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Investigation of aqueous biphasic systems for the separation of lignins from cellulose in the paper pulping process

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Abstract

In efforts to apply a polymer-based aqueous biphasic system (ABS) extraction to the paper pulping process, the study of the distribution of various lignin and cellulosic fractions in ABS and the effects of temperature on system composition and solute partitioning have been investigated. The partitioning of three lignin species (Indulin AT, Indulin C, and Reax 85A) have been studied in ABS prepared from stock solutions of 40% (w/w) poly(ethylene glycol) (PEG)-2000 and increasing concentrations of K_2CO_3, $(NH_4)_2SO_4$, and NaOH. The partitioning of these lignins is affected by the free energy of hydration of the salt forming the ABS, the tie line length, and the dissociation of the sulfonic acid and hydroxyl groups of the distributed solutes. The partitioning of fibrous cellulose and diethylaminoethyl cellulose have been studied in 40% (w/w) PEG-2000–$(NH_4)_2SO_4$ ABS. The hydrophilic nature of these species is important in terms of their phase preference when designing a polymer-based aqueous biphasic extraction process for use in a paper pulping process. Both cellulosic samples do not dissolve, but rather report to the salt-rich phase of an ABS. In both chemical pulping and Organosolv pulping, temperatures in excess of 120°C are needed to solubilize the lignin from the cellulose fraction of wood. To study the effects of temperature on the phase diagram and solute partitioning, phthalic acid and $NH_4^{99}TcO_4$ (as system probes) have been partitioned in 40% (w/w) PEG-2000–$(NH_4)_2SO_4$ ABS at known tie line lengths as a function of temperature. Temperature does not appear to affect the partitioning results beyond the expected increase in phase divergence as temperature is increased. The PEG-2000 polymer itself appears to be stable to chemical pulping conditions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aqueous two phase systems; Chemical pulping; Lignins; Cellulose

1. Introduction

The process of reengineering a typical chemical pulping process, in which raw paper pulp is prepared from wood pulp by delignification, is being examined. Typically, paper pulping is highly efficient and effective in delignification, but the process has a high chemical and energy demand [1]. Efforts in the past to reengineer such a process by traditional solvent extraction for greater efficiency and lower demands on chemicals and energy input have been made. These processes are known as Organosolv, and at the laboratory and pilot scale have demonstrated high efficiency for the delignification of raw paper pulp [2,3]. Due to the difficulty in engineering a high temperature/pressure solvent extraction process, only in relatively few instances, and only at relatively small scale, have these types of processes

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been applied in the pulp and paper industry. On the other hand, the results of the Organosolv experience suggest that the paper pulping process can be beneficially served by implementation of a solvent extraction step, or by its development as a reactive extraction process.

An aqueous biphasic extraction process may be designed and applied to the paper pulping process since traditional chemical processes (e.g., the Kraft process) provide salt concentrations that are close to that required for biphase formation with poly(ethylene glycol) (PEG). Elevated temperatures will also work in favor of biphase formation, and there are a wide range of polymers that are available which can be induced to phase separate under a continuum of less stringent conditions of temperature and salt concentration [4]. Previous results demonstrating that aromatic molecules prefer the PEG-rich phase of a PEG–salt ABS, suggest that lignins should have a similar behavior [5–8]. If lignins indeed prefer the PEG-rich phase, an extraction of lignin from cellulose could be effectively performed using ABS.

We have been examining PEG-2000 for its ability to extract various lignins from aqueous phases and its ability to extract lignin under conditions resembling chemical paper pulping. Ultimately, it would be desirable to engineer such an aqueous polymeric extraction step to minimize not only the consumption of chemical pulping feedstock, but to also minimize polymer usage. By studying the effectiveness of PEG-2000 in the extraction of lignin and rejection of cellulosic fractions, it is hoped to gain insight which can be utilized in the development of an appropriate ABS for use in the paper pulping industry.

