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Solubilization of Phenols by Intramolecular Micelles Formed by Copolymers of Maleic Acid and Olefins

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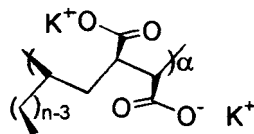
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ABSTRACT: The partition of a series of substituted phenols between water and polymer micelles formed by potassium salts of poly(maleic acid-co-1-olefins), PA-*n*K₂ with *n* ranging from 6 to 18, has been investigated. Steady-state and time-resolved fluorescence measurements have been used to study the formation and properties of these micelles. The data indicate that just PA-6K₂ exhibits a pH-induced conformational transition. All other copolymers adopt a compact configuration over the entire pH range. The hydrophobicity of these microdomains, as measured by the ratio III/I, increases with the length of the side alkyl chain. The aggregation number, i.e., the number of monomer units involved in the intramolecular micelle, has been found to be equal to the degree of polymerization, suggesting that one polymer chain forms one polymer micelle. The transfer free energies of *p*-alkyl-substituted phenols from water to PA-18K₂ and of phenol from water to PA-*n*K₂ have been measured. The contribution of each methylene group to the free energy is 0.97 and 0.34 kJ mol⁻¹ in the substituted phenol and the side alkyl chain, respectively. These values are lower than those determined for transfer of phenols to ionic micelles and to heptane.

Introduction

Polyelectrolytes with hydrophobic groups attached to the side chain may form hydrophobic microdomains under appropriate conditions. Polymers such as poly(methacrylic acid),^{1,2} PMA, copolymers of maleic acid with alkyl vinyl ethers,^{3–9} or styrene^{10–14} are known to perform a pH-induced conformational transition. At low pH these polymers adopt a compact form stabilized by hydrophobic interaction of the alkyl side chains, while at higher pH the macromolecule adopts a random coil conformation. It has also been shown that polyelectrolytes with long hydrocarbon side chain remain in the compact form in the whole range of pH.¹⁵ These structures, called “intramolecular micelles”, exhibit behavior analogue to micelles, including the capacity of solubilizing water-insoluble compounds. There have been relatively few studies of the solubilization of organic compounds by intramolecular micelles,^{9,15} although numerous studies discuss the properties and structure of these aggregates.

In the present study, the solubilization of phenols by alternating copolymers of maleic acid and olefins was investigated. The potassium salts of poly(maleic acid-co-1-olefins) of general formula



are referred as PA-*n*K₂ with *n* = 6, 8, 10, 12, 14, 16, and 18. Fluorescence probing of their aqueous solutions shows the presence of a hydrophobic microdomain, and the number of monomer units forming the intramolecular micelle has been determined.

The measurements of the solubilization of phenols in aqueous solution of PA-*n*K₂ were analyzed using the pseudophase model,^{16–18} where the incorporation of a substrate into micelles is treated as a distribution between the aqueous phase and the micellar phase. With this approach the thermodynamical parameters obtained are the partition coefficient and the standard free energy of transfer, $\Delta\mu_t^0$. Our results were compared to those obtained with micelles in order to assess the solubilization capacity of these intramolecular micelles.

Experimental Section

Materials. Poly(maleic anhydride-co-1-olefin) with olefins ranging from 1-hexene to 1-octadecene (PA-*n* with *n* = 6, 8, 10, 12, 14, 16, and 18) was obtained by polymerizing maleic anhydride (1 mol) and 1-olefins (1.5 mol) in 1,2-dichloroethane at 70 °C for 6 h and using benzoyl peroxide as initiator. The average molecular weights were determined by gel permeation chromatography, GPC, using poly(styrene) samples as standard and ranges between 9000 and 20 000. Further details will be given elsewhere.¹⁹

The potassium salts of these copolymers, PA-*n*K₂, were prepared by adding the polymers to an aqueous solution of KOH, while stirring, heated above 85 °C. After all solids dissolved, the salts were precipitated over an excess of methanol, washed with methanol, and redissolved in water. The remaining KOH was eliminated by ultrafiltration in a 50 mL Amicon cell with a PM-5 membrane which retains all molecules with a molecular weight above 5000. After filtering 20 mL an equal volume of water is added to the cell to keep constant the filtrand volume. This procedure is repeated until a constant conductivity measurement is reached. Finally, the solution was vacuum-dried at 40 °C. The degree of hydrolysis was complete, and it was determined by FTIR, measuring the disappearance of the absorption at 1779 cm⁻¹ which corresponds to the maleic anhydride residue.

