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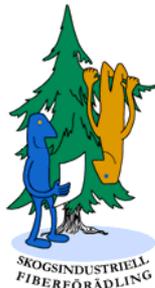


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Ion Specific Differences in Salt Induced Precipitation of Kraft Lignin

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ABSTRACT.

Precipitation of kraft lignin (KL) in alkaline solutions (pH = 10.5) at 70 °C in presence of various salts was investigated. Special concern was devoted to the influence of various quaternary ammonium bromides and different anions. In the latter case, KL precipitation, measured as turbidity, in presence of both sodium salts of uronic acids as well as various inorganic anions was studied. In case of inorganic anions, Cl⁻ and Br⁻ induced a higher degree of KL precipitation compared to NO₃⁻ and SCN⁻. The effects of the two tested sodium uronoates were found to diverge and, initially, galacturonoate showed a better KL stabilizing capacity than Cl⁻. The influence of various tetraalkyl ammonium bromides was compared with the effects of different alkali metal bromides. As the length of the alkyl chain was increased, the KL stability was found to be decreasing. However, at equal concentrations, (CH₃)₄NBr was found to induce a lower degree of KL precipitation than NaBr.

I. INTRODUCTION

In order to produce a chemical pulp of desired properties, it is of great importance to be aware of lignin solubility and stability under process conditions. Indirectly, this has been a considerable task in the development and modification of the kraft process (1) and, probably, it will increase in importance as the progress of chemical pulping proceeds. The effects of various ions on the lignin solution behavior during cooking as well as in the washing and bleaching stages are significant (1-3). The impact of multivalent metal ions, for example, magnesium, calcium, barium and aluminum on lignin solutions and pulp washing has been described in the literature (3,4). In general, very little has been presented regarding specific interactions between lignin and monovalent ions. Indeed, although being of limited industrial relevance, hydrotropic pulping, where high concentrations of various organophilic salts are added to improve the solvent (water) quality, was invented already in the early 1930's (5). Recently, it was reported that the phase behaviour of kraft lignin solution is differently affected by ions belonging to the so-called Hofmeister series (6). Hofmeister, or lyotropic effects are known to be present in many different macromolecular and colloidal systems (7-12). Especially, the effects of anions on negatively charged systems are notable, since the classical electrostatic approach do not fit at all. In spite of extensive research, the origin of the lyotropic effects is still not completely understood. Theories involving depletion of ions from regions immediately adjacent to the colloids, perturbations of the water structure at interfaces and extensions of Gibbs adsorption equation, have been proposed to explain the phenomena (8-12). In this investigation, ion specific differences in salt induced precipitation of kraft lignin in alkaline solutions are discussed.

II. EXPERIMENTAL

Chemicals. A commercial softwood KL (Indulin AT - lot 123H0189, $M_n = 1060 \text{ g mol}^{-1}$, $M_w/M_n = 5.2$ determined by SEC) was supplied by Aldrich. All salts used were of analytical grade and supplied by Riedel-deHaën or Aldrich. Deionised water was used throughout the investigation. Buffer solutions for pH calibration were supplied by Mallinckrodt Baker.

Turbidity measurements. Precipitation of KL was monitored by turbidity measurements. The turbidity was determined using a Hach RATIO/XR 43900 turbidimeter, equipped with a tungsten lamp and operating at all the wavelengths of visible light. All measurements were performed directly on the warm sample cuvettes. The difference in turbidity between a newly heated, still hot sample and the equivalent sample, first heated and chilled, then stored at room temperature for several weeks, was found to be below 10 %.

pH-measurements. A Mettler Delta 340 pH-meter equipped with an Ingold Inlab™ 404 electrode with automatic temperature correction was used. The electrode was calibrated against fresh buffer solutions at pH = 7.00 and 12.01. All samples were pH-adjusted to an initial pH-value of 10.52 ± 0.02 .