2. Experimental

The chemicals, $(NH_4)_2SO_4$, K_2CO_3, NaOH, Na_2S, Na_2CO_3, and PEG, were obtained from Aldrich (Milwaukee, WI, USA) and were of reagent-grade. Carbon-14 labeled phthalic acid was purchased from Sigma (St. Louis, MO, USA) and upon receipt, the tracer was diluted with water. $NH_4^{99}TcO_4$ was purchased from Amersham Life Science (Arlington Heights, IL, USA) and similarly diluted with water. Fibrous cellulose and DEAE (diethylaminoethyl) cellulose were obtained from Sigma. All water was purified using a Barnsted (Dubuque, IA, USA) commercial deionization system. For standard liquid scintillation analyses, Ultima Gold Scintillation Cocktail (Packard Instrument, Downers Grove, IL, USA) and a Packard Tri-Carb 1900 TR Liquid Scintillation Analyzer (Packard Instrument) were used.

The various lignins examined were obtained from Westvaco (Charleston, SC, USA). The physical and chemical properties of these lignin species are shown in Table 1. The lignins Indulin C and Indulin AT are closest to representing ‘‘natural lignin’’ since these lignins are derived directly from the alkaline pulping process. (This statement must be treated with caution, however, since they represent lignins resulting from a particular chemical delignification process and almost certainly differ from lignins from different processes.) Indulin AT is a desalted preparation of Indulin C. The remaining lignin species have all been treated by Westvaco to increase the preponderance of sulfonic acid groups in the preparation of surface active agents and dispersants [9].

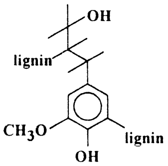
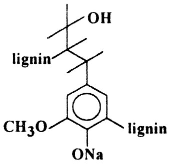
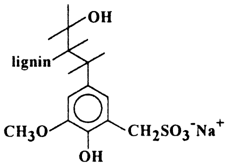
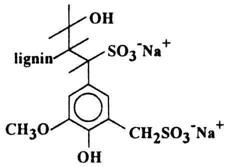
2.1. Phase diagram determination

The phase diagrams were determined by the cloud point method [10] and tie lines were assigned from the known relationship between the mass phase ratio and system composition using the mathematical methods of Merchuck et al. [11]. Phase diagrams were also determined at various temperatures using an HPLC Shimadzu LC 10 (Shimadzu Corporation, Kyoto, Japan) on an isochratic size exclusion chromatography column, Pharmacia Peptide HR 10/30 (Amersham Pharmacia Biotech, Piscataway, NJ, USA) coupled to a refractive index detector, Shimadzu RID10A (Shimadzu Corporation). The running buffer was a composition of 250 m*M* NaCl and water, and deionized water, running at a flow-rate of 1 ml/min. The temperature of the biphases was equilibrated using a Neslab RTE-110 water bath (Neslab Instruments, Newington, NH, USA).

2.2. Determination of lignin distribution ratios in ABS

Each lignin species (Reax 85A, Indulin AT, and Indulin C) was dissolved in 40% (w/w) PEG-2000 at 1 mg/g. The absorbance of the PEG–lignin solution

Table 1
Characterization of lignin species

Lignin	Sulfonation (mol/kg)	SO_3^- location	M_w	M_{z+1}	pH of reaction	Lignin structure
Indulin AT	0.0	–	2700	69 500	8.6	
Indulin C	0.0	–	2700	69 500	8.6	
Reax 85A	0.8	aryl	7900	189 000	10.4	
Polyfon T	2.0	alkyl, aryl	2900	13 000	10.5	

was measured at different concentrations to generate a calibration curve for each lignin species. This was done at 260 nm using a Cary 3C UV–Vis Spectrophotometer (Varian Optical Spectroscopy, Mulgrave, Victoria, Australia). Liquid–liquid distribution values were determined by mixing 2 ml of a salt stock solution of known concentration and 2 ml of a 40% (w/w) PEG-2000–lignin solution of known concentration. The systems thus prepared were vortex mixed for 5 min, centrifuged (2000 *g*) for 10 min, and then allowed to equilibrate for 30 min. Some lignin precipitation at the interface was observed, particularly in the PEG–NaOH ABS. The phases were separated so that any precipitation at the interface was not included in the test sample. A known volume of each phase was diluted with a known volume of deionized water and then each phase was analyzed on the spectrophotometer at 260 nm to determine its absorbance. From the calibration curves generated for each species of lignin analyzed, the concentration of lignin in each phase was determined and a distribution ratio calculated as in Eq. (1):

$$D = \frac{\text{Concentration of lignin in PEG-rich upper phase}}{\text{Concentration of lignin in salt-rich lower phase}} \qquad (1)$$

