

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

putting its parts together and initiating molecular diffusion. The chamber was kept vertically (horizontal liquid-liquid interface) during the experiments and all rapid movements were avoided while handling it. The solution of the substance whose molecular diffusivity was to be determined, was always placed in the lower part of the chamber and polyethylenepolypropylene glycol content in this part was set slightly higher than in the upper one - see tables 6.VII÷6.IX. Disassembling and assembling of the chamber parts were done by horizontal movement of the upper half, pushed slowly by means of a hand wheel. Initial trials conducted with aqueous solutions of hydrochloric acid and for negligible diffusion times showed that the described above procedure was sufficient to avoid accidental convective mixing.

The polymer solutions were always neutralized with 0.1N HCl before adding to them a diffusive substance. The experiments were conducted at 18°C and 25°C.

After each experiment mean concentrations of HCl and NaOH in both chamber parts were determined by conductometric titration. When experiments were conducted with ethyl chloroacetate, concentrations of ester were determined by means of high pressure liquid chromatography, as described in point 5. Diffusion coefficient was then calculated from the following expression

$$\frac{\bar{c}_u}{\bar{c}_u + \bar{c}_l} = \frac{1}{2} - \frac{4}{\pi^2} \cdot \sum_{k=0}^{\infty} \frac{1}{(2 \cdot k + 1)^2} \cdot \exp \left[- (2 \cdot k + 1)^2 \cdot \pi^2 \cdot \frac{D \cdot t}{L^2} \right], \quad (6.11)$$

where \bar{c}_u and \bar{c}_l are mean concentrations of a diffusing substance in upper and lower part of the chamber respectively, and L is the total length of the chamber. Equation (6.11) was obtained by integration of the solution of differential material balance in the diffusion chamber

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \quad (6.12a)$$

with the following boundary and initial conditions:

$$\left. \frac{\partial c}{\partial x} \right|_{x=0} = \left. \frac{\partial c}{\partial x} \right|_{x=L} = 0, \quad (6.12b)$$

$$c(x, t=0) = \begin{cases} c_0 & \text{if } 0 \leq x < L/2 & \text{- lower part} \\ 0 & \text{if } L/2 \leq x \leq L & \text{- upper part} \end{cases} \quad (6.12c)$$

The analytical solution of equations (6.12) is given by Carslaw and Jaeger [65, p.101]

Tables 6.VIIab, 6.VIIIab and 6.IXab present compositions of solutions in the chamber, diffusion times and diffusion coefficients recalculated from equation (6.11) for hydrochloric acid, sodium hydroxide and ethyl chloroacetate.

Table 6.VIIa. Molecular diffusivity of hydrochloric acid in aqueous solutions of the polymer at 18°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	29.90	1.47	85800	13.0
	lower	30.10	8.39		
2	upper	49.90	1.84	225000	8.79
	lower	50.10	7.43		

Table 6.VIIb. Molecular diffusivity of hydrochloric acid in aqueous solutions of the polymer at 25°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	0.0	2.29	69180	38.0
	lower	0.0	7.71		
2	upper	29.82	1.40	71520	13.9
	lower	29.88	8.54		
3	upper	39.96	1.19	73440	9.69
	lower	40.00	8.80		
4	upper	50.37	1.37	80730	11.4
	lower	50.73	8.77		
5	upper	60.40	1.25	95100	8.14
	lower	60.45	8.80		
6	upper	70.11	1.17	103500	6.58
	lower	70.35	8.88		
7	upper	80.14	0.85	103500	3.37
	lower	80.95	9.38		

Table 6.VIIIa. Molecular diffusivity of sodium hydroxide in aqueous solutions of the polymer at 18°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	39.90	1.32	169200	5.24
	lower	40.10	8.63		
2	upper	49.90	1.07	229020	2.69
	lower	50.10	8.58		

Table 6.VIIIb. Molecular diffusivity of sodium hydroxide in aqueous solutions of the polymer at 25°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	0.0	1.91	76200	24.1
	lower	0.0	8.09		
2	upper	29.50	1.33	72900	12.9
	lower	29.79	8.41		
3	upper	39.67	1.18	86400	6.78
	lower	40.03	9.73		
4	upper	49.73	0.87	103560	4.32
	lower	49.99	8.36		
5	upper	59.96	0.60	157800	1.40
	lower	60.29	8.44		
6	upper	69.79	0.51	163800	0.938
	lower	70.05	8.72		
7	upper	79.69	0.66	242040	0.775
	lower	80.18	10.09		

Table 6.IXa. Molecular diffusivity of ethyl chloroacetate in aqueous solutions of the polymer at 18°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	41.90	6.45	249300	1.07
	lower	42.10	82.3		

Table 6.IXb. Molecular diffusivity of ethyl chloroacetate in aqueous solutions of the polymer at 25°C.

