

POLYETHYLENE GLYCOL DERIVATIVES AND THE PHASE-TRANSFER CATALYSIS

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Abstract

The phase-transfer catalyst efficiency of polyethylene glycols were proven and analysed. The stability of their sodium complexes increases with the length of chain while the lipophilicity decreases.

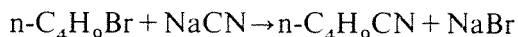
As a result the best phase-transfer catalyst PEO-s can be found among the medium chain-length ones.

Introduction [7]

The theory of phase-transfer catalysis has been developed from 1965. This method is a useful tool for the laboratory practice and for industrial processes.

A condition of chemical reactions is the proximity of the reactive particles. In a homogeneous medium it is fulfilled frequently as a consequence of the heat motion.

In many cases no homogeneous reaction mixture can be produced from the reaction partners, because their solubility is so entirely different. These reactions can be accomplished in heterogeneous system if there exists a phase in which all reaction partners are present at least in a small concentration. For example among the starting materials of the reaction:



the *n*-butyl bromide is soluble in organic solvents, the sodium cyanide is water-soluble. Nevertheless when stirring *n*-butyl bromide with a 33% aqueous NaCN solution, a slow reaction takes place giving 2% yield in 3 hours.^[11] This is because of the small but definite solubility of *n*-butyl bromide in water (0.058 g/100 g at 16°C).

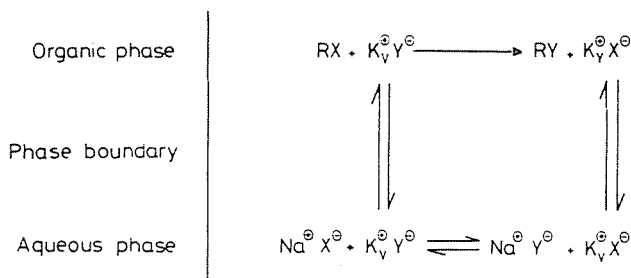
When the solubility is even smaller, no reaction can be detected at all. [12] The solubility differences are results of the structural differences between the starting materials. The ions of salt-like compounds (NaCN, NaI, KMnO₄) are held together in crystalline form by strong electrostatic forces. Only dipolar solvents (especially water) can decompose networks like this; the water molecules and the ions build up strong ion-dipole interactions. The hydrated

ions are built into the hydrogen-bonded structure of the water and are not able to step over a phase boundary, they can not enter an aprotic media. Their character is hydrophilic, lipophobic.

On the contrary, many apolar organic molecules can not interact with water molecules strongly enough to the intrusion among them. Materials like these are lipophilic, hydrophobic.

The lipophobic character is the stronger the larger charge is concentrated on a small particle. [13] The salt-like compounds are usually used in reactions where it is the anion which reacts. So the solubility can be improved simply by exchanging the cation. The quaternary ammonium ions can be suitable: n-butyl bromide can react with tetrabutyl ammonium cyanide in a homogeneous solution very fast.

Makosza [2], Starks [1] and Brandström [3] realized that a catalytic amount of quaternary salt reacts very well added together with the stoichiometric alkali salt. The quaternary ammonium ions carry the anions through phase boundaries and they are able to increase reaction rates as high as orders of magnitude. In the reaction mentioned above the conversion improves to 100% in 3 hours after adding 3% of tetrabutyl ammonium bromide. This method became known as phase transfer catalysis (see: Fig. 1).



The mass transport of the phase-transfer catalysis

Fig. 1. The mass transport of the phase-transfer catalysis

It has two different ways to run. By liquid-liquid phase-transfer catalysis the salt-like reagent is dissolved in water, and after the addition of catalyst it is vigorously stirred with the reaction partner being in organic solution. The reaction can proceed also if the salt is present in solid form; this is called solid-liquid phase-transfer reaction.

Besides the quaternary ammonium salt, some more types of catalysts were found, among others the crown ethers, the cyclic compounds containing $-\text{CH}_2\text{CH}_2\text{O}-$ units.

The catalytic activity of crown ethers is based upon their ability to complex cations.

