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Temperature effects on the solubilization behavior of some 3H-indoles in water and microheterogeneous media

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Abstract

The solubilization behavior of 3,3-dimethyl-2-phenyl-3H-indole (**I**) and its substituted derivative 2-[*p*-(dimethylamino)phenyl]-3,3-dimethyl-3H-indole (**II**) was studied in sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) aqueous micelles and dioctadecyldimethylammonium bromide (DODAB) surfactant vesicles. The site of solubilization of both probes in the micelles and vesicles was highly polar but moderately viscous, e.g. the interface. The effect of temperature on the fluorescence quantum yield of both molecules indicated that the gel to liquid crystalline phase transition temperature of DODAB was 309 K (36 °C). Molecule **II**, below the phase transition temperature, is locked in a site where rotation of the phenyl moiety is order limited, whereas molecule **I** occupies a site which is exclusively viscosity controlled. Molecule **I** may penetrate deeper into the hydrophobic region of DODAB above the phase transition temperature.

Keywords: Temperature effects; Solubilization behaviour; 3H-indoles; Microheterogeneous media

1. Introduction

Inherent complexities in biological membranes have been a driving force behind the development of membrane mimetic chemistry [1–3]. Interest in this subject has also been generated by its practical applications, e.g. drug encapsulation, energy storage, novel reaction media, etc. [4–8]. Micelles and vesicles are the most extensively studied membrane mimetic systems [9–12]. They are formed by the self-assembly of amphiphiles in aqueous solutions. Although micellar structures are in equilibrium with their monomers, the vesicular structures, once formed, are static entities on the time scale of most spectroscopic probe measurements [13]. A wide array of solubilization sites are accessible to guest molecules [14–18]. Major questions, such as the chain order, degree of wetness and permeability to solubilizates, have been addressed frequently but remain to be elucidated [19–23], and this domain of chemistry continues to be an active research area [24–33].

The potential of a guest molecule to probe the microstructure depends, to a large extent, on its behavior in homogeneous environments. A wide variation in spectral characteristics is vital for qualification as a probe candidate [9]. Since 3H-indoles are sensitive to homogeneous environments [34–38], their use as probes has been highlighted in reverse micelles [39], micelles [15,40] and vesicles [41,42]. Our continuing efforts in this direction are presented in this paper. 3,3-Dimethyl-2-phenyl-3H-indole (**I**) and 2-[*p*-(dimethylamino)phenyl-[3,3-dimethyl-3H-indole (**II**) were solubilized in sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) aqueous micelles and dioctadecyldimethylammonium bromide (DODAB) vesicles. Results show that the solubilization site of both probes in SDS, CTAB and DODAB is highly polar but moderately viscous. The viscosity gradient increases from the surface to the central region of DODAB bilayer vesicles, an observation in contrast with that made in phospholipids. The present investigation shows how a small chemical change in these molecular probes leads to a remarkably different physical behavior in heterogeneous media.

2. Experimental section

The synthesis and purification of molecules **I** and **II** were performed according to the modified methods of

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Skrabal et al. [43] and are reported in Popowycz [44]. Analytical grade reagents sodium hydroxide, sulfuric acid and methanol were used as received. Sephadex G-50 "fine" obtained from Sigma was used without purification. Surfactants SDS (Aldrich, 98%) and CTAB (Aldrich) were purified according to the method reported recently [40]. DODAB was received from Eastman Kodak and was purified in a 90:10 acetone–water mixture. All surfactants after purification were stored in a desiccator. The concentrations of CTAB and SDS used in all measurements were 0.01 and 0.06 M respectively; the concentration of the probes was in the range $(1–2)\times10^{-6}$ M.

