

Partition Isotherms and HPLC analysis of ethoxylated alkylphenol surfactant mixtures

Neudis Subero, Roberto Bauza, Ana Cáceres, Freddy Ysambertt* and Nelson Márquez*

Laboratorio de Petroquímica y Surfactantes, Departamento de Química
Facultad Experimental de Ciencias, La Universidad del Zulia
Apdo. Postal 526, Maracaibo, Venezuela

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Abstract

The partition isotherms of surfactants in the oil-water system over the entire concentration range below the CMC was determined. A normal-phase method for the separation of higher ethylene oxide number (EON) oligomers by High Performance Liquid Chromatography (HPLC) is described. Isocratic HPLC with mixed solvent on silica column allows to separate oligomers up to EON=18. Gradient programming moves the limit up to EON=20. For higher EON values (up to 50) a NH₂ column has to be used, either with isocratic or gradient mode. Detection was performed using UV detector.

Key words: Ethoxylated alkylphenol surfactants; HPLC analysis.

Isotermas de partición y análisis por HPLC de mezclas de surfactantes alquilfenol etoxilados

Resumen

En este trabajo se describe la separación de oligómeros con elevado número de óxido de etileno (EON) aplicando la Cromatografía Líquida de Alta Eficiencia (HPLC). HPLC en modo isocrático con mezclas de solventes, usando columnas de silica permitió la separación de oligómeros hasta EON = 18. Modo con gradiente desplazó el límite hasta EON = 20. Para EON hasta 50 se debe usar una columna de NH₂, en modo isocrático o en modo de gradiente. La detección se realizó usando detectores UV.

Palabras clave: Análisis por HPLC; surfactantes alquilfenol etoxilados.

Introduction

In the past ten years, surfactant mixtures have been dealt with ^{two} reasons: 1) because real systems are mixtures, generally for commercial reasons, and 2) mixtures allow the attainment of some average effect or some synergy, i. e., the enhancement of a property. It must be recalled that in the surfactant business an impurity may be the

cause, the culprit, or the savior of a problem, i. e., "a friend or a foe". In many applications it is of primary importance to know the composition of an effective mixture of surfactants.

Nonionic surfactants of the polyether type are synthesized by adding ethylene oxide to substances with a reactive hydrogen atom, such as alkylphenols (1). During the

* To whom correspondence should be addressed.

ethoxylation process, the adduction randomness results in a mixture of oligomers with different degrees of ethoxylation. The characteristic of each oligomer specie is the number of ethylene oxide group per alkylphenol molecule, so-called ethylene oxide number or EON. Various analytical procedures have been tried to separate the commercial ethoxylated alkylphenols into their different oligomers (2-3) mainly of the chromatographic type. Gas Chromatography (4-9) has been used only for the low average EON mixture, since it fails to separate higher oligomers (EON8), because of their volatility and the thermal degradation that can take place. For these reason, high performance liquid chromatography (HPLC) appears to be the choice method for the separation and characterization of ethoxylated alkylphenol surfactants (10-13). Ethoxylated alkylphenol surfactants have been separated by both reversed and normal phase HPLC. Octadecyl or octyl-silane columns have been used for such separations (14-19). Silica gel (10,15,16) and silica with chemically bonded nitrile (15,17), diol (16), and amino phases (16-25) have been also tested as column packings in normal phase HPLC separation. Several column packing materials used for normal phase separation were tested with aliphatic alcohols and hydrocarbon solvents (26) in order to compare the chromatographic behavior of underivatized ethoxylated nonylphenols on different stationary phases. A normal phase HPLC separation of ethoxylated nonylphenol oligomers has been described by Zhou et al. (27), who used a silica-diol column and a nonpolar solvent gradient elution. HPLC of an ethoxylated alkylphenol mixture having a low average EON was selected for interlaboratory testing, using a diol-bonded phase column under isocratic and gradient conditions (28-29).

In recent articles we have shown how to tune up both isocratic and gradient elution HPLC methods to separate ethoxylated alkylphenol surfactants (30-32). These meth-

ods were used to determine a general expressions for the partitioning coefficient of commercial alkyl phenol surfactants (33,34) between water and hydrocarbon. It is worth remarking that these surfactants generally contain an alkylate group that comes from the polymerization of a short olefin, e.g., propylene, with the corresponding branching due to Markovnikov's rule. Recently a simple way to separate the polyethylene glycol (PEG) oligomer species by isocratic elution with reverse phase columns was reported (35). A rapid reverse phase HPLC method was developed for separation and characterization of individual oligomers in polyethoxylated octylphenol (PEOP) surfactants, using a Cl trimethylsilyl (TMS) column (36). In a recent paper, an analysis by HPLC was proposed as a method to determine the isomeric purity of acid and esters (37) that could be completely resolved on a reversed-phase HPLC column using water-methanol-trifluoroacetic acid elution.