Pyrene (Aldrich), pyrenebutyltrimethylammonium bromide, PBTMA (Molecular Probes), and *p*-alkyl-substituted phenols (methyl-, ethyl-, and propyl-) (Aldrich) were used as received.

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Dodecylpyridinium chloride, DPC (Merck), was recrystallized twice from ethanol.

Measurement of Distribution Coefficients. In the pseudophase model the distribution constant can be expressed on a molar concentration basis, K_S , as

$$K_S = \frac{[S_M]}{[S_W][P_M]} \frac{f_M}{f_W} \quad (1)$$

where $[S_W]$ and $[S_M]$ denote molar concentrations of substrate in aqueous and micellar pseudophase, respectively, and $[P_M]$ is the concentration of polymer units forming the intramolecular micelles; f_W and f_M are the activity coefficient of the substrate in the respective phase. Alternatively, this equilibrium constant can be defined on a mole fraction basis, K_X , by

$$K_X = \frac{X_M}{X_W} \frac{f_M}{f_W} \quad (2)$$

where X_M and X_W are the substrate mole fractions in the micellar and aqueous phases.

Both quantities are related by

$$K_X = \frac{55.5K_S}{1 + K_S[S_W]} \quad (3)$$

At low substrate occupation numbers $K_S[S_W] = [S_M]/[P_M] \ll 1$, and eq 3 can be approximated by $K_X = 55.5K_S$. The transfer free energy from water to micellar phase is given by

$$\Delta\mu_t^0 = \mu_M^0 - \mu_W^0 = -RT \ln K_X \quad (4)$$

The distribution coefficients were determined by ultrafiltration in an Aminco 202 cell with a PM 5 membrane. Aqueous solutions of copolymer (1 g/L) at pH 7.0 with different concentrations of phenols were filtered, and the absorbances of the filtrate were measured at 275 nm. The molar concentration of phenols in the filtrate were obtained from a calibration curve and plotted according to eq 1. The equilibrium constants, K_S , were calculated from the initial slope where the activity coefficients can be assumed to be unity.

Fluorescence Probing. The concentrations used were 1 g/L and 2 μ M for the copolymers and pyrene, respectively. All samples were prepared with deionized water. Fluorescence emission spectra were obtained on a ISS PC1 photon counting spectrophotofluorometer. The ratio III/I corresponds to the ratio of intensities of peak three ($\lambda = 384$ nm) to peak one ($\lambda = 373$ nm). This ratio report on the polarity of the pyrene microenvironment.²⁰ The fluorescence decay of the singlet excited pyrene was monitored at 400 nm, following excitation with pulses from a LSI nitrogen laser, model VSL-337ND-S (<4 ns fwhm, 300 μ J, 337.1 nm). The emission was detected with a Hamamatsu IP-28 photomultiplier tube through a grating monochromator (Oriol 77250). Signals were digitized and stored with a TDS 430A digitizing oscilloscope (Tektronik). The data were analyzed in an IBM-compatible PC. A double exponential (eq 6) was fitted to the decay data

$$I(t) = I(0)\{\alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t)\} \quad (5)$$

where k_1 and k_2 are the rate constants for two different decays, and α indicates the fraction of singlet excited pyrene that decays with the slower rate constant k_1 . In all PA- n K₂ $\alpha = 0.7$ –0.8, and the fluorescence lifetime was taken as $1/k_1$.

