

Report on project week project

Raman scattering of micellar and liquid crystalline solutions

Christian Wald

September 2003

Tutor: Dr. Holger Gibhardt
Eckold group, IPC, Universität Göttingen

Fellows: Isabell Heller and Adriana Textor

During the project week we prepared aqueous solutions of ionic surfactants and salt. Using Raman spectroscopy we studied the thermally induced transition from the micellar to the liquid crystalline state and measured the melting temperature as a function of the surfactant and salt concentrations.

Contents

1	Classical theory of Raman scattering	2
1.1	Raman scattering in solution	3
2	Aqueous solutions of ionic surfactants	3
2.1	Detection of crystallisation with Raman spectroscopy	4
3	Experiment: Raman scattering of TMAB solutions	4

1 Classical theory of Raman scattering

A full and quantitative theory of the Raman effect requires a quantum mechanical description. Nevertheless, the semiclassical description provides a good insight into the basic principles.

In this picture, the electron cloud of the scattering object (e.g. a molecule or a crystal) serves as an antenna, being periodically polarised by the incident light and in turn emitting secondary light as a Hertzian dipole. In more detail, the electrical field \underline{E} of the incident light induces a dipole moment $\underline{d} = \underline{\alpha} \underline{E}$, where $\underline{\alpha}$ denotes the polarisability of the scattering object.

The polarisability of the electron cloud depends on the relative positions of the nuclei, thus it is modulated by rotations and vibrations. For small deviations R from the equilibrium position¹ $\underline{\alpha}$ can be expanded in a series

$$\underline{\alpha} \approx \underline{\alpha}|_0 + \left. \frac{\partial \underline{\alpha}}{\partial R} \right|_0 \cdot R =: \underline{\alpha}_0 + \underline{\alpha}'_0 R$$

(For instance, in the case of a two-atomic molecule, the natural choice for R is the distance between the two nuclei minus the equilibrium distance.)

Upon molecular vibration,

$$R = R_0 \cos(\omega_v t + \varphi_0)$$

and therefore

$$\underline{\alpha} \approx \underline{\alpha}_0 + \underline{\alpha}'_0 R_0 \cos(\omega_v t + \varphi_0)$$

Hence, an incident electromagnetic wave

$$\underline{E}(t) = \underline{E}_0 \cos(\omega_l t)$$

induces a dipole moment

$$\begin{aligned} \underline{d}(t) &\approx \underline{\alpha}_0 \underline{E}_0 \cos(\omega_l t) + \underline{\alpha}'_0 \underline{E}_0 R_0 \cos(\omega_l t) \cos(\omega_v t + \varphi_0) \\ &= \underline{\alpha}_0 \underline{E}_0 \cos(\omega_l t) + \underline{\alpha}'_0 \underline{E}_0 R_0 c_- \cos((\omega_l - \omega_v)t) + \underline{\alpha}'_0 \underline{E}_0 R_0 c_+ \cos((\omega_l + \omega_v)t) \end{aligned} \quad (1)$$

where $c_{\pm} = \frac{\cos \varphi \pm \sin \varphi}{2}$. The first term in (1) (frequency unchanged) represents Rayleigh scattering, whereas the second and third term represent first order Raman scattering with energy loss and gain, called *stokes* and *anti-stokes* lines, respectively. Expansion of $\underline{\alpha}$ to higher order induces (weaker) higher order Raman terms with frequencies $\omega_l \pm 2\omega_v$, $\omega_l \pm 3\omega_v$ etc.

(In a quantum mechanical picture, the stokes process is the excitation of a vibrational or rotational degree of freedom by one or multiple quanta. The energy is supplied by the absorption of a photon and the subsequent emission of a secondary one with slightly lower frequency. The stokes process is the analogous relaxation process.)

The intensity of the scattered light is proportional to the projection of \underline{d} onto the direction of polarisation of the outgoing light,

$$I_{out} = n_{out} \underline{R} n_{in}$$

¹In general, R is a multidimensional vector

where $\underline{n}_{in,out}$ denote the polarisations of incident and outgoing light. The Raman tensor \underline{R} is essentially the derivative of the polarisability in the “direction” of the vibration or rotation and thus dependent on the mode taken into consideration. Remarkably, the intensity does not depend on the directions of the incident and outgoing light (apart from the fact that they restrict the range of possible polarisations).

The Raman tensors can be classified according to their symmetry. The symmetry follows both, the symmetry of the scattering electron cloud and the symmetry of the vibration or rotation involved. This determines whether a given mode is Raman active or not. The symmetry properties of Raman tensors are tabulated for many individual molecule and crystal geometries.

