ISOTHERMAL SOLUBILITY DIAGRAM OF THE SODIUM HYDROXIDE – HUMIC ACID – WATER SYSTEM AT 25 °C

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Abstract

The article presents data from a study of solubility in the sodium hydroxide – humic acid – water system at 25^0C isothermal method and data from a study of the rheological properties of solutions formed by adding humic acid to 0.5 and 1.0% aqueous solutions of sodium hydroxide. The formation of a new compounds based on the initial components, for which the concentration limits of existence at 25 °C have been determined. By studying the rheological properties of solutions formed by adding humic acid to 0.5 and 1.0% aqueous solutions of sodium hydroxide, we have established that when sodium hydroxide interacts with humic acid in aqueous solutions, a complex compound of the composition NaOH•HA (1:1) is formed. These characteristic inflection points are less clearly manifested in the pH values of the solutions.

Keywords: *sodium hydroxide, humic acid, sodium humate, ternary system, complex salt, growth stimulator, isothermal diagram, synthesis*

Introduction

The authors (Fakerov G. M., Erkaev A. U., Sharipova H. T., Mirzoev B., 2022; Fakerov G. M., Erkaev A. U., Sharipova H. T., Mirzoev B., 2023; Fakerov G. M., Erkaev A. U., Sharipova H. T., Mirzoev B., 2022) obtained the following data based on the results of physicochemical and technological studies of the oxidation stages and extraction of alkali metal humates. The optimal oxidation mode of brown coal from the Shurabskoye deposit with nitric acid was found: nitric acid concentration of 50%, oxidation temperature of 45 °C, process duration of 1 hour, and the ratio of the organic part of coal to nitric acid monohydrate of 0.81:1. As a result of oxidation of Shurabskoye brown coal with nitric acid, the content of active functional groups in the latter increases, both in the coal itself and in humic acids.

Optimal conditions for humic acid extraction from oxidized brown coal of the Shurab deposit have been determined. It has been established that the greatest amount of humic acids, more than 80%, is extracted from coal with a 10% sodium hydroxide solution at 80 °C and 30-minute extraction. Increasing the L: S ratio from 5 to 20 leads to an increase in the yield of humic acids. The yield of humic acids in the case of using 10% sodium hydroxide at 80 °C, L: S = 15 and 30 min is 84.43; 70.75%, respectively, when using sodium and potassium hydroxides.

Along with sodium humate, included in the "List of preparations permitted for use in agriculture," plant growth stimulants such as ammonium and potassium humates, obtained by treating oxidized coals with ammonium and potassium hydroxides, have undergone extensive production testing.

The positive influence of ammonium humate on the cultivation of wheat, sugar beets, corn, potatoes, cabbage, and cotton was already discussed in the analysis of works (Gizatullin Slicks of adenumates on the yield of agricultural crops, 1963; Petrik G. K., 1971; Imakova S. T., Mukhanova V. L., Sultanov A. S., 1968; Abolina G. I., Tashkhodjaev A. T. 1968; Abolina G. I., Tashkhodjaev A. T., 1965; Imakova S. T., Mukhanova V. L., 1965).

When comparing the methods of applying ammonium humate to grain crops, the best results were obtained with a combination of seed soaking and sprout irrigation in the concentration range of 10−5−10−6%. On cucumber (Vyaznikovsky variety), the best results were obtained when using the preparation in a concentration of 10−4−10−5% for seed soaking and 10−5−10−6% for sprout irrigation (Bulli V. A., Antonova, Oleynik N. A., 1994). Spraying wheat in the tillering phase with ammonium humate solutions of 0.5; 0.05 and 0.005% concentration increased the yield by 2.5−3.5 c/ha (Larina V. A., Astrakhantseva G., Vasilyeva N., Galaganova A., Zhuravleva N., Markadanova E., Pokul T. V., Sokolova N., Starovoitova E.). In addition to increasing the wheat yield, its quality significantly improves. An increase in protein in wheat grain by 0.69−0.85% is noted, which increases the protein harvest from 1 ha from 461.3 kg to 529.9 kg, i.e. by 14.8%. Good results were also obtained when spraying corn, potatoes and other vegetables. Quite positive results were shown by testing the stimulating effect of ammonium humates in closed ground when growing cucumbers and tomatoes. The best concentration of ammonium humates in this case is 0.05%. This solution was used for soaking seeds, spraying plants during vegetation and watering plants under the root. The increase in cucumber yield was 23.6% when soaking, 15.0% when spraying and 15.7% when watering under the root. The quality of cucumbers also increased. The content of vitamin C in them increased from 11.64 to 14.06 mg.

