

Figure 6.4. Limiting NaOH concentrations in aqueous solutions of polyethylene-polypropylene glycol at 25°C.

a few percents different from the values obtained for solutions without NaOH but containing the same amount of the polymer.

Density, viscosity of the solutions were thus measured before and after each experiment. pH-titrations of aqueous solutions of the viscosity increasing agent containing up to 1 mol/dm³ of either HCl or NaOH showed that falls in hydrogen and hydroxide ions concentration are practically undetectable after 24 hours since preparation of solution.

Similarly as in the case of HCl and NaOH, concentration of ethyl chloroacetate in aqueous solutions of the polymer is slightly decreased after 24 hours. Additionally, it was found that polyethylenepolypropylene glycol considerably increases solubility of ethyl chloroacetate as well as solubility of other aliphatic esters in water.

6.2.5. Alkalinity of Aqueous Solutions.

Aqueous solutions of the viscosity increasing agent have alkaline reaction. pH-titration of solution containing 9.1 weight percents of the polymer was performed to determine alkalinity of this substance. Titration was conducted by means of 0.1N HCl, whereas pH values were determined with a standard, combined, pH electrode. Figure 6.5 shows titration curve obtained in this test. An equilibrium point can be found close to pH=7, which confirms the presence of 9.7 mmol of base per kilogram of the polymer. A theoretical pH-titration

curve, computed for strong base, as plotted in figure 6.5, is steeper near equilibrium point. The discrepancy between the experimental and the theoretical curve indicates a slight buffering action of the investigated polymer, which should not interfere with the course of the test reactions.

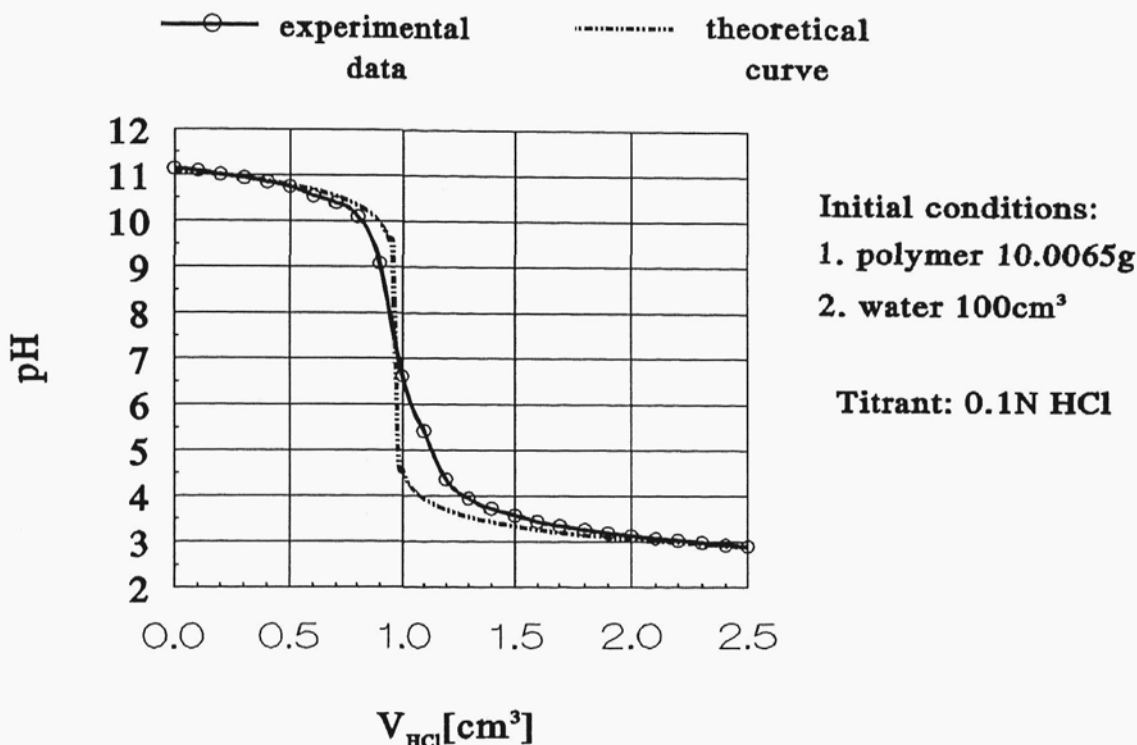


Figure 6.5. PH-titration of aqueous solution of the polymer.

Alkaline reaction of the polymer solutions can be caused by alkaline impurities, e.g. remainings of a polymerization catalyst; polymerization reactions leading to formation of polyethylenepolypropylene glycol may be catalyzed by alkaline compounds such as potassium hydroxide [79].

To identify substance causing alkaline reaction of the polymer solutions three type of analyses were performed: anion, monovalent cation and divalent cation liquid chromatography. Samples of the viscosity increasing agent diluted in redistilled water ($w_p=0.2\div2\%$) were chromatographed by means of Waters HPLC equipment - for details see table 6.V. Ions eluted from IC-Pak columns were analyzed by Waters conductometric detector - type 431.

No anions and no divalent cations were detected in analyzed samples. Only in chromatography of monovalent cations were the results positive. Table 6.VI presents these results.

As it can be seen, the average amount of potassium cations equals 12.2 mmol per kg of the polymer, whereas the average amount of sodium cations equals 0.5 mmol/kg. The concentration of ammonium cations in the analyzed samples is not correlated with the polymer

Table 6.V. Description of ion chromatographic analyses.

analysis type	column	pre-column	eluent		
			composition	pH	flow
anion	IC-Pak A	none	sodium gluconate, boric acid, sodium tetraborate decahydrate, n-butanol, acetonitrile	8.5	1.2[cm ³ /min]
monovalent cations	IC-Pak C	IC-Pak Guard	0.05mM EDTA, 2mM HNO ₃	2.7	
divalent cations	IC-Pak C	none	0.5mM EDA, 1mM HNO ₃	6.0	

content. The above results indicate presence of potassium hydroxide in the polymer in the quantity similar to that detected earlier by pH-titration. Thus, to avoid unwanted hydrolysis of ethyl chloroacetate during dissolving it in aqueous solution of the polymer, one should first neutralize alkaline impurities with hydrochloric acid.

Table 6.VI. Monovalent cations in the polymer.

w _p [%]	Na ⁺ [ppm]	NH ₄ ⁺ [ppm]	K ⁺ [ppm]
0.253	0.00	0.05	1.22
2.55	0.29	0.05	12.12

6.3. Measurements of Coefficients of Molecular Diffusivity in Aqueous Solutions of Polyethylenepolypropylene Glycol.

Coefficients of molecular diffusivity of the test reactants: HCl, NaOH and CH₂ClCOOC₂H₅ were measured in aqueous solutions of the viscosity increasing agent. Knowledge of these coefficients is inevitable for modelling laminar micromixing. As it was shown in chapter 3, molecular diffusion is an important elementary process governing micromixing in very viscous liquids.

Measurements were conducted in a cylindrical chamber 8 cm long and with diameter equal to 2 cm. The chamber consisted of two equal parts, each 4 cm long, which could be separated, independently filled up with liquid, joined together, drawn aside after a desired period of time and then independently emptied. In order to avoid thermal convection and consequently disturbance of the liquid-liquid interface, the chamber was thermostated one hour before