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Novel Method of Fluid-Phase Spectroscopy

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Abstract. In order to measure UV/VIS spectra and run small scale reactions under supercritical conditions an autoclave was built using the technique of an immersion-cell UV/VIS spectrophotometer which allows the use of just one optical window and a reflection unit inside the pressure chamber. The discussed system is easily installed into any existing autoclave and offers maximum security due to complete separation of measuring and pressure unit. The system was constructed to observe solvatochromic dyes in the supercritical phase in dependence of pressure and temperature.

1. Introduction

Highly compressible fluid mixtures in the critical and supercritical region have been of considerable research interest in recent years. A remarkable amount of reaction methods have been successfully developed using this new media. The potential advantages of using a supercritical fluid reaction medium are that it may be possible to increase the selectivity of a reaction while maintaining high conversions, to dissolve reactants and catalyst in a single fluid phase so that the reaction occurs homogeneously, and to improve or greatly facilitate the separation of product species from reactants, catalyst, and unwanted by-products by utilizing the phase behavior exhibited by the mixture in its critical region. Also, reaction rates may be enhanced while operating in the critical region of the mixture due to a favorable pressure dependence of the reaction rate constant as well as the unusual volumetric behavior of heavy solutes solubilized in a supercritical solvent [1].

We describe here an autoclave to contain supercritical fluids at pressures up to 1000 bar and temperatures up to 150° (limit given by the temperature range of the temperature probe) that is equipped with an optical window for the transmission of UV/VIS light. The system was adapted to fit a UV/VIS spectrophotometer (*Otsuka MCPD 1100*) with an optical immersion cell. It has been in use in our laboratory for UV/VIS spectroscopic studies of supercritical solutions for over two years. The autoclave design sought to accomplish the following: the window unit is easily installed into any type of pressure vessel, the pressurized system can be fully isolated from the measuring unit allowing maximum security, only one optical window is necessary compared to conventional two-window transmission systems [2], variation of the optical pathlength is possible under pressure due to an adjustable mirror holder.

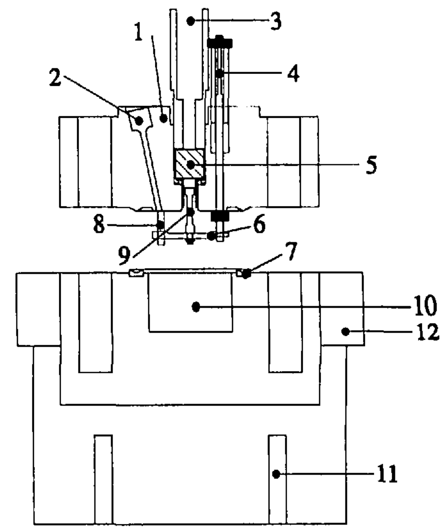

Fig. 1. *Cross-sectional view of the autoclave in a vertical plane through the center.* 1 autoclave lid, 2 outlet, 3 UV/VIS quartz-fibre-probe holder, 4 mirror adjustment, 5 sapphire window, 6 mirror holder, 7 copper gasket, 8 temperature probe container, 9 stainless steel mirror, 10 reaction vessel, 11 heating elements, 12 cooling element.

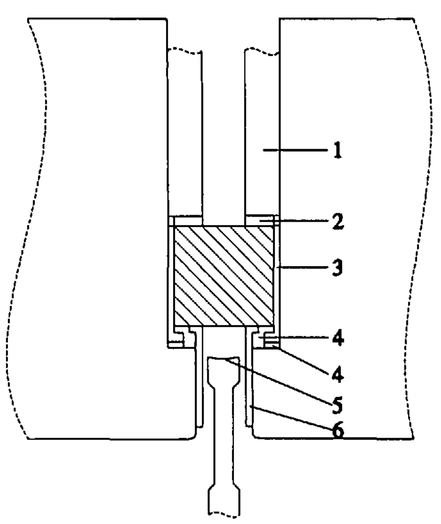

Fig. 2. *Expanded view of the window/mirror section.* 1 UV/VIS quartz-fibre-probe holder, 2 copper gasket, 3 stainless steel tube surrounding sapphire window, 4 *Teflon* gasket, 5 mirror, 6 stainless steel tube leading down the shaft in the center of the lid.

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2. Autoclave Design

The autoclave (*Fig. 1*) was designed and built by *W. Eisele* in the mechanical workshop of the Organisch-chemisches Institut of the University of Zurich. The system contains two parts. The lid with the built-in optical *Poulter*-type sapphire window (width 16 mm, height 16 mm) [3], the adjustable stainless steel mirror (ø 5 mm) with concave polished top (radius 25 mm) for beam reflection, the temperature probe (Pt 100) with container for measurement of reaction vessel temperature, the inlet, the outlet and the pressure measuring device (*Burster* Präzisionsmesstechnik Gernsbach, *type 81530*). The second part consists of a 60-ml-reaction vessel with heating (4 resistance heating rods) and cooling elements (water-cooled aluminum housing surrounding autoclave base) and temperature probe for heating regulation. The temperature is regulated by a controller (*Tecon 501*, *Tecon AG*) with an accuracy of ± 0.1°. The body was machined from stainless steel (*type 304*) and the UV/VIS probe holder is made of steel (*type VCN 150*). The inlet in the lid consists of a two-way stainless steel valve (*Nova Werke AG*) connected to a high pressure compressor (*Andreas Hofer Hochdrucktechnik GmbH*, model *MKZ 80-100*). The outlet consists of a two-way stainless-steel-valve with a stainless-steel tube (ø 2 mm) attached to it.