Materials and methods

The study of phase equilibria in physicochemical systems was carried out using the isothermal solubility method (Van't Hoff J. G., 1936).

The solubility of salts was studied by the isothermal method by mixing the solutions of the studied compounds at a constant temperature while maintaining a sufficient amount of solid phases in the mixture. The study was conducted in a therabolic flask with a stirrer placed in a thermostat, the temperature in which was maintained by a thermostat and a contact thermometer with an accuracy of ± 0.1 °C. After equilibrium was established, samples were taken from the liquid and solid phases for analysis and the location of the figurative point of the system was determined. The composition of the liquid and solid phases was established by chemical analysis.

The composition of solid phases was determined according to Skreinemakers. The essence of the method is that in the equilibrium system under study, the liquid phase is separated from the sediment and their composition is determined. Then, they are found along the lines corresponding to the compositions of their wet residues. The true composition of the desired solid phase is established at the intersection point of these lines (Dukelsky M., 1911).

The specific gravity of the samples of the studied compounds and solutions was determined by the pycnometric method (Zdanovsky A. B. Hallurgy, 1972) using a capillary pycnometer with a volume of 10 sm³. To determine the volume, the pyc-

nometer was filled with bidistilled water, thermostatted at 25 ˚C and weighed. Knowing the weight of the dry pycnometer, the density of water at 25 ˚C and the weight of the pycnometer filled with water, its volume was calculated. Weighing was carried out with an accuracy of ± 0.00005 mg. The results are presented with an accuracy of ± 0.1 kg/m^3.

Measuring the pH value of solutions in a laboratory ion meter I-130M with an electrode system of ESL 63–07, EVL-1M3.1 and TKA-7 electrodes with an accuracy of up to 0.05 pH units (GOST 24596. 5–81).

The kinematic viscosity of the solutions was determined using a VPZh capillary viscometer (Florov Yu.G., 1982) with a capillary diameter of 1.16–2.75 mm. The accuracy of the results was ± 0.0001 10–1 mm^2/s.

The phase characteristics of the samples under study were measured using a Panalytical Empyrean powder X-ray diffractometer. The equipment operation was controlled by a computer using the Data Collector program, and the X-ray diffraction pattern was analyzed using the High Score program with the PDF 2013 database. The X-ray phase analysis of the powders under study was performed using a Panalytical Empyrean X-ray diffractometer equipped with a Cu tube (Kα1 = 1.5406Å). The measurements were performed at room temperature in the 2θ angle range from 5 ˚ to 90 ˚ in the step-by-step scanning mode with a step of 0.013 degrees and a signal accumulation time at a point of 5 s.

Results and discussion

The extraction process was carried out at a ratio of OC: NaOH (10% solution) equal to 1:15; a temperature of 20–25 °C and stirring for 60 min. To obtain the first batch of fractions of HA (humic acids) samples, settling was carried out for 24 hours, then after separation of the liquid part, the system was thickened. The liquid part was acidified with 40% nitric acid to pH 0.80–0.85.

The resulting sediment was separated using a centrifuge at 2000 rpm for 15 minutes. The wet sediment was dried in a drying apparatus at a temperature of no more than 90 °C. The yield of HA was calculated based on the dry mass obtained.

1500 ml of distilled water were added to the remaining thick mass, and the process was continued for 12 hours, thus obtaining humic acid fractions and calculating the yield of the fractions. The first fraction was obtained by settling for 3 hours (Yunusova M. V., Erkayev A. U., Kucharov B. X., Yo'lbarsova M.V., Zakirov B. S., Reymov A. M., 2024).

