SHORT COMMUNICATION

Feasibility study of naphthalene removal: Naphthalene solubilization in aqueous solutions of a triblock copolymer of ethylene oxide and 1,2-butylene oxide, $E_{64}B_{20}E_{64}$

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Abstract

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Feasibility study of naphthalene removal: Naphthalene solubilization in aqueous solutions of a triblock copolymer of ethylene oxide and 1,2-butylene oxide, $E_{64}B_{20}E_{64}$

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Block copolymer $E_{64}B_{20}E_{64}$, where E denotes oxyethylene, OCH_2CH_2, B denotes oxybutylene, $OCH_2CH(C_2H_5)$, and the subscripts denote number-average block lengths in repeat units, was synthesized by sequential anionic polymerization. Characterization was by gel permeation chromatography (for molar mass distribution) and ^{13}C-NMR spectroscopy (for absolute molar mass and conformation of block architecture). Dynamic and static light scattering were used to study micellization and micelle properties of this copolymer in dilute aqueous solution and in the presence of naphthalene. Dynamic light scattering was used to analyze hydrodynamic radius, r_h and hydrodynamic expansion factor, δ_h. Static light scattering was used to study micelle association number, N_w, thermodynamic expansion factor, δ_t, and thermodynamic radius, r_t. The presence of naphthalene in micellar core increased N_w by 50% and increased micellar size.

Key words : copolymer, solubilization, light scattering, micelle

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การศึกษาการความสามารถในการแยก naphthalene ในสารละลายน้ำโดยการใช้ copolymer ชนิด $E_{64}B_{20}E_{64}$ ที่สังเคราะห์จาก ethylene oxide และ 1,2-butylene oxide

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โคพอลิเมอร์ชนิด $E_{64}B_{20}E_{64}$ (เมื่อ E แทน oxyethylene (OCH_2CH_2) และ B แทน oxybutylene ($OCH_2CH(C_2H_5)$) สังเคราะห์โดยปฏิกิริยาพอลิเมอร์ไรเซชันแบบแอนไอออนิกที่เป็นลำดับ การตรวจสอบคุณลักษณะของโคพอลิเมอร์โดยใช้ GPC เพื่อหาการกระจายของมวล และ ^{13}C-NMR สเปกโทรสโคปีเพื่อหามวลโมเลกุลและโครงสร้าง การศึกษาการเกิดไมเซลล์ในสารละลายน้ำ และในสารละลายน้ำที่มีแนพทาลีน โดยใช้เครื่องไลท์สแคทเทอร์ริงไดนามิกส์ไลท์สแคทเทอร์ริงจะให้รัศมีไฮโดรไดนามิกส์ (r_h) และสัมประสิทธ์การขยายตัวทางไฮโดรไดนามิกส์ (δ_h) การศึกษาสมบัติของไมเซลล์โดยใช้สแททิกส์ไลท์สแคทเทอร์ริง ใช้ศึกษาจำนวนของโคพอลิเมอร์ในไมเซลล์ (N_w) สัมประสิทธ์การขยายตัวทางเทอร์โมไดนามิกส์ (δ_t) และรัศมีเทอร์โมไดนามิกส์ (r_t) การที่แนพทาลีนละลายอยู่ในไมเซลล์ทำให้ N_w เพิ่มขึ้น 50% และทำให้ขนาดของไมเซลล์ใหญ่ขึ้น

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Block copolymers of $E_mB_nE_m$ type where E denotes oxyethylene, OCH_2CH_2, B denotes oxybutylene, $OCH_2CH(C_2H_5)$, and the subscripts denote number-average block lengths in repeat units, are important polymer surfactants produced by Dow Chemical Company, USA. These and other E/B copolymers have been extensively studied at the university of Manchester, UK. They associate to form micelles in aqueous solution, as reviewed in ref. 2 (Booth and Attwood, 2000).

In aqueous solution, micelle formation provides hydrophobic environment in the core of micelles. Hydrophobic compounds can transfer into the core of micelles and the effect can be used to extract the organic hydrocarbons from water (Paterson *et al.*, 1999; Calvert *et al.*, 1994) and deliver drug to target organ (Chaibundit *et al.*, 2002). In this paper we report a study by dynamic and static light scattering of the solubilization of naphthalene in aqueous solutions of copolymer $E_{64}B_{20}E_{64}$.

