

related to the history of mixing.

It should be noted that ethyl chloroacetate also undergoes neutral and acid-catalyzed hydrolysis but these reactions are too slow to interfere with alkaline hydrolysis; according to Jencks and Carriuolo [94] the rate constants of neutral and acid-catalyzed hydrolysis are equal to $1.08 \cdot 10^{-7} \text{ s}^{-1}$ and $3.67 \cdot 10^{-5} \text{ dm}^3/(\text{mol} \cdot \text{s})$ at 298.15 K, respectively.

6.2. Properties of Polyethylenepolypropylene Glycol.

6.2.1. Molecular Structure.

Polyethylenepolypropylene glycol was chosen as substance increasing viscosity of aqueous solutions of the test reactants. Polyethylenepolypropylene glycol is a polymer of ethylene oxide and propylene oxide, as shown in figure 6.1. The polymer is a non-volatile, non-toxic, highly viscous and transparent liquid.

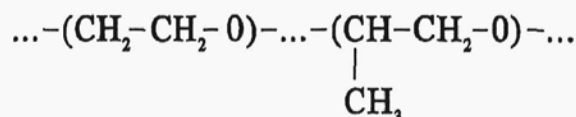


Figure 6.1. Molecular structure of polyethylenepolypropylene glycol.

Polyethylenepolypropylene glycol belongs to the family of polyethers, which results in its low polarity and increased ability to form hydrogen bonds [78]. These features should make the polymer soluble both in organic solvents and in water. Indeed, the experimental tests confirmed that the polymer is miscible in all proportions with: non-polar solvents e.g. tetrachloride and methylene chloride, moderate-polar solvents e.g. ethyl chloroacetate and polar solvents e.g. ethyl alcohol and water. According to literature [79] only paraffin hydrocarbons are immiscible with polyethylenepolypropylene glycol.

The polyalkylene glycol used in the experiments was manufactured by BP Chemicals Ltd. under the trade name Breox 75W 18000.

6.2.2. Viscosity of Aqueous Solutions.

Viscosity of aqueous solutions of the polyethylenepolypropylene glycol was measured with the use of viscometer - Rheotest 2.1 in a system of two coaxial cylinders at shear rates ranging from 13.25 s^{-1} to 1325 s^{-1} . Polymer contents in these solutions were ranging from 30

to 90 weight percents. It was found that all tested solutions behaved like Newtonian liquids. The measured viscosities were affected neither by the shear rate nor by the measurement time. Standard deviations of the viscosity values obtained for the same solution at various shear rates were not higher than 3%; the instrument error is equal to 3÷4%.

Tables 6.Iab present viscosities measured at 18°C and 25°C for different contents of the polymer, expressed in weight percents

- w_p .

Table 6.Ia. Viscosity of the polymer aqueous solutions at 18°C.

w_p [%]	30.00	40.00	50.00
μ [Pa·s]	0.134	0.416	1.197

Table 6.Ib. Viscosity of the polymer aqueous solutions at 25°C.

w_p [%]	30.08	39.69	49.67	59.50	67.75	79.39	89.95
μ [Pa·s]	0.096	0.261	0.732	2.09	4.28	10.69	20.88

Data shown in tables 6.I can also be approximated by the following expressions:

- at 18°C $\log_{10}\mu = -2.292 + 4.752 \cdot w_p$, (6.5a)

- at 25°C $\log_{10}\mu = -2.169 + 2.872 \cdot w_p + 4.196 \cdot w_p^2 - 3.422 \cdot w_p^3$. (6.5b)

Both the experimental points and expressions (6.5) are plotted in figure 6.2.

