Study of the aggregation of 1-alkanoylperylenes in 1,4-dioxane-H₂O binary solvents—Derivation of a new empirical equation relating CAgC to both chain-length and solvent aggregating power

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Aggregation behaviors of 1-alkanoylperylenes (Pe-n, n = 4, 8, 12) driven by hydrophobic-lipophilic interaction (HLI) have been investigated in dioxane (DX)-H₂O binary aquiorgano solvents by means of fluorescence spectroscopy. A novel empirical equation, which rationalizes CAgC (critical aggregate concentration) dependence of the aggregates both on the chain-length of the substituent alkyl group and on the solvent aggregating power (SAgP) for Pe-n, has been derived.

Keywords   1-Alkanoylperylene, aggregation, fluorescence spectra, new empirical equation

Introduction

It has been well established that in aqueous or aquiorgano binary mixtures with solvent aggregating power (SAgP), electrically neutral organic molecules tend to form aggregates (Ags).[1-4] These organic molecules are called aggregators (Agrs), and their aggregating tendencies are generally evaluated by critical aggregate concentrations (CAgCs), which are the concentrations of the Agrs at the onset of aggregation. Under identical experimental conditions, a smaller CAgC value signifies a greater aggregating tendency.[5]

Various internal and external factors can affect the aggregating tendency of a molecule, among them molecular structure is an important internal factor.[6] Previous works suggest that usually analogues with longer hydrocarbon chains have greater aggregating tendencies than those with shorter chains.[7] Moreover, there exists a good linear correlation between logCAgC and chain length, i.e., logCAgC = $kn + b$, where k is negative so that CAgC will decrease with increasing n, i.e., the number of carbon atoms in the chain.[8] In addition to molecular structure, SAgP is another important factor. In general, for a particular Agr, its CAgC will increase with decreasing SAgP, which usually parallels solvent hydrophilicity. If we designate the volume fraction of the organic component of an aquiorgano mixture by Φ, then SAgPs will decrease with increasing Φ values. Good linear correlation between logCAgC and Φ value has also been observed, i.e., logCAgC = $k\Phi + b$, where k is positive, thus CAgC will increase with increasing Φ.[9]

In the present work, the aggregation behaviors of 1-alkanoylperylenes (Pe-n, n = 4, 8 or 12) in dioxane-water (DX-H₂O) mixtures have been investigated by measuring their CAgCs at different Φ values. Results show that CAgC is a function of both Φ and n, where n represents the number of carbon atoms in the substituent alkyl chain (cf. Daul parameter eg. 4).

Experimental

Apparatus

Melting points were not corrected. Mass spectra were obtained by using an HP 5989A spectrometer at an ionization potential of 70 eV. δ_H spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer with TMS as the internal standard. UV-Vis spectra were obtained

by using a Perkin-Elmer Lambda 2 spectrometer.

Materials

The new compounds **Pe-n** were prepared from perylene through the Friedel-Crafts reaction in refluxed 1,2-chloroethane.[10] Their spectral and analytical data are reported below. Water was deionized, and dioxane (DX) was purified by a standard procedure.

1-*Butyrylperylene* (**Pe-4**)   Yellow solid, mp 185—186 °C. δ_H(CDCl$_3$):1.05(t, J = 7.5Hz,3H);1.83—1.94(m, 2H), 3.03(t, J=7.5 Hz, 2H), 7.45—7.65(m, 3H), 7.70—7.73(m, 2H), 7.83(d, J = 8.0Hz,1H),8.14(d, J = 8.0Hz,1H),8.22—8.44(m, 3H), 8.50(d, J = 8.6 Hz, 1H). λ_{max} (CH$_2$Cl$_2$): 258(ϵ = 4.3 × 10^4(mol/L)$^{-1}$·cm^{-1}), 446(ϵ =3.3 × 10^4(mol/L)$^{-1}$·cm^{-1})nm. m/z:251(72.45), 279(100.00), 322(M$^+$, 74.67). Anal. C$_{24}$H$_{18}$O. Calcd : C, 89.41, H, 5.63. Found: C, 89.45; H, 5.76.

1 - *Octanoylperylene* (**Pe-8**)   Yellow solid, mp 172.5—173.5 °C. δ_H(CDCl$_3$): 0.89(t, J = 6.7 Hz, 3H), 1.29—1.41(m, 8H), 1.78—1.87(m, 2H), 3.01(t, J = 7.3Hz,2H),7.43—7.53(m,3H), 7.72—7.81(m, 2H), 7.83(d, J = 7.9 Hz, 1H), 8.07(d, J = 7.9Hz,1H),8.09—8.37(m,3H), 8.47(d, J = 8.4Hz,1H). λ_{max}(CH$_2$Cl$_2$):258(ϵ = 3.2 × 10^4(mol/L)$^{-1}$·cm^{-1}), 446(ϵ = 2.6 × 10^4(mol/ L)$^{-1}$·cm^{-1}) nm. m/z: 251(65.68), 279(100.00), 378(M$^+$, 88.21). Anal. C$_{28}$H$_{26}$O. Calcd: C, 88.85, H, 6.92. Found: C, 88.56; H, 6.71.