Materials and Methods

Materials

Ethylene oxide (Fluka Chemical, 99.8%, b.p.=10.5-11.5°C) was transferred under vacuum from a cylinder through the vacuum line into the round-buttom flask onto powered CaH_2, and stirred at -70°C with solid carbon dioxide for 6 hours. The ethylene oxide then was distilled under vacuum onto powdered CaH_2 and stir for 8 hours before use.

1,2-Butylene oxide (Fluka Chemical, 99%) was stirred with powered CaH_2 under dry nitrogen for 6 hours. The 1,2-butylene oxide was then distilled under vacuum line onto powered CaH_2 and stirred for 12 hours before use.

1,2-Butanediol (Fluka Chemical, 98%) was distilled under reduced pressure and a mid-cut collected and stored over molecular sieve (type 4A) under dry nitrogen.

Potassium metal (BDH chemicals Ltd) was stored under liquid Paraffin and freshly cut before use.

Methods

1. Blockcopolymer Synthesis

Triblock copolymer was prepared by sequential anionic polymerization of 1,2-butylene oxide followed by ethylene oxide. The method of preparation, which has been described previously (Altinok *et al.*, 1997; Chaibundit *et al.*, 2000) was by a vacuum line and ampoule technique. This technique was used to minimize the introduction of moisture during transfer of monomers. The difunctional initiator, 1,2-butanediol, was activated with potassium metal. The mole ratio of OH/K was *ca.*10. The required amount of dry 1,2-butylene oxide was transferred into the ampoule containing the initiator. The reaction ampoule was put into a water bath at 45ºC for 7 days, at 65ºC for 10 days and at 85ºC until the reaction was completed. Solid carbon dioxide was used to check for the condensation on the neck of the ampoule. The α-hydro, ω-hydroxypoly(oxybythylene) was obtained. A small amount of this homopolymer was removed under a dry nitrogen atmosphere and characterized by GPC to get molar mass distribution and by ^{13}C-NMR to get number-average molar mass (M_n) using the assignments of Heatley (Heatley *et al.*, 1990). Then, this ampoule was evacuated and the required amount of ethylene oxide was transferred. The ampoule was put in the water bath and the temperature was raised over 14 days from 45 to 85ºC until the reaction completed. The copolymer was characterized by GPC and ^{13}C-MNR.

2. Polymer Characterization

2.1 GPC

Tetrahydrofuran was used as a solvent. The instrument was operated at 25ºC with flow rate of 1 cm^{3}min^{-1} using three 30 cm PL-gel columns; i.e. a 500Å and two mixed-B columns. This system was used to analyze homopoly(oxybutylene). The copolymer was characterized by similar column set using N,N-dimethylacetamide as eluent at 65ºC.

In each case the sample concentration was 2 g dm^{-3}, and the sample solution was injected through a 100 mm^3 loop. The emerging sample was detected by a differential refractometer. Poly(ethylene oxide) standards of known molar mass and narrow distribution were used for calibration to obtain a reliable measurement of molar mass distribution width (M_w/M_n). The results are listed in Table 1.

2.2 ^{13}C-NMR

High resolution liquid-state NMR spectra were obtained by means of a Varian Unity spectrometer operated at a frequency of 125.8 MHz. Deuterated chloroform was used as a solvent. Solution containing *ca.* 250 mg of polymer/cm^3 of solvent was used. Pulse interval of 10 s with pulse width of 90º was used.

3. Light Scattering measurement

Light scattering tubes were cleaned using chromic acid. An acetone vapour bath was used to remove dust inside the tubes. Solutions were clarified by filtering through Millipore Millex Filters (Triton free, 0.22 μm) at least five times, the final filtration being poured directly into the cleaned scattering cell.

3.1 Static light scattering

SLS intensities were measured by means of a Brookhaven BI 200S instrument using vertically polarized incident light of wavelength λ=488 nm supplied by an argon-ion laser operated at 500 mW or less. The intensity scale was calibrated using benzene acting as a secondary standard. The scattering angle was 90º.

3.2 Dynamic light scattering

DLS measurements were made under similar conditions, using a Brookhaven BI 9000AT digital correlator to acquire data.