The preparation of DODAB vesicles was carried out as follows: an aliquot of a 10^{-3} M solution of molecule **I** or **II** in methanol was added to a methanol solution of DODAB (18 mg) in a vial. This mixture was mixed by slight shaking and dried in vacuum desiccator. A thin film was formed along the sides of the vial. To this was added 2 ml of aqueous solution (pH ≈ 8). This solution was sonicated on a probe-type sonicator (Fisher-300), set at 50 W with a relative output of 70%, at 70 °C for 10 min. The solution was cooled to room temperature and transferred into Eppendorf standard micro-test-tubes. These were centrifuged on a megafuge supplied by Baxter Products (model 2630) at 3000 rev min^{-1} for 15 min. This helps to homogenize the vesicles and, in addition, removes titanium particles released by the tip of the sonicator. A measured amount of this solution was passed through a Sephadex column (15 cm × 1.5 cm). Fractions of equal volume were collected in glass vials and the presence of vesicles containing solubilized probes was monitored by UV spectrometry. All the fractions obtained from the column containing vesicles were mixed together. The dilution of the vesicles was 3–4 times. Since DODAB vesicles show absorbance between 250 and 400 nm, vesicles without probes were prepared in a similar fashion for use in the reference compartment of the UV spectrophotometer. DODAB vesicles did not show any spurious emission. The pH of all solutions was adjusted using sodium hydroxide and sulfuric acid.

The absorption spectra were recorded on a Philips PU-8800 UV–visible spectrophotometer. Corrected fluorescence spectra were measured on a Spex Fluorolog-2 spectrofluorometer with an F2T11 special configuration. Fluorescence lifetime measurements [34] for molecule **II** were made on a multiplexed, time-correlated, single-photon counting fluorimeter (Edinburgh Instruments, model 299T). Fluorescence quantum yields were measured using *p*-(dimethylamino)phenyl-3,3-dimethyl-3H-indole in methanol as a standard ($\Phi_F = 0.24$) [37].

Temperature variation was achieved by placing the sample in a cell compartment whose walls were accessible to water circulation. Water from a thermostatically controlled water bath was allowed to circulate through the walls of the sample compartment. The final temperature of the sample was measured by a thermocouple immersed in the sample solution and connected to a Fluke 51 digital meter.

3. Results and discussion

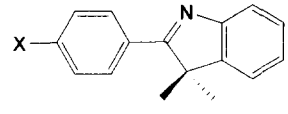
3.1. Nature of the solubilization site

The structures of molecules **I** and **II** are shown in Scheme 1. They were solubilized in water, SDS and CTAB micelles and DODAB surfactant vesicles. The spectral characteristics of the molecules in these media are listed in Table 1. The fluorescence spectra of both molecules in DODAB vesicles are displayed in Fig. 1.

Recent studies on substituted 3H-indoles in solvents of varying polarity and/or hydrogen bonding and viscosity have demonstrated that molecule **I** belongs to a unique class of fluorophores in which the deactivation of the excited singlet state is primarily governed by non-radiative internal conversion ascribed to an intramolecular torsional relaxation channel [37]. It was emphasized that since the excited state dipole moment of this molecule is much lower than that of its substituted homologs, the polarity and hydrogen-bonding ability of the solvents do not affect the rotational motion of the phenyl moiety. Therefore any restrictions imposed on the excited state phenyl torsion, e.g. viscosity of the solvating medium, are essentially reflected in the quantum yield of the fluorophore. There is an excellent linear correlation (correlation coefficient $r = 0.99$) between the fluorescence quantum yield and solvent viscosity (η in cP) as shown by the following equation which obeys the well-known Förster and Hoffman mechanism [37]

$$\Phi_F = (9.4 \pm 0.3) \times 10^{-4}\ \eta^{2/3} \quad (1)$$

On the other hand, molecule **II** shows a dependence of phenyl torsion on the viscosity in non-polar solvents only [34,35]. However, increasing dipole–dipole interactions in polar environments and hydrogen-bonding complexation in protic solvents also influence the first excited state geometry. The molecule becomes more



I X = H

II X = $N(CH_3)_2$

Scheme 1.

Table 1
Spectral characteristics and photophysical parameters of molecules I and II at the peak maxima in various media

Medium	I					II			
	$\bar{\nu}_A$ (cm^{-1})	$\bar{\nu}_F$ (cm^{-1})	Φ_F	$k_F^l \times 10^{-8}$ (s^{-1})	τ_F[a] (ps)	$\bar{\nu}_A$ (cm^{-1})	$\bar{\nu}_F$ (cm^{-1})	Φ_F	τ_F (ns)
Water	33300	23900	0.0011	2.1	5.2	27300	21800	0.21	1.1
SDS	32900	24300	0.0022	2.5	8.9	27200	21900	0.32	2.2
CTAB	32800	24600	0.0033	2.2	15	27000	22000	0.33	2.1
DODAB	32800	24700	0.0034	–	–	27100	22000	0.25	2.1

[a] Values calculated from $\tau_F = \Phi_F / k_F^l$ (the theoretical decay rate constant obtained from the integrated absorption spectra and the Strickler and Berg relationship [38,45]).

