected for MCR-ALS analysis for removing the effects of scattering at  $\lambda_{\text{em}} = \lambda_{\text{ex}}$  and  $\lambda_{\text{em}} = 2\lambda_{\text{ex}}$ .

For each asphaltene sample, the concentration–emission data matrix was composed of  $10 \times 66$  data points, where 10 is the number of solutions and 66 is number of emission wavelengths. The augmented data matrix for all sample solutions of a specified asphaltene sample was arranged by setting the data matrices alongside of each other and keeping the common concentrations in the same row (sample wise). The obtained augmented data matrix possesses a dimension of  $10 \times 726$  (comprised of 10 concentrations, 66 emission wavelengths for each of 11 excitation wavelengths).

The first step in MCR-ALS analysis is to find the number of existing components in the system under study. The number of components was elucidated by using Eigen-analysis and EFA. MCR-ALS requires good initial estimations of the spectral or the concentration profiles for each component to start the iterations.<sup>38</sup> Generally, EFA<sup>35</sup> or simple-to-use interactive self-modeling mixture analysis (SIMPLISMA) can be used to obtain initial estimates for concentration or spectral profiles, respectively.<sup>39</sup> Here, we used concentration profile as an initial estimate. Since the intensity in fluorescence is expected to have positive values, a non-negative constraint was imposed on both spectral and concentration profiles. The unimodality constraint was also imposed on concentration profiles. Identical constraints were imposed on all experiments. MCR-ALS optimization was stopped when the relative difference in lack of fit (% LOF) values between consecutive iterations was less than a threshold value (usually 0.1%).<sup>40</sup>

The experiments were done in duplicate, and the percent of relative standard deviation (% RSD) for two repetitive experiments were in the

ranges 0.9–9.5, 3.8–15, and 0.6–8.8 for Bangestan, Gachsaran, and Kuh-e-Mond, respectively.