Results and Discussion

Hydrophobic Microdomains in PA- n K₂. Measurements of the ratio III/I as a function of pH are shown in Figure 1. In the case of PA- n K₂ with $n \geq 8$, the ratio III/I decreases slightly with increasing pH and remains above 0.85 over the entire pH range. On the other hand, the PA-6K₂ shows a sharp decrease of the ratio III/I from

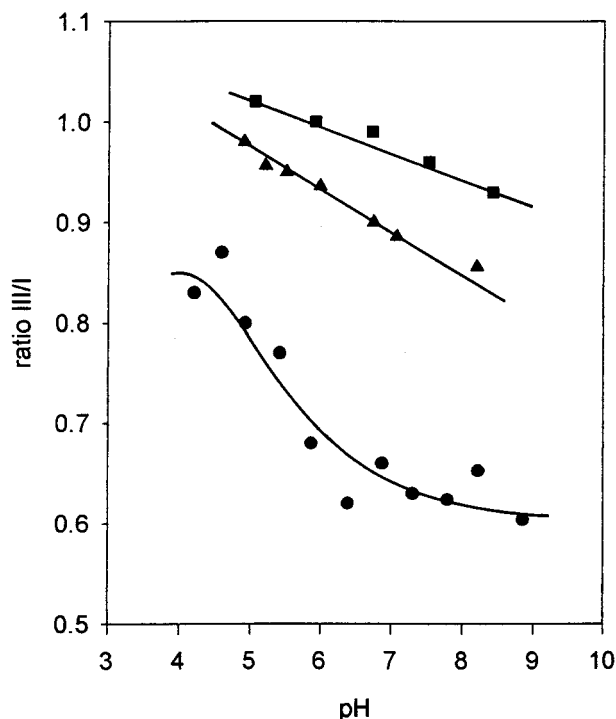


Figure 1. Fluorescence intensity ratio III/I of pyrene (2 μ M) as a function of pH in PA- n K₂ (1 g/L) aqueous solution: ●, PA-6K₂; ▲, PA-8K₂; ■, PA-12K₂.

~0.85 to 0.63 at pH > 6.0. This kind of behavior has been explained in terms of a pH-induced conformational transition. At low pH the polymer adopts a random coil conformation due to hydrophobic interactions of the side alkyl chains, and the ratio III/I reflects a hydrophobic environment. Increasing neutralization of the carboxylic groups increases the electrostatic repulsion, and the polymer chain tends to a stretched form. During this process pyrene senses a more and more polar microdomain until eventually it is released to the aqueous phase. In the PA- n K₂ systems with $n \geq 8$ the hydrophobic interaction among the alkyl side chains stabilizes the compact form even at high degrees of neutralization. These results agree with those reported by Chu and Thomas¹⁵ for PA-18K₂ and confirm that these copolymers form hydrophobic microdomains and act as host over the entire pH range. In Figure 2 the ratio III/I and the fluorescence lifetime of pyrene, measured in aqueous solutions of PA- n K₂ at pH ~7.0, are plotted against the number of carbon atoms in the side alkyl chain. It is seen that both parameters increase with n , which indicates that the hydrophobicity of the polymer micelle increases with increasing size of the side chain.

Aggregation Numbers of PA- n K₂ Intramolecular Micelles. The aggregation number of polymer micelles, which is the number of monomer units involved in the intramolecular micelle, has been determined by fluorescence probing methods,^{8,15,21} which were developed for simple micellar systems.^{18,22–25,26} In this work the time-resolved fluorescence quenching method was used. This method requires the measurement of the fluorescence intensity of a probe, that is dissolved completely into the micelle, in the presence of a quencher that is totally micellized; i.e., both probe and quencher are immobile. Under these conditions the time-dependent quenching data fit the equation