In part I and II we showed how the low ethylene oxide number (EON) oligomers can be separated by isocratic HPLC on silica column while higher EON oligomers can be separate using a NH_2 column and a solvent gradient (30,31). The suggested experimental conditions allow a satisfactory single run separation of a complex mixture. In this paper, we will address the problem of analyzing higher EON distribution mixture (higher than 20 EON) in isocratic and gradient elution form using UV detection.

Experimental Procedure

Partition measurements were carried out by placing 100 mL of oil containing the required amount of surfactant in a separatory funnel, adding 100 mL of water and allowing equilibrium to occur by diffusion at 25°C. The surfactant concentration in each phase was measured by UV spectrophotometry.

HPLC separations were performed using one or two Waters 510 HPLC pump, a

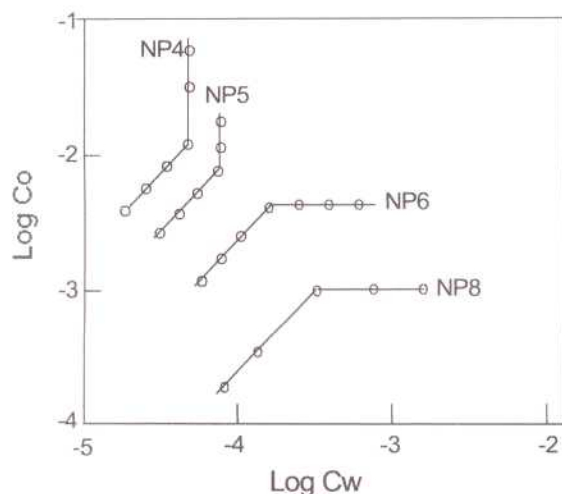


Figure 1. Partition isotherms of NP4, NP5, NP6 and NP8 in the n-heptane-water system at 25°C.

U6K injector, a Waters automated gradient controller, a Waters 484 turnable absorbance detector operate at 270 nm., a Waters 996 photodiode array detector coupled to an ACER computer loaded with Millennium software. The data was handle through an Action PC 5500 personal computer loaded with Turbochrom software with a PE Nelson 900 series interface.

Two columns were used: (1) a silica column, stainless steel, 250 mm x 4.6 mm, Li-chrosorb Si 60-10 μm , manufactured by Hibar-Merck. (2) Adsorbosphere NH_2 -10 μm , stainless steel, 250 mm x 4.6 mm, made by Alltech. The precolumns were filled with the same material than the analytical columns.

Whatever the origin of the surfactant sample, it is evaporate to dryness and then dilute with methanol down to 0.05 mol per liter range. Aliquots (5 or 10 μL) of these methanol samples were injected for chromatographic analysis.

N-heptane, chloroform and methanol are HPLC grade solvents from Baker Chemicals. Whenever a gradient elution is carried out solvent A refers to the initial solvent, while solvent B is the secondary one. The

solvent mixture composition is indicated on a volume percentage basis.

Commercial polyethoxylated nonylphenols were provided by Stepan Chemicals (Makon), Kao Atlas Japan (Emulgen), and Hoescht (Arkopal). All these products were found to be similar, with an ethylene oxide number (EON) distribution very close to the expected Poisson's. They are referred to as NPX, where X is a number which indicates the average number of ethylene oxide group per nonyl phenol molecule, calculated on a mol fraction basis, according to our HPLC data. These numbers are very similar to the manufacturers' claim. The identification of each peak was accomplished by comparison of the retention time with monodisperse alkylphenol polyethoxylated oligomers.