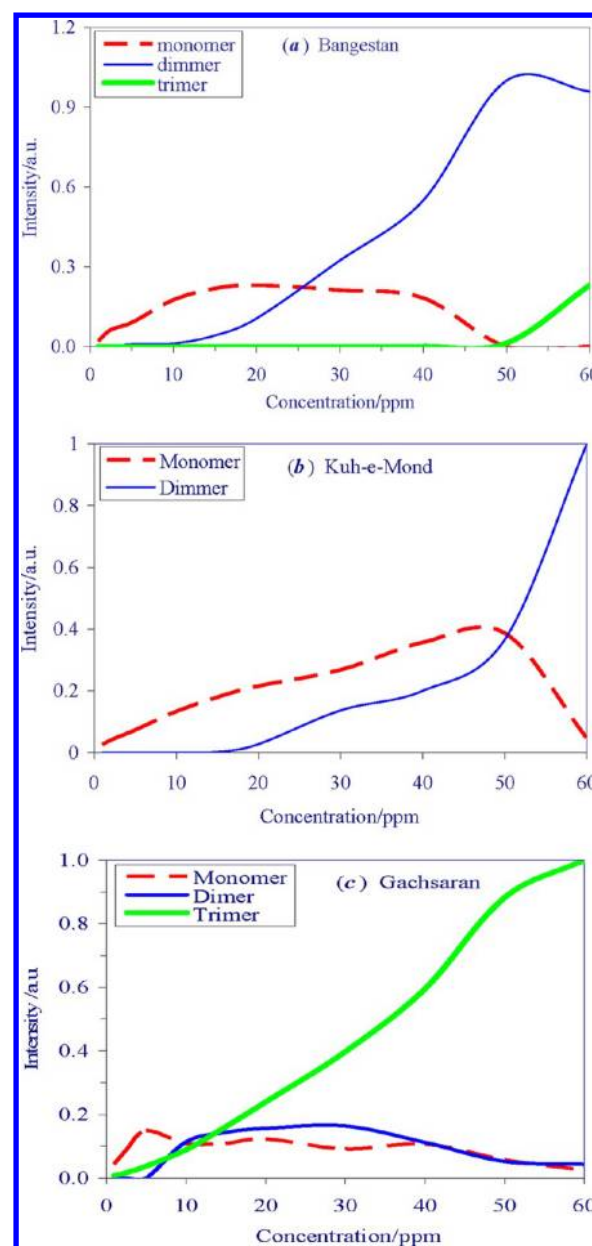
#### 4. RESULTS AND DISCUSSION

Fluorescence spectra of three samples at concentrations of 1, 30, 50, and 60 ppm are presented in the Supporting Information (Figures S1–S3). Figures 2–4 represents three-dimensional fluorescence spectra for different concentrations of the studied samples in the ranges from 320 to 700 nm in the emission domain (steps of 2 nm) and from 300 to 400 nm in the excitation domain (steps of 10 nm). One can observe a little difference between the spectra of the asphaltene samples, which can be attributed to the difference in the chemical structure of asphaltenes of different reservoir. By using the MCR-ALS analysis, we can resolve the components in each sample, whereas the whole spectra of three components show little differences.

The first step in MCR-ALS is determining the number of significant principal components, which can be attributed to the number of chemical species coexisting in the reaction system. The number of significant factors was extracted by application of the EFA method to the augmented data matrices. The evolutions of Eigen-values as a function of asphaltene concentration for the forward and backward analyses are given in the Supporting Information (Figure S4). According to the principal of factor analysis, the magnitude of the systematic Eigen-values is much larger than the noisy Eigen-values. The systematic Eigen-values in a data matrix can be considered as the number of independent chemical species coexisting in the evolutionary process. It is obvious from Figure S4 that there is a large separation between the third and fourth Eigen-values for the asphaltene samples of Bangestan and Kuh-e-Mond, whereas for that of Gachsaran, the largest separation is observed between the second and third Eigen-values. Accordingly, we considered three principal components for the Bangestan and Kuh-e-Mond samples and two principal components for Gachsaran sample.

The next step in MCR-ALS is to give an initial estimate for the concentration profile of each detected principal components (or chemical species). The concentration profiles obtained from EFA plots of Figure S4 (Supporting Information) are represented in Figure S5. These concentration profiles were obtained using intersection of the  $i$ th forward Eigen-value with  $(f - i + 1)$ th backward Eigen-value, where  $f$  is the number of significant principal components. These concentration profiles were used to start the MCR-ALS analysis for each one of the samples, separately. The optimal solutions were achieved after 9, 6, and 5 iterations, with a fitting error lack of fit (LOF) of 3.7%, 2.1%, 3.6% for Bangestan, Kuh-e-Mond, and Gachsaran samples, respectively. The respective percent of variances in the original data explained by the obtained models at convergence were 99.85%, 99.87%, and 99.86% for Bangestan, Kuh-e-Mond, and Gachsaran samples, respectively.

