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Use of an interactive carbohydrate polymer phenomenon for the separation of polyoxometalates

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Abstract

Keggin type polyoxometalates (POMs) have been proposed as agents for improving the feasibility of oxygen bleaching technique used in producing cellulose fibre in the wood pulping industry. To investigate the possible interactions between carbohydrate polymers and POMs, several different POM anions were eluted through a column containing dextran chromatography gel (Sephadex G-50). Solutions of KCl (0.05 and 0.10 mol/l) and NaCl (0.10 mol/l) were used as eluents. The elution volumes (V_e) of all the POMs tested were found to be greater than the V_e of the internal standard, glycine. The V_e of the POMs increased along with increasing electrolyte concentration. When eluted with 0.10 mol/l KCl solution, the V_e were greater than the respective values of the same POMs eluted with 0.10 mol/l NaCl solution. These facts suggest that POM and the Sephadex gel form complexes, and that the tendency for this to take place depends on the type and concentration of cations present in the system. The method described in this paper may be useful in analysing and purifying mixtures of POMs.

Keywords: Gel filtration; Sephadex gel; Separation; Polyoxometalate; Complexing; Chemical pulp

1. Introduction

This paper describes experiments where interaction of polyoxometalate (POM) anions and carbohydrate molecules was investigated by means of gel filtration through a dextran chromatography gel (Sephadex). In order to explain why such experimental procedure was chosen, a short introduction into the manufacture of bleached chemical pulp and the chemical structure of POMs will be presented below.

The main constituents of wood are two biopolymers, cellulose and lignin. Chemical pulp is prepared by dissolving lignin from wood material, thus retaining the desired product, cellulose fibre. Today this is most often achieved by a method called kraft process, where wood chips are cooked at a high temperature and pressure in highly alkaline conditions in the presence of sulphide ions. While the cooking proceeds, more and more cellulose dissolves along with the lignin. This means that the yield and quality of the product deteriorate (Sjöström, 1993). Therefore, the process is usually stopped at a point where the pulp still contains ca. 2–5% of lignin (Minor, 1996).

During cooking, the structure of lignin changes and light-absorbing unsaturated chemical structures called chromophores are formed. At this stage, the chemical pulp possesses a dark-brown colour, which is undesirable in most paper products. Therefore, the pulp has to be bleached, i.e. the chromophoric structures have to be removed before the fibre can be used to prepare high-quality paper products. Because bleaching of chemical pulps is connected with removing lignin from the pulp, the process is also called delignification (Sjöström, 1993).

Twenty to thirty years ago, chemical pulps were almost exclusively bleached with chlorine chemicals. At that time, elemental chlorine was the most widely used chemical. Although gaseous chlorine was a very potent delignifying agent, its use created environmental problems and the wood pulping industry was thus compelled to start searching for alternative bleaching techniques. Currently, the bleaching of chemical pulps is performed in a multi-step process called a sequence, where delignification is

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achieved in several treatment stages with bleaching chemicals and alkali (NaOH). At present, the only widely used chlorine chemical is chlorine dioxide, but because of ecological and economical reasons, the industry is keenly exploring new methods to improve the feasibility of totally chlorine-free (TCF) bleaching techniques (Sjöström, 1993).

Today, one of the well-established bleaching techniques in the pulping industry is oxygen delignification. The unlimited availability of oxygen makes it by far the cheapest of all bleaching chemicals. One disadvantage of this technique is the low selectivity at high degrees of delignification. During oxygen bleaching, extremely reactive radical species are formed. These radicals do not react only with lignin, but also damage the cellulose molecules, thus decreasing the quality of the product. Recently, several papers have been published on possible improvement of oxygen bleaching by use of POMs as agents in novel effluent-free oxygen delignification processes for chemical pulps (Evtuguin, Daniel, Silvestre, Amado, & Pascoal Neto, 2000; Evtuguin & Pascoal Neto, 1997, 2003; Evtuguin, Pascoal Neto, & Rocha, 2000; Gaspar, Evtuguin, & Pascoal Neto, 2003; Shatalov, Evtuguin, & Pascoal Neto, 2000; Weinstock, Atalla, Reiner, Houtman, & Hill, 1998; Weinstock, Atalla, Reiner, Moen, & Hammel, 1996; Weinstock et al., 1997, Weinstock, Hammel et al., 1998).