$$I(t) = I(0)\exp(-k_0 t) - \tilde{n}(1 - \exp(-k_q t)) \quad (6)$$

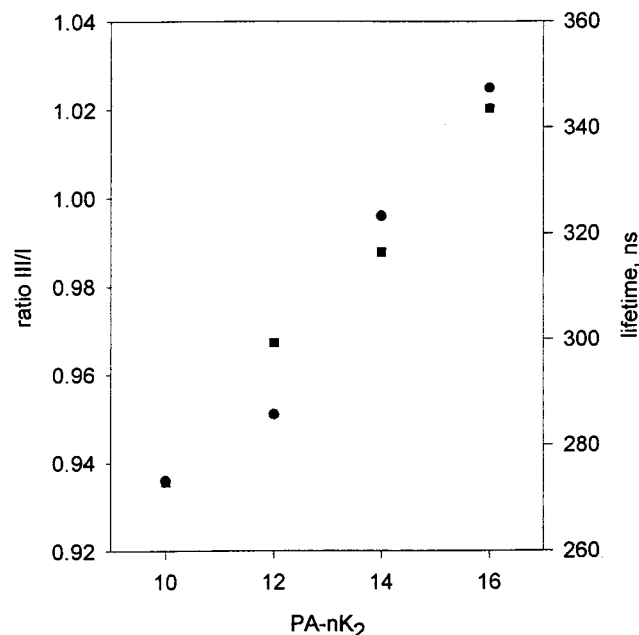


Figure 2. Plot of the ratio III/I (●) and the longest lifetime (■) of pyrene in aqueous solution of PA-*n*K₂ at pH = 7.0 as a function of side chain length.

Table 1. Molecular Weight of the Repetitive Unit, Degree of Polymerization, DP, Polydispersity Ratio, and Aggregation Number of Monomer Units in the Polymer Micelle, *N*, Calculated from Eq 8

copolymer	<i>M_n</i>	DP	<i>M_w</i> / <i>M_n</i>	<i>N</i>
PA-6K ₂	276	17	1.4010	
PA-8K ₂	304	33	1.5700	36
PA-10K ₂	332	35	1.4540	35
PA-12K ₂	360	29	1.6690	27
PA-14K ₂	388	30	1.3460	35
PA-16K ₂	416	26	1.4020	20
PA-18K ₂	444	23	1.4290	20

where \bar{n} denotes the mean number of quenchers in a micelle, and k_0 and k_q are the rate constant of decay in the absence and presence of quencher, respectively. In this work PBTMA and DPC have been used as probe and quencher, respectively. The aggregation number is calculated from \bar{n} , [DPC], and [PA-*n*K₂] according to eqs 7 and 8

$$\bar{n} = \frac{[\text{DPC}]}{[\text{micelle}]} \quad (7)$$

$$\bar{N} = \frac{[\text{PA-}n\text{K}_2] - [\text{PA-}n\text{K}_2]_F}{[\text{micelle}]} \quad (8)$$

where [PA-*n*K₂] is the concentration of polymer in mole of repetitive unit and [PA-*n*K₂]_F is the concentration of monomer unit that are not forming part of the polymer micelle. Considering that none of the copolymers with $n \geq 8$ show a conformational transition, we have assumed that all side alkyl chains are involved in the hydrophobic microdomain, i.e., [PA-*n*K₂]_F = 0. The aggregation numbers calculated by eq 8 are presented in Table 1. In agreement with Chu and Thomas,¹⁵ these numbers are equal to the degree of polymerization, within the experimental error. In a study of micellization of PA-*n*Li₂ using small-angle neutron scattering, Shih et al.^{27,28} arrived at a completely different conclusion. Their results indicated that the aggregation is produced by intermolecular association of several poly-

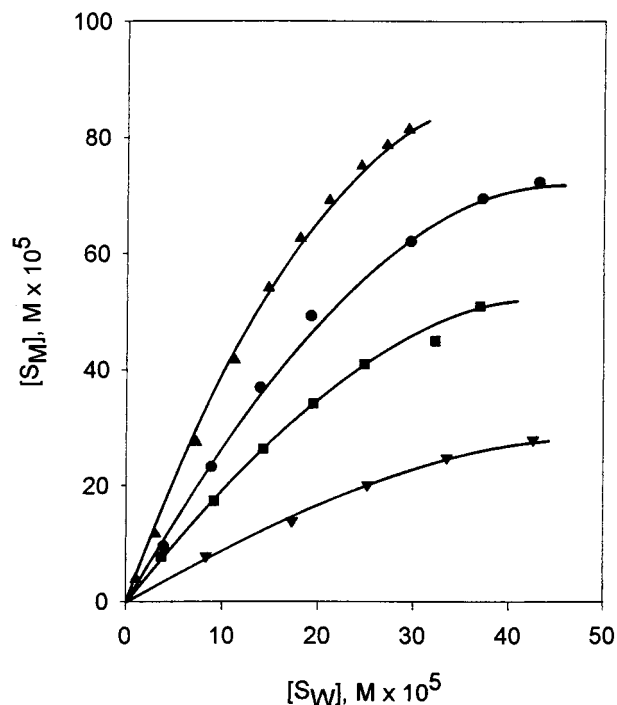


Figure 3. Plot of data for partition of *p*-alkylphenols between water and PA-18K₂ according to eq 1: ▼, phenol; ■, *p*-methylphenol; ●, *p*-ethylphenol; ▲, *p*-propylphenol.