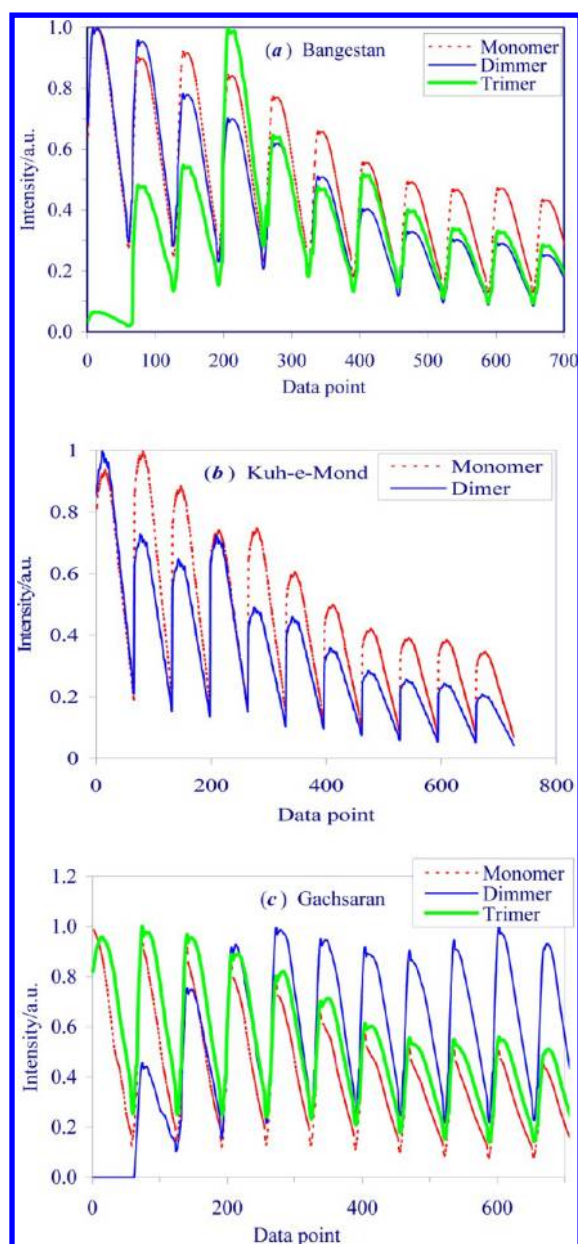
The final results of this analysis are the deconvoluted emission and excitation spectra and the concentration profiles (S and C matrices, respectively). Figures 5–7 show the concentration profiles and the deconvoluted emission and excitation spectra for three types of asphaltene samples. In fact, three chemical species detected as the results of this deconvolution are probably monomer, dimer, and trimer, knowing that asphaltene molecules are, in general, susceptible to undergoing self-aggregation.<sup>41,42</sup> For the Bangestan sample,



**Figure 5.** Concentration profiles obtained with MCR-ALS for different asphaltene samples.

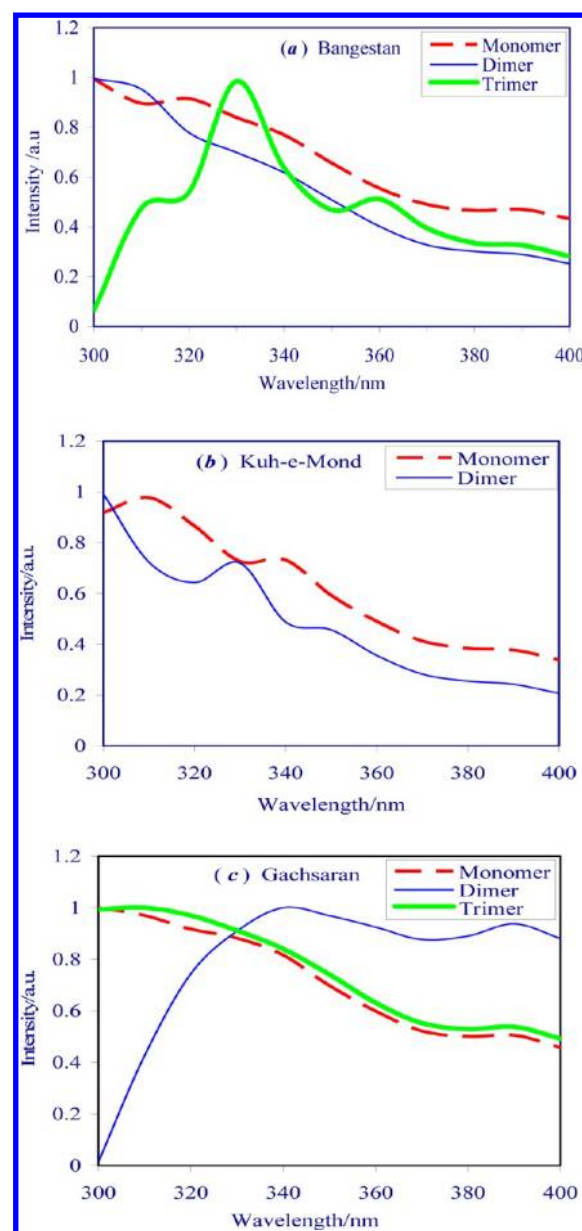
the results showed that three chemical species, probably monomer, dimer, and trimer, are present. At low concentration, we have only monomer, and by increasing the asphaltene concentration up to 20  $\mu\text{g/mL}$ , the dimer is evolved. By the successive increasing to 50  $\mu\text{g/mL}$ , the monomer portion is diminished and dimer formation is increased. At concentrations higher than 50  $\mu\text{g/mL}$ , the trimer species is evolved, while the dimer remains constant. In the concentration range 50–60  $\mu\text{g/mL}$ , we observe that all monomer, dimer, and trimer species are coexisting (Figure 5a). For Kuh-e-Mond sample, the identified two components can be attributed to the monomer and dimer species. At low concentration, only monomer species are present, and by increasing the asphaltene concentration up to 15  $\mu\text{g/mL}$ , the evolution of dimer species is observed. In the concentration range 20–60  $\mu\text{g/mL}$ , the monomer and dimer species are coexisting (Figure 5b). It should be noted that we could not detect the trimer species in the studied concentration