POMs are a large and structurally diverse group of early transition metal oxide clusters. The POMs that have been tested as agents in pulp bleaching belong to the family of Keggin structures (Shatalov et al., 2000; Weinstock, Atalla et al., 1998; Weinstock et al., 1997). The general formula of the Keggin structure is $[XM_{12}O_{40}]^{q-}$, where X is called the heteroatom and M are the addenda atoms. The structure is based on a central XO_4 tetrahedron which is surrounded by 12 MO_6 octahedra linked together with oxygen atoms. The heteroatom X is most commonly phosphorus or silicon, although other elements may also function as heteroatoms. The addenda atoms M are early transition metal atoms in high oxidation states, principally W^{VI} and Mo^{VI}, but it is also possible to prepare mixed-addenda Keggin structures where one or more M are substituted with V^{V} or some other metal atoms (Neumann, 1998).

Many properties make the Keggin structures suitable catalysts in pulp delignification. Firstly, they can be easily prepared from inexpensive compounds (e.g. WO_4^{2-}, MoO_4^{2-}, PO_4^{2-}, and SiO_3^{2-}) and their chemical properties (redox potential, acidity, solubility etc.) can be controlled by choice of synthetic precursors and conditions (Weinstock, Atalla et al., 1998). Furthermore, they can be, in many cases, readily reduced by one or more electrons, and the reduced POM anions can often be readily oxidized by O_2 (Kozhevnikov, 1998; Weinstock, 1998). Finally, their structure retains its stability over a wide pH and temperature range (Hill & Prosser-McCartha, 1995; Weinstock et al., 1997).

POM bleaching is based on two reactions

$$\mathrm{POM_{ox}} + \mathrm{Lignin} \rightarrow \mathrm{POM_{red}} + \mathrm{Lignin}^{*} + 2\mathrm{H}^{+} \quad (1)$$

$$\mathrm{POM_{red}} + 2\mathrm{H}^{+} + {}^{1}\!/_{2}\,\mathrm{O_2} \rightarrow \mathrm{POM_{ox}} + \mathrm{H_2O} \quad (2)$$

where $\mathrm{POM_{ox}}$, $\mathrm{POM_{red}}$, and Lignin* represent oxidized POM, reduced POM, and an oxidized lignin structure, respectively (Evtuguin & Pascoal Neto, 1997; Evtuguin, Pascoal Neto et al., 2000; Weinstock et al., 1997). From Eqs. (1) and (2) it is seen that, theoretically, when lignin is completely oxidized in POM bleaching, the final products are solely water and carbon dioxide.

Until now, POM bleaching has not been applied industrially. This is partly due to inefficiency of the processes presented. Very recently, we investigated the possible role of Donnan effect on distribution of POM in suspension of chemical pulp fibres (Ruuttunen & Vuorinen, 2004). It was observed that POM, which is highly anionic in aqueous solution, is repelled by the negatively charged fibre at near-neutral pH when ionic strength of the suspension is low. However, when the ionic strength of the suspension was high (0.50 and 1.00 mol/l), an attraction was observed between POM and the fibre. It was also observed that the attraction became stronger as the ionic strength of the suspension increased.

The repulsion of POM and the fibre was explained with the Donnan theory. Moreover, it was concluded that the repulsion most probably hinders the POM bleaching when it is performed at unfavourable conditions (i.e. low ionic strength and near-neutral to alkaline pH). In contrast, the attraction observed between POM and cellulosic fibre was highly unexpected, and its mechanism could not be explained. It was suggested that the transition metal oxides of POM form bonds with the hydroxyl groups of the carbohydrate molecules in cellulosic fibre (Ruuttunen & Vuorinen, 2004).

Gel filtration is a technique that is used to separate compounds according to their molecule size. Sephadex gels used in the technique are prepared by cross-linking dextran with epichlorohydrin (Anonymous, 1991). The Sephadex gels have some similar structural features with cellulose fibres: both materials swell in aqueous solution, but are not water soluble and both materials are formed of polymers containing glucose units, therefore possessing abundantly free hydroxyl groups. Because of this, gel filtration using Sephadex gel was chosen as a method to further investigate the attraction between POM and carbohydrates.