mer chains. However, it is not possible to compare these two set of measurements because of the big difference in polymer concentration (0.1% and 1%). Studies carried out with a similar copolymer, poly(maleic acid-*co*-alkyl vinyl ether), have shown that one macromolecule can give rise to many intramolecular micelles.^{8,21} In this case the different behavior can be attributed to the large difference in molecular weight between these two copolymers. Although the aggregation numbers in both systems are of the same order of magnitude, the degree of polymerization of the PA-*n*K₂ is ≤ 40 , whereas in the copolymers of maleic acid and alkyl vinyl ethers it is in the range 1700–4000. Hence, even when in both series of copolymer the intramolecular micelle are of similar size, just in the latter system it is possible to form more than one micelle by a macromolecule.

Thus, we can conclude that an aqueous solution of PA-*n*K₂ copolymers provides a hydrophobic microdomain in the whole range of pH, one polymer chain forms just one intramolecular micelle, and its hydrophobicity degree is determined by the length of the side alkyl chain.

Distribution of Phenols between Polymer Micelles and Aqueous Phase. The solubilization of *p*-alkyl-substituted phenols into the hydrophobic microdomains provided by the PA-*n*K₂ copolymers was analyzed using the pseudophase model (see above). The equilibrium constants, K_S , were obtained from the initial slope of plots of [S_W] against [S_M] according to eq 1 (see Figures 3 and 4). To assess the effect of the phenol and polymer structure on this equilibrium, two series of experiments were carried out: (i) a family of *p*-alkyl-substituted phenols were partitioned between water and the microdomain provided by PA-18K₂, and (ii) phenol was distributed between water and the polymer micelles formed by the PA-*n*K₂ copolymers. The values of K_S , K_X , and $\Delta\mu_t^0$ obtained in (i) and (ii) are collected in Tables 2 and 3, respectively. The data show that the equilibrium

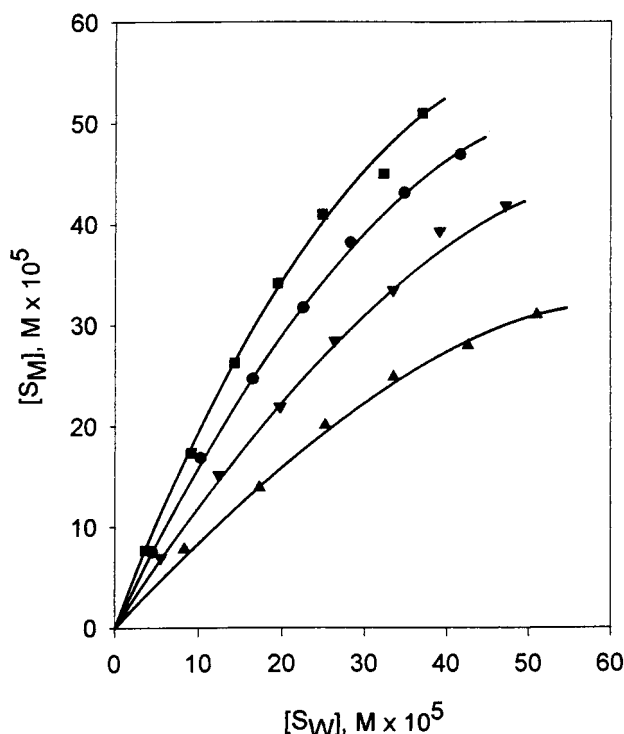


Figure 4. Plot of data for partition of phenol between water and PA-*n*K₂ according to eq 1: ■, PA-18K₂; ●, PA-16K₂; ▼, PA-14K₂; ▲, PA-12K₂.

