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Stacking phenomena in polyaromatic compounds

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Abstract

Solid–liquid equilibria (SLE) and formation of films at the air/water interface were investigated for binaries formed with 1-pyrenecarboxaldehyde (PCA) or fluorenone, mixed with pyrene or phenanthrene. In all systems studied, the components are non-miscible in the solid phase. Two eutectic points and the formation of a solid compound is observed in the diagram. The aggregation phenomena occurring in presence of water can lead to the formation of organized structures, similar to those observed in the case of surfactant/water systems. The results obtained suggest that these polyaromatic molecules have a tendency to stacking and agglomerating. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Aggregation of polyaromatics; Films at the air/water interface; Organized structures; Solid–liquid equilibria (SLE) of binary mixtures

1. Introduction

Polyaromatics and especially heteropolyaromatics show a strong tendency to stacking. This behavior can give rise to aggregation and consequently, formation of colloidal structures. Unusual rheological properties of asphaltes are due to the aggregation of asphaltenic structures present in the crude oil. These structures are mostly built with flat polyaromatic molecules containing oxygen, sulfur or nitrogen. Therefore, it seemed interesting to study molecular stacking in simpler compounds, which could be considered as precursors of complex systems present in heavy petroleum cuts [1]. In this paper, some selected properties of binaries formed with two polyaromatic molecules are presented. These binaries were formed with 9-fluorenone or 1-pyrenecarboxaldehyde (mixed with pyrene or phenanthrene). Solubility diagrams and film formation at the air/water interface were studied.

2. Experimental

2.1. Solubility diagrams

All materials used were purchased from Aldrich, excepting 1-pyrenecarboxaldehyde purchased from Fluka and used without further purification. The purity of 9-fluorenone, 1-pyrenecarboxaldehyde and pyrene was better than 99.0%, that of phenanthrene was better

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than 98.0%. The solid–liquid equilibria (SLE) diagrams and enthalpies of fusion were established using a differential scanning calorimeter DSC 111 (SETARAM). Experimental procedure and data handling were described elsewhere (Aoulmi [2,3], Mahmoud [4]). Mixtures of known concentrations were prepared by weighing. The quantities of samples used for each experiment were typically 50 mg. Before each experiment, the samples were melted and the liquid solutions were rapidly cooled with liquid air to obtain homogenous solid mixtures. The accuracy of temperature measurements was 0.1 K. The measurements were reproducible to within 0.5 K. Enthalpies and temperatures of fusion were measured and are reported in Table 1. In Table 1, the developed formulae of the compounds studied are reported. The solubility diagrams of three different binary systems were determined: 9-fluorenone with pyrene and 1-pyrenecarboxaldehyde with pyrene or phenanthrene.

2.2. Film formation at the air/water interface

The Langmuir balance KSV 5000 (KSV, Finland) was used to investigate the behavior of pure compounds and their mixtures when spread at the air/water interface [5,6]. All samples were dissolved in chloroform to the final concentration of around 1 mg/ml and the solutions (0.5–4 ml) were spread with a syringe on the water surface in a Teflon trough. The dimensions of the trough were: length 520 mm and width 150 mm. A symmetric compression of the film was done at the barrier speed of 1 cm/min.

2.3. Microscopic studies

The films formed at the air/water interface were transferred on microscope slides using Blodgett technique. Optical microscope with normal and polarized light was used to study the structures obtained. These techniques afforded a qualitative information only. Visual observations were helpful for discussing surface pression results (see Section 3).