The autoclave requires window to metal seals and metal to metal seals. The window to metal seal between the UV/VIS probe holder and the sapphire window is a copper gasket (*Fig. 2*). It was heated to a glow to achieve a high degree of flexibility so as to compensate for any unevenness on the surface of the window or the probe holder. The window is sealed with a *Teflon* gasket against pressure. To stabilize the *Teflon* seal against deformation two steel tubes were inserted. One around the window and one leading from the sapphire window down through the *Teflon* gasket and the shaft in the center of the lid. The steel tubes were made to fit both the sapphire window and autoclave shaft still allowing thermal expansion. The lid and the vessel are held together by 8 steel (*type 8.G8*) bolts, which are torqued to 215 Nm each. Sapphire is a chemically resistant window material with good optical transparency in the range of 200–5000 nm and it can withstand pressures up to 10 kbar [2].

After a reaction the supercritical phase is expanded through the steel tube which ends in a vessel filled with glass beads. The autoclave and the beads are then washed with the appropriate solvent to collect the reaction mixture.

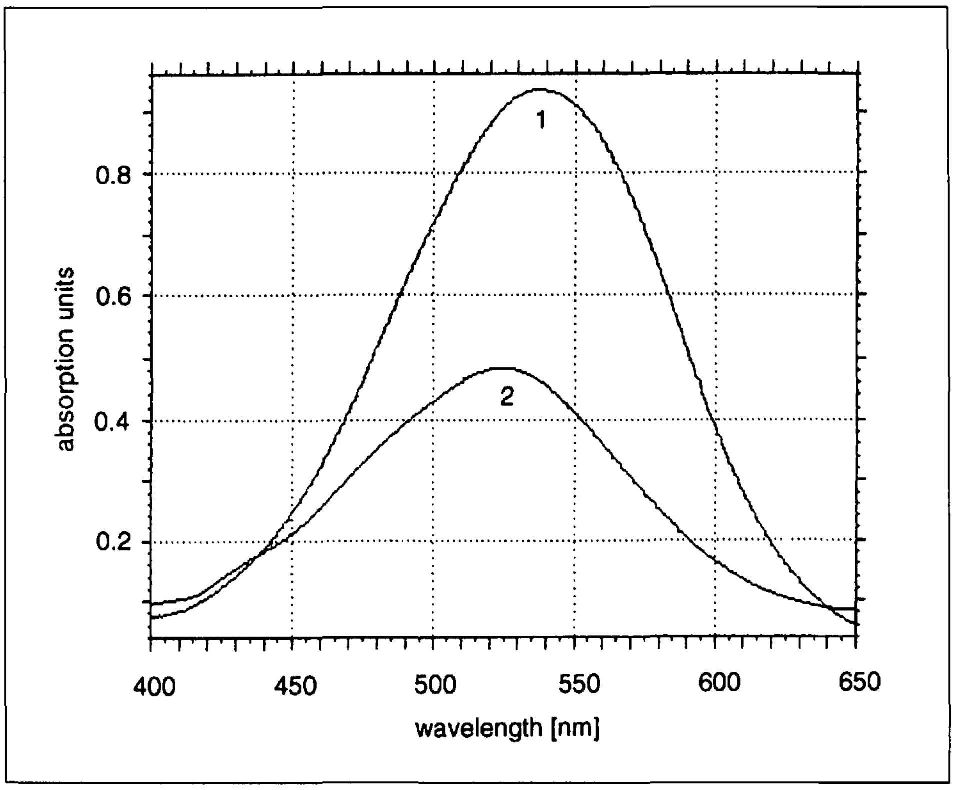

Fig. 3. *UV/VIS Spectrum of Phenol Blue in sc-CO_2.* 1: T = 60°, p = 864 bar, λ_{max} = 536.6 nm; 2: T = 60°, p = 93 bar, λ_{max} = 524.5 nm.

3. Measurement Procedure

UV measurements of compounds are usually performed in double beam UV/VIS spectrophotometers whereby a solution of the compound is measured against the solvent. The solution and the solvent are each filled into quartz-cuvettes. The cuvette containing the solvent is placed into the reference beam and the cuvette containing the solution into the measurement beam of the spectrophotometer.

Using an immersion-cell UV/VIS spectrophotometer measurements can be performed directly in a solution without having to transfer into a separate measuring flask. The probe is first placed into the solvent, the background measured, then into the solution where the spectrum can be registered sequentially. The UV/VIS light sources provide a light beam which is led to the solution by the center section of an optical quartz-fibre bundle. The light beam penetrates the solution and is reflected by a mirror, which is built into the probe, back through the solution onto the peripheral section of the quartz-fibre bundle, which leads the measurement beam back to the spectrophotometer where analysis follows.

In order to measure a spectrum under very high pressure using the method of an immersion cell, the described autoclave with a sapphire window (which is UV/VIS-penetrable) was built. The light is led by the inner bundle of the quartz fibres under normal pressure conditions to the sapphire window where it can penetrate and enter the supercritical solution. The beam is reflected on a mirror inside the pressure vessel back through the solution and the sapphire window on to the peripheral quartz fibres of the immersion-cell probe which leads the measurement beam back to the spectrophotometer to be analyzed. The distance between mirror and sapphire window can be adjusted from 1 to 20 mm. Standard UV/VIS spectroscopic measurements are usually performed in cuvettes with 10 mm width. This corresponds to 5 mm pathlength between mirror and window in the autoclave.

To measure a UV/VIS spectrum, the autoclave must first be heated to the desired temperature, then flushed and filled with the fluid at the desired pressure. After measuring the background, the autoclave is emptied, the compound to be measured loaded, then filled again under the same conditions as for background measurement. Two measurements of Phenol Blue in sc-CO_2 are shown in *Fig. 3*.

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