

## CELL-LESS MEASUREMENTS OF INFRARED ABSORPTION SPECTRA OF AQUEOUS SUSPENSIONS AND SOLUTIONS

L. BERÁK, J. MORAVEC and J. MÜNICH

*Institute of Nuclear Research,  
Prague-Řež*

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A simple through-flow device enabling measurements of infrared absorption spectra of solutions and suspensions in the form of a dynamic plane film of free liquid or suspension in a spindle-shaped frame made of a wettable material was developed and tested experimentally. The  $\nu_3(\text{SO}_4^{2-})$  absorption bands of aqueous suspensions of barium sulfate in the range of  $1300\text{--}1000\text{ cm}^{-1}$  were studied.

In relation to the preparation of selective sorbents for radiostrontium, we have studied the infrared spectra of mixed crystals of calcium sulfate and barium sulfate<sup>1-3</sup>. During further work, it appeared necessary to measure infrared spectra of aqueous suspensions of nascent precipitates of barium sulfate, prepared by continuous precipitation of sodium sulfate solutions with barium chloride. We have followed the number and relative intensities of the bands as well as the frequencies of their maxima.

The infrared spectrum of water displays very broad and intense absorption bands, therefore water is not very convenient as a solvent or suspending medium for infrared spectroscopy (the spectra can be measured only in limited wavenumber ranges using extremely thin sample layers). Beside the strong absorption of radiation, a further disadvantage of water consists in its reacting with most of the materials used as cell windows. Materials dissolved by water to a less extent exhibit either a limited transparency for infrared radiation (LiF) or considerable losses of energy due to the reflection of incident radiation (KRS-5, *i.e.* a TlI/TlBr mixed crystal). In order to avoid these difficulties, increased moreover by the need of measuring spectra in the through-flow arrangement in a constant, often very short time distance from the moment of precipitation, we measured the infrared spectra of aqueous suspensions or solutions in the form of a dynamic plane film.

### EXPERIMENTAL

The suspension of barium sulfate was formed continuously by mixing 0.5M solution of sodium sulfate and barium chloride in a through-flow reactor or in a special mixer, placed near the cell compartment of an infrared spectrometer UR 10 (Zeiss, Jena). The suspension of nascent pre-

precipitate formed (58 g  $\text{BaSO}_4/1$ ) was transported (the device for the formation and transportation of the suspension is identical with that used for X-ray studies<sup>4</sup>) into the spectrometer cell compartment, where a through-flow frame made of a wettable material was placed vertically in the sample beam. The duration of the sample transport could be controlled from fractions of seconds up to any time required. This made it possible to maintain approximately the predetermined history of the sample measured for the whole time of measurement.

For the systems followed, the best results were achieved with a spindle-shaped frame (Fig. 1) made of a copper wire, 1 mm thick, soldered with tin to the inner side of the copper supply tube (in the sectional view in Fig. 1). The frame allows a continuous impactless inlet and outlet of the liquid or suspension. The liquid measured flows through the frame in the direction downwards. On entering the frame, the liquid forms a plane film, which is continuously regenerated by the passage of the sample. In order to yield a good spectrum, the film must have constant optical properties, particularly its thickness must be constant and, regarding the strong absorption of radiation by water, as low as possible. A film possessing such properties was formed at the flow rate approximately 2 ml/min, when a frame with the dimensions given in Fig. 1 was used. For the spectral measurements, the most suitable appears the area lying closely below the point of intersection of the longitudinal and transversal axes of the frame.

The higher background of the spectrum, accounted for by the absorption by water, was compensated by a mechanical reference beam attenuator. The spectra of aqueous suspensions of barium



FIG. 1

The Through-Flow Spindle-Shaped Frame

The dimensions of the frame: 70–80 and 30–35 mm. ↓ Direction of flow of the liquid or suspension. The area crossed by the infrared radiation beam is indicated by a dotted line.