Results and Discussion

Partition Isotherms

In order to understand the relation between the partition behavior of emulsifiers and the type of emulsion produced, it is necessary to determine the partition isotherms of surfactants in the oil-water system over the entire concentration range below and above the CMC. Figure 1 shows the partition isotherm of NP4, NP5, NP6 and NP8 in the n-heptane-water system at 25°C. It is well known that the partition isotherm of a surfactant in an aqueous-organic two phase system exhibits an abrupt change of slope when the equilibrium concentration of the solute attains the CMC. Namely, the brake points in the partition isotherm indicate the beginning of micelle formation. At concentration below the CMC, partition coefficients for NP4, NP5, NP6 and NP8 were kept constant regardless of concentration, whereas those for NP4 and NP5 slightly increased with increased concentration. As shown in Figure 1, for the systems NP4-heptane-water and NP5-heptane-water, the surfactant concentration in the water phase (C_w) was held constant at concentrations above

the CMC, which suggest that micelles are formed in the oil phase. On the contrary, for the systems NP6-heptane-water and NP8-heptane-water, the surfactant concentration in the oil phase (C_o) was held constant at concentrations above the CMC, which indicates that micelles are formed in the water phase. These observed results reveal that micelle formation is a phenomenon similar to a phase separation. Namely, it would be thought that, at the break point in the partition isotherm, the saturation concentration for monomeric surfactants is reached in both the oil and water phases simultaneously. Therefore, it is reasonable to think that, at the break point in the partition isotherm, the equilibrium concentration of the solute attains the CMC in both the oil and water phases simultaneously. Above the CMC the micellar phase disperses in the oil phase for the systems NP4-heptane-water and NP6-heptane-water where w/o emulsions are formed, while it disperses in the water phase for the system NP8-heptane-water where o/w emulsion is formed. Thus, it can be concluded that the phase in which the micellar phase disperses as small aggregates of surfactant molecules is the continuous phase in the emulsion.

Isocratic and gradient HPLC on a silica column

Most commercially available nonionic surfactants are polyethoxy-lated alcohols or alkyl phenols which exhibit a wide distribution in their ethylene oxide chain length. In reverse phase chromatography the separation depends upon the alkyl group in the surfactant molecule and the retention mechanism is governed by hydrophobic interactions between the alkyl tail of the surfactant and the bonded stationary phase. However, the alkylate base material is often monoisomeric, and the main analysis problem is to separate the oligomers according to their ethylene oxide number; for such a separation, normal phase chromatography is the logical choice. This normal phase separation is based on the difference in affinity of the

polyether chain of the surfactant species, with respect to the stationary phase (silica) and the mobile phase, which must be less polar. The silica column tends to retain the different oligomers according to their EON. If n-heptane is used as a mobile phase to fractionate a mixture of surfactant species, the lipophilic ones elute with the solvent front while the hydrophilic ones are strongly retained by the column. On the other hand, if pure methanol is used, the hydrophilic surfactant species elute with the solvent front. Thus, the practical problem of isocratic HPLC lies in the finding of an appropriate mobile phase, so that both hydrophilic and lipophilic species might be fully separated. This difficulty has curtailed the application of this method, and many researchers have turned to gradient elution HPLC, a more fashionable and sophisticated technique. In this report, an optimized mobile phase is looked after in order to retain the user-friendly features of routine isocratic HPLC versus gradient HPLC. At first, it may be thought that a mixture of an apolar solvent, such as n-heptane with a polar one, such as methanol would produce a proper *polarity compromise*. Unfortunately these two solvents, and many others with the same characteristics, are not miscible. The miscibility gap may be reduced by the addition of a third component with intermediate polarity, as it is well known from general solution theory. In the present case chloroform, which is miscible with both heptane and methanol, is a choice candidate to attain a single phase elution solvent. Different ternary mixture proportions were tried in order to find out the optimum one. With mixture (a), which contains n-heptane-chloroform-methanol with respective 90:5:5 volume fractions, the hydrophilic surfactants are strongly retained in the column. On the contrary, mixture (b) which contains a 60:20:20 composition produces the quick elution of all surfactant species with a poor resolution. The optimum mixture (c) is found to be composed of n-heptane-chloroform-methanol in 70:10:20 volume