exp. no.	chamber part	w _p [%]	final conc. [mmol/kg]	t [s]	D·10 ¹⁰ [m ² /s]
1	upper	0.0	11.1	68400	9.02
	lower	0.0	89.1		
2	upper	29.92	6.2	76524	2.50
	lower	30.15	94.4		
3	upper	39.89	5.1	84472	1.53
	lower	40.13	95.3		
4	upper	49.87	4.5	141900	0.728
	lower	50.26	94.6		
5	upper	60.22	3.3	167220	0.325
	lower	61.17	97.0		

Diffusion coefficients presented in tables 6.VII÷IX were also plotted in figures (6.6)÷(6.8) versus the viscosity calculated from expressions (6.5) for the average polymer content in the diffusion chamber. As it can be seen, in all cases there is almost a linear correlation between $\log_{10}D$ and $\log_{10}\mu$. Thus, the diffusivity of the test reactants in the polymer solutions and at temperatures ranging from 18°C to 25°C can be approximated by the following equations:

$$D_{HCl} = 8.48 \cdot 10^{-10} / \mu^{0.238}, \quad (6.13)$$

$$D_{NaOH} = 2.97 \cdot 10^{-10} / \mu^{0.622}, \quad (6.14)$$

$$D_{ester} = 0.609 \cdot 10^{-10} / \mu^{0.649}, \quad (6.15)$$

It should be noted at this point that Reid et al. [81, p.606] report similar correlations for calculating molecular diffusivity in very viscous liquids.

Diffusion coefficients obtained for pure water solutions remain in quite good agreement with the values calculated either from Nernst equation ($D_{\text{HCl}}=3.33 \cdot 10^{-9} \text{ m}^2/\text{s}$, $D_{\text{NaOH}}=2.13 \cdot 10^{-9} \text{ m}^2/\text{s}$) or from Wilke-Chang expression ($D_{\text{ester}}=0.928 \cdot 10^{-9} \text{ m}^2/\text{s}$); for details see appendix D. This proves that the measurement method was correct.

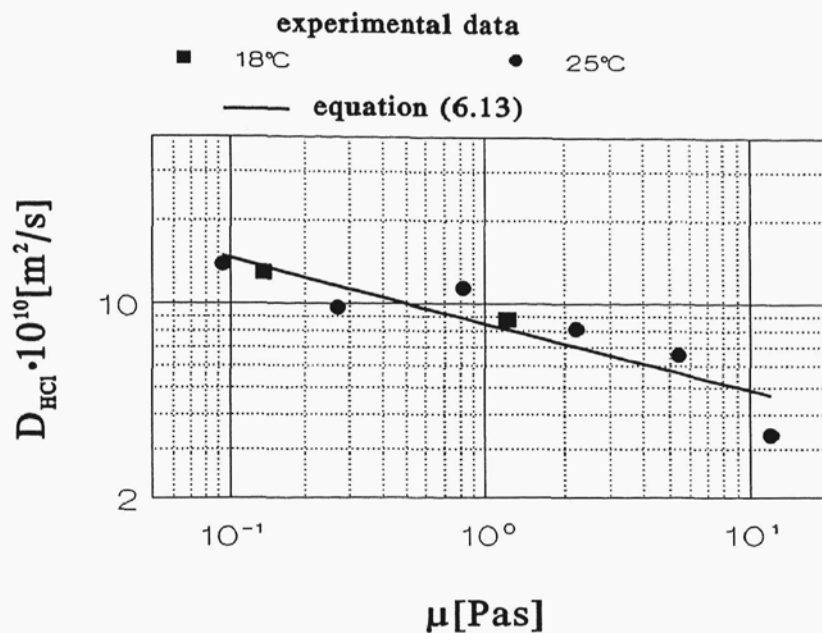


Figure 6.6. Molecular diffusivity of hydrochloric acid in aqueous solutions of the polymer.

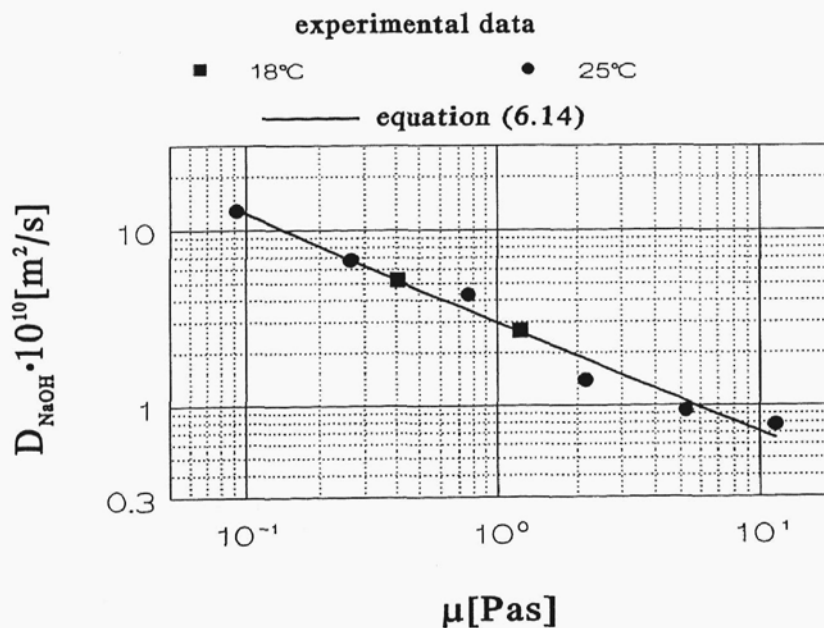


Figure 6.7. Molecular diffusivity of sodium hydroxide in aqueous solutions of the polymer.

