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Short communication

Analysis of aliphatic alcohol ethoxylates in terms of alkyl and ethylene oxide chain lengths by reversed-phase liquid chromatography with evaporative light scattering detection

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Abstract

Aliphatic alcohol ethoxylates are nonionic surfactants which are incorporated in many industrial formulations as complex mixtures of alkyl homologs and ethylene oxide oligomers. Determination of both the homolog and oligomer distributions is required for product control. The proposed method consisted of three reversed-phase liquid chromatographic separation steps carried out on the same C_{18}-bonded silica column. The first step was a preparative one: the sample mixture was fractionated according to the alkyl chain length without discrimination between ethylene oxide oligomers by using methanol–water eluent. The even homologs (EH) were collected together in a single fraction, the odd homologs (OH) in another. In the second and third steps, respectively, EH and OH fractions were separated according to the alkyl chain length and the number of ethylene oxide units simultaneously by changing the mobile phase composition to acetonitrile–water and by using evaporative light scattering detection.

Keywords: Surfactants; Aliphatic alcohol ethoxylates

1. Introduction

Nonionic surfactants are a class of surfactants widely used in many products and processes (laundry detergents, cleaning agents, cosmetics, herbicides . . .). Within this class, aliphatic alcohol ethoxylates (AAEs), of general formula C_nH_{2n+1}-$(OCH_2CH_2)_xOH$, are increasingly used [1], especially in order to replace alkyl phenol ethoxylates whose metabolites are more toxic [2] and less biodegradable [3]. AAEs are very complex two-dimensional mixtures which can include several tens to hundreds of components [4]. They are prepared by addition of ethylene oxide to aliphatic alcohol cuts. Consequently, first, the resulting product consists of several homologs of different alkyl chain lengths (generally ranging from 8 to 18 carbon atoms); according to the origin (oleochemical or petrochemical) of aliphatic alcohols, it comprises only even homologs or both even and odd homologs. Secondly, no homologs with a defined ethylene oxide chain result, but a distribution of oligomers (ranging from 1 to 30 ethoxy units) is found for each homolog.

Because surface activity, biodegradation and toxicity of AAEs are a function of their structure [4–7], product development and product control need efficient methods to determine both the homolog and oligomer distributions. Several recent reviews [8–10]

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and papers [11,12] discussed the use of chromatography and capillary electrophoresis for the characterization of AAEs. Liquid chromatography (LC) seemed to be the most suitable separation technique. However, since the resolution power of a single LC method was insufficient, the analysis of all the individual AAEs required either coupling of LC with an identification detection mode as mass spectrometry operating in selected ion monitoring mode [13–18] or on-line combination of two complementary LC methods that have the ability to resolve each distribution independently [19,20]. In these latter two-dimensional LC systems, the method used to provide information on the alkyl chain lengths was reversed-phase LC using a non-polar stationary phase eluted with a methanolic mobile phase; the ethylene oxide distributions were obtained either by complexation with a counter cation in an ion-exchange chromatographic system [19] or by normal-phase LC using unmodified silica as stationary phase and aqueous solvents as eluent [20]. In these two studies, the methods used for coupling the two separation systems were also different. In the automated apparatus proposed by Okada [19], all of each homolog peak eluted from the first separation column was collected on a short intermediate concentration column and, after the concentration was completed, the oligomer-by-oligomer separation was obtained by backflushing the concentration column content towards the second separation column. In the so-called comprehensive two-dimensional LC implemented by Murphy et al. [20], sequential aliquots from the first-dimension effluent were sampled on-line by the second-dimension separation system; the resulting data was a matrix, usually represented as a contour plot with each chromatographic separation along an axis.

In the present work, two reversed-phase LC methods using the same C_{18}-bonded silica column in association with two different gradient conditions, were off-line combined to separate the ethylene oxide and alkyl distributions of an AAE mixture presenting an average degree of ethoxylation of 7 and containing both even and odd homologs i.e., in total, about 120 individual AAEs. Evaporative light-scattering detection (ELSD) was chosen as detection method because AAEs can be analyzed under gradient elution without derivatization [20,21]. Moreover, the response factor in ELSD was shown to be equal for every AAE [22] and AAE formulations can be quantitatively analyzed as a function of their alkyl chains and of their degree of ethoxylation from only one calibration curve.