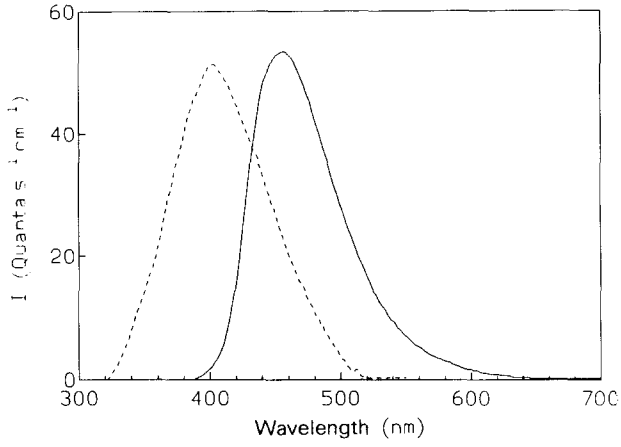


Fig. 1. Fluorescence spectra of molecules I (– – –) and II (——) in DODAB.

planar, such that the torsional movement of the phenyl moiety is hindered giving rise to higher quantum yield values.

Comparing the absorption and fluorescence wavenumber maxima for these molecules in microheterogeneous media (Table 1) with those observed in homogeneous solvents [34,35,37,38], it can be seen that both molecules are solubilized in a region of high polarity, similar to methanol or propanol. Since the polarity in the core of the micelles and in the bilayer region of the vesicles is close to that observed in non-polar solvents [1,13], it can be safely concluded that the solubilization site of these molecules is near the interface of SDS, CTAB and DODAB.

As stated above, the fluorescence quantum yield of molecule I responds to the viscosity of the solvent and follows Eq. (1) regardless of the polarity of the solvent (unlike molecule II), such that the microviscosity of the interfacial region of DODAB vesicles can be evaluated using molecule I. Substituting the value of the quantum yield of molecule I estimated in DODAB into Eq. (1), a viscosity value of 7 ± 2 cP is estimated. Viscosity values for SDS (4 cP) and CTAB (7 cP) micelles have also been estimated successfully by this probe [40]. The microviscosities are lower than those reported by earlier workers [20,25,46], e.g. Fendler and coworkers [25,46] have determined the viscosity in DODAB to be 144 cP. They used 2-methylanthracene, a completely hydrophobic probe [25]. This probe is known to be intercalated in the hydrophobic chain regions of the vesicles [46], in contrast with the interfacial location of molecule I. Thus our probe and the probe used by Fendler and coworkers [25,46] report the microviscosity of two very different regions of the vesicles. Lukac [20] has reported two values of the microviscosity, namely 41 and 11 cP, based on the scales constructed using straight chain alcohols and ethylene glycol respectively at different temperatures. Since the probe was reported to interact differently in different solvents, he suggested that the higher value (41 cP) could be discarded. The lower value (11 cP) is quite close to that obtained here. The probe used by Lukac was also found to be located in the highly polar regions, e.g. the interface. These experimental results show that, in DODAB surfactant vesicles, there is a high viscosity gradient which increases on going from the head group regions towards the hydrophobic chains, a phenomenon similar to that observed in aqueous micelles [1,12,13].

Similar observations have been made in previous studies using 2-[(*p*-methylamino)phenyl]-3,3-dimethyl-5-carboethoxy-3H-indole, a substituted derivative of molecule I [40,42]. This molecule migrated towards the chain region of the vesicles with an increase in temperature. The activation energy was determined to be higher above the phase transition temperature than below and the fluorescence quantum yield increased suddenly at the phase transition, indicating a higher viscosity in the hydrophobic chain region than at the interface. The same kind of observation has been made by Fendler and coworkers [47] in a different set of experiments and also by Whitten and coworkers [21]. Fendler and coworkers [47] used a pyranine probe to study the photopolymerization of surfactant vesicles of identical chain length as that of DODAB. From polarization and time-resolved anisotropy measurements, they established that pyranine moves to a hydrophobic and more ordered environment from its initial interfacial