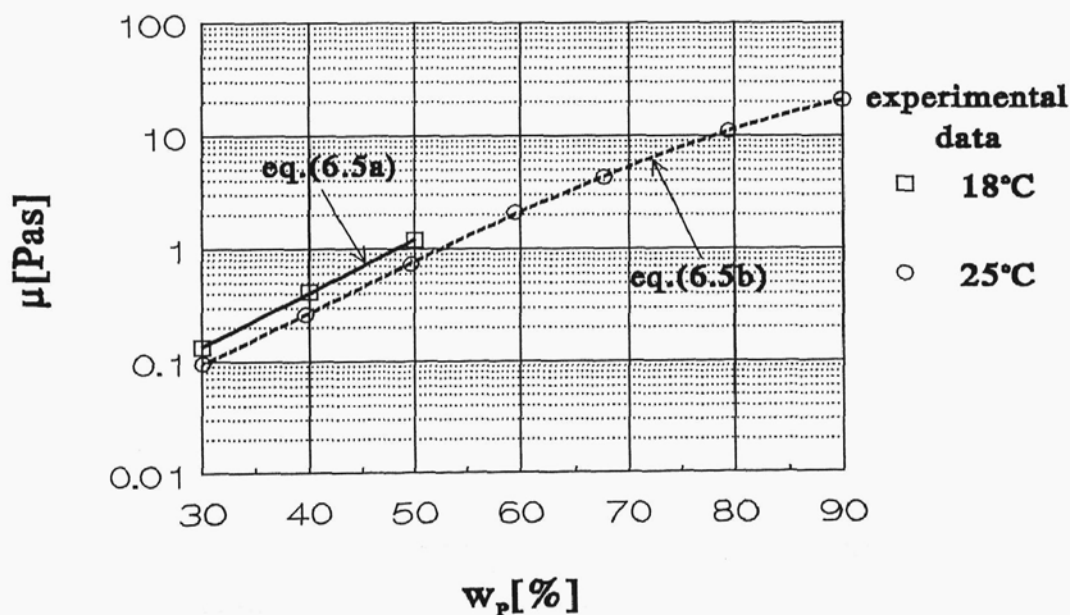


Figure 6.2. Viscosities of the polymer aqueous solutions.

As it can be seen, there is a very strong influence of the polymer content on viscosity of its aqueous solution; one can increase viscosity more than 20000 times using this substance.

To check if the viscosity increasing agent does not exhibit elastic features, oscillation tests were performed by means of Bohlin Rheometer System. During these experiments oscillating strain was applied to samples of the pure polymer and the resulting stress was measured. Table 6.II reports values of the phase shift between the strain and stress measured at different oscillation frequencies. The relaxation times computed from relation [80]:

$$\tau = 1/(2 \cdot \pi \cdot f \cdot \tan \delta) \quad (6.6)$$

are also presented in this table.

Table 6.II. Phase shifts and relaxation times obtained for the pure polymer at 22°C.

f[Hz]	0.1	0.2	0.5	1.0	2.0	5.0	10.0
δ [deg]	88.9	87.8	87.9	87.9	88.2	88.1	87.6
τ [s]	0.0306	0.0306	0.0117	0.0059	0.0025	0.0011	0.0007

These data clearly indicate that polyethylenepolypropylene glycol behaves almost like perfectly viscous liquid; the phase shift is close to 90 degrees and the relaxation times are very short (for perfectly viscous liquid $\delta=90^\circ$ and $\tau=0$). It should also be noted that so-called effect of "rod-climbing" was never observed when solutions containing the polymer were agitated.

6.2.3. Density of Aqueous Solutions.

Density of aqueous solutions of polyethylenepolypropylene glycol was measured by means of glass pycnometers, previously calibrated by redistilled water.

Tables 6.IIIab show densities measured at 18°C and 25°C for the polymer contents ranging from 30 to 90 weight percents.

Table 6.IIIa. Density of the polymer aqueous solutions at 18°C.

w_p [%]	30.00	40.00	50.00
ρ [g/cm ³]	1.048	1.065	1.080

Table 6.IIIb. Density of the polymer aqueous solutions at 25°C.

w_p [%]	30.08	39.69	49.67	59.50	67.75	79.39	89.95
ρ [g/cm ³]	1.043	1.058	1.073	1.085	1.090	1.093	1.095

Data reported in tables 6.III can be approximated by the following expressions:

- at 18°C ρ [g/cm³] = 0.9836 + 0.2505 · w_p - 0.1150 · w_p^2 , (6.7a)

- at 25°C ρ [g/cm³] = 0.9541 + 0.3865 · w_p - 0.3425 · w_p^2 + 0.0975 · w_p^3 . (6.7b)