2. Experimental

2.1. Samples and chemicals

The following terminology was used to characterize AAE samples: C_nAE_x designates the individual AAE with n carbon atoms in its alkyl chain and x ethylene oxide units while C_nAE globally describes all the oligomers with n carbon atoms in their alkyl chain. The AAE mixtures denoted by A and C were gifts from Lever-France (Haubourdin, France): A is a mixture of C_{13} and C_{15} homologs; C consists of homologs with an even number of carbon atoms ranging from C_{10} to C_{16}; A and C have similar average degrees of ethoxylation, i.e. 7.2 and 6.5, respectively. The test sample containing both even and odd homologs and denoted by A+C, was prepared by dissolving 5 g l^{-1} of each previous AAE mixture in water.

Acetonitrile and methanol, of HPLC grade from SDS (Peypin, France), were used without further purification. Water was deionized and purified using an Elgastat UHQ II system (Elga, Buckinghamshire, UK). HP45-grade nitrogen was supplied by Carboxyque Française (Venissieux, France).

2.2. Equipment and procedures

Separations were carried out on a liquid chromatograph composed of a LC-10AD high-pressure binary gradient system (Shimadzu, Tokyo, Japan), a 7725i sampling valve equipped with a 2-ml loop (Rheodyne, Cotati, CA, USA), a 150×4.6 mm I.D. column packed with Kromasil C_{18}, 5 μm (Eka Chemicals, Bohus, Sweden) as stationary phase, a Sedex 55 evaporative light scattering detector (Sedere, Alfortville, France) and a C-R5A data processor (Shimadzu). ELSD being a destructive detection mode, the detector was connected to the column in derivation by means of an Acurate post-column

splitflow (LC Packings, Amsterdam, The Netherlands), with only 5% of the column effluent being diverted to the detector which was equipped with a micronebulizer (without any decantation chamber).

Two different mobile phase conditions were used: for acetonitrile–water gradient, the acetonitrile proportion was linearly increased from 50 to 100% in 100 min; for methanol–water gradient, the methanol proportion was linearly increased from 75 to 100% in 50 min. Whatever the elution conditions used, the mobile phase flow-rate was 1 $ml\,min^{-1}$and the ELSD parameters were set as follows: drift tube temperature, 50°C; nebulizing nitrogen pressure, 1.5 bar; and photomultiplier gain, 7.

3. Results and discussion

Depending on organic modifier, different selectivities can be obtained. With methanol-based eluents, only alkyl homologs are separated [19,20,23–27]. The chromatogram of the test sample obtained with the methanol–water gradient is reported in Fig. 1 and, as expected, the homologs are eluted according to the length of their alkyl chain with co-elution of the oligomers belonging to a given homolog. Acetonitrile is known to enhance the effect of the ethoxylation degree on the differentiation of the retention times and, with acetonitrile-based eluents, the homolog peaks split into oligomer peaks

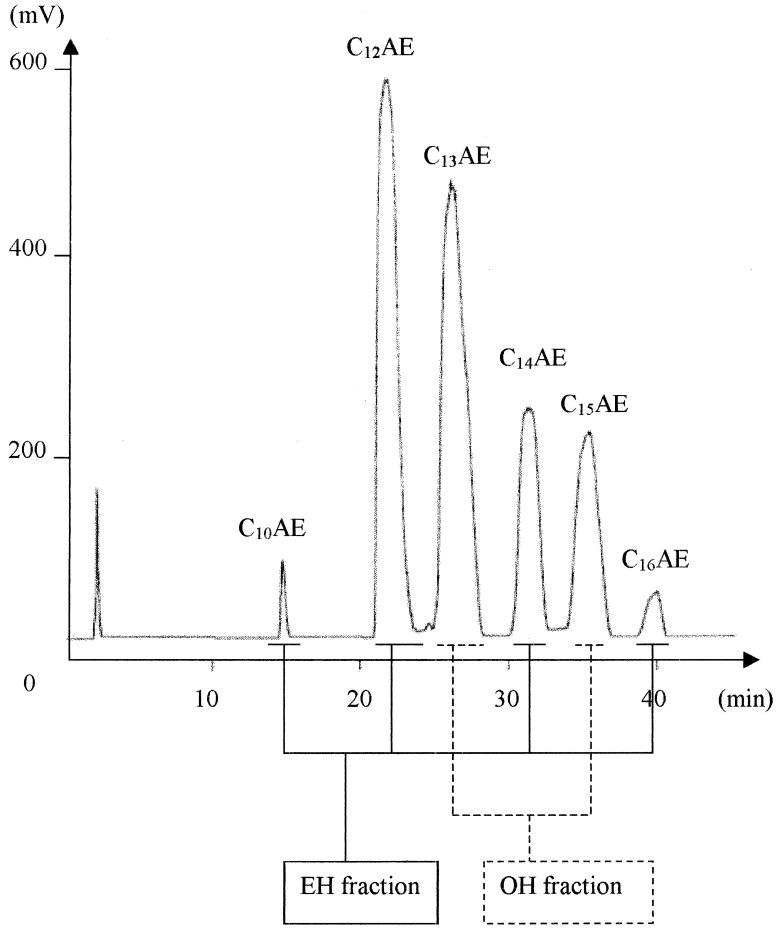

Fig. 1. Chromatogram obtained for the test sample with the methanol–water gradient. Injected volume, 200 μl.