2. Experimental

2.1. General aspects

To test the possible interaction of POM with carbohydrates at different electrolyte concentrations, experiments were designed where POM was eluted through a Sephadex

G-50 column. As eluent, KCl solution at concentrations 0.05 and 0.10 mol/l was chosen for the experiments. To test whether changing the electrolyte affected the results, some gel filtration experiments were planned to be performed with 0.10 mol/l NaCl as eluent. The minimum salt concentration was set at 0.05 mol/l to avoid the distortion of results caused by electronic interaction between the acidic groups attached to the Sephadex gel and the eluting molecules possessing an electrical charge (Neddermeyer & Rogers, 1968). The pH of the eluent was not adjusted; therefore the pH during filtration experiments was ca. 7.

The fractionation range of Sephadex G-50 gel for dextrans is 500–10,000 g/mol (Anonymous, 1991), which corresponds to dextran molecules containing ca. 3–60 glucose units. The diameter of a Keggin structure (i.e. POM anions used in this work) is ca. 1.1 nm (Weinstock, Atalla et al., 1998), which equals approximately the length of a cellobiose molecule (Sjöström, 1993) a disaccharide comprising of two glucose units. Based on these facts it is reasonable to draw a conclusion that the pores in Sephadex G-50 gel are large enough to accommodate a single POM anion.

The amino acid glycine (H_2NCH_2COOH) has a molecular mass of 75.07 g/mol, which is considerably less than the fractionation range of the Sephadex G-50 gel. Because both glycine molecules and the POM anions are able to penetrate into the pores in Sephadex G-50 gel, they should have approximately equal elution volumes (V_e) in the system designed for the experiments, assuming that no interaction (i.e. bonding) between the eluting compounds and the column material takes place.

2.2. Materials

All commercial reagents were of analytical grade. Sephadex G-50 (manufactured by Pharmacia LKB Biotechnology) gel material was swelled in distilled water. Glycine and Blue Dextran 2000 were manufactured by FF-Chemicals and Pharmacia Fine Chemicals, respectively. The POMs used in the experiments were $K_6[SiV^{IV}W_{11}O_{40}]$ (**1**), $K_5[SiV^{V}W_{11}O_{40}]$ (**2**), $K_5[SiMn^{III}W_{11}O_{39}]$ (**3**), $K_6[AlMn^{III}W_{11}O_{39}]$ (**4**), $Na_4[PMn^{III}W_{11}O_{39}]$ (**5**), and $Na_5[PMn^{II}W_{11}O_{39}]$ (**6**). Compounds **1–4** were synthesized in Forest Products Laboratory, USDA (Madison, USA) (Cowan et al., 2001; Domaille, 1984), and compounds **5** and **6** at the Department of Chemistry at Emory University (Atlanta, USA) (Zhang, Pope, Chance, & Jameson, 1995).

2.3. Equipment

The gel filtration equipment consisted of pump (HPLC 2248), UV/vis detector (Unicord VW 2251), fraction collector (Redi Frac), and a column. The equipment was manufactured by Pharmacia LKB. The dimensions of the column were 130 mm (length) and 16 mm (diameter). The column was packed according to the manufacturer's orders.

Table 1
Elution volumes (V_e) of POMs at different KCl concentrations

POM	V_e/ml	
	0.05 mol/l KCl	0.10 mol/l KCl
1	44	47
2	41	49
3	34, 53	37, 66
4	35	39
5	37, 45, 53	39, 48, 59
6	45	53

The pump was set to a flow rate of 0.400 ml/min. The actual flow rate was determined after each run by weighing the fractions collected. UV detection at wavelength 220 nm was used for glycine and the POMs. Blue Dextran 2000 was detected at 610 nm. In all of the experiments the fractions were collected at 20 min intervals. All experiments were performed at room temperature.

2.4. Sample preparation

Samples were prepared by mixing glycine, aqueous solution of POM (10 mmol/l), and the eluent. The concentrations of glycine and POM in the samples were 0.53 mol/l (40 g/l) and 0.20 mmol/l (ca. 0.6 g/l), respectively. The sample volume introduced to each gel filtration experiment was 0.500 ml.

