THE COEFFICIENTS OF DIFFUSION OF SMALL MOLECULES MIXTURES, MICELLAR MILIEUX AND THEIR EXPLANATIONS ON THE BASIS OF LASER SCATTERING MEASUREMENTS

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Abstract

The scattering of He-Ne laser and Ar^+ ion laser on two and three components mixtures of small molecules and biological and medical interesting milieux are performed. The measurements were carried out with the solutions from the small molecules to the micellar concentrations with macromolecules. For some of them, sells were also added. The conclusions for liquid materials are very interesting concerning the coefficients of diffusion, state of materials and molecular, micellar and mutual counter ions interactions. The measurements of diffusion coefficients are on the basis of the Rayleigh linewidth, on the basis of photon beating techniques (correlations techniques). Some data can be explained as with „correct" or „incorrect" optical purety.

INTRODUCTION

The contemporary notion explaining the mechanisms in connection with the relaxation characteristics of liquids, solubilied and half solubilised materials, concentric melt and polymers in high energy states, depends on the rheological features and polymers in high energy states, depends on the rheological features of macromolecules, magnetic and optical features, laws of chemical reactions and other nonequilibric processes in polymer and biopolymers, connected with formations and functions of macromolecules.

The history of theoretical concepts (1) is circulary so that today the late tendences are that general laws and general statistics are linked with Monte Carlo methods, too.

Flory, Volkenstine works and their schools and the statistical approach for multicomponents mixtures and calculations of coefficients concerned with macromolecules and sudden expansions and instigations with new technics and theories of dynamical light scattering and in connections with quantum electronics, quantum optics, photoelectronstatistics, technics of photon beating and mixing technics.

THE SHORT THEORETICAL INTRODUCTIONS

The laser scattering can be treated statically and dynamically. The statical approach for τ_E — turbidity in excess (3) is in formulas:

$$H\,(c - C^{+})/\tau_E = \left\{ \left(\frac{1}{b_3 M_m} \left[1 + \frac{C - C^{+}}{2 n_3 M_m} \quad (p^2 + p - p/b_3) \right] \right. \right. \cdot$$

(for high sell concentrations, $N_4 << N_3$)

$$\frac{1}{b_4 M_m} \quad | 1 + \frac{C - C^{+}}{2c\, m_a} \quad (p^2 + p - p/b_4) | \quad \text{(if there is no/sell } N_3 = 0)$$

$$b_4 = 1 - \alpha^2 + \alpha^2/2 + \alpha/2m$$

$$b_3 = 1 - f\alpha + f^2\, \alpha^2/2 + f^2\, \alpha/2m_a \qquad f = \psi_3/\psi_4.$$

Here m_a is aggregation number, M_s — molecular mass of surface active monomers, n_3 and n_4 are concentrations of sell (mol/mi) and surface active monomers, p-charge, $m_a = M_m/m$.

Another concept is with matric calculations of diffusion intensity I $(c_1, c_2 ... 0)$ of volume V, at distances r and under the angle with primary light wave vector, leading to the Rayleigh coefficients and definitions (3).

$$\mathrm{I}\,(c_1, c_2 \ldots 0) = \left[\frac{2\pi^2 \nu^2 V}{\lambda^4 T^2 N} \; \frac{1 + \cos RT \;|-D|}{\sin \qquad |A'|} + I_s \right] / \mathrm{I}$$

$$D = \begin{vmatrix} 0 & d\nu/dn_1 & dV/\partial n_2 \\ \dfrac{\partial \nu}{\partial n_2} & a_{11} & a_{12} \\ \ldots & \ldots & a_{22} \end{vmatrix} \qquad A = 1/B = \left\{ a_{ij} \right\} = \left\{ \frac{\partial \mu_j}{\partial n_j} \right\}$$

$$\nu^2{}_b V_b = V \nu^2$$

Another concept of I_{dif} $(c_1, c_2 ... 0)$ with light scattering and volume V and with(5) definitions.

The dynamical light scattering is concerned with coefficients of diffusion and whatever molecular mass was in the past, the diffusion coefficients are in modern treatments but more sophisticated. The theory deals with correlations functions of electric field or intensity correlation functions i.e. second, or forth order (respective to E) with a pair correlation .functions of materials$^{(4)}$.

Experimentally the third component (sell) makes the situation more „calm" while, as far as the substance is concerned, the sells accelerate micelar formations.

Here the theory starts with

$$I_d(t) = a^2 \sum_{ll'} \sum_{mm'} e^{i\vec{K}(\vec{R}_1(t)-\vec{R}_{l1}(t))} e^{(\vec{K}\vec{r}\,(\vec{r}_{em}(t)-r_{l'm'}(t))} \qquad T = 2\pi/\omega_o$$

and by averaging $< I > = < I_d\ (t) > = a^2 NS\ (K)\ F\ (K)$

$$S\ (K) = \frac{1}{N} < | \sum_{i=1}^{N} e^{(\vec{K}\vec{R}_1\ (t)} |^2 > \text{ structure factor}$$

$$K = K_d - K_i \qquad |K| = \frac{\pi}{\Lambda} \sin \theta/2$$

EXPERIMENTS

The apparatus is explained in$^{(5)}$. There are the He-Ne and Ar^+ion lasers in two geometries and the corresponding apparatusses and electronic data processing.

