6.5. An Analytical Method to Determine Concentration of Ethyl Chloroacetate.

To find a final product distribution in the reaction system (6.1) one has to know precisely initial amounts of all test reactants (HCl, NaOH and $CH_2ClCOOC_2H_5$) and either the final amount of ester or acid in the post-reaction mixture.

High pressure liquid chromatography was chosen as an analytical method allowing to determine both initial and final concentration of ethyl chloroacetate in the reactor content.

A reversed phase chromatography was performed on Waters Nova-Pak C-18 steel cartridge column. The column was 15 cm long and its diameter was equal to 3.9mm. The diameter of packing particles was equal to 4 μm. An eluent was composed of analytically pure water and acetonitrile (Merck LiChrosolv) in proportion H_2O:CH_3CN=60:40. Rheodyne valve with 50 μl loop was used to inject analyzed samples into the column. Composition of the solution eluted from the column was analyzed by means of Waters multi-wave UV detector - type 486. Wavelength chosen in measurements was equal to 220 nm. According to Pryde and Gilbert [82] absorption maxima for aliphatic esters are placed between 200nm and 210nm. However, when the wavelength was set at 210 nm or below this value the viscosity increasing agent (polyethylenepolypropylene glycol) also contained in the analyzed samples was disturbing a baseline and it was impossible to precisely detect starts and ends of peaks.

Typical retention times for ethyl acetate were close to 6 minutes, whereas for ethyl chloroacetate to 8.5 minutes for eluent flow equal to 0.35 cm^3/min. Figure 6.10 shows a typical chromatogram.

Concentration of ethyl chloroacetate was determined from the calibration curve:

$$c_{ester}[ppm] = -0.2938 + 104.68 \cdot \frac{A_{ester}}{A_{std}} - 2.7482 \cdot \left(\frac{A_{ester}}{A_{std}}\right)^2, \qquad \textbf{(6.19)}$$

where $\mathbf{A_{ester}}$ and $\mathbf{A_{std}}$ are areas under peaks of ethyl chloroacetate and an internal standard respectively. The concentration of the internal standard, in this case ethyl acetate, was the same in each analyzed sample and equal to 146 ppm.

The described above analytical method allows to determine ethyl chloroacetate concentration with 1.5 % error provided that the polymer content in the analyzed solution is not higher than 2 weight percents. The lowest concentration of $CH_2ClCOOC_2H_5$ which can still be determined with this accuracy is about 10 ppm.

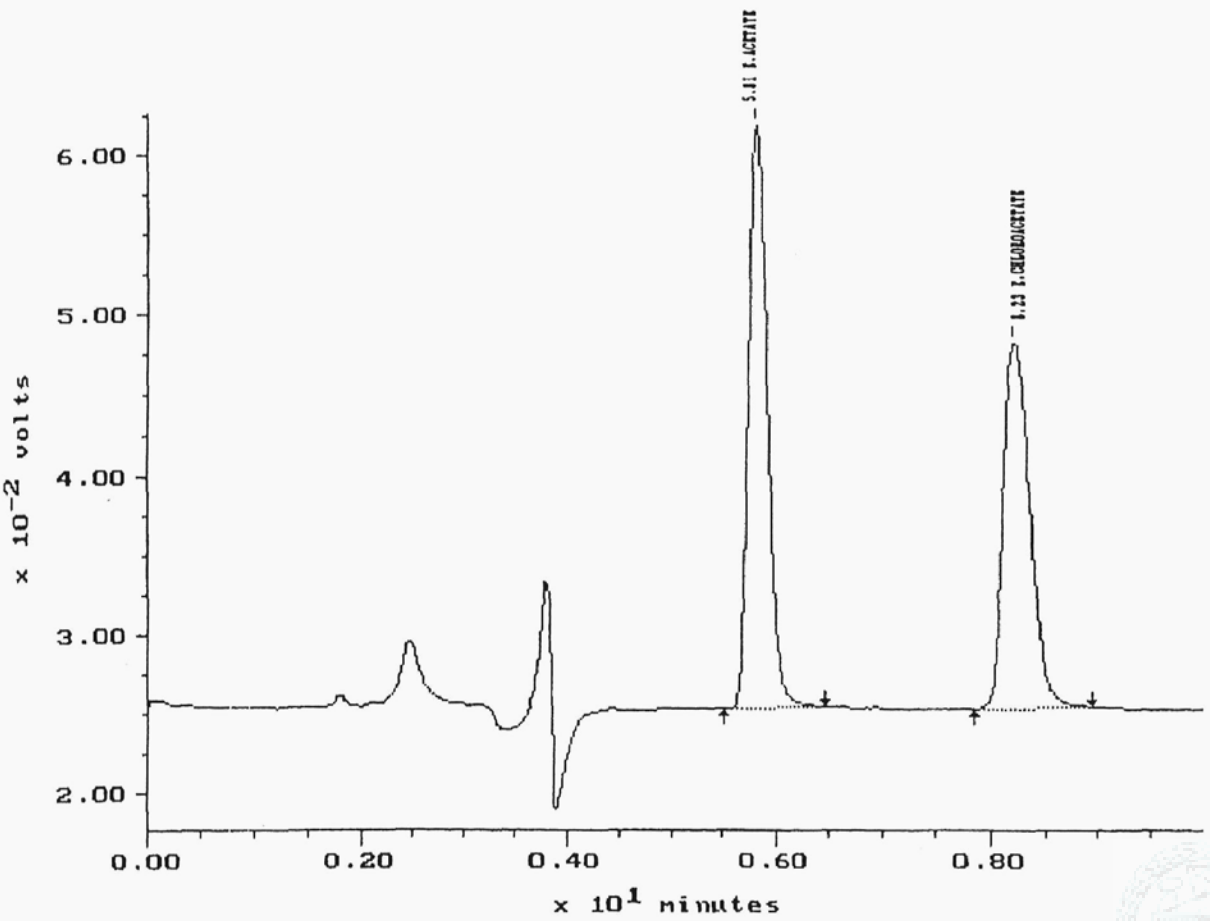

Figure 6.10. A typical chromatogram of sample containing 146 ppm of ethyl acetate (first peak) and 90 ppm of ethyl chloroacetate (second peak).