3. Results and discussion

The void volume (V_o) determined for the column was 10 ml. This value shows the smallest possible V_e for our system. The actual flow rate differed from the nominal flow rate (0.400 ml/min) and fluctuated slightly, being between 0.31 and 0.39 ml/min. Therefore, some variation in the results is seen; the V_e of the internal standard, glycine, was determined to be 24–25 ml. This value represents the largest possible V_e in our system for a compound that behaves ideally in gel filtration, i.e. does not interact with the gel material.

The elution volumes of POMs at different KCl and NaCl concentrations are summarized in Tables 1 and 2. It can be seen that all of the POMs have larger elution volumes than glycine. This indicates that POMs interact with the column material. For only two POMs (**3** and **5**) more than one peak was obtained. It is known that compounds **1** and **2** are structurally stable in the conditions used in the experiments (Weinstock et al., 1997). Compound **4** is synthesized at pH

Table 2
Elution volumes (V_e) of POMs eluted with 0.10 mol/l NaCl

POM	V_e/ml
5	29, 39, 49
6	39

ca. 3–5 (Cowan et al., 2001) and the estimation for the pH stability range of compounds **5** and **6** is ca. 2.5–6.5 (Botar & Weinstock, 2003). No data in the literature was found on the pH stability of compound **3**. Based on these facts, it is possible that the additional peaks for compounds **3** and **5** are due to degradation of the compounds during sample preparation or gel filtration. Nevertheless, because the shape of the peaks in all cases is Gaussian and there are no indications on tailing (Figs. 1 and 2), the additional peaks for **3** and **5** may also be due to impurities that the synthesized POMs potentially contain. Because the V_e values of the hypothetical impurities are larger than the V_e of glycine, compounds **3** and **5** may also contain other POMs than $K_5[SiMn^{III}W_{11}O_{39}]$ and $Na_4[PMn^{III}W_{11}O_{39}]$. Comparing the results for **5** and **6** (Tables 1 and 2, Figs. 1 and 2) it seems that **5** possibly contains traces of **6** as an impurity: in the experiments, for both compounds a peak was detected at $V_e = 45$ and 39 ml, when 0.05 mol/l KCl and 0.10 mol/l NaCl, respectively, were used as eluents. However, no common peaks were detected when the same compounds were eluted with 0.10 mol/l KCl.

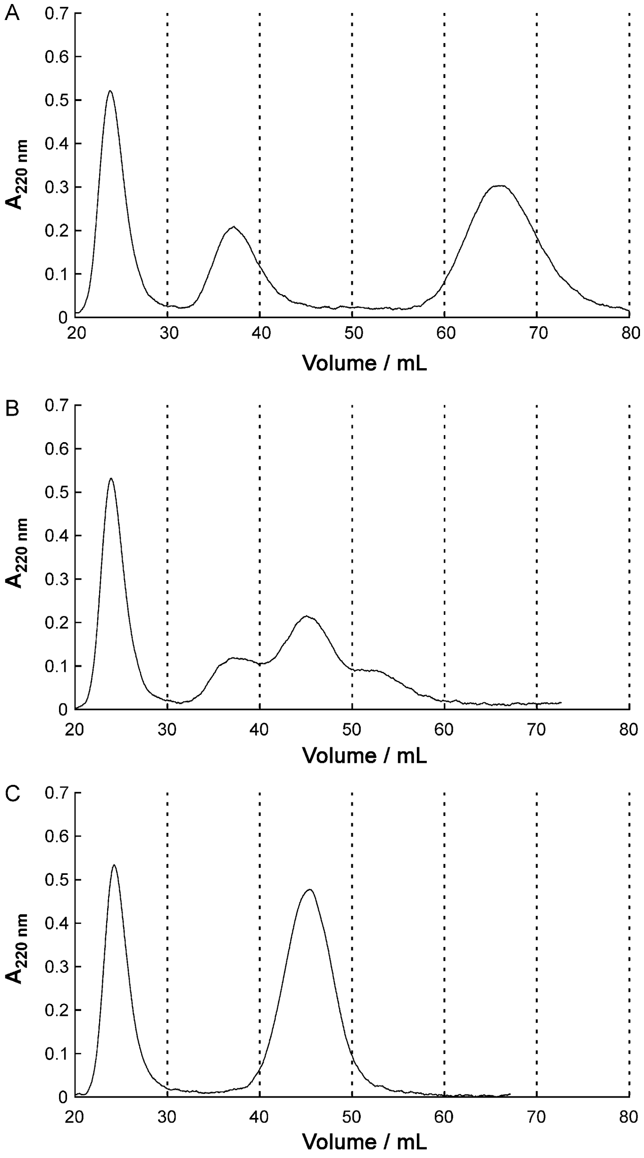

Fig. 1. Gel filtration of POMs. The leftmost peak in each chromatogram is due to the internal standard, glycine. (A) Compound **3** in 0.10 mol/l KCl; (B) compound **5** in 0.05 mol/l KCl; (C) compound **6** in 0.05 mol/l KCl.

