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Effect of sodium chloride on the solubility and hydrolysis of epichlorohydrin in water

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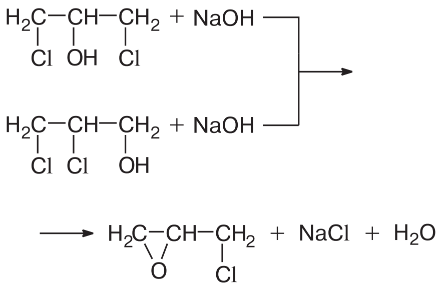
The mutual solubility of the components in the epichlorhydrin—water—sodium chloride system was studied in the temperature range of 20—90 °C. It was found that epichlorohydrin is salted out as the concentration of NaCl increases. The Sechenov coefficient was determined to be equal to 0.29. It was found that epichlorohydrin reacts with an aqueous solution of sodium chloride to form glycerol dichlorohydrins. Alkali formed during this reaction catalyzes the hydrolysis of epichlorohydrin to glycerol monochlorohydrin, acts as a reagent in the glycidol formation and accelerates its subsequent conversion to glycerol.

Key words: epichlorohydrin, water, sodium chloride, solubility, hydrolysis.

Epichlorohydrin (ECH) is a large-tonnage product of organic synthesis used for the production of epoxy and ion-exchange resins, epichlorohydrin rubbers, surfactants, and much more.

In industry, ECH is produced by alkaline dehydrochlorination of glycerol dichlorohydrins[1] (Scheme 1). The reaction products are ECH and an aqueous solution of sodium chloride. As a rule, the addition of salts to aqueous solutions of organic compounds with limited solubility such as ECH[2] leads to their salting out, *i.e.*, to a decrease in the solubility of the substances in the salt solution.[3]

Scheme 1



To optimize the dehydrochlorination of glycerol dichlorohydrins, the data on the solubility of ECH in sodium chloride solutions of various concentrations and at different temperatures, as well as the information on the composition of the organic phase equilibrated with the aqueous salt layer, may be of practical importance, but they are not available from the literature.

The purpose of the present work is the study of the mutual solubility of components in the ECH—water—NaCl system.

Experimental

Epichlorohydrin (99.9%, Sigma-Aldrich), NaCl (reagent grade), and distilled water were used in the work.

The experiments were carried out in a 200 mL glass reactor equipped with a jacket, a thermocouple sleeve and a reflux condenser. Stirring was carried out with a magnetic stirrer. Aqueous NaCl (120 g) and ECH (40 g) were placed into the reactor. The reaction mixture was heated to a desired temperature (20—90 °C) with stirring and kept for 20 min. After the stirring was stopped, the formation of layers was observed: the upper layer was the aqueous NaCl and the lower one was ECH. The composition of each layer was analyzed.

The analysis of water, ECH, and organic products of its hydrolysis was carried out by GLC on a Tsvet-800 chromatograph with a thermal conductivity detector. The column (2 m×3 mm) was packed with a polysorb-1 phase, the detector temperature was 200 °C, the injector temperature was 220 °C, the column temperature was programmed from 70 to180 °C.

The NaCl content was determined by potentiometric titration of the chloride anion with aqueous $AgNO_3$.

Results and Discussion

The solubility of the components of the system under study in each other is limited in both binary and trinary mixtures.

The limiting solubility of these components in binary mixtures at 20 °C is 6.55 wt.% for ECH in water,[2] 1.42 wt.% for water in ECH,[2] 26.39 wt.% for NaCl in water,[4] and

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0.073 wt.% for NaCl in anhydrous ECH (experimental data).

The results of experiments on determination of the solubility of ECH in aqueous solutions of NaCl of various concentrations at 20 and 60 °C are presented in Table 1.

As it was expected, ECH undergoes salting out by sodium chloride. The concentration of ECH in the saturated solution of the salt at 20 °C is 5.8 times lower than in water and is only 1.1 wt.%.

The ECH phase is in equilibrium with the aqueous salt layer. The content of NaCl in this phase is 0.08—0.10 wt.%. The increase in the solubility of NaCl in ECH is caused by the presence of water dissolved in it. The ECH phase contains 0.5—0.6 and 1.9—2.0 wt.% of water at 20 and 60 °C, respectively. Note that an increase in the concentration of NaCl reduces the solubility not only of ECH in the aqueous salt layer, but also that of water in ECH. The presence of NaCl in the ECH phase leads to a decrease in the concentration of water in it by about 2.5 times at 20 °C and 1.6 times at 60 °C (the solubility of water in ECH at 60 °C is 3.23 wt.%).[2]

The salting out process of nonelectrolytes is described by the Sechenov equation:[3]

$$\ln C = \ln C_0 + kC_{\text{salt}}, \qquad (1)$$

where C is the nonelectrolyte concentration, mol L^{-1}; C_0 is the solubility of nonelectrolyte in pure water, mol L^{-1}; C_{salt} is the concentration of salt solution, mol L^{-1}.