Table 2
Experimental results of solid–liquid equilibria determinations

x_1	T/K	x_1	T/K	x_1	T/K
Pyrene (1) +9-Fluorenone (2)					
0.0000	355.9	0.3000	361.7	0.6000	378.2
0.0514	352.7	0.3500	361.7	0.6500	387.1
0.1001	350.4	0.4009	361.0	0.7000	392.2
0.1503	352.1	0.4510	361.2	0.7994	404.1
0.2001	357.3	0.5000	360.8	0.8991	415.8
0.2509	360.3	0.5500	370.0	1.0000	422.7
Pyrene (1) +1-pyrenecarboxaldehyde (2)					
0.0000	398.4	0.3006	399.2	0.6504	389.2
0.0506	396.4	0.3505	407.2	0.7009	392.6
0.1016	392.4	0.4500	410.6	0.7986	404.5
0.1507	389.2	0.4995	410.3	0.8998	414.2
0.2000	388.1	0.5501	405.2	0.9475	419.3
0.2501	394.2	0.6004	396.2	1.0000	422.7
Phenanthrene (1) +1-pyrenecarboxaldehyde (2)					
0.0000	398.4	0.4502	379.8	0.7999	358.6
0.1015	391.6	0.5000	387.2	0.8498	360.7
0.2014	380.6	0.5500	389.2	0.9000	364.9
0.2495	372.5	0.5998	388.2	0.9498	368.3
0.2997	366.2	0.6498	385.5	1.0000	372.4
0.3502	361.7	0.7001	380.4		
0.4006	370.2	0.7504	364.2		

3. Results and discussion

Experimental results of SLE determination are given in Table 2 and in Figs. 1–3. In all systems studied, the components are non-miscible in the solid phase and exhibit two eutectic points with a solid compound formation. The stoichiometry of this compound was close to 1 : 1 with two of three binary systems studied. This confirms a tendency of polyaromatic molecules to stacking. Therefore, aggregation of these molecules at the air/water interface could

Table 1
Temperature and enthalpy of fusion of compounds considered in this paper. All results were obtained using DSC 111 SETARAM calorimeter

Component	Pyrene	Phenanthrene	9-Fluorenone	PCA
$\Delta H_{i,T_\mathrm{m}}$/kJ mol^{-1}	17.313	16.474	14.848	8.987
T_m/K	422.7	372.4	355.8	398.5

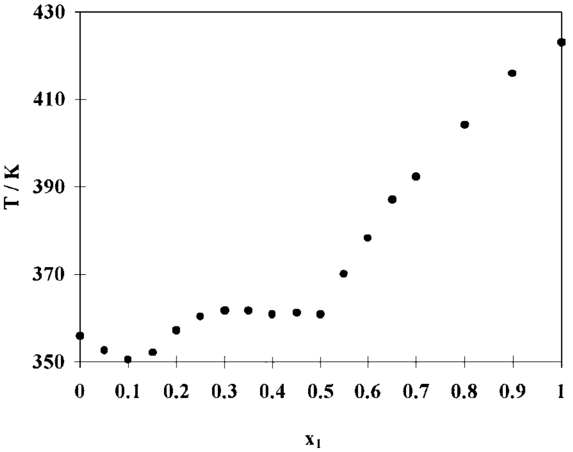


Fig. 1. Experimental results of SLE determination of the Pyrene (1) +9-Fluorenone (2) system.

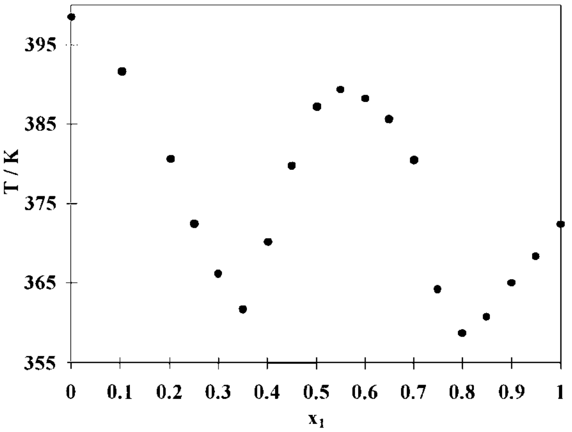


Fig. 2. Experimental results of SLE determination of the Phenantrene (1) +1-pyrenecarboxaldehyde (2) system.

