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Thermodynamic parameters of the chromatographic equilibrium distribution process of amphiphilic compound by HPLC. Part II: Nonylphenol Polyethoxylated

Bélgica Bravo*, Gerson Chávez, Ana Cáceres, Fredy Ysambertt y Nelson Márquez
Laboratorio de Petroquímica y Surfactantes, Facultad de Ciencias,
Universidad del Zulia, Venezuela.

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Abstract

The oligomer distribution of polyethoxylated surfactants was determined by isocratic normal-phase HPLC on amino column at variable column temperature. As temperature increases, both the absolute retention and selectivity decrease, with a resulting decrease in the separation of the individual oligomers. The effect is correlated with the rising lipophilic character of surfactant species as temperature increases, hence decreasing the interaction with the polar stationary phase. Therefore, the resolution and elution time of the surfactant oligomers can be adjusted by simply changing the temperature. HPLC experiments carried out at different temperatures allow to obtained Van't Hoff plot, and to calculate the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of transfer of one oligomer molecule from the mobile phase to the stationary phase.

Key words: Effect of the temperature in HPLC separation; HPLC of non-ionic surfactants; polyethoxylated surfactants.

Parámetros termodinámicos del proceso de distribución de equilibrio cromatográfico de compuestos anfifílicos por HPLC. Parte II: Nonilfenol polietoxilados

Resumen

En este trabajo se determinó la distribución de oligómeros de surfactantes polietoxilados por HPLC en fase normal en condiciones isocráticas, empleando una columna amino y variando la temperatura de la misma. Con el aumento de la temperatura, tanto la retención absoluta como la selectividad disminuyen, y por consiguiente ocurre un decrecimiento en la separación de los oligómeros individuales. Este efecto esta relacionado con el creciente carácter lipofílico del surfactante con el aumento de la temperatura, trayendo como consecuencia que su interacción con la fase estacionaria polar disminuya. Por consiguiente, la resolución y el tiempo de elusión de los oligómeros del surfactante pueden ajustarse simplemente cambiando la temperatura de la columna. Los experimentos realizados por HPLC a

* Autor para la correspondencia. Teléfonos: 0416-7532127, 0261-7598125; E-mail: belgicabravo@yahoo.es

diferentes temperaturas permitieron obtener la curva de Van't Hoff y calcular la energía libre (ΔG°), entalpía (ΔH°) y entropía (ΔS°) de transferencia de una molécula de oligómero de la fase móvil a la fase estacionaria.

Palabras clave: Efecto de la temperatura en la separación por HPLC; HPLC de surfectantes no iónicos; surfectantes polietoxilados.

Introduction

Surfactants are amphiphilic compounds, which are often used as mixtures, either for cost reasons or because of voluntary mixing to attain some average property or some synergistic effect (1-6). In many applications it is of primary importance to know the exact composition of an effective mixture of surfactants. Most non-ionic surfactants are of the polyether-type, and are synthesized by the addition of ethylene oxide to substances with a reactive hydrogen atom, such as alkylphenol (7). During the ethoxylation process, the adduction randomness results in a mixture of oligomers with a variable degree of ethoxylation, which often varies according to a Poisson's law. As a consequence of its ethylene oxide number (EON) distribution, a commercial surfactant may contain substances with widely different properties from the physicochemical point of view. For instance a commercial nonylphenol with an average of 5 EO groups per nonylphenol molecule contains about 50% of substances which are not water soluble. In presence of both oil and water phases, this can result in an independent solution behaviour of each substance, in particular with the low EON species migrating into the oil phase and leaving the remaining species to go to the interface (8, 9). This situation is often worsened by a current practice in surfactant formulation, i.e., mixing different surfactants in order to attain some average value or some synergistic effect. Such mixing may result in a very wide range EON distribution (10).

Various chromatographic methods have been proposed for the analysis of polyethoxylated surfactants. Individual oligomers are eluted in the order of increasing number of ethylene oxide units in normal-phase methods (11-22), whereas in reversed-phase techniques (11, 15, 21, 23-27), the order of elution depends on the lipophilic group. Both in reversed- and normal-phase cases, the logarithm of the retention factor K', has been found to linearly vary with the number of the repeated structural units (28).