Further, in order to obtain stimulants, we studied the mutual solubility of salts in the sodium hydroxide – humic acid (HA) – H_2O system using the isothermal method at a temperature of 250 ˚C. Equilibrium in the system was established within three days. Based on the chemical analysis of the compositions of the liquid and solid phases, an isothermal diagram of the solubility of this system was constructed (Figure 1).

**Figure 1.** *Isothermal diagram of solubility of the NaOH-HA-H_2O system at 25 ˚C*
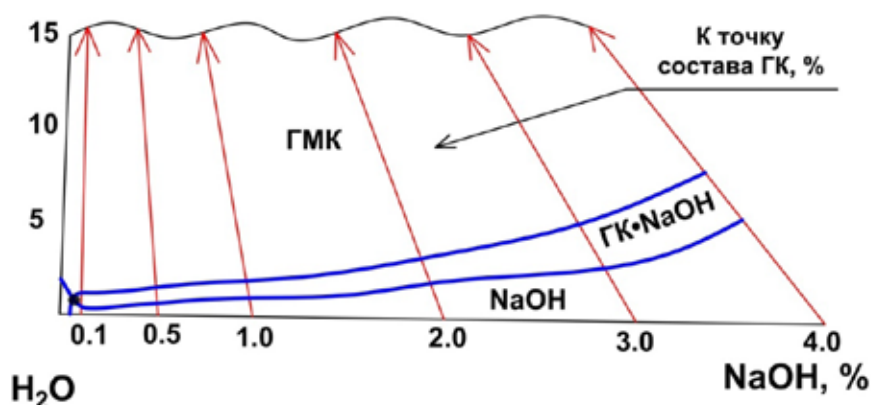
Data on solubility in the ternary system sodium hydroxide – humic acid (HA) – H_2O are presented in Figure 1, from which it follows that the components of the system have a salting-out effect on each other, therefore, with an increase in the concentration of the initial components, the crystallization region of the formed compound expands. This is obviously

associated with complex formation in the system. Indeed, the liquidus curve of the solubility diagram breaks down into three branches corresponding to the crystallization of two initial components – sodium hydroxide and humic acid and the compound NaOH • HA.