III. RESULTS AND DISCUSSION

Lyotropic effects are present in various macromolar and colloidal systems (8). In Figs. 1a-b, the influence of some different cations and anions on KL system stability followed by turbidity measurements is shown. From Fig. 1a, it can be seen that among the tested cations, the lowest stability is obtained in the presence of cesium ions. Within the series of tested metal ion chlorides, the mutually order in causing precipitation is found to be $\text{Cs}^+ > \text{Na}^+ > \text{K}^+$. Concerning the anions, the lowest KL stability is obtained for Cl^- , followed by Br^- and NO_3^- respectively.

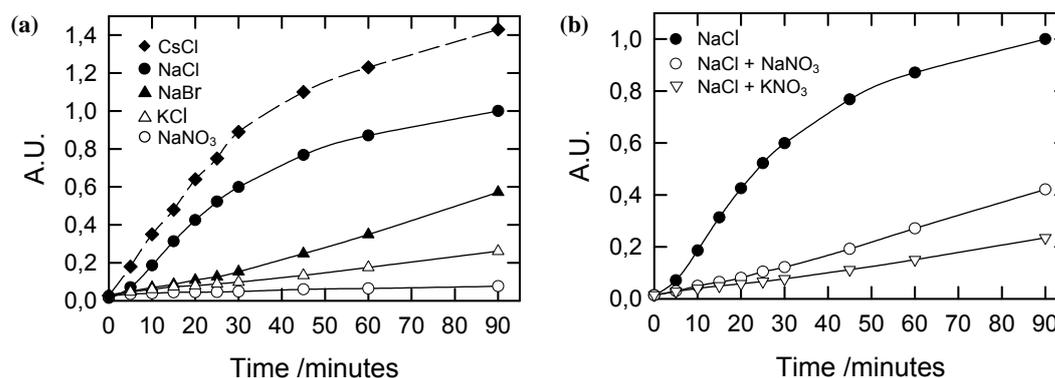


Figure. 1: The figures show the effect of various monovalent metal ion salts on the stability of KL as monitored by turbidity measurements versus time. **(a)** The effect of various salts in the Hofmeister series is shown. In **(b)**, the additive effect of anions and cations is demonstrated. *Note:* All turbidity values are normalized against the end-turbidity of the NaCl sample in each figure.

The mutually order of cations in precipitating KL presented in Fig. 1a, show a reasonable correspondence to the Hofmeister series (7,8). The potency of these cations also follows the sequence for decreasing power in destroying the so-called water structure, which has been determined by IR-measurements on aqueous electrolyte solutions (9). According to this, a decrease in KL precipitation could be caused by water structure breaking cations i.e. $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Cs}^+$. As the Hofmeister series of monovalent cations proposes a higher macromolecular stability/solubility for some ammonium ions than for alkali metal ions, this was investigated in