Experimental duration was 10 min. Each experiment was carried out twice or more times. The scattering angle for DLS was normally 90º to the incident beam. The correlation functions obtained from DLS were analyzed by constrained regularized CONTIN method (Provencher, 1977) which provided distributions of decay rates (Γ) and the corresponding distributions of an apparent mutual diffusion coefficient [$D_{app} = \Gamma q^2$, $q = (4\pi n/\lambda)\sin\theta/2$, n=refractive index of the solvent]. Values of the apparent hydrodynamic radius ($r_{h,app}$, radius of gyration of the hydrodynamically equivalent hard sphere) were obtained through Stoke-Einstein equation

$$r_{h,app} = kT/(6\pi\eta D_{app}) \qquad (1)$$

where k is the Boltzmann constant, and η is the viscosity of the solvent at temperature T. Intensity I(Γ) data delivered using the CONTIN program at logarithmically space values of decay rate were transformed to $I(\log \Gamma)=I(\Gamma)\Gamma$ to get intensity distributions of $\log(\Gamma)$ and corresponding distributions of $\log(r_{h,app})$. Normalization of $I(\log r_{h,app})$ gave the intensity fraction distribution. Intensity-average values of Γ obtained by integration over the intensity distibutions were converted to intensity-average values of $r_{h,app}$.

The analysis of SLS was by the Debye equation

$$K^*c/(I-I_s) = 1/M_w + 2A_2c + ... \quad (2)$$

where I is the intensity of light scattering from solution relative to that from benzene, I_s is the corresponding quantity for the solvent, c is the concentration (in g dm^{-3}), M_w is the mass-average molar mass of the solute, A_2 is the second virial coefficient (higher coefficient being neglected in eq 2), and K* is the appropriate optical constant. Values of K* included specific refractive index increment, dn/dc, which were determined at a given temperature. At 25°C value of dn/dc for E/B system was 0.132 and for the system containing naphthalene was 0.133.

3.3 Naphthalene Solubilization

The solubilization was carried out by preparing saturated solutions of naphthalene. Saturation was ensured by the presence of a separated solid naphthalene crystalline phase. The small amount of solid naphthalene was added in to the small vial containing aqueous solutions of $E_{64}B_{20}E_{64}$. Each solution was slightly stirred using magnetic bar at 25°C for 24 hrs. Then, each solution was filtered through Millpore Millex filters (Triton Free, 0.22 μm) at least five times before light scattering measurement was made.

Results and Discussion

Table 1 shows the molecular characterization of $E_{64}B_{20}E_{64}$ copolymer.

1. Hydrodynamic Radius

Copolymer solutions with concentrations in the range 1-60 g dm^{-3} were investigated at 25°C, including those containing solubilized naphthalene. All solutions were clear at this temperature.

Figure 1(a) shows the intensity fraction distributions curve obtained from DLS for aqueous solutions of $E_{64}B_{20}E_{64}$. At all concentrations, the intensity fraction distribution of $\log(r_{h,app})$ showed a single peak. The average values of $r_{h,app}$ are 5-9 nm. Figure 1 (b) shows the intensity fraction distributions obtained from aqueous solutions of $E_{64}B_{20}E_{64}$ saturated with naphthalene. The average values of $r_{h,app}$ are 6-11 nm. The narrow peaks in the distributions of hydrodynamic radii indicated that micelles were form by closed association. The effect of an increase in concentration was to decrease the value of $r_{h,app}$ at the peak maximum, which is the expected effect of intermicellar interaction. The increase in peak width at very low concentrations is a result of scatter of data points in the CONTIN analysis.

Figure 2 shows the effect of the concentration on reciprocal hydrodynamic radius of the micelles of the copolymer with and without naphthalene. The positive gradient of the plot indicates micelles interacting as hard spheres. The

Table 1. Molecular characterization of copolymer[a]

Polymer/copolymer	wt%/E (NMR)	M_n/g mol^{-1} (NMR)	M_w/M_n (GPC)	M_w/g mol^{-1}
B_{20}	-	1460	1.02	1490
$E_{64}B_{20}E_{64}$	80	7070	1.09	7700

[a] Estimated uncertainty: ±2% in wt% E; ±3% in M_n, M_w/M_n, and block lengths; ±4% in M_w. M_w calculated from M_n and M_w/M_n.