whose retention increases with decreasing number of ethylene oxide units [9,24,26–32]. As an example, Fig. 2 shows the chromatogram of the mixture A+C obtained with the acetonitrile–water gradient. The additional separation of the oligomers of each homolog is obtained, but the oligomer distributions are distinctly observed only if homologs differ by at least two carbon atoms: the C_{10}AE and C_{12}AE distributions are separated, but the C_{12}AE and C_{13}AE, C_{13}AE and C_{14}AE, C_{14}AE and C_{15}AE, C_{15}AE and C_{16}AE distributions overlap. By modifying the gradient profile, it was impossible to obtain a complete separation of the oligomer distributions of two adjacent homologs. Consequently, the complete analysis of AAEs in terms of alkyl and ethylene oxide chain lengths is only possible for AAE mixtures containing exclusively even or odd homologs.

Taking these results into account, we experimented with an analysis scheme including three successive steps. In the first step, the mixture A+C was fractionated into two fractions by performing its homolog-by-homolog separation with the methanol–water gradient (as in Fig. 1) and collecting all the even homologs in a single flask (EH fraction) and all the odd homologs in another (OH fraction). In the second and third steps, the EH and OH fractions were separately analyzed in terms of homologs and oligomers with the acetonitrile–water gradient (Fig. 3a and b, respectively). Before injection, the EH and OH fractions were treated in order to analyze their total content: the methanolic eluate of the first step was first evaporated to dryness under a gentle flow of nitrogen; then the residual material was dissolved in 1 ml of acetonitrile–water (20:80, v/v) and the total volume was injected into the separation column. From the chromatograms obtained for the two fractions, the fractionation of the mixture A+C was a success: no even homolog is observed in OH frac-

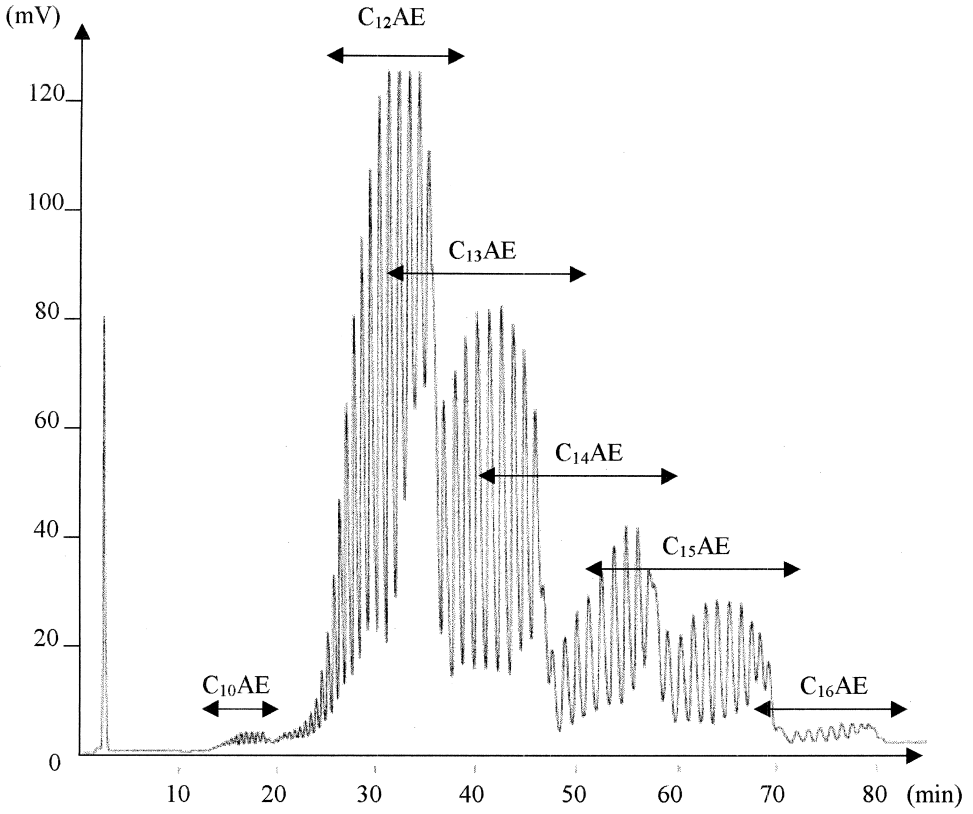

Fig. 2. Chromatogram obtained for the test sample with the acetonitrile–water gradient. Injected volume, 200 μl.