When temperatures increases, the affinity of polyethoxylated non-ionic surfactants change from hydrophilic to lipophilic (29-32). Such change in affinity of the surfactant is mainly due to the desolvatation of the polyethylene oxide chain as temperature increases. As a consequence this phenomenon is likely to notably influence the interactions of a polyethoxylated surfactant molecule with the polar stationary phase in a HPLC process (31, 33-35). This is the subject of the present paper. On the other hand, it is known that the thermodynamic characteristic of the adsorption-desorption process taking place in HPLC can be obtained from the so-called van't Hoff plot (see Ecuación [1] later on) in which the neperian logarithm of the capacity factor is plotted versus the reciprocate temperature (36). If such a plot is linear, then the enthalpic and entropic contributions to the free energy of transfer are independent of temperature and the retention can be easily predicted as a function of temperature. This paper will report an estimate of the thermodynamic characteristic data in normal phase HPLC and will use the oligomer separation by adjusting the temperature.

Experimental procedure

HPLC separations were performed on a liquid chromatography equipment consisting of a M6000A pump, a U6K injector from

Waters Associates, and a Waters 996 Photodiode Array Detector operated at 276 nm coupled to a PC loaded with Millennium software. A 5 μm Lichrospher NH_2 column (250 x 4 μm; made by Merck) was used. All surfactant samples were first evaporated to dryness and then diluted with methanol down to a concentration in the 0.05 mol/liter range. Aliquots (10 μL) of these methanol samples were injected in the HPLC system. The column temperature was varied from 15°C to 50°C either by using an Eppendorf CH-30 column heater or by immersing the column in a VWR heating/refrigerated circulating water bath from Merck. N-heptane, isopropanol, used as mobile phase were HPLC grade from Baker Chemicals. All mobile phase solvents were ultrasonically degassed. The flow-rate was set to 1 mL min^{-1}.

Commercial polyethoxylated nonylphenols were provided by Stepan Chemicals (Makon), Kao Atlas Japan (Emulgen), and Clariant (Arkopal). All these products were found to be similar, with an ethylene oxide number (EON) distribution very close to the expected Poisson's law. They are referred to as NPX, where X indicates the average number of ethylene oxide groups per nonylphenol molecule, calculated on a mole fraction basis, according to our HPLC data. Each peak was identified by comparison of the retention time in experiments carried out with monodisperse alkylphenol polyethoxylated oligomers.

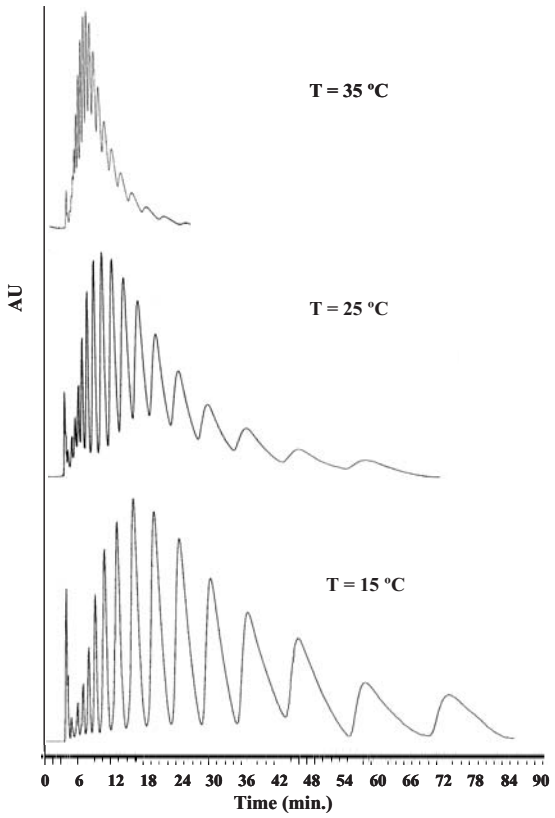

Figure 1. HPLC chromatograms from the separation of NP20 on NH_2 column at different temperatures, using *n*-heptane/isopropanol/water 70:20:10 as mobile phase. Conditions: Lichrospher NH2 column (5μm, 250 x 4 mm); flow rate, 1 mL/min; Detection, UV at 276 nm.