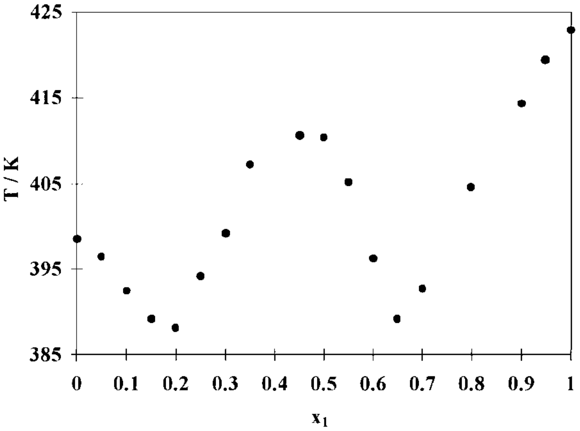


Fig. 3. Experimental results of SLE determination of the Pyrene (1) +1-pyrenecarboxaldehyde (2) system.

be expected. It can be observed in Figs. 4 and 5 that molecular areas are much smaller than it could be expected with investigated molecules. This proves that the water surface is covered by a film formed with bulky, three-dimensional aggregates of polyaromatics. However, these films while compressed produced isotherms analogous to those obtained with surfactants. The forward and backward branches of isotherms are not superposable, giving rise to hysteresis. The irreversible formation of aggregates upon the compression of the film could be responsible for this phenomenon. This is also consistent with thermodynamic and microscopic observations showing aggregate formation.

3.1. 1-Pyrenecarboxaldehyde

Results obtained in the case of 1-pyrenecarboxaldehyde are presented in Fig. 4. Five compression isotherms were obtained as follows. The compression of a film obtained with 2 ml of the solution spread on the water surface is presented in Fig. 4(a). After decompression of this film, 2 ml more of the solution were added and the film was compressed again to the collapse pressure (Fig. 4(b)). Three consecutive cycles of decompression and recompression gave the isotherms presented in Fig. 4(c–e). Several observations concerning these compression isotherms can be done. At first, very small molecular areas indicate that the films are multilayer. It is difficult to estimate the exact number of the layers. In the case of the first isotherm (Fig. 4(a)), the area per molecule measured at the collapse pressure is 5.3×10^{-3} nm^2. This should be compared to 0.4 nm^2, which is estimated to be roughly the area per molecule in a closely packed, hypothetical monolayer of 1-pyrenecarboxaldehyde. The number of eighty layers obtained as a ratio of these two values cannot be considered as a definitive structural parameter. Indeed, the following compression/decompression cycles gave decreasing values of the molecular areas. This decrease was slower with each cycle. The two last cycles gave at the collapse pressure very similar molecular areas, corresponding

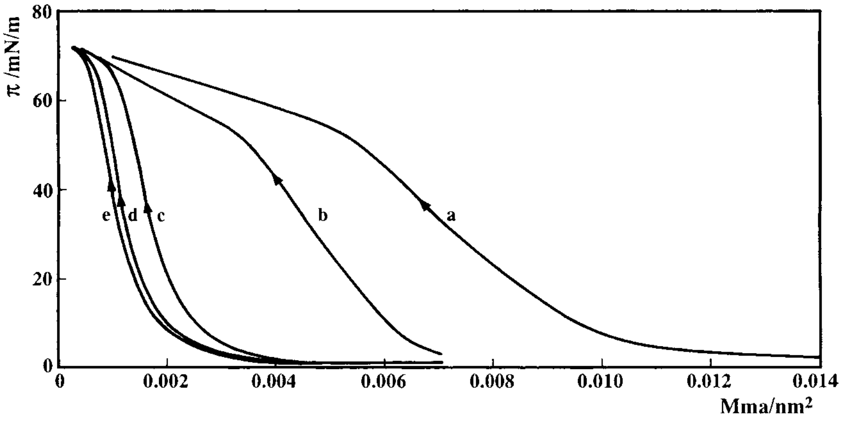


Fig. 4. Compression isotherms of films formed with 1-pyrenecarboxaldehyde. (a) First compression of the film obtained by spreading 2 ml of the chloroform solution. (b) Second compression done after a decompression of the first film and spreading of 2 ml more of the solution. (c–e) Consecutive compressions of the film obtained in point b.