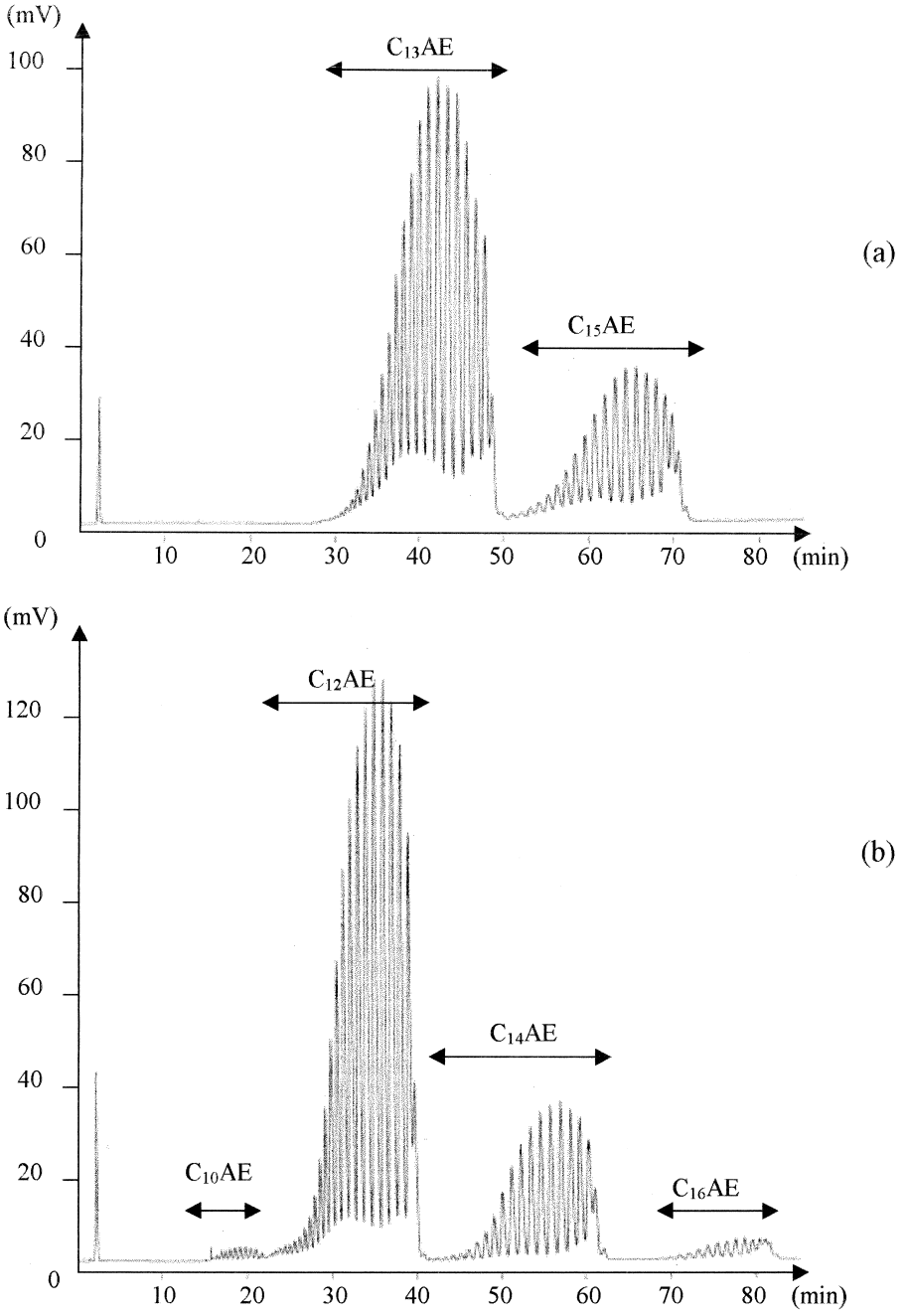

Fig. 3. Chromatograms obtained for the OH (a) and EH (b) fractions with the acetonitrile–water gradient. EH and OH fractions were collected from the separation of the test sample with the methanol–water gradient (see Fig. 1).

tion, no odd homolog is observed in EH fraction and there is no overlapping between the oligomer distributions in each fraction.