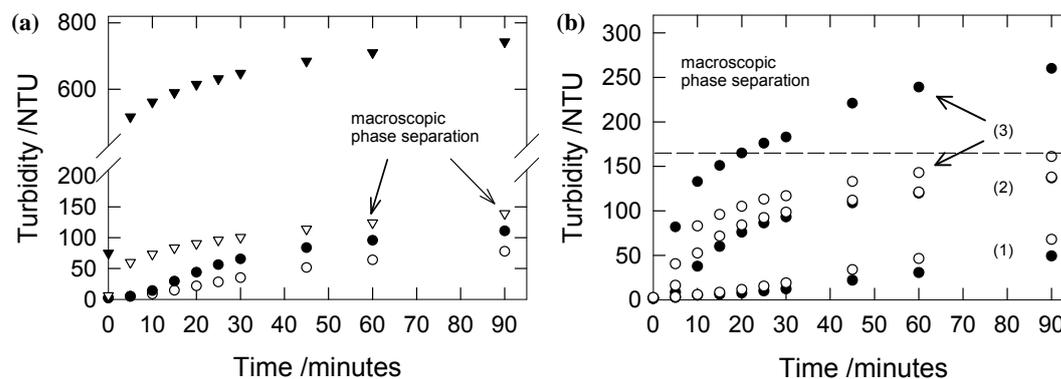


Figure. 2: The figures show the effect of some bromide salts on the stability of KL at $T = 70$ °C as monitored by turbidity measurements versus time. **(a)** The effect of various alkyl ammonium bromides XBr (\circ $N(CH_3)_4Br$, ∇ $N(C_2H_5)_4Br$, \blacktriangledown $N(C_4H_9)_4Br$) and sodium bromide (\bullet), $[XBr] = 0.50$ M, $[NaCl] = 0.50$ M in all the samples. **(b)** A comparison of $N(CH_3)_4Br$ (\circ) and NaBr (\bullet) at different concentrations, (1) 0.10 M, (2) 0.30 M, (3) 0.50 M. $[NaCl] = 0.75$ M in all the samples.

the KL system. The simplest ion, NH_4^+ , was not tested due to possibilities of NH_3 formation at the present alkalinities. In Fig. 2a-b, the results of the comparison between sodium bromide and some quaternary ammonium bromides are shown. From the results presented in Fig. 2a it can be seen that tetramethyl ammonium ions are more efficient KL stabilizers than sodium ions. Furthermore, from Fig. 2b it can be observed that compared to the case of sodium ions, the KL solution becomes increasingly more stable when the concentration of tetramethyl ammonium ions increases. In the context of chemical pulping this might be a notable observation, since the QUATAM-process, which is based on tetramethyl ammonium hydroxide instead of sodium hydroxide, shows a higher rate of delignification than the kraft process at otherwise equivalent process conditions (13).

For the investigated anions, on the other hand, the outcome of the test shows upon an inversed correlation to the classical classification according to Hofmeister. As shown in Fig. 1a-b and Fig. 3a, NO_3^- and SCN^- are the best and Cl^- is the worst among the tested inorganic anions in providing stability for the alkaline KL system. Interestingly enough, this coincides with the trend of decreasing surface tension at air-water interface, where SCN^- shows the lowest value and CO_3^{2-} and SO_4^{2-} the highest (8). Furthermore, SCN^- and NO_3^- are considered as very potent water structure breakers (chaotropes), whereas, for instance SO_4^{2-} belongs to the group of polar water-structure makers (kosmotropes). Moreover, Napper has shown that for poly(oxyethylene) stabilizing moieties, SO_4^{2-} is the most effective anionic flocculant (9). Similar solution behaviour regarding various oxyethylene-containing polymers has been observed by others (12). In the latter case, the phenomenon is explained to be due to adsorption of, for instance SCN^- , on the non-ionic polymer chain. This would create a pseudo-polyelectrolyte and, thus, enhanced solubility is obtained.

Lyotropic effects are often found to be additive among anions and cations (8,9). Fig. 1b shows the aggregation behaviour after additions of sodium chloride and alkali metal ion nitrates to samples containing a fixed standard sodium chloride concentration. As can be

seen in Fig. 1b, when sodium chloride is the only electrolyte, extensive aggregation by time occurs. In samples containing a mixture of both 0.375 M NaCl and 0.375 M NaNO₃ or 0.375 M KNO₃, the aggregation is much less pronounced. The results of the salt test clearly indicates that the effects of cations and anions are additive in case of KL precipitation.