RESULTS-DISCUSSION

The materials chosen for discussions were: 1) sodiumdodecysulphate (SDS) in 2-times destilated water, 2) solutions core particles$^{(2)}$, 3) phytol-quionoline mixtures (small molecules).

Some of results are in Table 1.

Table 1a. — Some data for diffusion coefficients 59/100 Cc-0.175 M in water 2 times destilated Ar ion laser, A = 514,5 m, P ≤ 500 mW

No.	a	θ°	τ/us	Γ (H z)	$q^2\ cm^{-2}$		r^2
1	0,201080	45	0.2	14001 274	0,1464466	2,832	0,98322
2	0,487853	30	1	6793 871	0,0669873	3,004	0,94239
3	0,202309	36	0.2	14086 85	$9{,}5491 \cdot 10^{-2}$	4,36997	0,995853

Table 1b. — Some data for diffusion coefficients and small angle dispositions for 59/1 SDS in 2 times destilated water

$U_{PM}V$	filtar Hz	$\theta_{appear.}$	θ_{right}	$g^2 cm^{-2}$	Γ_{right}	$D_T - 10^6 cm^2/s$
1150	5	4	3,0064551	$4{,}8004 \cdot 10^7$	3,40	8,716
900	15	8	6,006	1,914	6,724	

Table 1c. — Polystirol $\phi = 0{,}199\ \mu$

	Δt, $K_2/\Gamma_2^2 \sim$ 0,05 small poly.			
Δt	Γ_1	Γ_2	K_2/Γ_2^2	$\Gamma = 180\ \ 7$
20	166	175	0,01	$\Gamma = 180 \pm 7$
10	171	175	0,02	$\Gamma_{exp} > \Gamma_{oal}$
5	174	196	0,16	
2	177	206	0,24	

Standard processes lead to the diffusion coefficients with respective calculations, that usually are coefficients of diffusion of monomers, small or macromolecules in diluted solutions, where the situations is „pure" and below of the concentrations for micellar formations (if it is possible): after wards we measure coefficients of diffusion for micelles (big differences in order of magnitude). But with the concentration growth the interactions increase too, and we measure the effective coefficients of diffusions. Some possible clear conclusions in this situations are: (1) if known dependences D (k), k-scattering vector) exist: long range interactions exist, (2) if D is constant with scattering angle, there are no long range interactions, and we must investigate further, (3) if D is constant with concentrations, there are no short range interactions, (4) if D growts with concentrations (salinity), that can be the case of confirmations change (case core particles), (5) if the behaviour is not usuall, we can consider and calculate polydispersity (the case of polystirene solutions), (6) if there are concentrated solutions, the situation is not so simple, the effects of Difour and Soret may be of interest, (7) concerning phytol and quinoline case, there are some experimental problems except basides purety and what is „optical pure case". There is a problem or concentrated solutions when explaining what is there the coefficients of diffusions, in any case, the effective diffusion coefficients are involved. If we can imagine that there is phytol in quinoline D is one and for the case quinoline in phytol, D is another. But it is sure that the coefficients of linewidth are concentrated to two values, the difference is double, (8) if there are polydispersity, the methods of cululant and the Pussey give the order of magnitude of polydispersity in second term or linewidth (Γ_2) i.e. Γ/K^2, if polydispersity is of small degree such measurements are very constructive in a case when polystirene is for calibrations of light scattering apparatus. The answer is more exact if polydispersity is stronger. But, the degression from D and D_{th} means that the interactions exist. If D_{cal} is smaller than measured, that means for sure that electrostatic interactions exist. For phytol and quinoline, measurements are discussed in a link with an earlier version of apparatusses and we will repeat the measurements, later only the order of magnitude is sure, but the question of purety of solutions is to be resolved. On the basis of measurements we can say that different types of conclusions, depending on partial situations in solutions can be made.

This paper is not intended to give the number of regular laws for any case, while the situations when light scattering can be very fine, but we have to be careful, but for D we get some conclusions on the basis of our measurements (core particles-confirmations change), polystirene (smail polydispersity), and the order of magnitude for phytol and the conclusions that sell added makes the micellar growth faster. There are also comparisons with the possibility of apparatusses in connection with different milieus, as from the point of view of small molecules, as well as, with the case of micellar or core particles, and SDS.

From the experimental point of view, Table 1 provides an example also of difficulties with which the explanations begin what, is pure, what is stable,how to determine exact statistical calculations, what is better:r^2 nearer to 1, or a lower background, and that the experients and experiences are very important. Small change is the coefficients of linear regression coefficients connected to linewidth, what is related to D explanations.

REFERENCES

1. J. J. Gotlieb, S. A. Darinskij, J. E. Svetlov, Fizičeskaja kinetika makromolekul, Himija, Leningrad 1986.
2. F. Rochen, P. Pieranski, La recherche, 17, 312, 1986.
3. Kerker M.: Light Scattering and other electromagnetic radiations, N. Holl. Amsterdam 76.
4. M. Srećković: Teza, Beograd 1979.
5. M. Srećković, M. Drifford, J. P. Dalibez, to be publish; M. Srećković and oth. Trends in Quantum Electronics, Bukarest, 1985„; M. Srećković, Drifford M., int. publ. CEA 1980.
6. Hantz E., Lai A., Tailander P., Tivant P., Drifford M., Deffer J., Biochimie, 63, 891, 1981.
7. M. Srećković, M. Drifford, J. P. Dalibez, P. Osmokrović, YUKEM, Beograd, 1986.