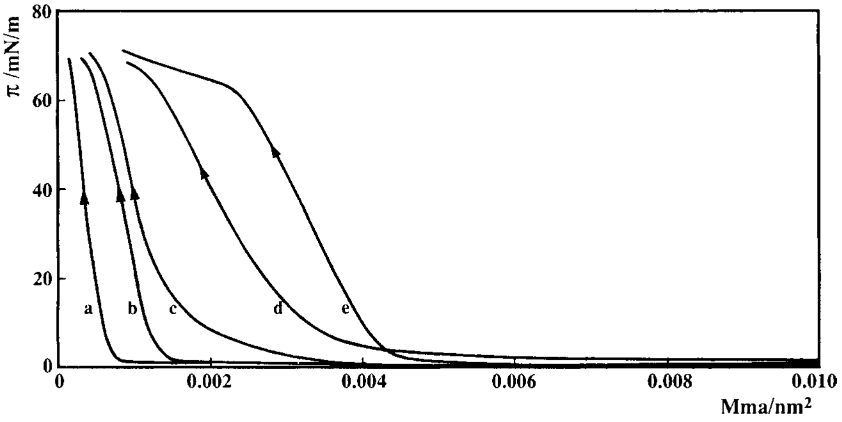


Fig. 5. Compression isotherms of pure or mixed films formed with (a) phenanthrene, (b) pyrene, (c) 1-pyrenecarboxaldehyde, (d) 1-pyrenecarboxaldehyde and phenanthrene, (e) 1-pyrenecarboxaldehyde and pyrene.

to ca. 800 layers of molecules. It can be concluded that after several cycles of compression/decompression, the film has a structure which does not evolve any more and its behavior is reminiscent of this of a Langmuir monolayer. Beyond the collapse point, the film which could be directly observed, formed a tissue-like structure, made of fibers parallel to the barriers. The film was transferred on a glass slide using Blodgett technique and observed under optical microscope using polarized light. The patterns observed were reminiscent of those characteristic of lamellar and hexagonal phases described for different surfactants. This observation supports the hypothesis that the compound studied forms at the air/water interface aggregates which can be compressed in a similar way as monomeric molecules.

3.2. 9-Fluorenone

9-Fluorenone spread from chloroform solution at the air/water interface forms a viscous liquid, depositing at the bottom of the Langmuir trough. Consequently, no further investigation of the film was possible. However, the small amounts of the compound resting on the water surface and transferred on the microscope slide showed with polarized light

Table 3
Surface pressure $\prod^{\mathrm{coll}}$ and mean molecular area $\mathrm{Mma}^{\mathrm{coll}}$ at collapse conditions in function of the nature of the sample and the number of compression cycles

Compounds	Collapse conditions		Sample, volume/ml	Number of cycles
	$\prod^{\mathrm{coll}}/\mathrm{mN\ m}^{-1}$	$10^2\ \mathrm{Mma}^{\mathrm{coll}}/\mathrm{nm}^2$		
Phenanthrene	69.5	0.01	5	2
Pyrene	63.3	0.05	2	1
	64.1	0.05	3	1
	66.2	0.04	3	2
PCA	52.5	0.53	2	1
	54.0	0.31	4	1
	64.4	0.11	4	2
	69.5	0.05	4	4
PCA/Phenanthrene	66.6	0.12	1	1
	66.6	0.12	2	1
PCA/Pyrene	61.2	0.33	2	1
	64.1	0.22	2	2
	62.3	0.20	2	3

patterns reminiscent of hexagonal-type phases, as it was the case with 1-pyrenecarboxaldehyde.

3.3. Pyrene

In the case of pyrene, formation of snowflake-like aggregates, separated by domains where the film was thinner, could be observed at the air/water interface. As can be seen in Table 3, the number of aggregate layers calculated at the collapse point is high. The compression isotherm becomes reproducible after two compression/decompression cycles. The film is more rigid than this obtained with 1-pyrenecarboxaldehyde, as it can be judged from the steep slope of the isotherm. The film observed under the microscope with polarized light is a network of regular circular bright spots which might be hydrated crystals imbedded in a thin, homogenous film.

3.4. Phenanthrene

At low surface pressure the behavior of phenanthrene at the air/water interface is very similar to this observed with pyrene. The compression isotherm for the second compression/decompression cycle is very steep in its low molecular areas region and gives a very high value of the collapse pressure (69 $\mathrm{mN\ m}^{-1}$). The presence of regular, circular bright spots was detected under optical microscope with polarized light. These structures are similar to those observed in the case of pyrene but they are more numerous and more homogeneously distributed.