2.3. Determination of distribution ratios for tracer solutes in ABS

Both ^{14}C-labeled phthalic acid and $NH_4^{99}TcO_4$ served as non-volatile probes for the study of temperature effects on phase partitioning in ABS. Liquid–liquid distribution ratios were determined by mixing 2 ml of a 40% (w/w) PEG-2000 solution with 2 ml of a salt stock solution of known concentration. Then the prepared systems were vortex-mixed for 2 min and equilibrated at the experimental temperatures for 30 min using a Neslab RTE-110 water bath (Neslab Instruments). ^{14}C tracer and $NH_4^{99}TcO_4$ were diluted with water to an activity of approximately 0.06–0.08 μCi/μl for use as the "spike" in the partitioning experiment. Tracer quantities (1–4 μCi) of the radionuclide of interest were added, the system centrifuged (2 min, 2000 *g*), and then vortex-mixed for 2 min. The phases were disengaged by allowing the systems to equilibrate at experimental temperatures for 1–2 h in the water bath. Equal aliquots of each phase were then removed for standard liquid scintillation analysis. All measurements were carried out in duplicate at least.

The distribution ratios measured for phthalic acid and $^{99}TcO_4^-$ are defined as the total concentration of solute in the upper PEG-rich phase divided by the concentration of the total tracer concentration in the lower salt-rich phase. Since equal aliquots of each phase were analyzed, and the activity of the tracers is directly proportional to their concentration, the distribution ratios were determined as in Eq. (2):

$$D = \frac{\text{Activity in counts per minute in the upper PEG-rich phase}}{\text{Activity in counts per minute in the lower salt-rich phase}} \tag{2}$$

For the complete detail of this method see Ref. [12].

2.4. Cellulose determination in ABS

A series of 40% (w/w) PEG-2000–20% (w/w) $(NH_4)_2SO_4$ ABS were prepared at different volume ratios. Fibrous cellulose and diethylaminoethyl (DEAE) cellulose materials were treated with deionized water and filtered under vacuum. A known amount of cellulose (6–13 mg) was added to each ABS. The ABS were mixed and allowed to equilibrate. The cellulose materials did not dissolve in the ABS. The phase preference of the cellulose, in particulate form, was qualitatively determined by visual inspection.

2.5. Lignin solubility

Each lignin species (Indulin C, Reax 85A, and Polyfon T) was solubilized in 100 m*M* K_3PO_4, and the absorbance of these solutions was monitored as the pH of the solutions was adjusted with concentrated H_3PO_4. The absorbance was measured at 260 nm using a Cary 3C UV–Vis Spectrophotometer (Varian Optical Spectroscopy). The pH of the solutions was measured using a Corning pH meter 220 (Corning Incorporated Science Products Division, Corning, NY, USA).

3. Results and discussion

3.1. Lignin partitioning in ABS

Given the current demand for paper products and the increase in environmental regulations, efforts to reengineer a typical chemical pulping process have led to the development of technologies that are environmentally benign and more efficient in the separation of lignins from cellulose. In the so called "Organosolv Process", a traditional solvent extraction technique has been developed which utilizes high temperature and pressure to chemically breakdown the lignin before dissolving and extracting the lignin away from the pulp. Such a process has greater efficiency and lower demand on chemicals and energy input [2,3]. This process inspired us to attempt to develop a wholly aqueous solvent extraction operation based on the use of aqueous polymers applicable to the paper pulping process. Such a process could eliminate the need for volatile, flammable organic effluents, and still retain solvent selectivity for lignin. We have recently been examining PEG-2000 for its ability to extract lignins from aqueous phases and its ability to extract lignin under conditions resembling chemical paper pulping.