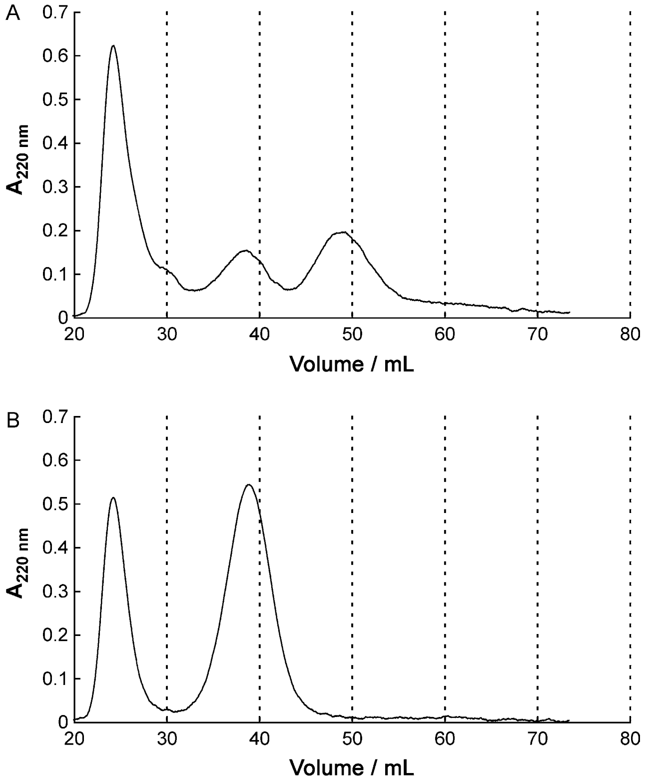

Fig. 2. Gel filtration of POMs. The leftmost peak in both chromatograms is due to the internal standard, glycine. (A) Compound **5** in 0.10 mol/l NaCl; (B) compound **6** in 0.10 mol/l NaCl.

The results in Table 1 show that there is a positive correlation of V_e values of POMs with the KCl concentration of the eluent. Also, when the results in Tables 1 and 2 are compared, it is seen that in the gel filtration experiments where NaCl solution was used as an eluent, smaller V_e values were obtained than in the experiments where POMs were eluted with KCl. The explanation for these observations may be ion pairing of POMs (Grigoriev, Cheng, Hill, & Weinstock, 2001; Grigoriev, Hill, & Weinstock, 2000; Kirby & Baker, 1998). Grigoriev et al. (2001) observed that in a solution containing acetate buffered water and *t*-butanol (2:3, v/v) POMs formed ion pairs with alkali metal cations and the tendency for ion-pairing increased with increasing electrolyte concentration and cation size. Therefore, if complexing of POM with Sephadex gel involves forming of ion pairs, complexing is more pronounced in an environment where potassium ions are present compared to a system consisting of sodium ions, POM and Sephadex gel. However, since the tendency of ion-pairing decreases with increasing hydration of the cations (Kirby & Baker, 1998), it is somewhat doubtful that the phenomenon exists in our system, where no organic solvents are present.

The valence of the POM anion does not seem to affect its V_e. In Table 1 it is seen that the compounds with valence $6-$ (**1** and **4**) and the compounds with valence $5-$ (**2**, **3**, and **6**) have all very different elution volumes. Moreover, it is difficult to find any pattern between the oxidation state of the addenda atoms and the V_e values of the POMs. This can be seen by comparing the results for the compounds **1** and **2** (containing V^{IV} and V^{V}, respectively) as well as for the compounds **5** and **6** (containing Mn^{III} and Mn^{II}).