1 - *Lauroylperylene* ((**Pe-12**)   Yellow solid, mp 164.5—165.5 °C. δ_H(CDCl$_3$): 0.88(t, J = 6.7 Hz, 3H), 1.24—1.52(m, 16H), 1.78—1.93(m, 2H), 3.03(t, J = 7.3Hz,2H),7.43—7.62(m,3H),7.68—7.72(m, 2H), 7.82(d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.05—8.34(m, 3H), 8.48 (d, J = 8.5 Hz, 1H). λ_{max}(CH$_2$Cl$_2$): 258(ϵ = 3.0 × 10^4(mol/L)$^{-1}$·cm^{-1}), 446(ϵ = 2.5 × 10^4(mol/L)$^{-1}$· cm^{-1}) nm. m/z: 251(49.90), 279(90.88), 434 (M$^+$, 100.00). Anal. C$_{32}$H$_{34}$O. Calcd: C, 88.43; H, 7.89. Found: C, 88.30; H, 7.85.

Fluorescence measurement

The samples were shaken vigorously in a mechani-

cal shaker for 30 min, then warmed in a 35 °C water-bath for 3 h. The fluorescence spectra of **Pe-n** were run on a Perkin-Elmer LS-50 Luminescence spectrometer at 35 °C by using the excitation wavelength of 446 nm.

Results and discussion

Among the various methods employed to determine CAgC, fluorescence probe (FP) analysis is often used.[4b] This approach is based on the fact that if aggregation takes place, the high local concentration of FP within Ags will favor excimer formation or self-quenching of its fluorescence. Thus, the concentration at which excimer or self-quenching is first observed can be defined as its CAgC. Under our experimental conditions, **Pe-n** does not seem to form excimers because there is no excimer fluorescence emission at the longer wavelength, *i. e.*, wavelength longer than that of 1-alkanoylperylene* emission. Fig. 1 illustrates a typical plot of the maximum FL intensities (I_m) of **Pe-n**. *vs*. their concentrations ([**Pe-n**]). Such plots show three regions. In region (a) **Pe-n** exists only as monomers and their maximum FL intensities increase linearly with their concentrations. In region (c), after saturation of the monomeric **Pe-n**, Ags are formed. Due to self-quenching inside the Ags, I_m does not increase proportionally with the increase of the aggregate concentration. Region (b) is a transitional region between (a) and (c). The concentration at the crossing point of straight lines extrapolated from (a) and (c) represents the CAgC.
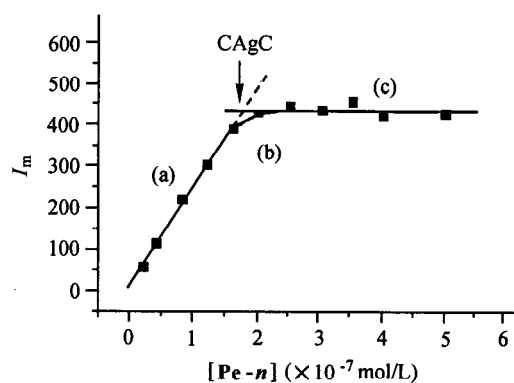

Fig. 1   Dependence of the maximum FL intensities of **Pe-n** on its concentration at 35 °C.

In Table 1 are listed the CAgCs of **Pe-n** at 35 °C in DX-H$_2$O mixtures at different Φ values. The range of Φ

value is determined mainly by the measuring range of the fluorescence spectroscopy. If Φ is too small, the CAgC of Pe-n will be so low that the FL intensity of monomeric Pe-n will be hard to measure with reasonable precision. Meanwhile, if Φ is too large, no aggregation can be determined because Pe-n's FL intensity moves out of

the upper measure limit of the instrument. That is also the reason of why we can not obtain the CAgC of all of the three Pe-n in a solvent with the same Φ value. However, from Table 1, we still can conclude that in likeness to previous results, lower CAgC corresponds to smaller Φ value or longer length of the side chain.

Table 1 CAgCs of Pe-n ($n = 4, 8,$ or 12) at $35^\circ C$ in DX-H_2O mixtures at different Φ values

n				4				
Φ	0.20	0.22	0.25	0.28	0.30	0.32	0.35	
CAgC ($\times 10^{-7}$mol/L)	2.21	3.32	6.41	10.17	16.9	24.8	56.4	
n				8				
Φ	0.35	0.36	0.38	0.40	0.42	0.44	0.45	0.46
CAgC ($\times 10^{-7}$mol/L)	2.05	2.69	4.85	9.67	14.0	26.6	33.9	41.9
n				12				
Φ	0.46	0.48	0.50	0.52	0.54			
CAgC ($\times 10^{-7}$mol/L)	1.77	3.42	5.87	12.29	24.37			

The uncertainty of CAgCs is less than $\pm 10\%$.