Next, with the aim of synthesizing sodium humate, we studied the rheological properties of solutions formed by adding humic acid to 0.5 and 1.0% aqueous solutions of sodium hydroxide (Figures 2 and 3).
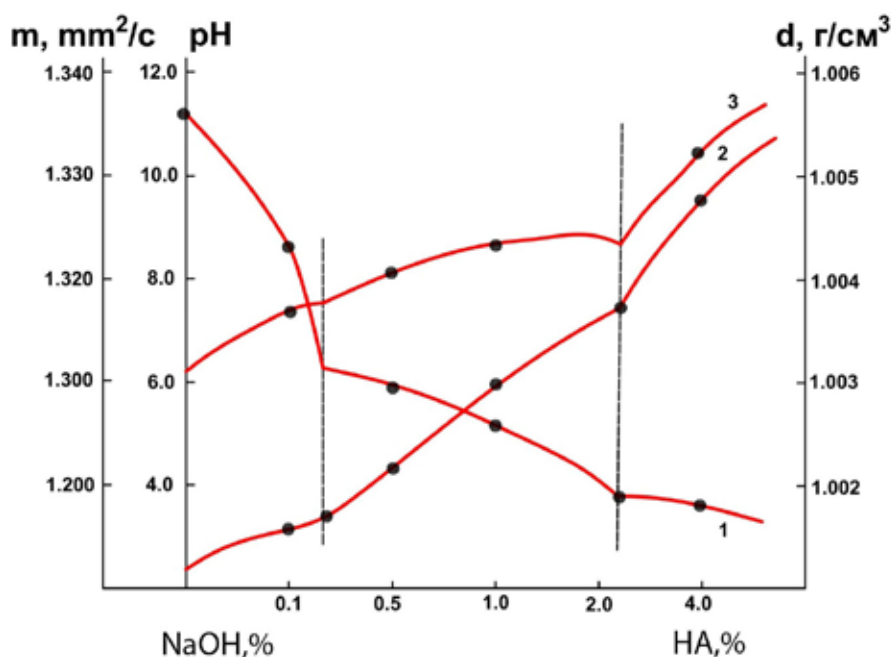
Figure 2. *Dependence of pH of the medium (1), density (2) and viscosity (3) on the concentration of humic acid in a 0.5% sodium hydroxide solution*
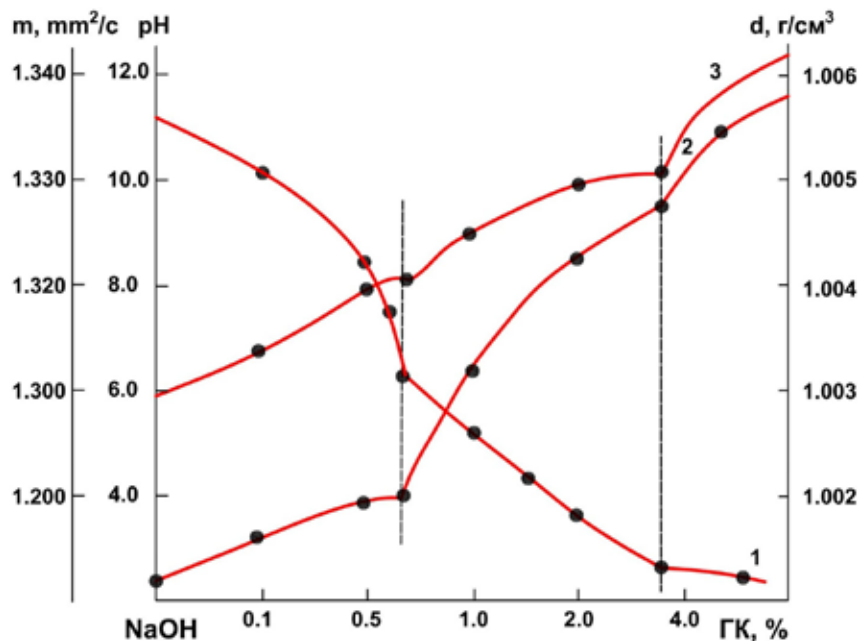
The pH, density and viscosity of solutions of these systems were determined depending on the content of components at a tempera-ture of 25 °C. Based on the data obtained, diagrams of the "composition-properties" of the above components were constructed.

Figure 3. *Dependence of pH of the medium (1), density (2) and viscosity (3) on the concentration of humic acid in a 1.0% sodium hydroxide solution*

From the diagram of the dependence of the pH of the solution medium on the concentration of humic acid in a 0.5% sodium hydroxide solution, it is evident that with an increase in the concentration of humic acid in the solution, a sharp decrease in the pH of the solutions is observed, and an increase in the density and viscosity of the system is observed in the density and viscosity of the solutions.

A study of the sodium hydroxide – humic acid – water system of viscosity, density and pH of the medium showed that the constructed "composition – properties" diagram has two breaks corresponding to a change in the crystallizing phases of the system at the double cryohydrate point, which indicate the formation of a double compound of the composition: NaOH • HA.

The diagram of the dependence of pH, density and viscosity of solutions on the con-

centration of humic acid in a 1.0% sodium hydroxide solution is of a similar nature. It is evident from the diagram that in a 1.0% sodium hydroxide solution in the humic acid concentration range of 0.27–2.12%, a decrease in the pH of solutions is observed in the curves of the dependences and a sharp increase in the values of density and viscosity of solutions is observed (Figure 3). Thus, it can be assumed that when sodium hydroxide interacts with humic acid in aqueous solutions, a complex compound of the composition NaOH • HA (1:1) is formed. These characteristic inflection points are less clearly manifested in the pH values of solutions.

The complex salt NaOH • HA was synthesized on the basis of solutions of sodium hydroxide and crystalline humic acid in a molar ratio resulting from the results of the study of the "Composition-properties" diagram.