Compounds **3–5** have identical composition of addenda atoms, i.e. their structure differs only with respect to heteroatoms (Si, Al, and P, respectively). Even though the several peaks that were obtained in the experiments for **3** and **5** make interpretation of the results difficult, it is evident that the three POMs have different elution volumes. Therefore, it seems possible that the heteroatom affects the V_e values of POMs. However, the mechanism for this effect remains unclear in the light of the results.

4. Conclusions

Based on the results it is clear that POMs interact with the Sephadex G-50 gel. At the moment we are not sure what the mechanism of the interaction is. It is probable, nonetheless, that the interaction occurs between the metal oxides of POMs and the hydroxyl groups of dextran molecules because these are the most abundant functional groups present in our system. The role of alkali metal cations in the complexing mechanism is obscured, although a complexing mechanism including ion-pairing between the cations and POM anions would explain some of the experimental results.

The method presented in this paper may be used in purifying aqueous POM solutions. So far, only few methods have been published for chromatographic separation of POMs. To our knowledge, none of the methods previously published are based on chromatography on gel filtration gels. Instead, the techniques utilized are high performance liquid chromatography (HPLC) (Braungart & Ruessel, 1984; Hettiarachchi, Ha, Tran & Cheung, 1995; Kirk, Riske, Finke, Lyon & Rapko, 1989) and capillary zone electrophoresis (CZE) (Hettiarachchi et al., 1995). The method presented in this paper is technically less demanding than the aforementioned methods.

It is obvious that investigation on many aspects of gel filtration of POMs is still needed. Nevertheless, the results presented in this paper show a previously unknown property of POMs, namely their ability to form complexes with carbohydrate gels in electrolyte solution.

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References

Anonymous (1991). *Gel filtration: Principles and methods*. Sweden: Pharmacia LKB Biotechnology.

Botar, B., & Weinstock, I.A. (2003). Personal communication.

Braungart, M., & Ruessel, H. (1984). Separation of molybdoheteropoly acids of phosphorus, arsenic, silicon and germanium as ion-associates by HPLC. Application to quantitative determination in water. *Chromatographia*, *19*, 185–187.

Cowan, J. J., Bailey, A. J., Heintz, R. A., Do, B. T., Hardcastle, K. I., Hill, C. L., & Weinstock, I. A. (2001). Formation, isomerization, and derivatization of keggin tungstoaluminates. *Inorganic Chemistry*, *40*(26), 6666–6675.

Domaille, P. J. (1984). The 1- and 2-dimensional tungsten-183 and vanadium-51 NMR characterization of isopolymetalates and heteropolymetalates. *Journal of the American Chemical Society*, *106*(25), 7677–7687.

Evtuguin, D. V., Daniel, A. I. D., Silvestre, A. J. D., Amado, F. M. L., & Neto, C. P. (2000). Lignin aerobic oxidation promoted by molybdovanadophosphate polyanion $[PMo_7V_5O_{40}]^{8-}$. Study on the oxidative cleavage of β-O-4 aryl ether structures using model compounds. *Journal of Molecular Catalysis A: Chemical*, *154*(1/2), 217–224.

Evtuguin, D. V., & Pascoal Neto, C. (1997). New polyoxometalate-promoted method of oxygen delignification. *Holzforschung*, *51*(4), 338–342.

Evtuguin, D. V., Pascoal Neto, C., & Rocha, J. (2000). Lignin degradation in oxygen delignification catalyzed by $[PMo_7V_5O_{40}]^{8-}$ polyanion. Part I. Study on wood lignin. *Holzforschung*, *54*(4), 381–389.

Gaspar, A., Evtuguin, D. V., & Pascoal Neto, C. (2003). Oxygen bleaching of kraft pulp catalysed by Mn(III)-substituted polyoxometalates. *Applied Catalysis, A: General*, *239*(1/2), 157–168.

Grigoriev, V. A., Cheng, D., Hill, C. L., & Weinstock, I. A. (2001). Role of alkali metal cation size in the energy and rate of electron transfer to solvent-separated 1:1 $[(M^+)(\text{acceptor})]$ $(M^+=Li^+, Na^+, K^+)$ ion pairs. *Journal of the American Chemical Society*, *123*(22), 5292–5307.