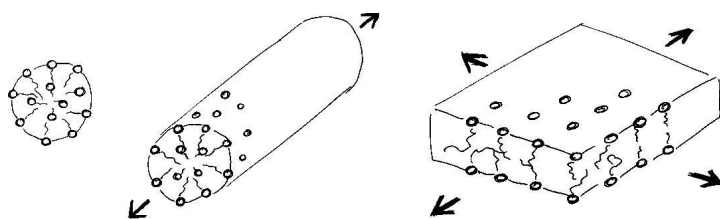
1.1 Raman scattering in solution

In general the orientations of molecules in solution is completely random and the solution is isotropic, the only reference is the polarisation of the incident light. A Raman scattering experiment measures an averaged Raman tensor characterised by only two numbers, the so called *mean value* $\bar{R} := \frac{1}{3}(R_{11} + R_{22} + R_{33})$ and the *anisotropy* $\gamma := (R_{11} - R_{22})^2 + (R_{22} - R_{33})^2 + (R_{33} - R_{11})^2 + 6(R_{12}^2 + R_{23}^2 + R_{31}^2)$, where \underline{R} denotes the Raman tensor of a single molecule. The intensity of the so-called “isotropic scattering” where incident and scattered light have parallel polarisations is proportional to $\overline{R_{ii}^2} := \bar{\alpha}^2 + \gamma^2/45$. The intensity of the “anisotropically scattered” part with polarisation perpendicular to the incident light is proportional to $\overline{R_{i \neq j}^2} := \gamma^2/60$.

A typical measurand is the ratio of both contributions, the *depolarisation ratio*.

2 Aqueous solutions of ionic surfactants

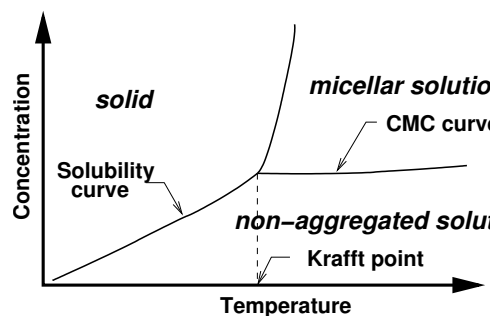
In an aqueous solution, contacts between the solvent and the lipophilic parts of surfactant molecules are energetically unfavourable. Hence, a solution of single isolated molecules is rather disadvantageous. The surfactant molecules can lower their energy by swimming at the water surface, their tails directed upwards or by aggregation in micelles, the tails pointing inwards, the hydrophilic heads exposed to the solvent.



As micelles are neither hollow nor filled with water, the radius of spherical micelles is determined by the length of the surfactant molecules; growth requires deformation. A rodlike micelle can grow in one dimension, two dimensions become available for discoidal ones.

This way, the energy is further decreased by lowering the curvature of the surfactant monolayers forming its surface.

On the other hand, each step of lowering the energy brings about a loss of entropy. Therefore the predominant state depends on temperature and concentration. At low concentration and high temperature, the surfactant will be mainly dissolved as single molecules. On increasing concentration or decreasing temperature, spherical micelles will predominate. (The according point, not sharply defined, is called *critical micelle concentration* or *cmc* in short.) Subsequently, the micelles will turn into rods and later discs (which can again aggregate). In large micelles the surfactant molecules are arranged like on a lattice; the solution of them is said to be liquid crystalline.



Ionic surfactants in solution partly dissociate and become charged. Electrostatic repulsion counteracts aggregation. Addition of salt pushes the equilibrium towards undissociated surfactants and screens the Coulomb interaction, hence salt promotes “liquid crystallisation”.

2.1 Detection of crystallisation with Raman spectroscopy

The vibrational modes of the lipophilic tails are strongly affected by their environment. For the surfactant studied in our experiment, the antisymmetric CH_2 stretching vibration is suppressed by permanent collisions with the surrounding water molecules, except in the liquid crystalline state. In contrast, the symmetric mode is always present. The change in the intensity ratio of the corresponding Raman lines enables the detection of the transition from small micelles to liquid crystals. In addition, due to the length scales of the growing aggregates, the solution becomes turbid on crystallisation, causing a decrease in the overall Raman scattering intensity.

3 Experiment: Raman scattering of TMAB solutions

During the project week we prepared aqueous solutions of tetramethylammonium bromide (chiefly 0.4m) with different concentrations (between 0m and 2m) of sodium bromide added. The positive effect of salt on the aggregation of surfactants was immediately observable in an increased viscosity.

The solutions were filled into cuvettes at normal pressure and placed in a Raman spectrometer (backscattering geometry). Starting from temperatures above the melting point, the temperature was kept constant for a certain time to observe the Raman spectrum of the solution (and, with the naked eye, its turbidity). This procedure was repeated with lower and lower temperatures until the spectrum (or the turbidity) indicated crystallisation. To determine the melting point more accurately, the solution was heated up noticeably above the melting point to accelerate melting and then cooled to the desired temperature.

Especially high salt concentrations and temperatures slightly below the melting point involved large time scales (from tenth of minutes to tenths of hours). Time turned out to be too

short to measure the melting curve (melting temperature as a function of the salt concentration) accurately.

Nevertheless, the project offered the opportunity to experience the behaviour of surfactants practically and to learn more about the Raman effect and the method of Raman scattering.

Acknowledgements

I would like to thank the Eckold group for offering the project including the opportunity to use their spectrometer. In particular thanks to Holger Gibhardt who helped us and answered our questions anytime and even set the IPC hike aside for our project.