Results and Discussion

As mentioned previously an increases in temperature is expected to turn the surfactant less hydrophilic, and consequently to reduce its interaction with the stationary polar phase. Furthermore, the pressure in the column is found to decrease as temperature increases (i.e. 1500 psi to 300 psi at 40°C). The influence of temperature on the separation is shown in Figure 1, using amino column and n-heptane/isopropanol/water 70:20:10 as mobile phase. It is seen that the surfactant oligomers are strongly retained on the stationary phase at 15°C. Increasing the temperature up to 25°C the separation of the hydrophilic oligomers was decreased. The best separation is attained at 25 and 35°C, since a large number of oligomers can be separated in reasonable time with acceptable resolution. At Temperature higher than 40°C the fractionation is no longer satisfactory. Moreover, it can be said that increasing temperature has two additional benefits: (1) The run time is lower than in normal isocratic mode

and it competes with the solvent gradient case, saving time and solvent; (2) the pressure reduction extends the life-time of the column.

The surfactants retention increases with increasing length of its hydrophilic polyethylene oxide chain. This confirms that the surfactants is adsorbed on the polar stationary phase by its polyethylene oxide chain, and that the hydrophobic moiety is pointing away from the column surface. The chromatographic equilibrium distribution process of solutes between a stationary phase and a mobile phase is related to changes of the standards free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated with the transfer of one mole of analyte from the mobile to the stationary phase (36-38):

$$\ln k = -\frac{\Delta G^\circ}{RT} + \ln\phi = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln\phi \qquad [1]$$

where, k= (t_r - t_0) / t_0 (t_r and t_0 are the retention time of the solute and the total dead time of the column, respectively), R is the gas constant (R= 8.314 J.mol^{-1} K^{-1}), T is the absolute temperature (T= 298.15 K) and ϕ is the phase ratio of the column (i.e., the volume of stationary to that of mobile phase). Using the approach proposed by Jandera et al. (37), ϕ is estimated to be 0.54. The data on the influence of temperature on the capacity factor (k), i.e., on the retention time of the oligomers under isocratic conditions, is charted according to a Van't Hoff plot. Figure 2 deals with the separation of a NP20 commercial mixture on an amino column in the conditions indicated in Figure 1. Figure 2 definitely shows that there is a linear relationship between ln k and the reciprocate temperature for all oligomers. It is worth noting that the slope is positive. This represents a diminishing retention as temperature rises. At a given temperature, ln k is found to increase as the oligomer ethoxylation degree increases. All the data indicate that the decrease in the capacity factor with increasing temperature can be represented by a Van't Hoff type expression:

$$\ln k = a + \frac{b}{T} \qquad [2]$$

where, a and b are the intercept and slope of the linear regression line, respectively. The values of these parameters are reported in Table 1, together with the standard devia-