The partitioning behavior of various lignins was studied in ABS prepared from stock solutions of 40% (w/w) PEG-2000 and increasing concentrations of three water structuring salts: K_2CO_3, $(NH_4)_2SO_4$, and NaOH. Fig. 1 shows the distribution ratios for model lignin species in relation to the salt concentration used to form the ABS. The distribution ratios increase with increasing salt stock solution concentration, for each lignin species, in each ABS, formed with each different salt. In common with macromolecular and ionic solutes, the increase in distribution with increasing salt stock solution con-

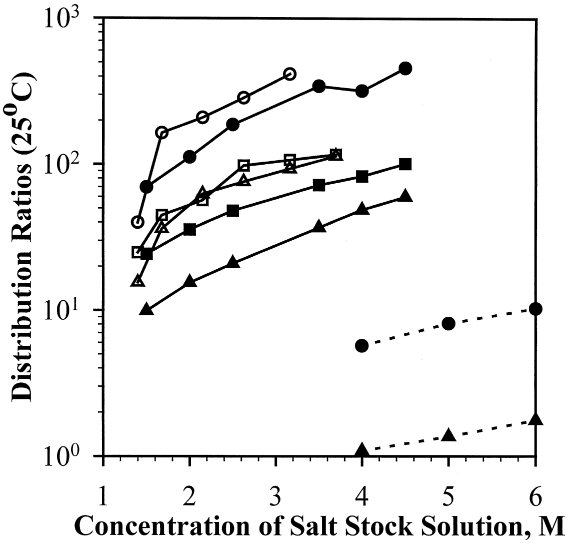


Fig. 1. Distribution ratios for Indulin AT (●), Indulin C (■), and Reax 85A (▲) in 40% (w/w) PEG-2000–$(NH_4)_2SO_4$ (○, □, △), –K_2CO_3 (●, ■, ▲), and –NaOH (--●--, --▲--) ABS as a function of increasing salt stock solution concentration.

centration is related to the increasing divergence of the phase compositions and the increase in free energy of transfer of a solute between the phases [7,8,13,14]. These results confirm the well known relationship in Eq. (3):

$$\mathrm{Ln}\, K = k\, \Delta w_2 \tag{3}$$

where K is the partition coefficient, k is a constant, and Δw_2 is the concentration difference between the phases of the phase-forming components [7,8,15–17].

The filled symbols in Fig. 1 represent the distribution ratios of the lignins in a PEG-2000–K_2CO_3 ABS (pH 12–13). The distribution ratios of the unsulfonated lignins, Indulin AT and Indulin C, have the highest distribution ratios at all concentrations of salt, whereas the sulfonated lignin Reax 85A has lower distribution ratios due to the degree of sulfonation. Sulfonation decreases the hydrophobicity of the lignin and, therefore, lowers the distribution to the PEG-rich phase.

A similar relationship is shown for the distribution ratios of lignins in a PEG-2000–$(NH_4)_2SO_4$ ABS (Fig. 1: open symbols/solid lines) (pH 5.5–6.5). However, the effect of system pH on the dissociation of the charged groups, primarily sulfonic acid and hydroxyl groups in the lignin polymer, is also observed for these systems. The sulfonated lignin Reax 85A has similar distribution ratios as Indulin C. The lower system pH decreases the dissociation of the hydroxyl groups in $(NH_4)_2SO_4$ allowing Reax 85A to partition to the PEG-rich phase as a less charged moiety.

Our current understanding of solute partitioning in ABS, predicts that the higher the charge on the molecule the lower the distribution ratio of the solute (i.e., a lower preference for the PEG-rich phase) [18]. This means that solutes that are negatively charged above their pK_a should be characterized by a lower distribution ratio than if partitioned as a neutral species. For organic bases, having a positive charge below their pK_a, the same considerations will apply. Fortunately this is, no different from distribution of charged solutes between organic–aqueous phases [19], although there will be differences at the molecular level. It is worth noting, however, some models for charged partitioning in ABS predict a higher partition coefficient for negatively charged solutes over neutral solutes [20].