Table 2. Distribution Constants and Standard Free Energies for Transfer of Phenol and *p*-Alkylphenols between the Aqueous Phase and Polymer Micelles Formed by PA-18K₂

substrate	K_S	$K_X (\times 10^{-4})$	$\Delta\mu_t^0$, kJ mol ⁻¹
phenol	215.7	1.20	-23.3
<i>p</i> -methylphenol	337.3	1.87	-24.4
<i>p</i> -ethylphenol	489.1	2.71	-25.3
<i>p</i> -propylphenol	705.9	3.92	-26.2

Table 3. Distribution Constants and Standard Free Energies for Transfer of Phenol between the Aqueous Phase and the Polymer Micelles Formed by PA-*n*K₂

copolymer	K_S	$K_X (\times 10^{-3})$	$\Delta\mu_t^0$, kJ mol ⁻¹
PA-10K ₂	38.4	2.13	-19.0
PA-12K ₂	96.3	5.34	-21.3
PA-14K ₂	131.2	7.28	-22.0
PA-16K ₂	177.4	9.85	-22.8
PA-18K ₂	215.7	11.97	-23.3

constant increases with increasing size of both the side alkyl chain and the alkyl group of the phenol and that the value of K_S is more affected by changes in the phenol structure. The standard free energy of transfer of phenols from the aqueous phase to the micellar phase, $\Delta\mu_t^0 = \mu_M^0 - \mu_W^0$, calculated from eq 5, is assumed to be composed of additive contributions from different groups:²⁹

$$\Delta\mu_t^0 = \Delta\mu_{Ar}^0 + n_C \Delta\mu_C^0 \quad (9)$$

where $\Delta\mu_{Ar}^0$ denotes the contribution of the parent aromatic group, $\Delta\mu_C^0$ is the incremental free energy per methylene group, and n_C is the number of these groups attached to the parent group. In Figure 5 the values of $\Delta\mu_t^0$ are plotted against the number of carbon atom in the *p*-alkylphenol. For comparison, the results reported for transfer to sodium dodecyl sulfate micelles have been included.³⁰ The intercepts obtained from these plots are

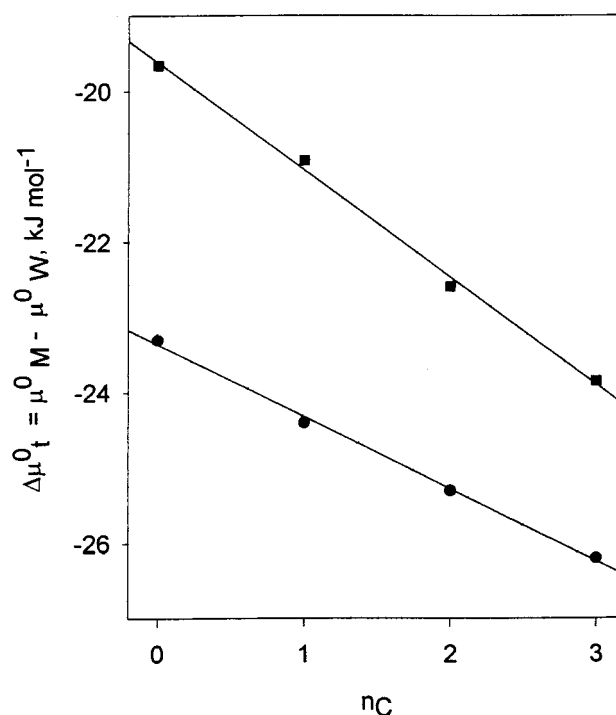


Figure 5. Free energies of transfer ($\Delta\mu_t^0$) of *p*-alkylphenols from water to PA-18K₂ (●) and to SDS (■) as a function of the number of carbon atoms of the *p*-alkyl chain of the phenol.

-23.4 and -19.6 kJ mol⁻¹ for PA-18K₂ and SDS micelles, respectively. This result suggests that the phenol group interacts more strongly with the polymer chain and consequently dissolves more in the PA-18K₂ than in SDS micelles. However, the values of $\Delta\mu_C^0$ obtained from the slope are quite similar (0.97 and 1.42 kJ mol⁻¹) but much lower than that determined for transfer to heptane (3.27 kJ mol⁻¹).³⁰ The low values of $\Delta\mu_C^0$, measured in ionic micelles, have been explained in terms of penetration of water molecules into the aggregate, which reduces the micelle hydrophobicity. However, a comparison of the ratio III/I values obtained in ionic micelles and in PA-18K₂ reveals that the hydrophobicity is higher in the polymer micelles. In addition, quenching studies suggest that the penetration of neutral molecules is more restricted in the polymer than in simple micellar systems.¹⁵ Thus, a possible explanation for the low value of $\Delta\mu_C^0$ for the transfer from water to the polymer micelle formed by PA-18K₂ is the need of a configurational reorganization of the polymer chains to accommodate the alkyl chain of the phenols.