As the open-chained—CH₂CH₂O—oligomers (oxyethylene oligomers) can complex alkali ions [7] similarly to the crown ethers we started a project to enlighten how they catalyse phase-transfer reactions.

The oxyethylene oligomers proved to be the better complexing agents the longer-chained they were [8] (see: Fig. 2). It seems to be advantageous to use oligomers above the hexaethylene glycol but compounds with substantially higher polymerisation degree could be chosen only from the commercial polyethylene glycols (polyoxyethylene compounds, PEG-s), which are mixtures of homologues. The PEG-s were found to be also complexing agents and increasing the average chain-length the tendency of complex stabilization continued (Fig. 2).

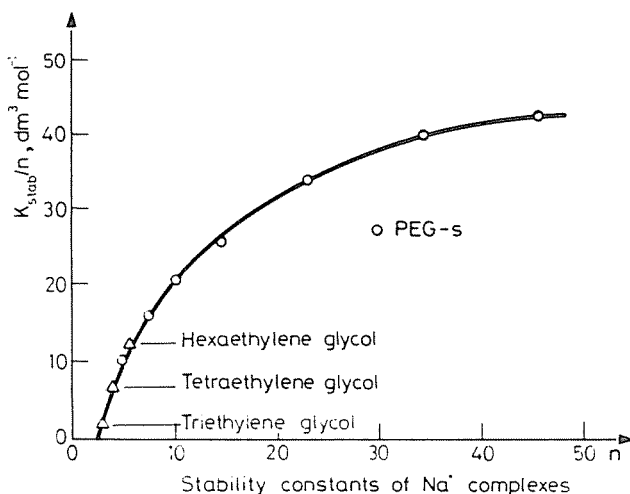


Fig. 2. Stability constant of Na⁺ complexes

Some investigations were used to estimate the average ligandum-number (~ 4 atoms of oxygen) and to study the role of end-group and the chain-length. [8]

The complexing constants are high enough to await phase-transfer catalytic effects of PEG-s. It was demonstrated [7] indeed (the preparation of NaI in benzene and a reaction was shown in a paper of ours) and the study of the features of PEG-s as phase-transfer catalysts were started.

Figures 3 and 4 show the ion concentrations produced by crown ethers in the organic phase of a phase-transfer catalysed system. Modelling the liquid-liquid version an aqueous salt solution was stirred with a benzene solution of PEG (Fig. 3).

The high complexation is not the only condition of a good phase-transfer catalyst. The medium chain-length PEG-s are the relatively most efficient ones

(Fig. 3) because the lipophilicity follows an opposite tendency with complex stability and together they give an optimum.

Nevertheless, the salt concentrations are too low to expect a strong phase-transfer catalytic effect of PEG-s in liquid-liquid systems.

This is not the case when using a solid salt instead of aqueous solutions (Fig. 4).

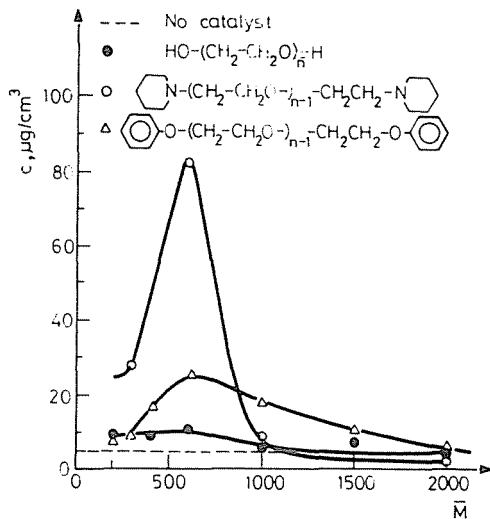


Fig. 3. Concentration of sodium 2,4-dinitrophenolate in the benzene phase vs. average molecular weight