In conclusion, the off-line combination of two reversed-phase LC method in three steps allowed us to separate all the oligomer distributions of an AAE mixture containing even and odd homologs. This analysis scheme, using only one column and two series of mobile phase conditions, is easy to implement. But, as in the two forms of two-dimensional separation previously used for characterization of AAE mixtures [19,20], it takes several hours for the analysis of individual AAEs to be completed.

References

[1] M. Raymond, Proceedings of the 4th World Surfactant Congress, Barcelona, 1996, Vol. 1, p. 21.
[2] S. Jobling, J.P. Sumpter, Aquat. Toxicol. 27 (1993) 361.
[3] M. Ahel, W. Giger, M. Koch, Wat. Res. 28 (1994) 1131.
[4] J. Cross (Ed.), Nonionic Surfactants: Chemical Analysis, Surfactant Science Series, Vol. 27, Marcel Dekker, 1987, p. 3.
[5] R.R. Birch, J. Am. Oil Chem. Soc. 61 (1984) 340.
[6] L. Kravetz, J.P. Salanitro, P.B. Dorn, K.F. Guin, J. Am. Oil Chem. Soc. 68 (1991) 610.
[7] S.T. Dubey, L. Kravetz, J.P. Salatrino, J. Am. Oil Chem. Soc. 72 (1995) 23.
[8] A.T. Kiewiet, P. de Voogt, J. Chromatogr. A 733 (1996) 185.
[9] A. Marcomini, M. Zanette, J. Chromatogr. A 733 (1996) 193.
[10] T. Cserhati, E. Forgacs, J. Chromatogr. A 774 (1997) 265.
[11] A. Di Corcia, J. Chromatogr. A 794 (1998) 165.
[12] K. Heinig, C. Vogt, G. Werner, Anal. Chem. 70 (1998) 1885.
[13] H.Fr. Schröder, J. Chromatogr. 647 (1993) 219.
[14] H.Fr. Schröder, J. Chromatogr. A 712 (1995) 123.
[15] H.Fr. Schröder, in: D. Barcelo (Ed.), Applications of LC–MS in Environmental Chemistry, J. Chromatogr. Library, Vol. 59, Elsevier, Amsterdam, 1996, p. 263.
[16] K.A. Evans, S.T. Dubey, L. Kravetz, I. Dzidic, J. Gumulka, Anal. Chem. 66 (1994) 699.
[17] D.D. Popenoe, S.J. Morris, P.S. Horn, K.T. Norwood, Anal. Chem. 66 (1994) 1620.
[18] C. Crescenzi, A. Di Corcia, R. Samperi, A. Marcomini, Anal. Chem. 67 (1995) 1797.
[19] T. Okada, J. Chromatogr. 609 (1992) 213.
[20] R.E. Murphy, M.R. Schure, J.P. Foley, Anal. Chem. 70 (1998) 4353.
[21] S. Brossard, M. Lafosse, M. Dreux, J. Chromatogr. 591 (1992) 149.
[22] F. Guerrero, Thesis, Lyon, 1995.
[23] N. Nakamura, Y. Morikawa, I. Matsumoto, J. Am. Oil Chem. Soc. 58 (1981) 72.
[24] P.L. Desbene, B. Desmazières, V. Even, A. Desbene-Monverney, J. Chromatogr. 461 (1989) 305.
[25] T. Ban, E. Papp, J. Inczedy, J. Chromatogr. 593 (1992) 227.
[26] K. Lemr, M. Zanette, A. Marcomini, J. Chromatogr. A 686 (1994) 219.
[27] P. Jandera, M. Holcapek, G. Theodoridis, J. Chromatogr. A 813 (1998) 299.
[28] A. Nozawa, T. Ohuma, J. Chromatogr. 187 (1980) 261.
[29] M. Kudoh, H. Ozawa, S. Fudano, K. Tsuij, J. Chromatogr. 287 (1984) 337.
[30] G. Barka, P. Hoffman, J. Chromatogr. 389 (1987) 273.
[31] H. Rothbächer, A. Korn, G. Maier, Tenside Surf. Det. 30 (1993) 165.
[32] P.L. Desbene, F.I. Portet, G.J. Goussot, J. Chromatogr. A 730 (1996) 209.