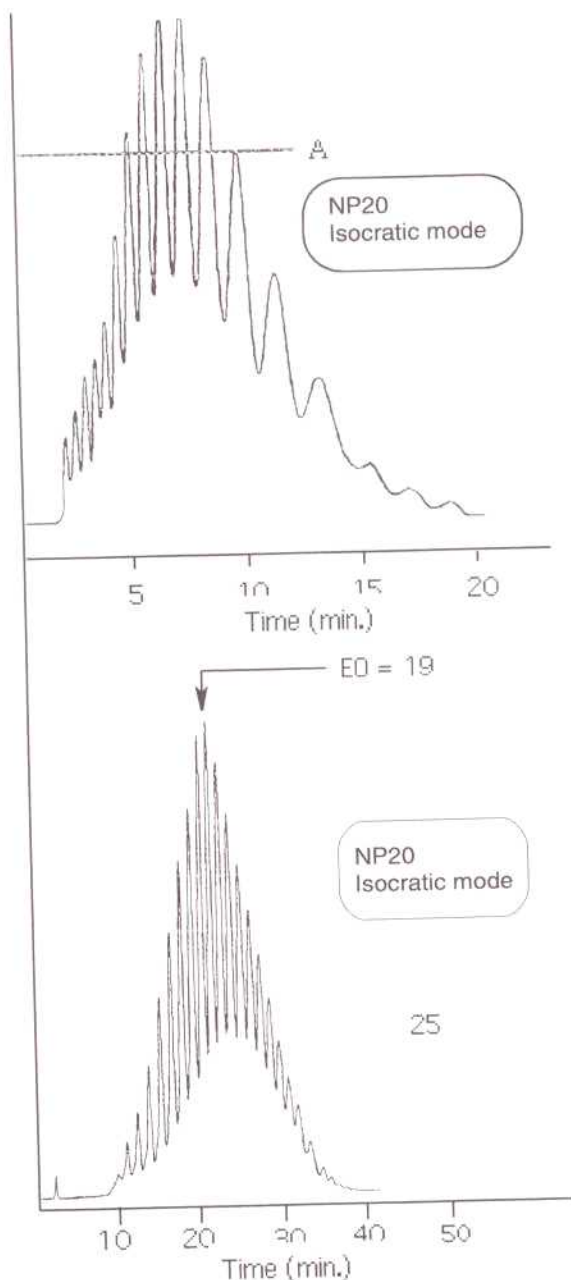


Figure 2. Chromatograms from the separation of NP20 on silica column. (A): Isocratic mode with heptane-chloroform-methanol 70/10/20. (B) Gradient mode according to Table 1. Flow-rate, 1 mL/min; detection, UV (270 nm), sample volume, 10 μ L.

fractions. The method is applied to an equimolar mixture of commercial products NP20. Figure 2 (A) shows that the resolution is good up to EON = 20, but this retention becomes too severe beyond EON = 25.

In order to reduce the retention time of the high EON oligomers, without affecting the retention time of the low EON oligomers, a solvent gradient technique must be used. The column is still the same, but this time the optimization variables are the solvents A and B nature and the mixing program. Base solvent A is n-heptane-chloroform-methanol 90-5-5 mixture, which would allow an excellent separation of low EON oligomers. Solvent B (chloroform-methanol 50-50) must be more polar, but its mixture with solvent A must not become too polar, because it would elute all high EON oligomers together. Trial and error experiments were carried out on nonylphenol ethoxylated surfactant mixture with 20 EON. The best performance was attained using the program shown in Table 1.

Figure 2(B) indicates that this separation is better than in the isocratic mode, with a better definition and resolution of the peaks in the whole EON range. The various oligomers with different ethoxyl groups can be separated effectively with a very short elution time.

Peak areas (or peak heights) were used to calculate the mole percent and average EO number of each NPX. This was accomplished by: (1) listing all peak areas, (2) adding all areas to find the total area, (3) calculating the area fraction (equivalent to mole fraction) of each ethoxymer and (4) multiplying each mole fraction by its ethoxymer numbers (addition of which gives average EO number). The chromatograms were handled through an Action PC 5500 personal computer loaded with Turbochrom software with a PE Nelson 900 series interface. Turbochrom acquires and analyzes data based on the values (parameters) we enter in the method. A method consists of three sec-

Tabla 1
Gradient programs to separate NP20 mixtures on silica column

Time (min)	Flow (mL/min.)	%A	%B	Curve*
Initial	1	100	0	-
15	1	85	15	linear gradient
30	1	75	25	linear gradient
40	1	70	30	linear gradient

* Curve: tipe of curve using by a Waters automated gradient controller.

Table 2
EO Distribution of NP20

EON	Peak Area	Mole Fraction x 100%	Mole Fraction x EON
10	135771	0.40	0.04
11	322719	0.96	0.11
12	507276	1.50	0.18
13	802969	2.38	0.31
14	1242754	3.69	0.52
15	1750221	5.19	0.78
16	2306221	6.84	1.09
17	2801135	8.31	1.41
18	3122100	9.26	1.67
19	3314700	9.84	1.87
20	3249027	9.64	1.93
21	3040769	9.02	1.89
22	2729356	8.10	1.78
23	2313568	6.87	1.58
24	1883117	5.59	1.34
25	1448540	4.30	1.08
26	1059478	3.14	0.82
27	729563	2.16	0.58
28	471626	1.40	0.39
29	271682	0.81	0.23
30	142667	0.42	0.13
31	54428	0.16	0.05
33	699687	99.98	Av EO = 19.78

