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TEMPERATURE EFFECTS ON POLYMER-BASED AQUEOUS BIPHASIC EXTRACTION TECHNOLOGY IN THE PAPER PULPING PROCESS

Mian Li[a]; Heather D. Willauer[a]; Jonathan G. Huddleston[a]; Robin D. Rogers[a]
[a] Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, Alabama, U.S.A.

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TEMPERATURE EFFECTS ON POLYMER-BASED AQUEOUS BIPHASIC EXTRACTION TECHNOLOGY IN THE PAPER PULPING PROCESS

Mian Li, Heather D. Willauer, Jonathan G. Huddleston, and Robin D. Rogers*

Department of Chemistry and Center for Green
Manufacturing, The University of Alabama, Tuscaloosa,
Alabama 35487

ABSTRACT

In order to apply a polymer-based aqueous biphasic system (ABS) extraction to the paper pulping process, the partitioning behavior of six model lignin species (Indulin AC, Indulin C, Reax 85 A, Reax 825 E, Polyfon T, and Alkali lignin) were studied in PEG-2000/NaOH ABS prepared from stock solutions of 40% (w/w) PEG-2000 and increasing concentrations of NaOH. In a given salt concentration, the distribution ratios increase in the order Polyfon T < Reax 825 E < Reax 85 A < Indulin C < Alkali lignin < Indulin AT due to the degree of sulfonation. In both chemical pulping and Organosolv pulping, temperatures in excess of 120 °C are needed to solubilize the lignin from the cellulose, however, the availability of data on all relevant ABS system parameters, especially phase diagrams under process conditions, is limited. Phase diagrams of PEG-2000/$(NH_4)_2SO_4$ at higher process temperatures

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*Corresponding author. Fax: (205) 348-9104; E-mail: RDRogers@bama.ua.edu

have thus been measured. The partitioning of phthalic acid was studied in order to understand temperature effects not only on system composition, but also on phase partitioning.

INTRODUCTION

The pulp and paper industry is a large and growing portion of the world's economy. More than 150 megatons of paper pulp and 50 megatons of lignin are produced annually, reflecting the high demand for paper products and the natural abundance of the raw materials. However, this industry is facing increasing pressure in terms of environmental regulations and energy usage; and new or greatly modified technologies will be necessary to carry the industry through the twenty-first century by reducing environmental emissions to air and water (1).

The alkaline or Kraft pulping process is by far the dominant chemical pulping process practiced on an industrial scale. Some major difficulties with the Kraft pulping process are the emission of reduced forms of sulfur, and the accompanying odor and high water usage. Various modifications to the Kraft process have been adopted to increase the cooking efficiency whilst maintaining the viscosity of the resultant cook. Improvements in the early stages of pulp preparation have big impacts downstream through reduction in the necessity for bleaching processes. Such modifications have included preimpregnation of wood chips with low caustic/high sulfide liquor, improved control of hydroxide ion concentration by the use of semi-batch methods, extension of the cook at lower temperatures, and the dilution of the lignin as the cook proceeds and the chemicals become exhausted (2).

There has been renewed interest in recent years in trying to find alternatives to the Kraft system that will yield pulp with Kraft-like strength properties, but without the environmental drawbacks, based on Organosolv pulping, that is, a process using organic solvents to aid in the removal of lignin from wood (3-4). At the laboratory and small pilot scale, Organosolv processes have been demonstrated to be highly efficient processes for the delignification of raw paper pulp. However, 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 been applied within 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. It was the results of the organosolv experience that inspired us to examine the effectiveness of polymer-based aqueous extraction processes applied to the delignification of cellulose in the paper pulping process.

Since most aqueous biphasic systems (ABS) have been applied at room temperature (5-9), and temperatures in excess of a 120 °C are conventionally used to solubilize the lignin from the cellulose fraction of wood, this application of ABS requires an understanding of the effect of the increase in temperature on the behavior of the polymer/salt system and on the distribution of partitioned solutes. Here we report detailed phase diagram and partitioning data currently used in wholly aqueous solvent extraction or reactive extraction processes, that may be applicable to delignification of cellulosic materials. The results of changes in polymer and salt concentrations, as well as temperatures on the composition of the systems and the partitioning behavior of representative solutes were critically examined. It is hoped that such data will be useful in engineering an aqueous polymeric extraction step to minimize not only the consumption of chemical pulping feedstock, but to also minimize polymer usage.

EXPERIMENTAL

Materials and Methods

The chemicals, $(NH_4)_2SO_4$, NaOH, poly(ethylene glycol) (PEG-2000), and phthalic acid 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 (to ca. 0.6-0.8 μCi/μL). All water used was purified using a Barnsted commercial deionization system (Dubuque, IA, USA). 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.

Alkali lignin was obtained from Aldrich (Milwaukee, WI, USA). The other lignins examined were from Westvaco (Charleston, SC, USA).

Phase Diagram Determination

The polymer and salt solutions were prepared on a mass basis from stock solutions. Phase separation was accelerated by centrifugation at 3000 rpm for 10 min.

