Trimer exciplex emission in benzopyrene

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Trimer exciplex emission in benzopyrene[a]

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Most hydrocarbon molecules in solid and in liquid phases tend to join together in pairs to form excimers.[1-5] In the case of 3, 4, 9, 10-dibenzopyrene, a potent carcinogen,[6] the molecules coagulate and stick together in groups of three to form trimers rather than excimers Typical emission spectra of 3, 4, 9, 10-dibenzopyrene in benzene, when the main pulsed N_2-laser beam (3371 Å) was used as a source of excitation, are shown in Fig. 1. All the spectra were taken under the same experimental conditions and used the same surface of the cell for both excitation and emission in order to avoid self-absorption. Oxygen was removed from the sample by bubbling ultra pure argon gas during data gathering.

In this work it was assumed that the emission spectrum of curve (1) is totally due to monomer emission. This has been confirmed by lifetime measurement.[7] The emission spectra of trimers were then obtained by subtracting curve (1) from the rest of the curves for wavelengths $\geq$ 4900 Å. The lifetimes of these longer wavelength bands were found to be completely different for those bands at shorter wavelengths.[7,8] Since a trimer is formed through the association of two unexcited (M) and one excited (M*) molecule, the relative intensity of the trimer (I_T) to that of the monomer (I_M) should be proportional to the square of the concentrations (C^2) of (M). This was found to be the case, as shown in Fig. 2. The trimer was also found to be unstable in the ground state. Absorption spectra (using Cary 14) showed no spectral change at any of the concentrations we used. That excluded the possibility of dimer formation.
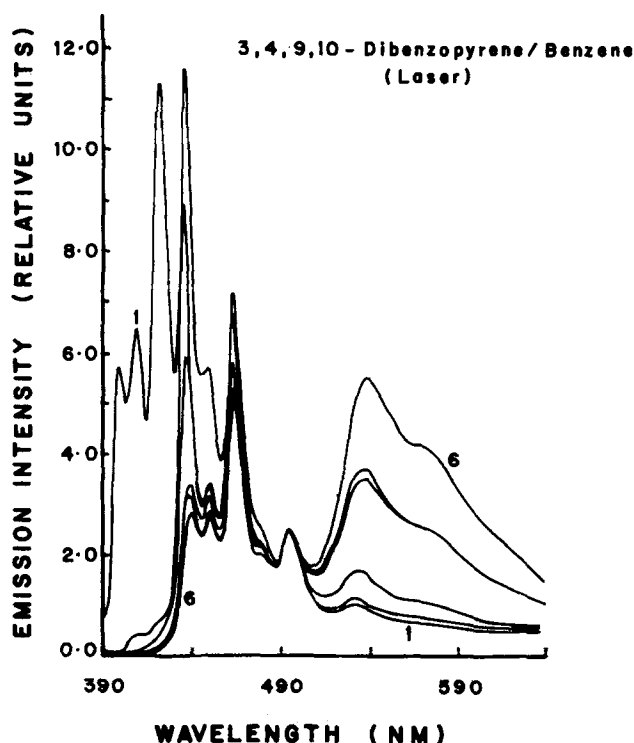
FIG. 1. Emission spectra of 3,4,9,10-dibenzopyrene in benzene at the following concentrations: 1(0.01 g/1); 2(0.02 g/1); 3(0.5 g/1); 4(1.0 g/1); 5(1.5 g/1); 6(2.0 g/1). The excitation wavelength is 3371 Å using the main N_2-laser beam.
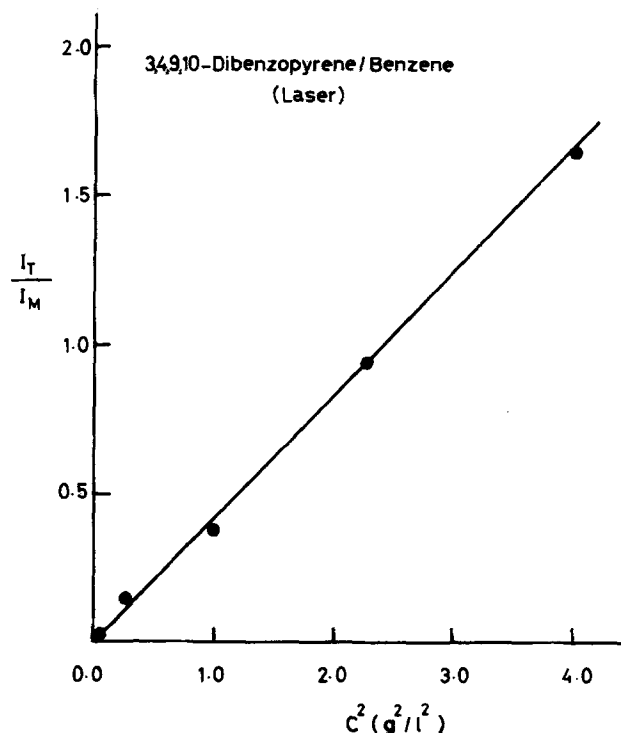

FIG. 2. Dependence of I_T/I_M on C^2 for 3,4,9,10-dibenzopyrene in benzene when N_2-laser was used as source of excitation ($\lambda_{ex} = 3371$ Å).