The result of processing the experimental data by Eq. (1) is shown in Fig. 1.

The salting-out constant of ECH from aqueous sodium chloride solutions at 20 °C is $k = 0.29$. The average error of approximation does not exceed 4%. For comparison, the salting-out constant of glycerol dichlorohydrin (the starting compound for the synthesis of ECH) by sodium chloride is 0.36 (calculated from reference data[2]). Epichlorohydrin is less soluble in water than glycerol dichlorohydrin (162 g L^{-1} at 20 °C).[2] The observed decrease in the salting-out coefficient with the growth of the nonelectrolyte hydrophobic properties is confirmed by the well-known regularities in the salting-out effect.[5]

Table 1. The solubility of ECH in aqueous solutions of NaCl of various concentrations at 20 and 60 °C

T/°C	Content of NaCl in aqueous solution (wt.%)	Solubility of ECH (wt.%)
20	0.00	6.55[2]
	1.9	5.9
	9.9	3.4
	14.9	2.4
	19.5	1.9
	25.8*	1.1
60	0.00	8.03[2]
	1.9	6.5
	9.5	3.8
	14.9	2.8
	19.4	2.2
	26.6*	1.4

* Saturated solution of NaCl.

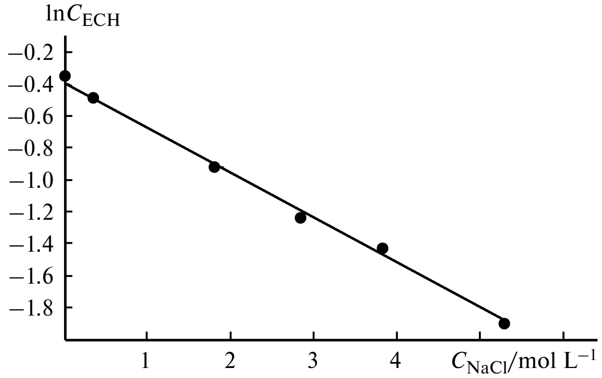
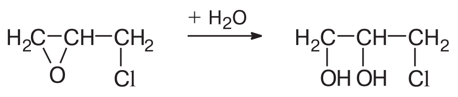


Fig. 1. Salting out of ECH with sodium chloride at 20 °C (linearization of the Sechenov equation).

It follows from the experimental data that an increase in temperature from 20 to 60 °C has very little effect on the solubility in water of separate components NaCl and ECH, as well as of ECH in NaCl solutions of various concentrations. As the salt concentration in the aqueous solution increases, the raising temperature has an increasingly less significant effect on the solubility of epichlorohydrin. If the increase in the solubility of epichlorohydrin in water with raising temperature from 20 to 60 °C is 1.48 wt.%, in the salt-saturated solution it is only 0.3 wt.%.

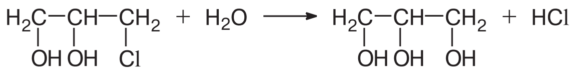
The contact of ECH with water leads to the formation of some by-products, the proportion of which increases with increasing temperature. The main product of the hydrolysis of ECH in water is glycerol 1-monochlorohydrin (Scheme 2).

Scheme 2



The pH value of the aqueous layer obtained by keeping ECH (25 wt.%) in distilled water for 4 h at 60 °C remains constant and equal to 6. When this mixture is refluxed at 90 °C, the pH of the solution decreases to 2—3, which indicates the formation of an acid in the reaction mixture. This results from the intensive reaction according to Scheme 2 and subsequent hydrolysis of glycerol monochlorohydrin with the evolution of hydrogen chloride (Scheme 3).

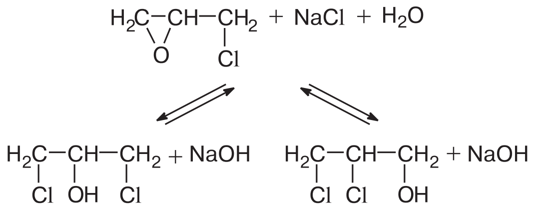
Scheme 3



The conversion of ECH to monochlorohydrin is 10%. The selectivity on glycerol does not exceed 0.3%.

The experimental data show that hydrolysis of epichlorohydrin in the presence of NaCl follows a different pathway. An aqueous salt solution of ECH is an alkaline medium with pH of 9—10. This solution also contains glycerol 1,3-dichlorohydrin and glycerol 1,2-dichlorohydrin, the starting compounds for obtaining ECH according to Scheme 1. Under conditions of the experiments, the conversion of epichlorohydrin is 0.8 wt.%, while the selectivity on glycerol dichlorohydrins is 100%. It should be noted that glycerol dichlorohydrins do not form in the absence of NaCl. The observed fact indicates that ECH reacts with an aqueous solution of NaCl to form glycerol dichlorohydrins and an alkali (Scheme 4).