In the distribution of phenol between water and the microdomains provided by PA-*n*K₂, the dependence of $\Delta\mu_t^0$ with the length of the side alkyl chain reflects the change in μ_M^0 due to a change in the polymer structure. It is interesting to note that a linear relation exists between the values of $\Delta\mu_t^0$ and the number of methylene groups in the side alkyl chain (see Figure 6). However, in this case the slope is just 0.34 kJ mol⁻¹, which is much lower than the contribution of one methylene group to the hydrophobic stabilization of the polymer micelle (1.67 kJ mol⁻¹), measured in copolymers of maleic acid and alkyl vinyl ethers.³ Thus, the small dependence of μ_M^0 with the polymer structure can be explained in terms of the small changes of hydrophobicity reflected by the ratio III/I when the length of

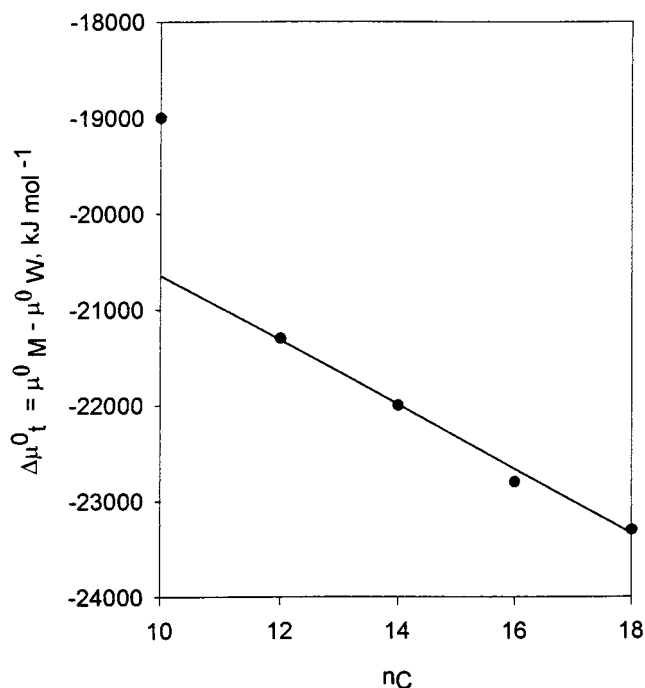


Figure 6. Free energies of transfer ($\Delta\mu_t^0$) of phenol from water to PA- nK_2 as a function of the number of carbon atoms of the side alkyl chain.

the side alkyl chain of the PA- nK_2 decreases from $n = 18$ to 12.

Conclusions

A pH-induced conformational transition has been observed in aqueous solution of PA-6K₂. For all other copolymers a hydrophobic microdomain is provided by the polymer in the whole range of pH. The hydrophobicity of these polymer micelles increases with increasing length of the side alkyl chain, and the aggregation number is equal to the degree of polymerization, within the experimental error. This means that just one polymer micelle arises from one polymer chain. This result is quite different from what has been found for copolymers of maleic acid and alkyl vinyl ethers, where several micelles are formed by one macromolecule. However, the values of N in both systems are in the same order of magnitude, which suggests that the different behavior is due mainly to the difference in molecular weights between these two systems.

The study of the solubilization of *p*-alkyl substituted phenols in the polymer micelles formed by PA-18K₂ has shown that the latter are a better host for these solutes. The value of $\Delta\mu_{Ar}^0$ is larger in PA-18K₂ than in SDS micelles, suggesting a strong interaction of the phenol

moiety with the polymer. On the other hand, the value of $\Delta\mu_C^0$ is lower in polymer micelles than in normal ionic micelles. This lowering in $\Delta\mu_C^0$ is ascribed to a configurational reorganization required to solubilize the alkyl chain of the organic substrate.

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