In Fig. 2 are shown the plots of the logarithms of the CAgCs of each Pe-n vs. Φ values of the solvent. Within experimental error these plots appear to be linear and fit Eq. (1).

$$\log CAgC = C_1 \Phi + C_2 \qquad (1)$$

For each Pe-n, values of C_1, C_2, and linear correlation coefficient r as well as the range of Φ values, are listed in Table 2.

Table 2 C_1 and C_2 values of Eq. (1) at corresponding Φ range

n	C_1	C_2	r	Range of Φ value
4	9.193	-8.517	0.998	0.20—0.35
8	12.037	-10.888	0.999	0.35—0.46
12	14.160	-13.274	0.999	0.46—0.54

In Figs. 3 and 4 are shown respectively the plots of C_1 and C_2 vs. number of carbon atoms in the side chain of Pe-n. These points fall on straight lines, which can be fitted with Eq. (2) and (3).

$$C_1 = a_1 n + b_1 = 0.62n + 6.83, \quad r = 0.997 \qquad (2)$$

$$C_2 = a_2 n + b_2 = -0.60n + (-6.14), \quad r = 1 \qquad (3)$$

From Eqs. (1), (2) and (3) we can obtain Eq. (4),

a dual-parameter equation of CAgC with Φ and n as the variables.

$$
\begin{aligned}
\log CAgC &= (a_1 \cdot n + b_1)\Phi + (a_2 \cdot n + b_2) \\
&= (a_1 \cdot \Phi + a_2) \cdot n + (b_1 \cdot \Phi + b_2) \\
&= (0.62\Phi - 0.60) \cdot n + (6.83\Phi - 6.14)
\end{aligned}
$$
$$\qquad (4)$$

It is clear that CAgC depends on both the lengths of side hydrocarbon chain and by the SAgP of solvent. If Φ is fixed, then $\log CAgC = kn + b$; if n is fixed, then $\log CAgC = k\Phi + b$. Eq. (4) can enable us to estimate the CAgC of Pe-n with any number of carbon atoms in it's side chain in DX-H_2O mixtures with any Φ value.
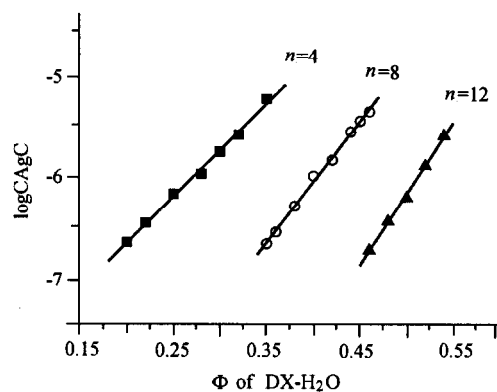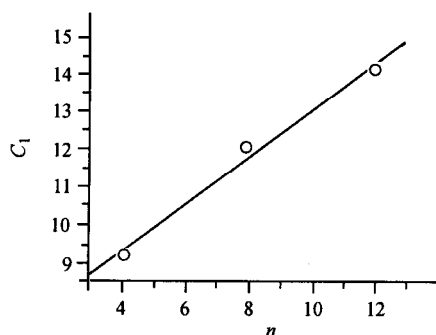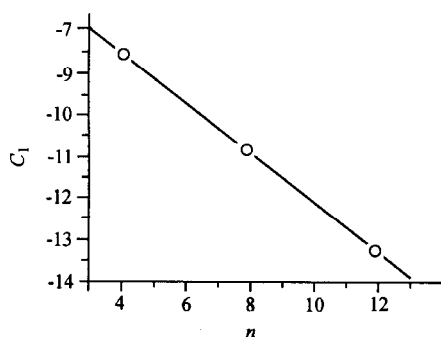

Fig. 2 Relation between the logarithm of the CAgC of Pe-n at $35^\circ C$ ($n = 4, 8, 12$) and the Φ value of DX-H_2O.

Fig. 3 Relation between coefficient C_1 of Eq. (1) and number of carbons in the side chain of Pe-*n*.

Fig. 4 Relation between coefficient C_2 of Eq. (1) and number of carbons in the side chain of Pe-*n*.

In conclusion, Pe-*n* may also be used as fluorescence probes for evaluating aggregatingtendencies or CAgC values. Furthermore, the SAgP and chain-length

dependence of these values can be described by a single dual-parameter equation.

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