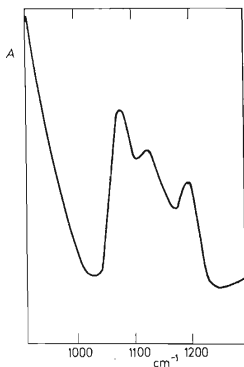


FIG. 2

IR Absorption Spectrum of a Nascent Suspension of Barium Sulfate in Water

The precipitate was formed from a low (10% mol.) excess of  $\text{BaCl}_2$ .

sulfate were measured in the range of the  $\nu_3(\text{SO}_4^{2-})$  vibrations, *i.e.* between  $1300\text{--}1000\text{ cm}^{-1}$  (NaCl prism). As a matter of fact, the band of the bending vibration  $\nu_4$  near  $600\text{ cm}^{-1}$  has a lower half band width than of the stretching vibration  $\nu_3$  and is more sensitive towards structural changes of the sample<sup>1-3</sup>; the water absorption is, however, too high to allow any measurements in the  $600\text{ cm}^{-1}$  range. The following parameters were set on the spectrometer: spectral slit width c.  $5\text{ cm}^{-1}$ , scanning speed  $32\text{ cm}^{-1}/\text{min}$ . In the same wavenumber region we measured also aqueous solutions of  $\text{NaClO}_4$  (5% wt.) and  $\text{Na}_2\text{SO}_4$  (2.5% wt.) and also proved the assumption, following from theory, that for pure water a stable large plane film cannot be prepared. In order to stabilize the dynamic membranes of solutions we added a surface-active agent (100 p.p.m.). The stability of films of nascent suspensions was sufficient without any addition of surface-active compounds, the latter were therefore not added to the suspensions.

## RESULTS AND DISCUSSION

Stability of a film of a liquid, containing surface-active compounds of the type of wetting agents, is governed by the same factors as that of hydrofobic colloids<sup>5</sup>. In the first approximation the equilibrium thickness of the film can be assumed to be determined by repulsive forces between the electric double layers, acting in favour of increasing the film thickness, and attractive van-der-Waals forces, acting in the opposite sense. These forces are summed with other occurring pressures, *e.g.* the pressures accounted for by sucking resulting from the withdrawal of liquid by gravitation or to the thicker parts of the film. The film thickness also decreases due to the increase of the concentration of dissolved salts which cause the compression of the electric double layer. It can be therefore assumed that the film will be most thin, homogeneous, and stationary in the region of the center of the frame, where the film is formed. The kinetic energy of the streaming liquid in our arrangement causes that area to be displaced slightly downwards, in the direction of the liquid flow. The mass of the liquid moving through the frame downwards is distributed in the area of the frame according to the hydrodynamic resistance, which is proportional to the pressure occurring inside the film. Therefore, most of the mass passes close to the frame and least of it in the center. The existence of reverse streaming was apparent in the case of suspensions. The time of aging of the suspension crossing the beam of infrared radiation in the area of rest can be therefore determined only approximately.

The spectrum of an aqueous suspension of nascent precipitate of barium sulfate, obtained by measuring the dynamic plane film of the free suspension, is given in Fig. 2. As apparent, the spectrum corresponds completely to the results obtained by measuring solid samples in a Nujol mull or in a KBr disk<sup>1</sup>. Spectra of aqueous solutions of  $\text{NaClO}_4$  and  $\text{Na}_2\text{SO}_4$ , exhibited essentially the absorption curves of the corresponding solids.

The method described could be probably used also for measurements of infrared spectra of other systems with low-volatile solvents, if they are capable of forming a sufficiently stable plane film of the free liquid or suspension. Heavy water can be also used as a solvent or suspension medium in order to extend the spectral region

for aqueous systems, since its absorption maxima appear in other regions than those of light water. The use of a spectrometer with a higher signal-to-noise ratio in the ranges of low transmittances would also improve the results obtained and enable measurements to be carried out in a wider spectral region.

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