solubilization site in non-polymerized vesicles as a function of incubation time. Whitten and coworkers [21] have carried out studies on the triplet–triplet absorption spectrum of 4-nitro-4′-methoxystilbene (NMS) in surfactant vesicles. NMS was shown to be solubilized at two distinctly different solubilization sites in dioctadecyldimethylammonium chloride (DODAC) vesicles. Lifetime measurements established that one of the solubilization sites was interfacial (more polar and less viscous) and the other was the hydrocarbon chains (lower polarity but higher viscosity). The microviscosity data observed in DODAB surfactant vesicles are in sharp contrast with the trend found in vesicles formed from phospholipids [48]. A reverse order of viscosity is reported in phospholipids, i.e. the chain mobility is shown to be higher on going to the bilayer interior from the head groups or interface. One possible reason for this could be the existence of highly charged head groups in DODAB. Once the vesicles are formed, repulsion of the head groups is expected as in SDS and CTAB micelles. This would bring the hydrophobic chains closer due to the hydrophobic effect, increasing the order in the chain region and possibly decreasing it in the head group region.

3.2. Effect of temperature

The effect of temperature in the range 283–343 K was studied for molecules **I** and **II** in water, SDS, CTAB and DODAB. Arrhenius plots of the non-radiative decay rate parameter ($\Phi_F^{-1}-1=k_{nr}/k_F$) are shown in Figs. 2–5. The calculated activation energies are given in Table 2. From the temperature dependence of Φ_F and τ_F of these 3H-indole probes, it has been confirmed that $k_F(=\Phi_F\tau_F^{-1})$ does not vary with temperature in the range used in the present work [41]. For molecule **I**, the Arrhenius plots are perfectly linear in water and both micelles as shown in Fig. 2. The activation energies calculated from these plots follow

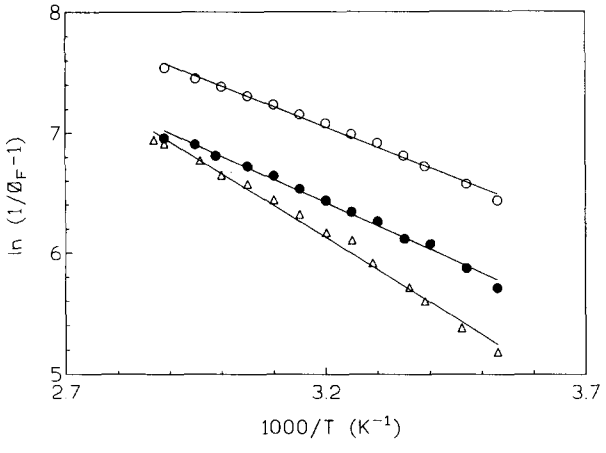


Fig. 2. Arrhenius plot for molecule **I** in water (○), SDS (●) and CTAB (△).

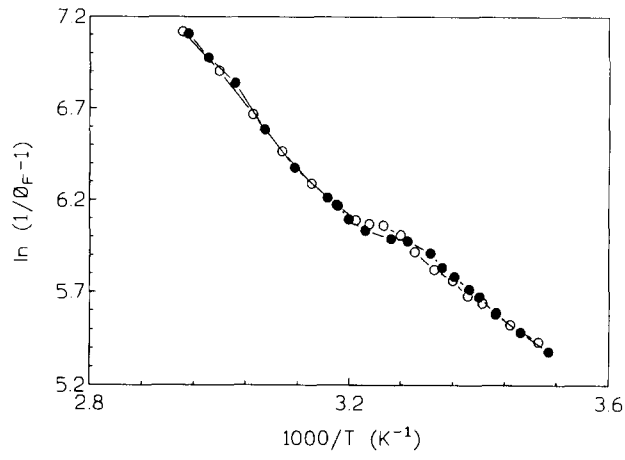


Fig. 3. Arrhenius plot for molecule **I** in DODAB; forward cycle (○); reverse cycle (●).