3.5. Mixed films of 1-pyrenecarboxaldehyde with pyrene or phenanthrene

Mixed films were prepared using chloroform solutions of mixtures of $\approx 1:1$ molar ratio, of the two polyaromatics. This molar ratio was chosen as corresponding to the stoichiometry of the solid compounds observed in SLE diagrams. 1-Pyrenecarboxaldehyde with pyrene form at the interface a film having the same macroscopic fibrous character as this observed with the pure 1-pyrenecarboxaldehyde. Microscopic view of the film showed a network of short fibers coexisting with ribbon-like structures. Films formed by 1-pyrenecarboxaldehyde with phenanthrene are quite different. The microscopic observations revealed in this case that the components are segregated. Indeed, structures observed with pure 1-pyrenecarboxaldehyde and with phenanthrene were present in this case but in addition numerous structures reminiscent of surfactant hydrated crystals were detected.

The compression isotherms obtained upon the second compression of the films of three pure compounds and two mixtures are given in Fig. 5. Pure phenanthrene gives a very steep isotherm confirming the 'solid-like' nature of the compressed film. The mixed films are much more compressible and have a more 'liquid-like' character.

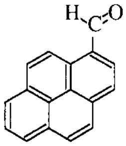
The data concerning the collapse parameters observed in the case of various systems are presented in Table 3. As it was stated above, the molecular area at the collapse pressure reflects the agglomeration of the molecules and consequently the thickness of the film. The films which show a more 'solid-like' character have higher collapse pressures and higher film thickness.

4. Conclusion

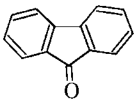
The phase behavior of polyaromatic hydrocarbons, as described in this paper, suggests the ability of these molecules to agglomerate. Aggregation phenomena occurring in presence of water can lead to the formation of organized structures similar to those observed in the case of surfactant/water systems. It must be noted that this organization depends strongly on the structure and on the physical properties of the molecules considered. All compounds used in this study have a very similar structure, chemical nature and molecular dimensions. The films they form at the water/air interface show, however, very disparate properties and organization. This result can be useful in understanding the behavior of polyaromatic hydrocarbons in complex environments such as petroleum fluid or soil/water systems. This latter case concerns the important problem of polyaromatic hydrocarbon migration through ecosystem compartments.

5. List of symbols

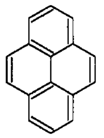
T/K	experimental equilibrium temperature
T_m/K	melting temperature of the pure component
x_1	mol fraction of component 1 in the liquid phase
$\Delta H_{i,T_m}$/ kJ mol^{-1}	molar enthalpy of fusion of component i at melting-point temperature
Π/mN m^{-1}	surface pressure
Mma/nm^2	mean molecular area



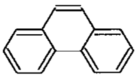
1-Pyrenecarboxaldehyde (PCA)



9-Fluorenone



Pyrene



Phenanthrene

References

[1] R. Mahmoud, C. Achard, N. Hasnaoui, R. Solimando, M. Rogalski, From Polyaromatics to Asphaltenes: Phase Behavior of Hydrocarbon Mixtures in Presence of Complex Aromatic Structure, Proceeding of the Eighth International Conference on Properties and Phase Equilibria for Product and Process Design, Noordwijkerhout, the Netherlands, 1998, p. 86.

[2] A. Aoulmi, M. Bouroukba, R. Solimando, M. Rogalski, Thermodynamics of mixtures formed by polycyclic aromatic hydrocarbons with long chain alkanes, Fluid Phase Equilibria 110 (1995) 283–297.

[3] A. Aoulmi, Ph. D. Thesis of Institut National Polytechnique de Lorraine, Nancy, France 1994.

[4] R. Mahmoud, Solubility of pyrene in long chain *n*-alkanes, Master of Sciences Thesis, Institut National Polytechnique de Lorraine, Nancy, France 1995.

[5] K.S. Birdi, Lipid and biopolymers at liquid interfaces, Plenum Press, New York, NY, 1989.

[6] G.L. Gaines, Insoluble monolayers at liquid–gas interfaces, John Wiley and Sons, Inc., New York, London, Sydney, 1966.