Fig. 1 also shows the distribution ratios of lignins in a PEG-2000–NaOH ABS (filled symbols/dashed lines), a system which most closely resembles the conditions present during alkaline pulping. The distribution ratios of the two species of lignin partitioned in this system are reduced, compared to the SO_4^{2-} and CO_3^{2-} ABS, and in particular the distribution of the sulfonated species Reax 85A is reduced to a distribution ratio approaching 1, indicating a near equal distribution between the two phases. For the unsulfonated lignin, Indulin AT, the distribution coefficients vary from 5 to 10 as the salt concentration is increased. Although the distribution ratios for theses systems are low, they are adequate for extraction.

We know from our studies of model aryl organic species, that for neutral aryl organics, the salt concentration of the system determines the point at which polymer–salt phase separation occurs, but thereafter solute distribution depends only on the degree of phase divergence as may be measured by empirical measures such as the tie line length, the

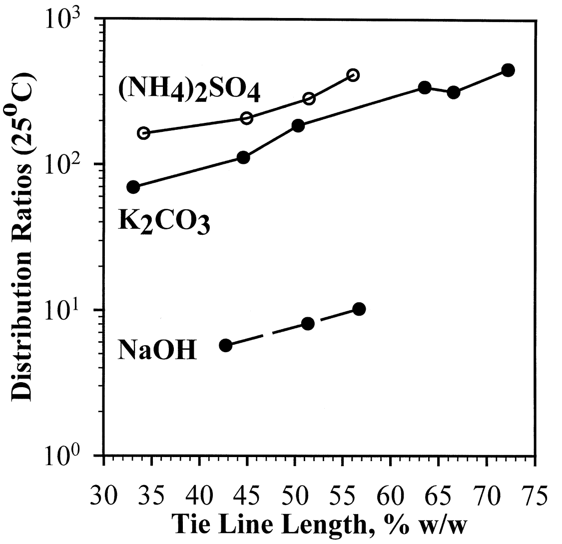


Fig. 2. Distribution ratios for Indulin AT in 40% (w/w) PEG-2000–$(NH_4)_2SO_4$ (○), $-K_2CO_3$ (●), and –NaOH (--●--) ABS as a function of tie line length.

system stability, or the difference in polymer concentration between the phases [7,8,18]. Fig. 2 shows the distribution ratios of Indulin AT vs. tie line length in PEG-2000–K_2CO_3, $(NH_4)_2SO_4$, and NaOH ABS. Tie line length is the traditional system descriptor of the phase diagram, although ΔPEG, the difference in PEG concentration between the phases, better describes the phase diagram [19]. TLL may be defined as in Eq. (4):

$$\text{TLL} = (\Delta\text{PEG}^2 + \Delta\text{Salt}^2)^{1/2} \tag{4}$$

The differences observed in the partitioning of Indulin AT, when expressed in terms of the degree of phase divergence, may be accounted for on the basis of differences in dissociation and charge on the lignin side chains and functional groups. The reduced distribution of the Indulin AT in the highly basic NaOH system may be ascribed to the ionization of the hydroxyl functionalities. The slight reduction in distribution in the carbonate system over the sulfate system may be ascribed to only partial ionization of the hydroxyl moieties.

3.2. Effect of temperature on ABS

Temperatures in excess of a 120°C are conventionally used to solublize the lignin from the cellulose fraction of wood in both chemical pulping and in the Organosolv processes. Currently, we are examining the fundamental effects of temperature on the PEG–salt phase behavior and solute phase partitioning. Fig. 3 shows the phase diagram and tie lines for PEG-2000–$(NH_4)_2SO_4$ ABS derived from the measurement of phase compositions using HPLC (see Section 2.1). There are several features that are apparent, including the shift of the binodal toward slightly lower concentrations of PEG and salt in the region examined between 10 and 70°C. This effect is small, but quite distinct and highlights the precision possible with this technique.