tions: instrument, processing, and calibration. These results are shown in Table 2 for NP20, whose average EON is found to be close agreement with 20. When the EON experimental values are compared with the theoretical Poisson distribution, a more or less accurate agreement is exhibited as mentioned by other authors (38, 39). The difference is not very significant, and it is not far away from the corresponding Poisson distribution with average EON = 20. Since surfactant mixture is the experimental way to reach an intermediate value of average EON, the HPLC fingerprints of these mixtures are evaluated prior to analysis of the partitioning data.

Trials with higher proportion of solvent B did not exhibit any improvement of separation nor a substantial reduction of the retention time of the high EON oligomers. As a consequence, a less polar column was selected, i.e., Adsorbosphere NH₂ (10 μ m) from Alltech.

Isocratic and gradient HPLC on a NH₂ column

As in the previous case, the NH₂ column is tested first in isocratic mode in order to optimize the solvent mixture. Since the purpose is to separate higher oligomers, a NP20 and NP30 commercial surfactants with an EON distribution from 20 to 40 is tested. Since the column is less polar than the previous one, the appropriate solvent mixture is probably less polar. Different ternary (heptane-chloroform-methanol) mixture proportions were tried in order to find out the optimum one. Mixture (a) 75-10-15, exhibits a quick elution and a poor separation. In mixture (c) 90-5-5, half the methanol and half the chloroform have been replaced by heptane, to make up a much less polar solvent. The separation is better than in the previous case (a), but the retention times are much longer. Mixture (b) 82-8-10, exhibits an intermediate polarity. Figure 3(A) shows the isocratic separation of NP20 on NH₂ column with n-heptane-

chloroform-methanol mixture 82-8-10. Also, Figure 3(B) shows the isocratic separation of NP30 on NH₂ column with n-heptane-chloroform-methanol mixture 70-15-15. The corresponding chromatogram displays a good compromise between separation and retention time. However, it is worth noting that the very high EON oligomers might not be well separated.

A wider EON range can be reached by using solvent gradient. In order to separate the very low EON species first, a slightly less polar solvent is taken as base solvent A (90/5/5 n-heptane/chloroform/methanol), then it is mixed with more polar solvent B (50/50 chloroform/methanol) according to a linear gradient program shown in Table 3. Figure 4A shows the chromatogram obtained with methanol solution of NP20 using NH₂ column. Also, Figure 4B shows the chromatogram obtained with methanol solution of NP30 in linear gradient mode shown in Table 4. It is seen that the separation is fairly satisfactory over the whole range, altogether with a reasonable retention time.

Such wide range EON distributions are encountered in surfactant fractionation, although the limitations of the GC analytical technique have restricted the studies to low EON mixtures up to now (38,40). Real non-ionic surfactant formulations can fairly well contain mixtures of very different products such as NP4 and NP20. These mixtures can exhibit a differential rather than collective behavior at interface; as a consequence, the different oligomers can fractionate between the two or three phases at equilibrium, as discussed elsewhere (30,31).

Conclusions

Break points in the partition isotherm indicate the beginning of micelle formation. The oligomers distribution in ethoxylated surfactants of the alkylphenol type with higher degree of ethoxylation can be determined by normal-phase HPLC on silica and