Figure 4. *X-ray diffraction pattern of formed NaOH • HA*
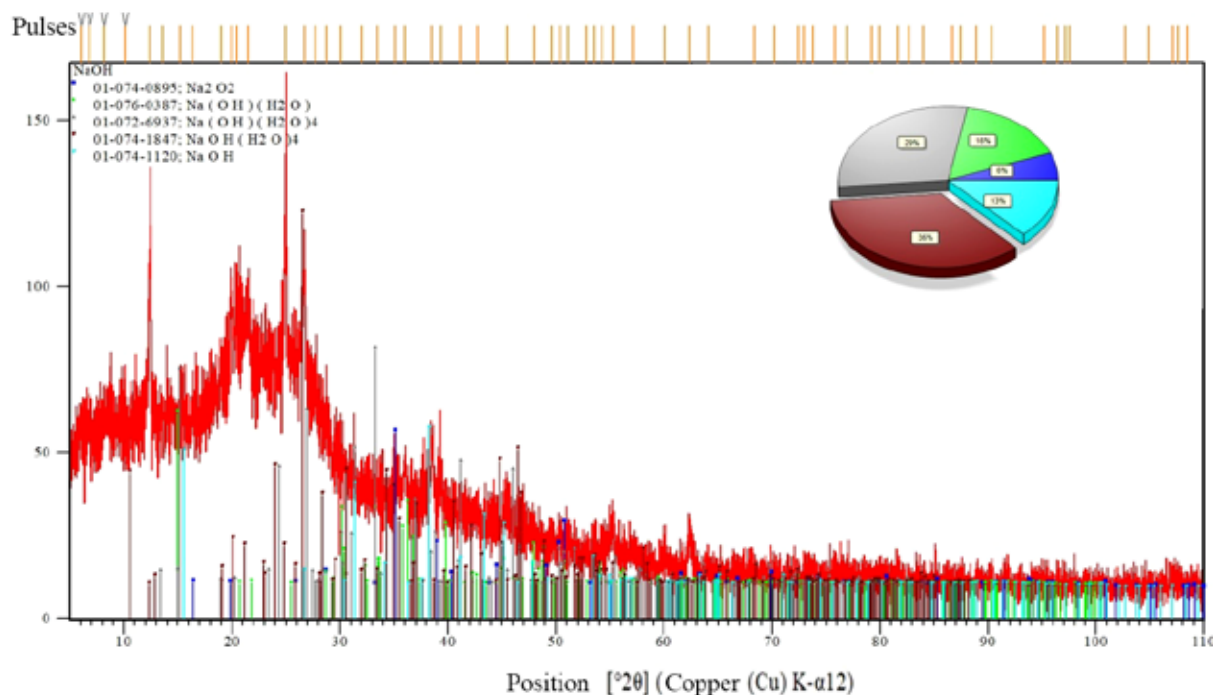
The data of X-ray phase analysis of the compound of sodium hydroxide with humic acid show that all reflections on the diffraction patterns are, as a rule, characterized by their own reflection angles, a set of interplanar distances and diffraction line intensities (Fig. 4). This indicates the individuality of the crystal lattices of the obtained compounds.

Conclusion

Thus, the mutual solubility of salts was studied by the isothermal method at a temperature of 25 °C in the sodium hydroxide – humic acid – water system, and an isothermal diagram of this system was constructed based on the analysis of the compositions of the liquid and solid phases. It was studied that due to complexation in the system, with an

increase in the concentrations of the original components, the crystallization region of the formed compound expands. It was investigated that the liquidus curve of the solubility diagram breaks down into three branches corresponding to the crystallization of two original components – sodium hydroxide, humic acid and the compound NaOH HA. Then, the rheological properties of the solutions formed by adding humic acid to 0.5 and 1.0% aqueous solutions of sodium hydroxide were studied. pH, density and viscosity of solutions of these systems were determined depending on the content of components at a temperature of 25 °C, and composition-property diagrams were constructed. It has been investigated that the constructed diagram «composition-properties» has a break corresponding to the change in crystallizing phases at the double cryohydrate point, which indicate the formation of a double compound of the composition: NaOH · GC. A complex salt of NaOH ·HA based on solutions of sodium hydroxide and crystalline humic acid has been synthesized.

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