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[8] Due to short lifetime of trimers and our inability to differentiate between excimer and trimer emission in the early stage of this work, lifetime of the long wavelength portion of the spectrum of 3, 4, 9, 10-dibenzopyrene was reported in Ref. 7 to be due to excimer.

Experimental evidence for the universality of the pseudospinodal

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There have been a number of experimental results[1-5] supporting the concept of a pseudospinodal for describing critical region data. Recently, Sorensen and Semon[6] have successfully used this concept to derive an equation of state for liquid–gas systems that fits PVT data as well as other phenomenological equations. In this note we have used available experimental evidence to test the existence of a *universal* pseudospinodal that describes all thermodynamic and transport properties of all liquid–gas and binary fluids systems with one curve.

The spinodal curve, first introduced by van der Waals, represents the limit of metastability of the one-phase state in the two-phase region. To describe critical region data off the critical isochore, Benedek[5] introduced the so-called *pseudospinodal assumption* that states that along any isochore, represented by density or concentration ρ, a given thermodynamic or transport property X diverges as the pseudospinodal temperature $T_s(\rho)$ is approached according to

$$X = X_0 \left[\frac{T - T_s(\rho)}{T_c} \right]^{-x} = X_0 [t + t_s(\rho)]^{-x} \tag{1}$$

with $t = (T - T_c)/T_c$ and $t_s(\rho) = [T_c - T_s(\rho)]/T_c$. Here X_0 and x are the critical amplitude and exponent found along the critical isochore. Note that $T_s(\rho_c) = T_c$, where ρ_c is the critical density. Under the assumption of Eq. (1), the locus of $T_s(\rho)$, called the pseudospinodal curve, is found to have the form

$$|\rho - \rho_c|/\rho_c = \tfrac{1}{2}(\rho' - \rho'')/\rho_c = B_s \left[\frac{T_c - T_s(\rho)}{T_c} \right]^{\beta\dagger} \tag{2}$$

where B_s is the amplitude of the curve and ρ' and ρ'' are the densities or concentrations of the two phases. It is expected from homogeneity or scaling[7,8] that $\beta\dagger = \beta$, the exponent describing the coexistence curve.[1,9]

To test the universality of the pseudospinodal, we have

attempted to use all available experimental results[1-4] specifically designed to test the pseudospinodal assumption. We have also analyzed experimental data not specifically designed for this problem but with ample off-critical isochore data to allow for our analysis. Such data are surprisingly rare. We have used specific heat data for He^4[10] and CO_2,[11] thermal diffusivity data for CO_2[12] and PVT data for He^4.[13] The PVT data were used to graphically obtain inverse isothermal compressibility data of He^4 along the off-critical isochores.

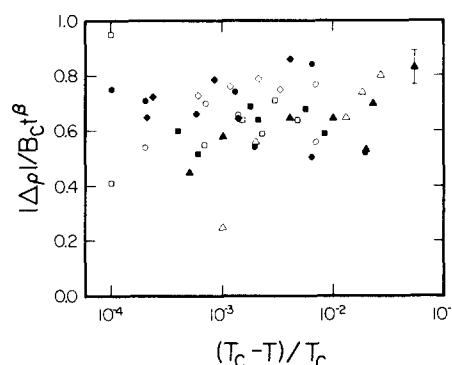In analyzing the data, a background term of the form

FIG. 1. Plot of pseudospinodal curve data $\Delta\rho_s$ normalized by the coexistence curve $B_c t^\beta$ versus the reduced temperature $t = (T_c - T)/T_c$. The symbols correspond to: ◆ diffusivity and correlation length of isobutyric acid + water (Ref. 1), ◊ osmotic compressibility and correlation length of polystyrene + diethyl malonate (Ref. 4), ● viscosity of isobutyric acid + water (Ref. 3), ○ correlation length of polystyrene + cyclohexane (Ref. 2), ▲ isothermal compressibility of He^4 (Ref. 13), △ specific heat of CO_2 (Ref. 11), ■ specific heat of He^4 (Ref. 10), and □ thermal conductivity of CO_2 (Ref. 12). The value $|\Delta\rho|/B_c t^\beta = 1.0$ represents the coexistence curve. A typical error bar is also shown.

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