The binodals connecting the compositions of the coexisting top and bottom phases become longer, and the slope of the tie lines become steeper as the temperature is increased. It is apparent that increases in temperature produces results which appear to be identical to the addition of the salt to the PEG solution. Increases in temperature and in salt concentration cause an increase in the degree of phase divergence, as measured by the tie line length, for these biphasic systems. Both an increase in temperature and an increase in the salting-out strength of the salt (by change of salt type) causes an increase in the tie line slope and a shift of the binodal to lower concentrations of PEG and salt.

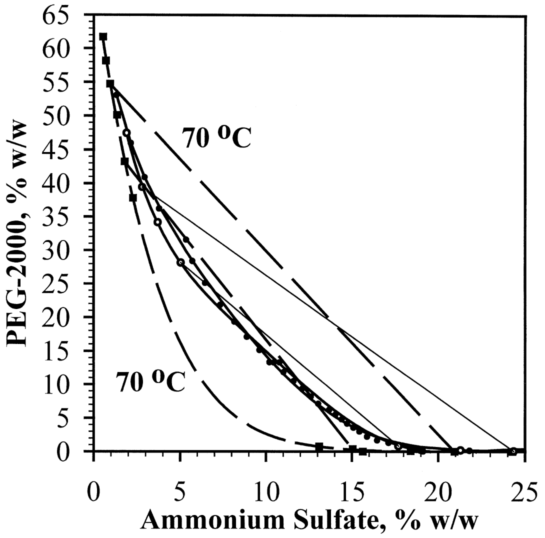


Fig. 3. Experimentally determined phase diagrams for a PEG-2000–$(NH_4)_2SO_4$ ABS as a function of temperature: (– ● –, 25°C; – ○ –, 10°C; – ■ –, 70°C) binodal curves; (–) tie lines determined at 10°C; (– –) tie lines determined at 70°C.

The quantitative partitioning of the probe solutes, phthalic acid and $NH_4^{99}TcO_4$, in PEG-2000–$(NH_4)_2SO_4$ ABS was studied in order to understand the temperature effects on both phase divergence and solute behavior. These two solutes were chosen because they are non-volatile and their behavior is well known in PEG–salt ABS [8,12,21,22]. Increasing the temperature of a given ABS studied here increases the phase divergence (see Fig. 3) and thus as expected, solutes such as phthalic acid and $^{99}TcO_4^-$ (which prefer the PEG-rich phase) exhibit higher distribution ratios just as distribution ratios for these solutes increase as salt concentration increases.

If the data is expressed in terms of the degree of phase divergence of the systems, (tie line length, as shown in Fig. 4 or the difference in PEG concentration between the phases, ΔPEG, data not shown) it is apparent that the difference in partition coefficient for the different temperatures of various systems is almost eliminated by this procedure. There is very little effect of temperature on the partition itself, the effect manifested solely on the degree of phase divergence. Increasing the salt concentration of any salt is identical to the effect of increasing temperature on partitioning, thus *systems composed of different salts and at different temperatures can all be related through the degree of phase divergence* [18].