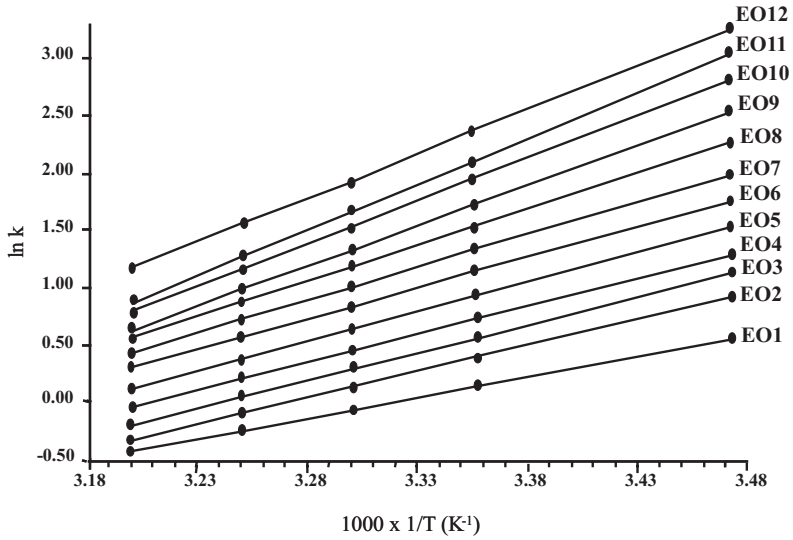

Figure 2. The Van't Hoff plots for selected oligomers of NP20 from the HPLC chromatograms shown in Figure 1. Other condition as Figure 1.

Table 1
Regression parameters of Equation [1] for NP20 surfactant on the amino column

Oligomer	Intercept (a= -ΔH°/R)	Slope (b= ΔS°/R + Ln ϕ)	SD[a]	r [b]
1	-11.918	3.588	0.03	0.9999
2	-15.132	4.624	0.05	0.9998
3	-15.682	4.839	0.03	0.9999
4	-15.545	4.845	0.02	0.9989
5	-16.615	5.227	0.01	0.9998
6	-16.801	5.344	0.04	0.9998
7	-17.891	5.724	0.03	0.9999
8	-19.522	6.275	0.02	0.9988
9	-21.876	7.031	0.02	0.9998
10	-23.178	7.489	0.03	0.9999
11	-23.594	7.656	0.03	0.9999
12	-24.406	7.978	0.04	0.9899

[a]SD, standard deviation of the slope. [b]r , linear correlation coefficient.

Table 2
Free energy (ΔGº), standard enthalpy (ΔHº) and entropy (ΔSº) to transfer the oligomeric unit of NP20 from eluent to the bonded phase of the amino column

Oligomer	ΔG° (KJ mol^{-1})	ΔH° (KJ mol^{-1})	ΔS° (KJ $mol^{-1}K^{-1}$)
1	-1.455	-29.833	-0.094
2	-1.994	-38.442	-0.121
3	-2.403	-40.233	-0.125
4	-2.796	-40.282	-0.124
5	-3.283	-43.455	-0.133
6	-3.790	-44.429	-0.135
7	-4.215	-47.592	-0.144
8	-4.705	-52.176	-0.157
9	-5.073	-58.455	-0.177
10	-5.612	-62.263	-0.188
11	-5.960	-63.656	-0.191
12	-6.600	-66.335	-0.198

tion of the slope (SD) and the regression coefficients *r*. Hence ΔH° and ΔS° are temperature-independent and can be readily calculated from Equation [1] provided that the column phase ratio has been estimated (ϕ = 0.54). ΔG°, ΔH° and ΔS° of transfer from the mobile to the stationary phase were calculated for each oligomer of NP20 commercial mixture and the results are summarized in Table 2. The negative ΔH° indicates that the adsorption of EO chains onto the stationary phase is an exothermic process dictated by a favorable energetic interaction between the surfactant head group and the amino substrate. As expected, ΔH° is more negative as the degree of ethoxylation increases, i.e., as the surfactant becomes more hydrophilic. On the other hand, the negative ΔS° values indicate an increased molecular order resulting from the association of analyte with the hydrophilic ligands of the stationary phase. The trends of ΔH°, -TΔS° and ΔG° vs. the oligomer number (n_{EO}) of the NP20 on amino column and other condition as Figure 1 is illustrated in Figure 3. These plot suggest linear relationships between the thermodynamic parameters of retention and the degree of ethoxylation. The eluites are supposed to orient so as to minimize the energy of binding the hydrophilic moieties to the polar chromatographic surface. Since the surfactant molecule has two moieties, one may admit that the retention occurs by penetration of the hydrophilic group within the interligate space of the polar stationary phase and the hydrophobic alkyl chains are oriented towards the bulk of the less polar mobile phase layer.