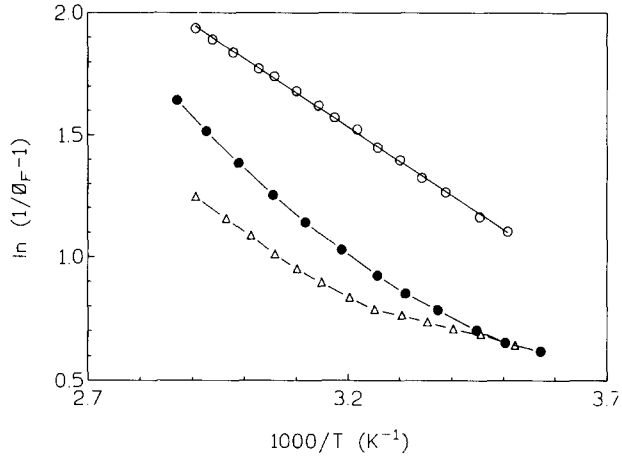


Fig. 4. Arrhenius plot for molecule **II** in water (○), SDS (●) and CTAB (△).

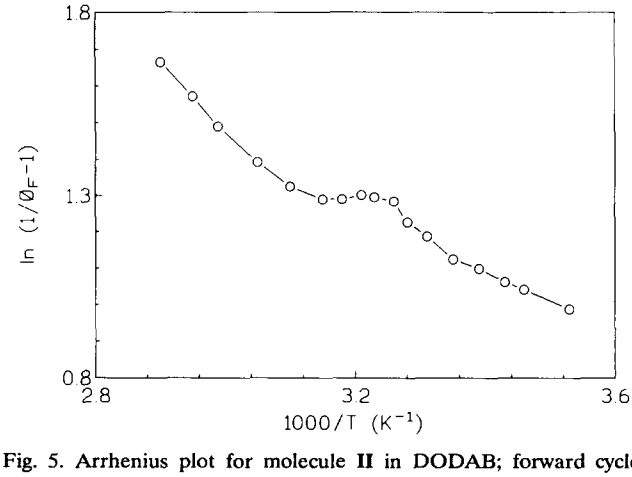


Fig. 5. Arrhenius plot for molecule **II** in DODAB; forward cycle (○).

the order CTAB > SDS > water (Table 2). As stated earlier, the torsional relaxation dynamics of this molecule is controlled by the viscosity of the medium only and the molecule experiences the highest viscosity in

Table 2
Activation energies (±1 kJ mol^{-1}) correlated to the non-radiative fluorescence decay processes of the probes in various media

Molecule	Medium			
	Water	SDS	CTAB	DODAB
	14	16	22	Below T_c=23 Above T_c=35
II	12	–	–	–

CTAB. This argument is in accord with the viscosity determined using this molecule in SDS and CTAB [40] and that reported by earlier workers [13]. Fig. 3 shows the Arrhenius plot for this molecule in DODAB vesicles. A distinct break is observed at around 309 K (36 °C). Heating and cooling cycle curves overlap, and no hysteresis is observed. The discontinuity at around 309 K may be correlated with the phase transition of DODAB vesicles from the gel to the liquid crystalline phase [20,27,41,42]. The activation energies estimated from the linear portions of the plots (heating cycle), both below and above the phase transition temperature, are presented in Table 2. The value of the activation energy in DODAB (23 kJ mol^{-1}) below the phase transition temperature is similar to that obtained in CTAB (22 kJ mol^{-1}). Above the phase transition temperature, a higher value of the activation energy (35 kJ mol^{-1}) is observed.

As stated earlier, the torsional relaxation of molecule I can be controlled by the viscosity of the surrounding environment [37]. The DODAB vesicles in their gel state have an ordered structure and thus low mobility. This leads to high viscosity values in all regions of DODAB vesicles in the gel state in contrast with the liquid crystalline state. Above the phase transition temperature, the hydrocarbon chains melt by assuming mobile liquid-like arrangements, providing a lower viscosity in the liquid crystalline state [25]. However, the decrease in viscosity is expected to be concentrated mainly in the hydrophobic chains rather than in the head group region. Therefore the activation energy should be lower in the liquid crystalline state of DODAB vesicles than in the gel state. Thus a different mechanism seems to be operative in this case. As stated previously the viscosity values in DODAB increase on going from the surface of the vesicles to the interior. It is probable that during chain melting, probe molecule I starts to move towards the hydrocarbon chain region of the vesicles, thus experiencing a higher viscosity. Since the absorption and fluorescence spectra of molecule I are not very sensitive to small polarity changes, it was not possible to observe any spectral changes as a function of temperature that would confirm this mechanism. In other words, molecule I does not penetrate deep enough into the hydrophobic chains, where the viscosity is remarkably high and the polarity is extremely low. This sort of penetration has been observed in one of the substituted derivatives of molecules I [41,42] and has also been reported by Lukac [20].