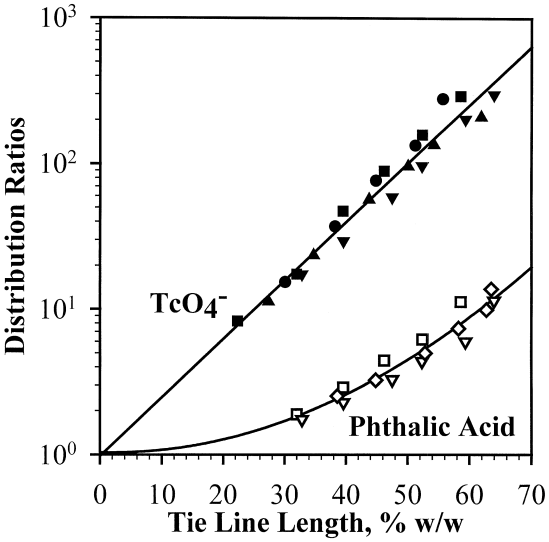


Fig. 4. Distribution ratios for phthalic acid (open symbols) and $NH_4^{99}TcO_4$ (closed symbols) versus tie line length for 40% (w/w) PEG-2000–$(NH_4)_2SO_4$ ABS of increasing salt stock solution concentration or increasing temperature. Symbols refer to solutes partitioned and the temperature at which the biphase was formed: phthalic acid (□) 25°C; (▽) 55°C; (◇) 70°C; TcO_4^-: (●) 10°C; (■) 25°C; (▲) 40°C; (▼) 55°C.

At elevated temperatures used in chemical pulping, biphase formation can be expected at lower salt concentrations, since the phase separation of PEG–salt ABS is enhanced by temperature [23]. There is no evidence of any decline of the partition coefficient over this range, due to polymer dehydration, and no reason at this stage to suppose that PEG–salt systems would not be effective at higher temperatures. Fig. 4 does, however, also show a nonlinear relationship between the distribution of phthalic acid and tie length in the PEG-2000–$(NH_4)_2SO_4$ ABS. This relationship could be the result of partial ionization of phthalic acid ($pK_{a,1} = 2.89$, $pK_{a,2} = 5.51$) due to the effect of increasing pH differences between the phases as a function of increasing phase divergence in a PEG–salt ABS and will be the subject of a separate publication [18].

One other potential effect of temperature used in pulping is on the degradation of the PEG polymer. In order to study this, an experiment was designed to study the molecular size of PEG polymers after long term exposure to heat and alkaline pH. Fig. 5 plots

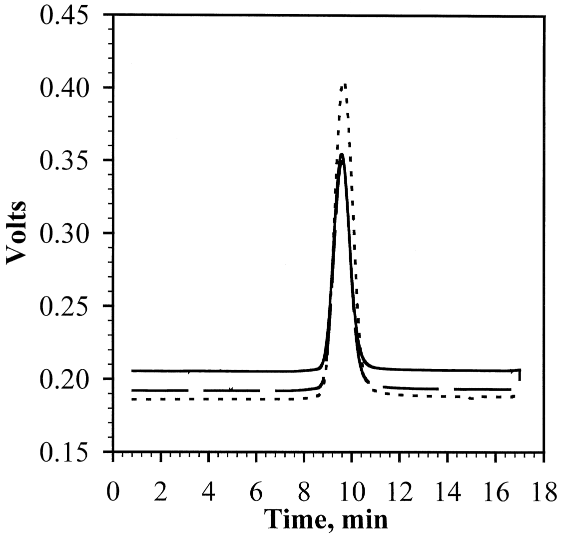


Fig. 5. Size exclusion chromatograms of PEG-2000–(1.75 *M* NaOH, 0.38 *M* Na_2S, 0.19 *M* Na_2CO_3) ABS as a function of temperature. Symbols refer to the temperature and day at which the polymer phase was sampled: (—) day 1 at 25°C; (– –) day 4 at 71°C; (----) day 8 at 71°C.

the detector signal obtained during size exclusion chromatography of PEG after contact with a formulated solution that maintains the molar proportions of an alkaline paper pulping solution (1.75 *M* NaOH, 0.38 *M* Na_2S, and 0.19 *M* Na_2CO_3 [24]). The chromatogram obtained after 1 day at 25°C is the same as that obtained after exposure to the mock pulping solution for 8 days at 71°C. The chromatograms also show no degradation in the peak shape of the polymer. Our current experimental program is directed toward the investigation of the behavior of these systems at temperatures in excess of 120°C.