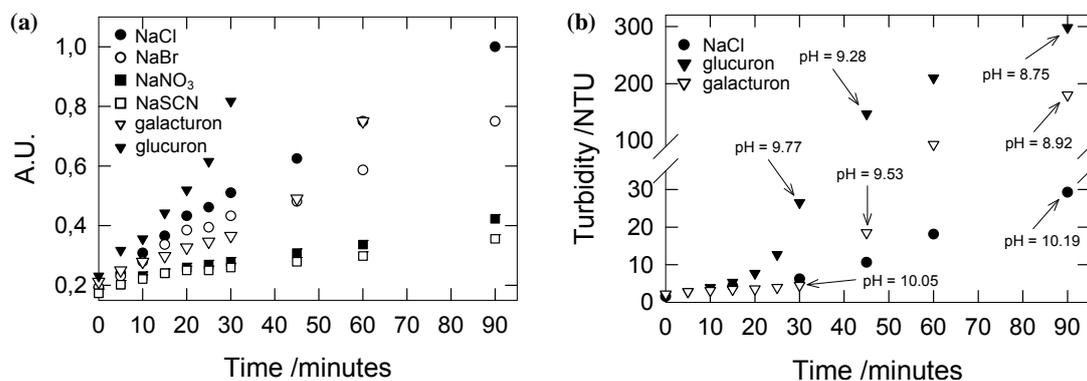


Figure 3: (a) The effect of various anions on the stability of KL at T = 70 °C as monitored by turbidity measurements versus time. The sodium chloride concentration was 0.375 M in all the samples and 0.375 M of the specific salt was added. The turbidity values are normalized against the end-turbidity of the NaCl sample. (b) The effects of sodium chloride and sodium salts of glucuronic and galacturonic acids on KL stability. [NaCl] = 0.800 M, [glucuronate⁻, galacturonate⁻] = 0.400 M + 0.400 M NaCl.

Several of the ions tested in this investigation are of course not expected at important concentrations in ordinary cooking liquors. However, the ion specific interactions between KL and simple ions are of fundamental importance and might provide useful information for the understanding of the stability and solubility of lignin in chemical pulping processes. On the other hand, lyotropic effects are not exclusively caused by inorganic ions (7-12). Therefore, KL precipitation in presence of two different organic sodium salts, D-glucuronoate and D-galacturonoate, was compared with anions in the Hofmeister series. As can be seen in Fig. 3a, glucuronoate gives the overall lowest KL stability of all the tested anions. Compared with the studied inorganic ions, the effect of glucuronoate ions on KL stability shows a marked time dependency. Initially, the presence of galacturonoate induces less significant KL precipitation than Cl⁻ and Br⁻. At above 30 minutes, the slope of a thought turbidity curve representing the KL-galacturonoate sample, rapidly increases and finally the turbidity of the KL-galacturonoate sample exceeds the turbidity of the Cl⁻ and Br⁻ samples. However, the comparison between the various anions is not straightforward due the possibilities of further reactions of the uronoates with a following decrease in alkalinity, which certainly promotes KL precipitation. The final pH-value of the samples in Fig. 3a was 10.2 for the KL-inorganic salt samples, whereas for the KL-galacturonoate and the KL-glucuronoate samples, the pH-values were 9.0 and 8.7, respectively. In order to clarify the different effects of pH and ion specificity, the pH-values in the uronoate samples were measured at different heating times. From the results shown in Fig. 3b it can be observed that the pH-value in the KL-uronoate samples is rapidly decreasing by time of heating and at the same time the turbidity increases. However, despite lowering the pH-

value, galacturonoate seems to possess a precipitation decreasing ability that is totally absent in KL-glucuronoate samples. Starting at an initial turbidity of 1.5 NTU for KL-Cl⁻ and 2.2 NTU for the KL-galacturonoate samples. After 15 minutes at 70 °C, the turbidity was increased to 4.3 and 3.4 NTU (pH = 10.36) and after 30 minutes it was 6.2 and 4.5 NTU, respectively. Thereafter, the turbidity of the KL-galacturonoate samples steadily increased above a thought trend line of the KL-Cl⁻ sample, which is mainly due to the decrease in the pH-value.

IV. CONCLUSIONS

Ion specific interactions are present in macromolecular systems, aqueous alkaline KL solutions is no exception. An exact clarification of the phenomenon is not provided in the literature. Different adsorption/desorption of certain ions at macromolecular interfaces is one suggested explanation. Differences in solution behaviour due to perturbations of the water-structure by some ions, is another theory. From the latter school, it is adopted that destabilization of biological macromolecules by salt generally requires a mixture of so-called kosmotropic cations with chaotropic anions. However, in alkaline KL systems the effect seems to be vice versa. More extensive investigations of these ion specific effects are needed. For instance, the degradation of hemicelluloses during alkaline cooking creates relatively high concentrations of hydroxy carboxylate residues in the black liquor. The effect of these anions on KL solubility/stability should be of fundamental interest for further investigations.

V. ACKNOWLEDGEMENTS

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