The effect of temperature on molecule II is quite different and more complex. However, a distinct break around 309 K (36 °C) is observed in DODAB vesicles, corresponding to the phase transition temperature (as observed using molecule I). Except for water, the Arrhenius plots in micelles and vesicles are non-linear (Figs. 4 and 5). These results do not indicate the multiple site occupancy of molecule II in these microheterogeneous media, an observation commonly made in these systems. Indeed, it is well known, that small solubilized molecules, such as NMS, which is similar in size to molecule II, can reside in at least two distinctly different environments within bilayer vesicles (such as DODAC and dipalmitoyllecithin (DPL)), and that exchange between these sites below the phase transition temperature is slow ($k < 10^4$ s^{-1}) [49]. Because fluorescence lifetime analysis shows that the decay curves are single exponential [15], a different mechanism seems to be operative in this case. The photophysics of molecule II in solution has been studied extensively and conformational analysis using Austin model package (AMPAC) and intermediate neglect of differential overlap for spectroscopy (INDO-S) has been performed [34,35]. These studies show that the phenyl moiety can oscillate to some extent in both the ground and excited states. This allows for many possible conformers within the kT barrier. This torsional relaxation is the main cause of the decrease in the fluorescence quantum yield and lifetime. Thus the photophysical parameters (Φ_F, τ_F) of this molecule, like molecule I, are affected by the viscosity of the medium, but only in non-polar solvents, whereas in polar solvents hydrogen bonding plays the dominant role in reducing the torsional movement. The non-linearity of the Arrhenius plots for molecule II in micelles and vesicles cannot be simply treated as a viscosity effect. Since this molecule occupies only one solubilization site, the tendency of the Arrhenius plots to nearly level off at low temperatures (below the phase transition temperature in DODAB) can be assumed to be due to the locking of the molecule into a site where the probability of twisting of the phenyl portion is order limited rather than viscosity controlled. This idea is reinforced by the behavior of this molecule in water (Fig. 4), where no such sites exist and the plot is linear at all temperatures studied. Above the phase transition temperature in DODAB, the hydrophobic chains melt and the order is reduced in both the head group region and the core of the vesicles, leading to near-linearity of the plots. Due to these non-linear effects, the calculation of the activation energy in micelles and vesicles was not attempted with molecule II. A similar behavior has been observed by

Whitten and coworkers [14] using stilbenes in different organized media.

4. Conclusions

A comparison of the spectral shifts observed for molecules I and II in various solvents with those in SDS and CTAB micelles and DODAB surfactant vesicles shows that the solubilization site is quite polar, similar to that at the interface. Since the torsional relaxation of molecule I and, consequently, the fluorescence quantum yield are proportional to the two-thirds power of the viscosity of the solvating medium, a viscosity value of 7 cP was estimated for DODAB vesicles. This value is in close agreement with that reported by Lukac [20] using a probe with a similar location. The viscosity is higher (by at least an order of magnitude) in the hydrophobic chain region of the vesicles than at the interface. This is in contrast with the viscosity gradient observed in phospholipids. The phase transition temperature for DODAB vesicles was estimated to be approximately 309 K (36 °C) from both probes. Arrhenius plots of molecule I in water and heterogeneous media were found to be linear and the estimated activation energies were a function of the viscosity of the medium. Molecule I is thought to move towards the central chain region of the vesicles above the phase transition temperature as shown by the higher activation energy. Below the phase transition, molecule II is locked in a site where the rotation of the phenyl portion is order limited, but this rotation becomes viscosity controlled above the phase transition temperature due to chain melting. This work shows the effectiveness of chemical substitution for probing the physical characteristics of heterogeneous media.

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