3.3. Cellulose partitioning in a PEG–salt ABS

In the process of developing an aqueous polymeric extraction of lignin from cellulose in a paper pulping process, a survey of cellulose phase preference was completed in a PEG–salt ABS. The phase preference of charged and uncharged cellulose, in particulate form, in a PEG–$(NH_4)_2SO_4$ ABS at different volume ratios was determined by visual inspection. None of the cellulosic materials studied dissolved and the particulates remained in the salt-rich lower phase. Distribution to the salt-rich phase is likely because of the hydrophilic nature of the cellulose particulates [25]. This preference of the cellulose materials for the salt-rich phase is desirable, and continues to support the idea that a wholly aqueous polymer extraction process could be feasible for the separation of lignin from the cellulose fraction of wood. There is no evidence of any variation in cellulose phase preference with volume ratio as has been noted for biomass [26].

3.4. Effects of pH on solubility of lignin fractions

The various lignin fractions were examined for their solubility in aqueous solution of 100 m*M* K_3PO_4 over a wide pH range. Fig. 6 plots the UV absorbance of Indulin C, Reax 85A, and Polyfon T as a function of aqueous pH. These lignins are, for the most part, water soluble at alkaline pH, but solubility decreases with protonation of the hydroxyl groups as the pH is reduced. This is important as it defines the likely effective operational pH of any polymer-based extraction system. It also suggests a rather facile regime whereby lignin fractions may be recovered from polymeric phases effectively. Fig. 6 also shows that the modified lignins having greater stoichiometric amounts of sulfonic acid groups show increased solubility over the acidic pH range.

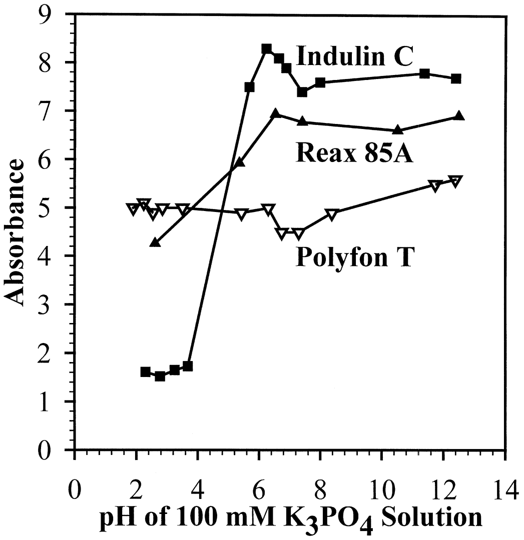


Fig. 6. The solubility of lignin species as measured by absorbance in 100 m*M* K_3PO_4 as a function of pH: (■) Indulin C; (▲) Reax 85A; (▽) Polyfon T.

4. Conclusions

Partitioning studies of a number of lignin species and cellulosic materials in PEG-2000–salt ABS have demonstrated the potential for a wholly aqueous lignin–cellulose separation in wood pulping. Distribution values ranging from 1 to >400 have been found for the three lignin species studied, while the cellulosic materials were found to show an absolute preference for the salt-rich phase of the PEG–salt ABS. A direct relationship between the degree of sulfonation of the lignin species and their partition coefficient in a PEG–salt ABS was observed. Examination of the effects of pH on the solubility of lignin fractions suggests a plausible means of recovering lignin fractions from the polymeric phases effectively. These results also suggest that it should be possible to quantitatively extract the lignin into the polymer-rich phase while leaving the cellulose fibers in the salt-rich phase.

Quantitative partitioning of solutes has been demonstrated as a function of temperature and salt concentration used to form the biphase in a PEG–salt ABS. A suitable system parameter (e.g., tie line length or ΔPEG) can be used to measure the degree of phase divergence of the systems as a result of increasing the concentration of salt used to form the biphase or increasing the temperature at which the biphase is formed. Thus, it has been determined that temperature has similar effects on phase behavior and solute partitioning as the type and concentration of salt. We have not observed, at higher temperatures, any reduction in partition coefficient or degradation of the polymer, so the effectiveness of a PEG–salt extraction at the higher temperatures needed in a pulping process seems possible.

Further research is underway to continue our survey of the practical applicability of various aqueous polymers to use in the alkaline pulping process. We are currently trying to understand the entropic and enthalpic contributions to the free energy of transfer of solutes in ABS [27] by thorough examination of the effects of temperature on the phase diagrams and on solute partitioning.

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