Grigoriev, V. A., Hill, C. L., & Weinstock, I. A. (2000). Role of cation size in the energy of electron transfer to 1:1 polyoxometalate ion pairs $\{(M^+)(X^{n+}VW_{11}O_{40})\}^{(8-n)-}$ (M=Li, Na, K). *Journal of the American Chemical Society*, *122*(14), 3544–3545.

Hettiarachchi, K., Ha, Y., Tran, T., & Cheung, A. P. (1995). Application of HPLC and CZE to the analysis of polyoxometalates. *Journal of Pharmaceutical and Biomedical Analysis*, *13*(4/5), 515–523.

Hill, C. L., & Prosser-McCartha, C. M. (1995). Homogeneous catalysis by transition metal oxygen anion clusters. *Coordination Chemistry Reviews*, *143*, 407–455.

Kirby, J. F., & Baker, L. C. W. (1998). Effects of counterions in heteropoly electrolyte chemistry. 1. Evaluations of relative interactions by NMR on kozik salts. *Inorgic Chemistry*, *37*(21), 5537–5543.

Kirk, A. D., Riske, W., Finke, R. G., Lyon, D. K., & Rapko, B. (1989). Rapid, high-resolution, reversed-phase HPLC separation of highly charged polyoxometalates using ion-interaction reagents and competing ions. *Inorganic Chemistry*, *28*(4), 792–797.

Kozhevnikov, I. V. (1998). Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chemical Reviews*, *98*(1), 171–198.

Minor, J. L. (1996). Production of unbleached pulp. In C. W. Dence, & D. W. Reeve (Eds.), *Pulp bleaching: Principles and practice*. Atlanta, USA: Tappi Press pp. 25.

Neddermeyer, P. A., & Rogers, L. B. (1968). Gel filtration behavior of inorganic salts. *Analytical Chemistry*, *40*(4), 755–762.

Neumann, R. (1998). Polyoxometalate complexes in organic oxidation chemistry. *Progress in Inorganic Chemistry*, *47*, 317–370.

Ruuttunen, K., & Vuorinen, T. (2004). Donnan effect and distribution of $[SiV^{IV}W_{11}O_{40}]^{6-}$ anion in pulp suspension. *Journal of Pulp and Paper Science*, *30*(1), 9–14.

Shatalov, A. A., Evtuguin, D. V., & Pascoal Neto, C. (2000). Cellulose degradation in the reaction system O_2/heteropolyanions of series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$. *Carbohydrate Polymers*, *43*(1), 23–32.

Sjöström, E. (1993). *Wood chemistry: Fundamentals and applications*. San Diego, USA: Academic Press.

Weinstock, I. A. (1998). Homogeneous-phase electron-transfer reactions of polyoxometalates. *Chemical Reviews*, *98*(1), 113–170.

Weinstock, I. A., Atalla, R. H., Reiner, R. S., Houtman, C. J., & Hill, C. L. (1998). Selective transition-metal catalysis of oxygen delignification using water-soluble salts of polyoxometalate (POM) anions. Part I. Chemical principles and process concepts. *Holzforschung*, *52*(3), 304.

Weinstock, I. A., Atalla, R. H., Reiner, R. S., Moen, M. A., & Hammel, K. E. (1996). A new environmentally benign technology and approach to bleaching kraft pulp. Polyoxometalates for selective delignification. *New Journal of Chemistry*, *20*(2), 269–275.

Weinstock, I. A., Atalla, R. H., Reiner, R. S., Moen, M. A., Hammel, K. E., Houtman, C. J., Hill, C. L., & Harrup, M. K. (1997). A new environmentally benign technology for transforming wood pulp into paper. Engineering polyoxometalates as catalysts for multiple processes. *Journal of Molecular Catalysis A: Chemical*, *116*(1/2), 59–84.

Weinstock, I. A., Hammel, K. E., Moen, M. A., Landucci, L. L., Ralph, S., Sullivan, C. E., & Reiner, R. S. (1998). Selective transition-metal catalysis of oxygen delignification using water-soluble salts of polyoxometalate (POM) anions. Part II. Reactions of alpha vanadoundecatungstosilicate with phenolic lignin-model compounds. *Holzforschung*, *52*(3), 311.

Zhang, X., Pope, M. T., Chance, M. R., & Jameson, G. B. (1995). High-valent manganese in polyoxotungstates. 1. Magnesium(IV) Keggin derivatives. *Polyhedron*, *14*(10), 1381–1392.