

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 (250cm^3) reactor immersed in thermostating bath, equipped with a three-blade propeller, a conductometric electrode and a resistance thermometer, as shown in figure 6.9.

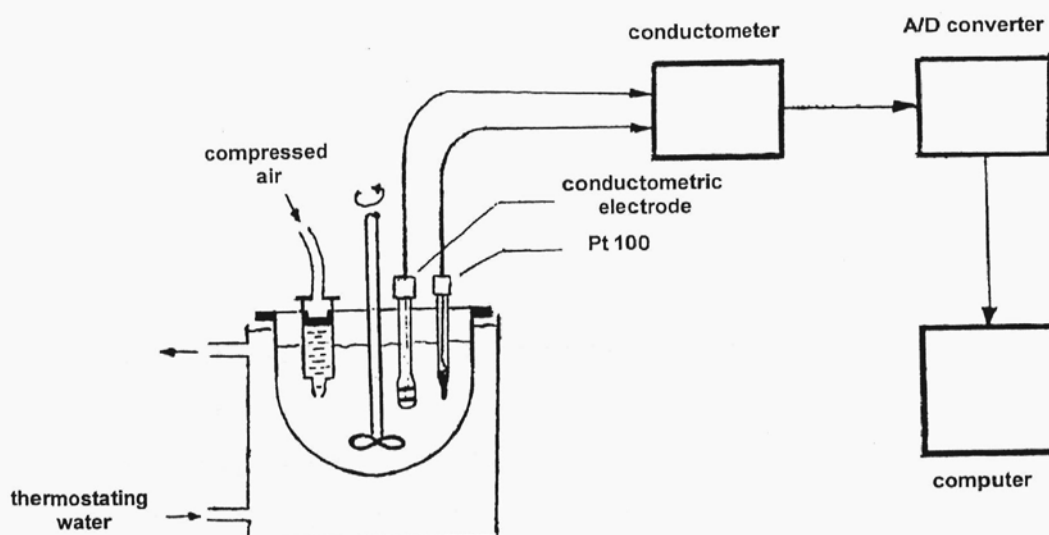


Figure 6.9. Experimental system for measurement of reaction kinetics.

Both the electrode and the thermometric probe were connected to Metrohm conductometer - type 660, allowing to perform conductivity measurements with 2% error. Analog output signal (0÷1 V) from the conductometer, proportional to the measured conductivity, was converted by A/D card and recorded by a computer.

Solution containing sodium hydroxide (6.0÷6.6 mmol/dm³) was poured into the reactor and thermostated at 25°C. Solution containing ethyl chloroacetate (62÷80 mmol/dm³) was also thermostated at 25°C, then quickly transferred to a syringe, injected into the reactor under pressure within 1 second and quickly mixed with the reactor content. Conductivity of the resulting mixture was recorded by a computer with a sampling frequency equal to 25 Hz.

In all experiments equimolar amounts of base and ester were mixed (deviations were not higher than 0.1 % of the total amount). The polymer content in the mixed solution was identical and ranged from 0 to 40 weight percents. During preparation of the solution the main reactants were always added after the polymer neutralization by 0.1N hydrochloric acid.

The mixing times in the experimental system were determined by monitoring conductivity fluctuations after injection of samples containing potassium chloride. Times at which the conductivity fluctuations were smaller than 1% were ranging from 3 to 4 s in the case when the most viscous solutions were mixed ($w_p \cong 40\%$).

According to the literature [77] in aqueous and non-aqueous solutions alkaline hydrolysis of aliphatic esters is a second-order reaction. In this case the reaction rate is given by:

$$R_{OH^-} = R_{ester} = -k_2 \cdot c_{OH^-} \cdot c_{ester} \quad (6.16)$$

Thus, in an equimolar and perfectly mixed solution, the material balance of the base can be written as follows:

$$\frac{dc}{dt} = -k_2 \cdot c^2, \quad (6.17)$$

where for simplicity c_{OH^-} is replaced by c . Integration of equation (6.17) yields

$$\frac{1}{c} - \frac{1}{c_0} = k_2 \cdot (t - t_0) \quad (6.18)$$

Hence, even not knowing t_0 and c_0 one can estimate the rate constant - k_2 from the slope of curve $1/c$ versus time.

It was experimentally checked that the conductivity of the aqueous solution of sodium hydroxide and the viscosity increasing agent is directly proportional to the concentration of sodium hydroxide; the correlation coefficients, r , of linear calibration curves are not lower than 0.996, as it is shown in table 6.X. This allows to compute $1/c$ at any instant of time,

measure the slope of the resulting curve and finally determine the rate constant - k_2 .

Table 6.XI reports initial compositions of mixed solutions and values of reaction rate constants recalculated from $\text{kg}/(\text{mol} \cdot \text{s})$ to $\text{dm}^3/(\text{mol} \cdot \text{s})$ with the use of equation (6.7b).

Table 6.X. Calibration curves at 25°C;
 $c_{\text{OH}}[\text{mol/kg}] = A \cdot x[\text{mS/cm}] + B$.

exp.no.	w_p [%]	$A \cdot 10^{-2}$	$B \cdot 10^{-3}$	r
1÷3	0.0	0.6665	3.239	0.9989
4÷6	30.15	1.316	3.329	0.9960
7÷9	30.00	1.398	3.785	0.9968
10÷12	39.93	2.207	3.983	0.9991

Table 6.XI. Initial solutions parameters and reaction rate constants measured at 25°C.

exp. no.	reactor solution			syringe			k_2 [$\text{dm}^3/\text{mol/s}$]
	w_p [%]	$c_{\text{OH-}}$ [mmol/kg]	m_s [g]	w_p [%]	c_{ester} [mmol/kg]	m_s [g]	
1	0.0	5.975	200.03	0.0	79.61	15.02	30.70
2	0.0	5.975	200.01	0.0	79.61	15.00	29.71
3	0.0	5.975	200.00	0.0	79.61	15.00	31.53
4	30.15	6.628	210.12	30.00	62.53	22.25	29.80
5	30.15	6.628	210.03	30.00	62.53	22.34	28.56
6	30.15	6.628	210.02	30.00	62.53	22.26	29.75
7	30.00	6.255	210.06	30.00	62.44	20.70	27.95
8	30.00	6.255	209.98	30.00	62.44	20.82	28.60
9	30.00	6.255	210.03	30.00	62.44	20.76	29.15
10	39.93	6.239	215.01	39.92	62.60	21.45	34.17
11	39.93	6.239	214.98	39.92	62.60	21.28	33.87
12	39.93	6.239	214.99	39.92	62.60	21.44	35.69

Summarizing, the mean values of the rate constants are equal to:

- a) for 0% polymer content - 30.7 [$\text{dm}^3/\text{s/mol}$],
- b) for 30% polymer content - 29.0 [$\text{dm}^3/\text{s/mol}$],
- b) for 40% polymer content - 34.6 [$\text{dm}^3/\text{s/mol}$].

The above results remain in a good agreement with the literature data for pure water solutions [77]; $25.8 \text{ dm}^3/\text{mol/s} \leq k_2 \leq 33.2 \text{ dm}^3/\text{mol/s}$, which indicates that the presence of polyalkylene glycol, up to 40 weight percents, has a very limited effect on k_2 .