**Figure 6.** Emission spectra obtained with MCR-ALS for different asphaltene samples.

range and higher concentrations of asphaltene might be useful to detect the trimer species. However, we had a limitation in collecting fluorescence data as a result of the inner filter effect of asphaltene samples at high concentrations. It is observed from Figure 5c that for the Gachsaran sample the monomer is not so stable, and by a small increase in the concentration, dimer and trimer species are formed. Interestingly, the trimer species represented the highest stability and evolved at concentrations as low as  $1.0 \mu\text{g/mL}$ . The higher stability of trimer can be related to the difference in the chemical structures of the asphaltene samples, such as molecular size, hydrophobicity, and presence of polar functional groups. Quite interestingly, the observation we had could be the reflection of facts and can be attributed to the role of molecular structure of each asphaltene, as we have recently reported.<sup>43</sup> The asphaltene sample could be a polydisperse distribution of molecules, though it can be assumed there is a narrow distribution around



**Figure 7.** Excitation spectra obtained with MCR-ALS for different asphaltene samples.

the major component from which the excitation–emission data were collected.

Both Bangestan and Kuh-e-Mond reservoirs contain heavy oils with serious asphaltene deposition problems in reservoirs and in pipelines, whereas no asphaltene deposition is reported for Gachsaran field. These facts simply imply that self-aggregation characteristic of most asphaltene samples<sup>41,42</sup> can be ruled out for Gachsaran. Also, these facts, in conjunction with the data given for API° and SARA,<sup>43–45</sup> in Table 1 and for compositions,<sup>46</sup> in Tables 2, unravel that the natures of Bagestan and Kuh-e-Mond asphaltenes are different from that of Gachsaran asphaltenes. The tables show that asphaltene and resin contents of Gachsaran are almost the same as Bangestan and they are much lower than Kuh-e-Mond, which substantiates that molecular structure has certain role in deposition (besides other factors). Our recent investigations for the determination of molecular structure of these three asphaltenes have led to a smaller molecular weight and smaller



**Table 1. SARA Tests (wt %) and API° of Oils Used in This Work**

test name	Kuh-e-Mond <sup>41</sup>	Gachsaran <sup>42</sup>	Bangestan <sup>43</sup>
saturates (wt %)	12.8	53.4802	42.0
aromatics (wt %)	21.83	34.45	43.0
resins (wt %)	53.39	8.5	8.0
asphaltene (wt %)	14.7	5.3	7.0
API°	12.8	31	23.8