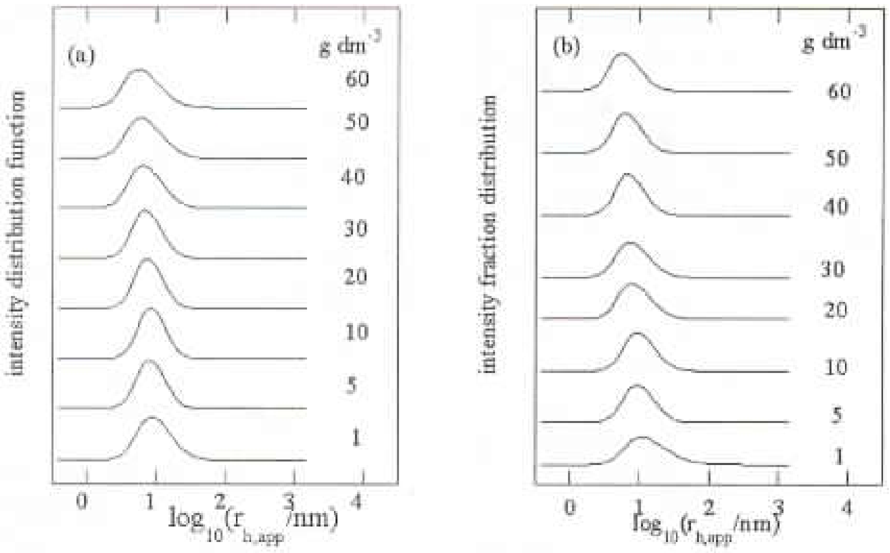

Figure 1. Dynamic light scattering. Intensity fraction distributions of the logarithm of apparent hydrodynamic radii at 25ºC of $E_{64}B_{20}E_{64}$ (a) in aqueous solution and (b) in aqueous solution containing naphthalene.

values of r_h obtained by extrapolating individual data sets to zero concentration are shown in Table 2. The hydrodynamic expansion factor was derived from

$$\delta_h = \nu_h/\nu_a \qquad (3)$$

where ν_h is the average hydrodynamic volume, and ν_a is the average anhydrous volume of the micelles. The value of ν_a ($\nu_a = M_{w,mic}/N_A\rho_a$, N_A= Avogadro's constant) was calculated from the micellar molar mass determined by SLS (see section 2) and the density of the anhydrous liquid copolymer at 25ºC (ρ_a=1.09 g cm^{-3}) (Mai *et al.*, 1997).

2. Association Number and Thermodynamic Radius

SLS was carried out at 25ºC. The scattering angle was 90º. Eq 2 assumes small particles relative to the wavelength of the light. Radii of gyration estimated to be 0.775r_h (i.e., as if the micelles were uniform spheres) are 7 and 9 nm for copolymer solutions and solution containing naphthalene, respectively. Consequently only a small effect from intraparticle interference is expected (Casassa, 1989). The Debye equation (eq 2) was used to analyze the data. The interparticle interference caused the curvature, as seen in Figure 3.

Table 2. Properties of micelles of $E_{64}B_{20}E_{64}$ copolymer in aqueous solution[a]

Copolymer	T/ºC	r_h/nm	δ_h	$M_{w,mic}$/ 10^5g mol^{-1}	N_w	δ_t	r_t/nm
$E_{64}B_{20}E_{64}$	25	8.8	9.4	2.0	28	5.8	7.6
$E_{64}B_{20}E_{64}$+ Naphthalene	25	11.0	12.2	3.0	42	5.9	8.7

[a] **Estimated uncertainties are ±5% in r_h and r_t, ±10% in $M_{w,mic}$, N_w, δ_h, and δ_t.**

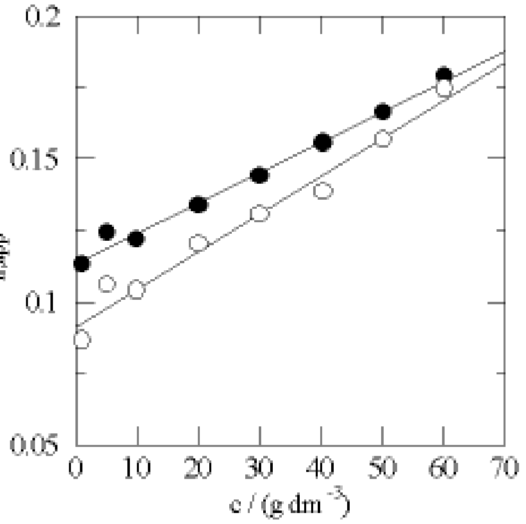

Figure 2. Reciprocal of apparent hydrodynamic radius versus copolymer concentration of $E_{64}B_{20}E_{64}$ at 25ºC: (●) in aqueous solution, and (o) in aqueous solution containing naphthalene. The base lines are obtained by a least square fit through all the data points.