We have developed methods where we can perform small scale (25 mL) phase equilibrium and solute partitioning experiments at elevated temperatures up to 150 °C, utilizing a small PTFE-lined stainless steel bomb (Fisher, Norcross, GA, USA), and a laboratory oven. Since phase separation is promoted by increase in temperature and vice versa, provided equilibrium is achieved at the operating temperature, the system may be cooled to a safe handling temperature to perform separation and analysis. Over the time scales involved, thermal motion alone is insufficient to remix the phases. (We have experimentally determined (unpublished results) that the time required to cool and separate the phases is insufficient to affect the equilibrium values obtained as long as the phases are not mixed or agitated.) Thus, we have been able to take our studies of the phase behavior of PEG-salt ABS and the distribution of partitioned solutes up to temperatures and pressures equivalent to current alkaline paper-pulping practice.

The compositions of phases at 150 °C were 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, Inc., Piscataway, NJ, USA) coupled to a refractive index detector, Shimadzu RID 10 A. The mobile phase was 250 mM NaCl solution and the flow rate was 1 mL/min.

Lignin Partitioning

Each lignin species (Indulin AT, Indulin C, Reax 85 A, Reax 825 E, Polyfon T, and Alkali lignin; Table 1) was dissolved in 40% (w/w) PEG-2000 at 1 mg/mL. ABS were prepared by mixing 20 mL 40% PEG-2000-lignin stock solutions with 20 mL NaOH stock solutions of varying concentration. The systems thus prepared were vortex mixed for 5 min, centrifuged at 3000 rpm for 10 min, and then allowed to equilibrate for 30 min. Phase volumes were then measured in order to further check mass balance. The top and bottom phases were withdrawn separately. Each phase was diluted 20-50 x with 0.1 M NaOH and then analyzed at 280 nm (10) using a Cary 3C UV-visible Spectrophotometer (Varian Optical Spectroscopy, Mulgrave, Victoria, Australia). From the calibration curves for each species of lignin analyzed, the concentration of lignin in each phase was determined and the distribution ratio obtained as in eq. 1.

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

Phthalic Acid Partitioning

Phthalic acid (both ^{14}C-labeled and non-radioactive) was used as a nonvolatile probe for the study of temperature effects on phase partitioning in ABS. All systems were mixed and allowed to equilibrate at experimental temperatures using a Neslab RTE-110 water bath (Neslab Instruments Inc., Newington, NH, USA). The distribution ratios measured for ^{14}C-labeled phthalic acid were defined as the total tracer concentration of solute in the upper PEG-rich phase divided by the concentration of the total tracer in the lower salt-rich phase. Since equal aliquots of each phase were analyzed, and the activity of the tracer is directly proportional to its concentration, the distribution ratios were determined as in eq. 2.

$$D = \frac{\text{Activity in counts per minute PEG-rich phase}}{\text{Activity in counts per minute salt-rich phase}} \qquad (2)$$

For the complete detail of this method see reference (11).

For non-radioactive phthalic acid, an aliquot of stock solution (5.0 mg/mL) was added to the ABS prepared and the final concentration of phthalic acid was adjusted to ca. 1 mM in the whole system. The concentration of phthalic acid was measured by an HPLC Shimadzu LC 10 coupled with a UV-VIS spectrophotometric detector, Shimadzu SPD 10 AVvp (Shimadzu Corporation, Kyoto, Japan). The column and the mobile phase used was the same as described above for the determination of phase diagrams.

RESULTS AND DISCUSSION

Lignin Partitioning in ABS

The physical and chemical properties of lignin species are shown in Table 1. Experiments were performed to measure the distribution ratio for the model lignin species in PEG-2000/NaOH ABS prepared from stock solutions of 40% (w/w) PEG-2000 and increasing concentrations of NaOH. PEG-2000/NaOH ABS were selected for the initial lignin partitioning studies because the caustic conditions closely resemble the chemical paper pulping process, but the ABS under study remains a simple single-polymer, single-salt system.

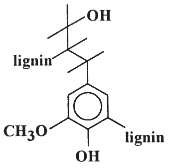
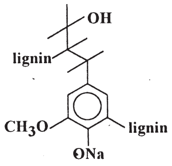
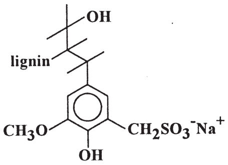
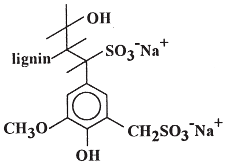
Fig. 1 shows the distribution ratios for model lignin species in relation to the salt stock concentration in ABS. The distribution ratios increase with increasing salt concentration for each lignin species. In common with macromolecular and ionic solutes, the increase in distribution with increasing salt concentration is related to the increasing divergence of the phase compositions and the increase in free energy of transfer of a solute between the phases (12-15). These results confirm the well-known relationship in eq. 3:

$$\text{Ln } K = k\Delta w_2 \qquad (3)$$

where K is the partition coefficient, k is a constant, and Δw_2 is the concentration difference between the phase of the phase-forming components (12-13, 16-18).