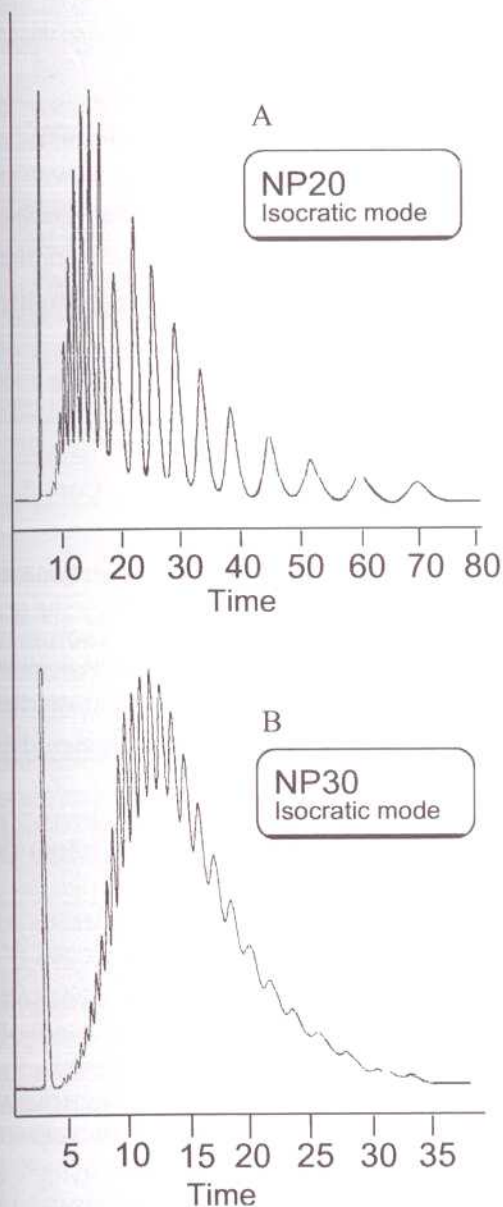


Figure 3. Chromatograms from the separation of NP20 and NP30 on NH_2 column with UV detection. (A) Isocratic separation of NP20 on NH_2 column with n-heptane-chloroform-methanol mixture 82-8-10. (B) Isocratic separation of NP30 on NH_2 column with n-heptane-chloroform-methanol mixture 70-15-15. Other conditions as in Fig. 1.

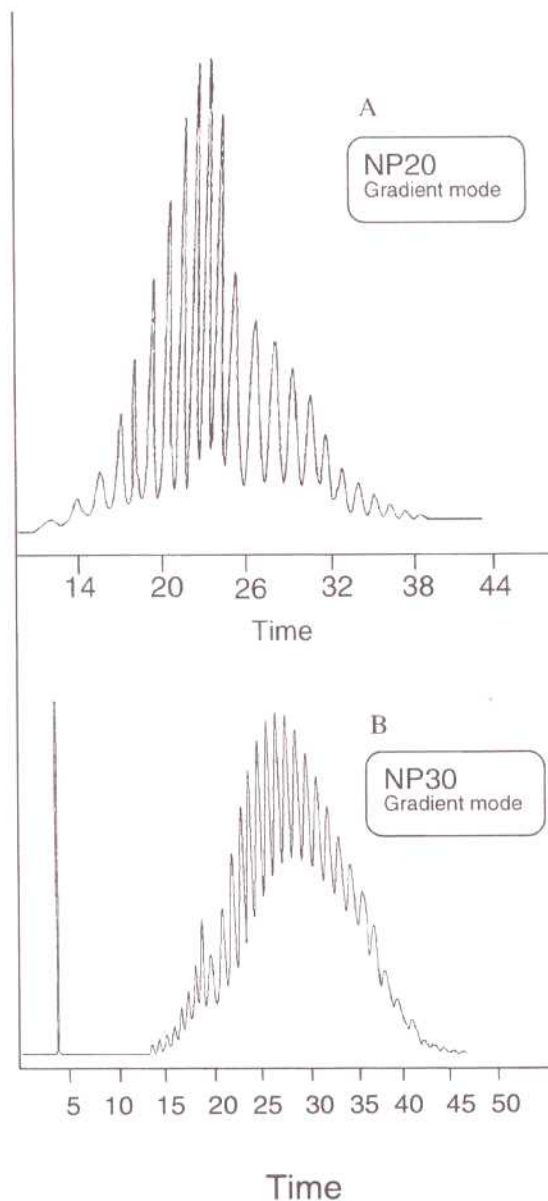


Figure 4. Gradient elution separation of NP20 (A) and NP30 (B) on NH_2 column with UV detection. For conditions see Table 3 and Table 6.

Table 3
Gradient programs to separate NP20 mixtures on NH₂ column

Time (min.)	Flow (mL/min.)	%A	%B	Curve*
Initial	1	100	0	-
15	1	85	15	linear gradient
30	1	75	25	inear gradient
40	1	70	30	inear gradient

* Curve: tipe of curve using by a Waters automated gradient controller.

Table 4
Gradient programs to separate NP30 mixtures on NH₂ column

Time (min.)	Flow (mL/min.)	%A	%B	Curve*
Initial	1	100	0	-
5	1	90	10	linear gradient
15	1	80	20	linear gradient
30	1	75	25	linear gradient
40	1	70	30	linear gradient
50	1	65	35	linear gradient

* Curve: tipe of curve using by a Waters automated gradient controller.

NH₂ columns using UV detection under isocratic and gradient elution with n-heptane-chloroform-methanol mobile phases.

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