**Table 2. Reservoir Crude Oil Compositions (wt %)<sup>46</sup>**

components	compositions		
	Gachsaran	Bangestan	Kuh-Mond
H <sub>2</sub> S	0.24	0.16	0
N <sub>2</sub>	0.01	0.45	0.66
CO <sub>2</sub>	0.77	1.55	0.23
C <sub>1</sub>	35.46	22.90	10.35
C <sub>2</sub>	6.03	7.64	2.35
C <sub>3</sub>	4.93	5.35	1.95
iC <sub>4</sub>	1.14	1.16	1.62
nC <sub>4</sub>	2.92	2.74	4
iC <sub>5</sub>	1.26	0.93	3.6
nC <sub>5</sub>	1.27	1.12	2.28
C <sub>6</sub>	4.67	4.27	2.74
C <sub>7</sub>	5.12	4.29	2.15
C <sub>8</sub>	3.42	3.60	2.42
C <sub>9</sub>	3.60	3.31	2.15
C <sub>10</sub>	3.02	2.95	3.13
C <sub>11</sub>	2.37	2.72	2.52
C <sub>12</sub> <sup>+</sup>	23.69	34.86	57.86
Other Properties			
C <sub>12</sub> <sup>+</sup> mol wt (g/mol)	333		485
C <sub>12</sub> <sup>+</sup> sp gr at 293 K	0.9640		1.0473

number of fused aromatic rings for Gachsaran than the other two.<sup>43</sup> On the other hand, it has been shown that the smaller asphaltene molecular weights imply greater asphaltene molecular heterogeneity, as well as indicating existence of a lower energy barrier to break apart asphaltene micelles, which may also have important operational implications.<sup>11</sup>

Then, considering the finding in this work for dimer and trimer formation of Gachsaran asphaltene at very low solution concentration lead to a conjecture: the smaller molecular size of the Gachsaran asphaltene has a higher molecular diffusivity, hence providing the possibility of dimer and trimer formation in a dynamic mode. That is, an excited asphaltene molecule can interact with another approaching diffused molecule to form an excited dimer, such as an excimer, with a repulsive character at ground state. The larger molecular size of Bagestan and Kuh-e-Mond asphaltenes molecules lead to lower molecular diffusivities, hence such dynamic dimer formation is unlikely. So, the dimer and trimer detected by the present method in low concentration solutions of Gachsaran asphaltene are formed when the sample gets excited (in the spectrofluorimetric spectroscopy) and may not exist in a static way. This could be consistent with the fact that no deposition problem has been encountered in Gachsaran reservoir and pipelines.

It should be pointed out that the data could be also analyzed by parallel factor analysis (PARAFAC) as a multiway data analysis method.<sup>29</sup> However, PARAFAC needs to pretreat the data matrix because the data need to be strictly trilinear. So, before PARAFAC is used, the sources of variability present in

the spectra that are not caused by variation in the concentrations of the analytes need to be eliminated. PARAFAC needs the experimental data to preserve their trilinear structure if it is to work correctly. MCR-ALS, however, only requires the data set to tend to trilinearity, but it is not a hard condition.<sup>34</sup> It is preferred here to analyze the data by MCR-ALS, since the data trilinearity were not verified.

## 5. CONCLUSIONS

MCR is a classical and, at the same time, a fully alive data analysis tool that is still in progress in terms of theoretical developments and new applications. Much development can still be foreseen in different areas, such as the incorporation of new kinds of information and models that respond to mathematical data structure and to properties of new measurements and processes. In this study, the usefulness of EFA and MCR-ALS to extract underlying information about the behavior of different asphaltene samples by changing the concentration in the range 1–60 µg/mL has been demonstrated. The formation of monomer, dimer, and trimer for each asphaltene sample was determined at different concentration. These results can be attributed to the difference in the chemical structure of each asphaltene sample. The information that shows that no problems of asphaltene deposition in Gachsaran reservoir and pipeline exist enhances the conjecture that dimer and trimer species deconvoluted in this work at low concentrations are not static but are formed in a dynamic mode. Although the fluorescence spectra of three samples have small differences at the first look, by employing the chemometry analysis, differences between the samples can be recognized.

## ■ ASSOCIATED CONTENT

### Supporting Information

Excel files and additional figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors are indebted to the research council of the Shiraz University for financial support. Financial support from Enhanced Oil Recovery (EOR) Research Center of the College of Engineering is greatly acknowledged. Help from Elnaz Zare is greatly acknowledged.

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