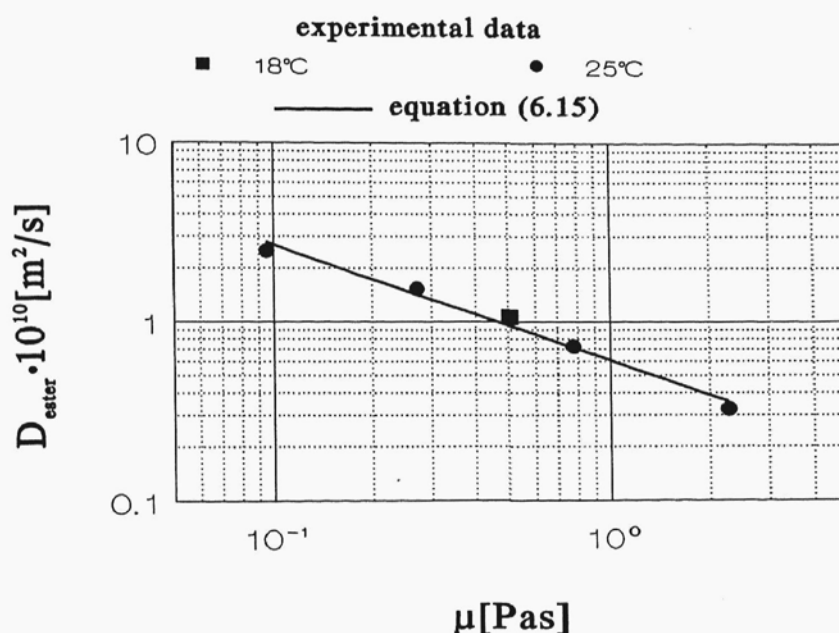


Figure 6.8. Molecular diffusivity of ethyl chloroacetate in aqueous solutions of the polymer.

6.4. Measurements of Rate Constant of Alkaline Ester Hydrolysis in Aqueous Solutions of Polyethylenepolypropylene Glycol.

Measurements of rate constant of alkaline hydrolysis were conducted in a small (250cm³) reactor immersed in thermostating bath, equipped with a three-blade propeller, a conductometric electrode and a resistance thermometer, as shown in figure 6.9.

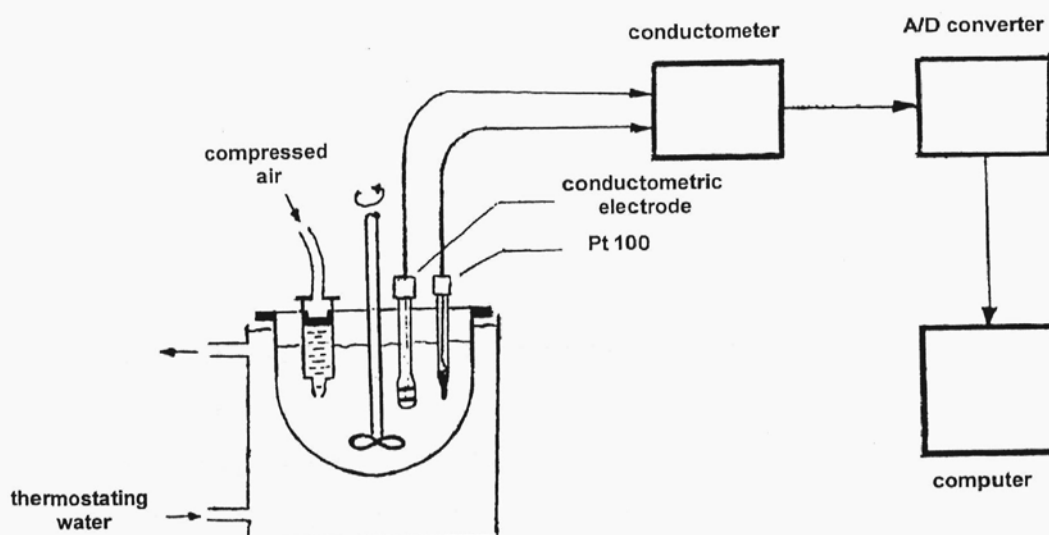


Figure 6.9. Experimental system for measurement of reaction kinetics.