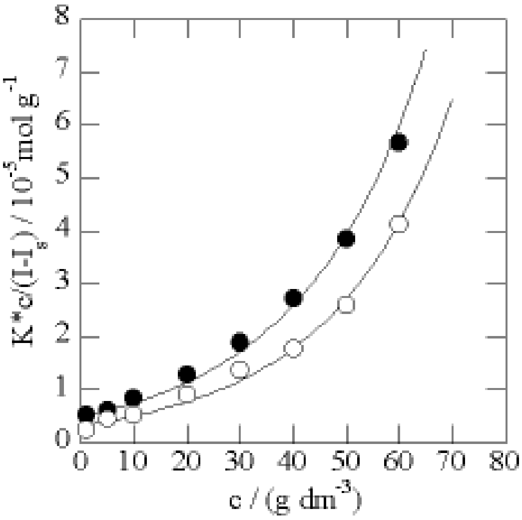

Figure 3. Static light scattering. Debye plots for aqueous solutions of copolymer $E_{64}B_{20}E_{64}$ at 25ºC: (●) in aqueous solution and (o) in aqueous solution containing naphthalene. The curves are based on the scattering theory for hard spheres.

A method based on Percus-Yevick theory for hard spheres, adapted by Virij, together with the Carnahan-Starling equation was used to fit the data (Percus and Yeick, 1958; Virij, 1978; Canahan and Starling, 1969). This method is equivalent to the use of the virial expansion for the structure factor for hard spheres taken to its seventh term by applying two parameters, M_w and δ_t. The thermodynamic expansion parameter, δ_t, relates to the volume excluded by another water-swollen micelle. The values of δ_t was calculated from

$$\delta_t = v_t/v_a \qquad (4)$$

where v_t is the thermodynamic volume which is one-eighth of the excluded volume for a micelle acting as an effective hard sphere, and v_a is the anhydrous volume of the micelle. The values of the association numbers of the micelles were calculated from

$$N_w = M_{w,mic}/M_{w,mol} \qquad (5)$$

Without knowing the amount of naphthalene solubilized per micelle it is impossible to calculate N_w precisely for the case of block copolymer in naphthalene solution, and the value listed can be described as apparent.

It can be seen from Table 2 that the presence of naphthalene in micellar solution leads to an increase of $M_{w,mic}$ by 50%, hence the apparent value of N_w by 50%, and an increase in radius of 25% (r_h) or 14% (r_t), that is an increase in radius cubed of 95% (r_h) or 48% (r_t). These increases in micellar mass and radius are caused, presumably, by naphthalene solubilized in cores of micelles. Regarding the molar mass, the amount of B in the copolymer is only 20 wt% (see Table 1). So an increase of 50% in $M_{w,mic}$ caused solely by solubilization of naphthalene in the original copolymer micelles would imply 70 wt% naphthalene in the core, which is most unlikely. Indeed, the fact that increases in N_w and the radii cubed are similar (particularly so for the thermodynamic radius which is closely related to the micelle hard sphere radius) means that the major effect of the presence of naphthalene is to promote an increase in N_w. The fact that dn/dc is little changed by the solubilization of naphthalene (see section 3.2 in Materials and Methods) is consistent with only a small proportion of solubilizate in the cores. The exact amount of naphthalene solubilized cannot be deduced from light scattering measurements alone, but would require other measurement for example by UV spectroscopy.

Concluding Remarks

Micelles of $E_{64}B_{20}E_{64}$ copolymer in aqueous solution can solubilize naphthalene. The presence of naphthalene promoted the increases in N_w, δ_h, δ_t, r_h and r_t. The amount of naphthalene solubilized in the cores of micelles cannot be deduced from the present results but will be determined in a further investigation. Ultimately it is hoped that the solubilization of naphthalene can be used to model that of other aromatic hydrocarbons, including aromatic drugs, in aqueous micellar solutions.

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