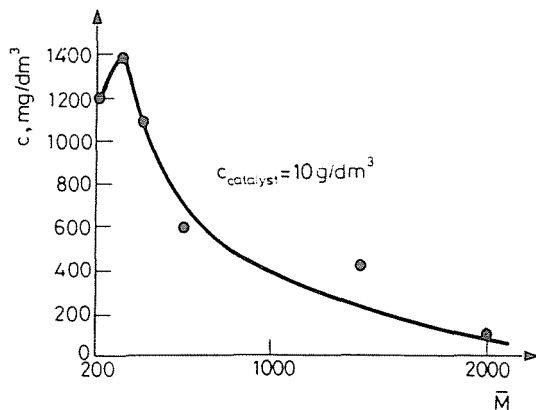


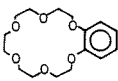
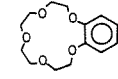
Fig. 4. Equilibrium DNP⁻ Me⁺ concentration of benzene solutions at $t=25^\circ\text{C}$ as a function of the average molecular weight of polyethylene glycol

The PEG can dissolve much more salt this way, and the medium chain-length ones are the best catalysts again. It can be in connection to the lipophilicity of the complex.

Using different solvents and different cations the solubility power of some PEG-s^[10] are collected in Table 1.

Table 1

K_{sol} and K_{stab} for solid-liquid phase-transfer equilibria in different solvents

Catalyst	Me	Benzene		Chlorobenzene		Dichloromethane		Acetonitrile	
		K_{sol}	$\log K_{stab}$	K_{sol}	$\log K_{stab}$	K_{sol}	$\log K_{stab}$	K_{sol}	$\log K_{stab}$
PEG 300	Li	0.095	5.4	0.79	4.3	1.9 ⁺			
	Na	0.20	5.1	0.38	4.0	0.63	5.0	0.61	1.6
	K	0.37	5.4	0.51	4.5	0.53	4.8	0.54	2.1
PEG 600	Li	0.22	5.8	1.4 ⁺		2.5 ⁺			
	Na	0.17	5.0	0.52	4.2	0.49	4.8	0.52	1.4
	K	0.27	5.2	0.83	5.2	0.78	5.3	0.62	2.3
PEG 2000	Li	0.031	5.0	1.8 ⁺		7.7 ⁺			
	Na	0.097	4.7	0.77	4.7	2.4 ⁺		0.26	1.0
	K	0.18 ⁺	5.0	2.1 ⁺		1.5 ⁺		1.8 ⁺	
	Li	0.011	4.4	0.97	5.3	0.89	5.1		
	Na	0.34	5.4	0.69	4.5	0.69	5.2	0.61	1.6
	K	0.019	3.9	0.30	4.1	0.41	4.6	0.65	2.3
	Li	0.036	4.9	0.32	3.5	0.78	4.7		
	Na	0.26	5.2	0.44	4.1	0.26	4.4	0.37	1.2
	K	0.73	6.1	0.69	4.8	0.41	4.6	1	
No catalyst	Li	$4.2 \cdot 10^{-7}$		$1.6 \cdot 10^{-4}$		$6.8 \cdot 10^{-5}$		> 1.3	
$C_{salt} \frac{mol}{dm^3}$	Na	$2.2 \cdot 10^{-6}$		$6.3 \cdot 10^{-5}$		$1.5 \cdot 10^{-5}$		$3.8 \cdot 10^{-2}$	
	K	$2.4 \cdot 10^{-6}$		$3.6 \cdot 10^{-5}$		$1.8 \cdot 10^{-5}$		$9.0 \cdot 10^{-3}$	

⁺ This high K_{sol} value may point to other than 1 : 1 complexation. The K_{sol} values mean ratios of the dissolved salt concentration to the concentration of ligandum, K_{stab} = the thermodynamic stability constant of the complex. Anion: 2,4-dinitro phenolate, $t = 25^\circ C$.

Changing a solvent for a more polar one the PEG-s (and crown ethers) become weaker complexing agents and stronger phase-transfer catalysts. Higher solvating power of a solvent makes easier the dissolution of a salt but in the same time it counteracts to the complexation.

The best alkali salts to dissolve are K^+ salts in apolar solvents and Li^+ salt in dipolar aprotic solvents. Sodium is a good compromise taken the prices of reagents into consideration.

These results can be used to design parameters for a phase-transfer catalyzed reaction.

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