Scheme 4

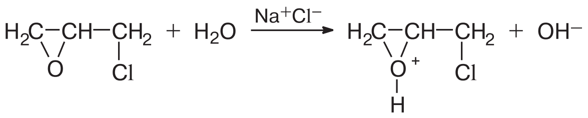


The obtained experimental data confirm the reversibility of the reaction of formation of ECH by dehydrochlorination of glycerol dichlorohydrins, which was not previously noted in the scientific and technical literature.

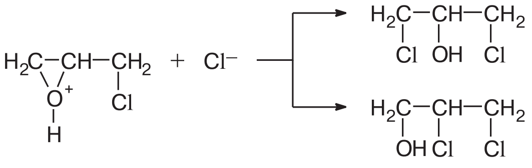
Another epoxy compound, ethylene oxide in an aqueous solution, also reacts with sodium chloride to form ECH and an alkali.[6] Apparently, the reaction with an aqueous solution of NaCl is characteristic of all epoxy compounds.

The reaction of ECH with an aqueous solution of NaCl can be represented by Schemes 5 and 6.

Scheme 5



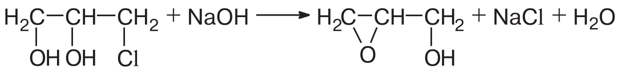
Scheme 6



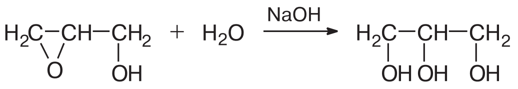
An oxonium form of ECH protonated at the oxygen atom is formed as an intermediate compound. Further addition of chloride anion results in the formation of two isomers of glycerol dichlorohydrins. In the ECH molecule, as well as in its oxonium form, the chlorine atom due to its negative inductive effect contributes to the formation of a partial positive charge on the carbon atom from the opposite end of the carbon chain. This substantiates the predominant formation of glycerol 1,3-dichlorohydrin through the nucleophilic attack by the agent according to Scheme 6.

Upon increase in temperature to 80 °C or higher, the solubility of ECH in salt solutions remains practically unchanged as compared to the process at 60 °C, but the processes of its hydrolysis to monochlorohydrin according to Scheme 2, as well as to glycidol (Scheme 7) and glycerol (Scheme 8), are accelerated due to the formation of an alkaline medium.

Scheme 7



Scheme 8



For the standard time of the experiments (heating from 20 to 40 min and maintaining the reaction mixture for 20 min at a given temperature), an increase in temperature from 60 to 80 °C led to an increase in the conversion of ECH from 0.8% to 4.3%, but the selectivity on glycerol dichlorohydrin decreased to 90% due to the reactions shown in Schemes 7 and 8.

The technology of preparation of ECH from glycerol[1] allows one to obtain concentrated solutions of glycerol dichlorohydrins with the content of the main compound more than 80 wt.%. Unlike the traditionally used method of dehydrochlorination of diluted (3—5%) aqueous solutions of glycerol dichlorohydrins in a distillation column with simultaneous hot-steam distillation off of forming ECH, the synthesis of ECH from the concentrated starting material can be carried out in a mixing reactor, followed by separation of the aqueous salt and epichlorohydrin phases formed. This can significantly reduce the energy consumption of the process.

The obtained results allow us to draw a conclusion about the optimal conditions for the synthesis. Since the solubility of epichlorohydrin in the aqueous salt layer decreases with increasing NaCl concentration, the process of dehydrochlorination of glycerol dichlorohydrins should be carried out with a 20 wt.% solution of NaOH. This will give a close to saturation concentration of NaCl in the solution with a minimum content of ECH dissolved in it. Despite the fact that the reaction rate and reactor productivity increase with increasing temperature, it is better to conduct the process at temperatures below 60 °C to avoid intensive hydrolysis of ECH. The results of the studies showed that the solubility of ECH in the NaCl solution varies insignificantly with the temperature increase from 20 to 60 °C and, consequently, practically does not depend on temperature and the loss of ECH with the aqueous salt layer. At the same time, the temperature increase practically does not affect the composition of the epichlorohydrin phase, which is subject to rectification for the production of a commercial product.

Thus, it follows from the results of the study that sodium chloride quite efficiently salts out ECH from its aqueous solution. So, the solubility of ECH at 20 °C in a saturated NaCl solution is 5.8 times lower than in distilled water. The salting-out coefficient determined by the Sechenov equation is 0.29. The increase in temperature has very little effect on the solubility of ECH in water. As the concentration of sodium chloride increases, this change becomes less pronounced and the solubility of ECH increases by only 0.3 wt.% in the saturated NaCl solution with a temperature change from 20 to 60 °C.

In the absence of sodium chloride, ECH in water undergoes hydrolysis to form glycerol monochlorohydrin, with the medium pH shifting to the acidic region. In the presence of sodium chloride, the reaction of ECH proceeds with an aqueous solution of NaCl to form glycerol dichlorohydrins. The formed alkali (pH 9—10) accelerates the hydrolysis of ECH to glycerol monochlorohydrin and is involved in further transformations with the formation of glycidol and glycerol.

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