On the other hand at temperature higher than 40°C the different oligomer peaks are not separated and merge in a distribution curve. Figure 4 shows the oligomer distribution of the commercial products NP10 (A), NP15 (B), NP20 (C), NP30 (D) and NP40 (E) at 50°C. The EO numbers at the apex of the respective distribution correspond to the average EON. It is seen in this Figure 4 that as the average EON of the surfactant increase, the Poisson distribution becomes broadly.

Conclusions

Although isocratic HPLC has been considered by some authors as not flexible enough to analyse surfactant mixtures, changing the column temperature a few de-

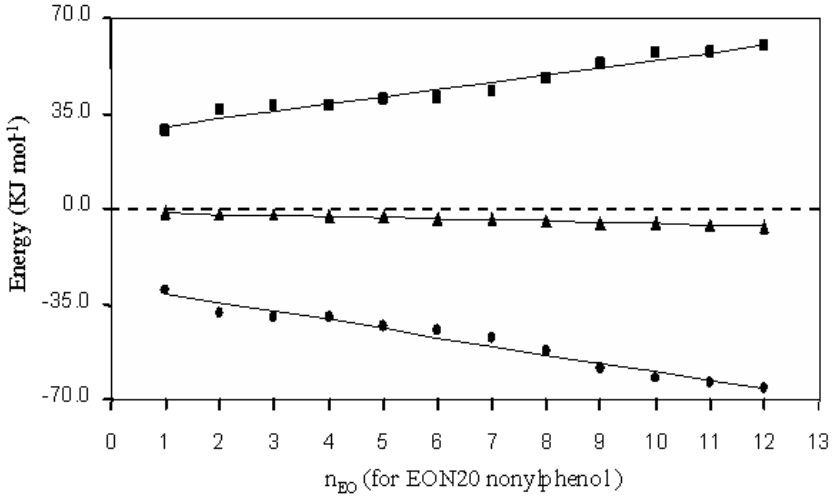

Figure 3. The thermodynamic parameters, ΔH° (●), -TΔS° (■) and ΔG° (▲), vs. The oligomer number (n_{EO}) of the ethoxylated chain for ethoxylated nonylphenol surfactant of EON20. Other condition as Figure 1.

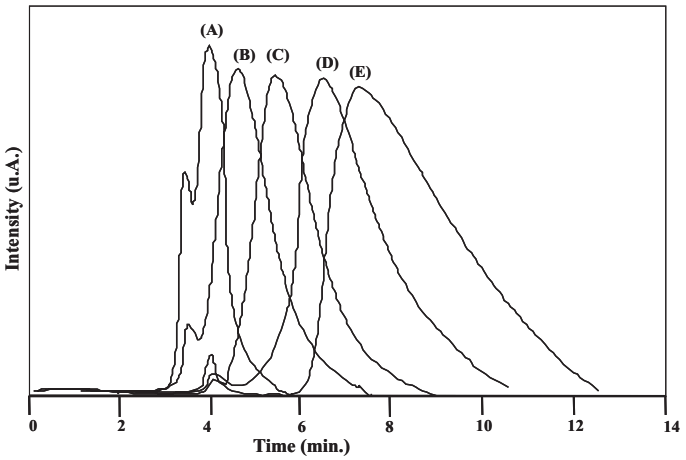

Figure 4. Oligomer distribution of NP10, NP15, NP20, NP30 and NP40 determined by HPLC at 50C. Other condition as Figure 1.

grees may turn it into the simplest method to determine the oligomer distribution in polyethoxylated non-ionic surfactants. The resolution and elution times for the oligomers can be easily adjusted by simply changing the temperature. The negative values of enthalpy of transfer of a surfactant molecule from the mobile phase to the amino stationary substrate indicates the spontaneity of surfactant adsorption. Both $\Delta H°$ and $\Delta S°$ are negative and increase in absolute value with an increase in the ethylene oxide chain length. Furthermore, the determination of the oligomer distribution and the average EON is easily carried out by normal phase HPLC at 50°C.

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