Distribution ratios ranging from 0.5 to more than 40 have been found for the six species. The distribution ratios of the unsulfonated lignins, Indulin AT, Indulin C, and alkali lignin, have the highest distribution ratios at all concentrations of salt, while the sulfonated lignins, Polyfon T (3.4 mol/kg sulfonic acid groups),

Table 1. Characterization of Lignin Species

Lignin	Sulfonation, mol/kg	M_w	pH of reaction	Lignin Structure
Indulin AT	0	2700	8.6	
Indulin C	0	2700	8.6	
Alkali Lignin	0	5000	-	
Reax 825E	3.4	3700	12.0	
Reax 85A	0.8	7900	10.4	
Polyfon T	2.0	2900	10.4	

Reax 825 E (2.0 mol/kg sulfonic acid groups), and Reax 85 A (0.8 mol/kg sulfonic acid groups) have lower distribution ratios. In particular, the distribution ratios of the sulfonated species of Polyfon T and Reax 825E are reduced to less than 1 when the concentration of NaOH is below 6 M.

Sulfonation decreases the hydrophobicity of the solute being partitioned in ABS and thereby lowers the distribution ratios of lignin to the PEG-rich phase.

Compared with the distribution ratios of lignin in other ABS such as PEG-2000/$(NH_4)_2SO_4$ and PEG-2000/K_2CO_3 (19), it is observed that the distribution of all species is reduced in PEG-2000/NaOH ABS at the same tie line length. The reduction may be ascribed to the ionization of the hydroxyl functions. However, a significant extraction of lignin can still be achieved according to the partitioning of Indulin AT, Indulin C, and alkali lignin since these lignins are closest to representing 'natural lignin' derived directly from the alkaline pulping process.

Effects of Temperature on ABS Phase Diagrams

Current alkaline pulping processes operate at temperatures in the region 120 to 160 °C. It is important, therefore, to develop an understanding of the effect of increase in equilibrium temperature on the behavior of ABS and on the distribution of partitioned solutes. PEG-2000/$(NH_4)_2SO_4$ ABS were initially chosen for our studies at elevated temperatures, because their phase behavior at room temperature is well known (5, 19).

In previous work (19) the phase diagrams of PEG-2000/$(NH_4)_2SO_4$ were measured from 10-70 °C, and we have now extended this range to 150 °C. Fig. 2

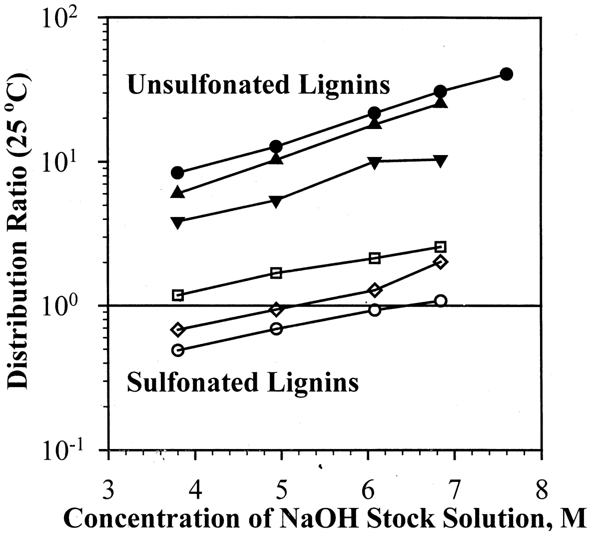


Figure 1. Distribution ratios for Indulin AT (●); Alkali lignin (▲); Indulin C (▼);Reax 85 A (□); Reax 825 E (◊) and Polyfon T (○) in PEG-2000/NaOH ABS. The closed symbols refer to unsulfonated lignins; the open symbols sulfonated lignins.

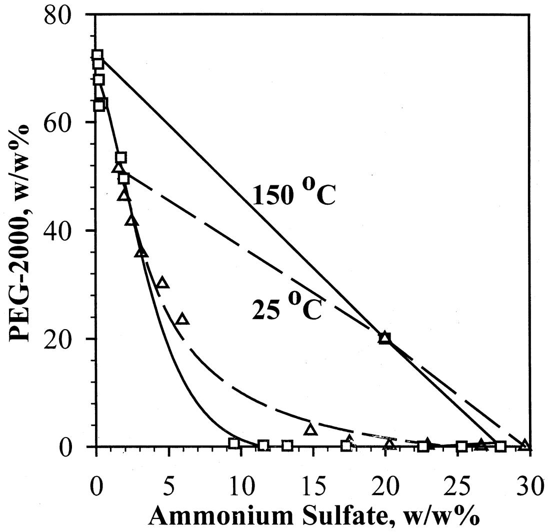


Figure 2. Phase diagrams for PEG-2000/$(NH_4)_2SO_4$ ABS at 25 oC (△) and 150 °C (□).

shows the effect of changing the temperature on the composition of the equilibrium phases of PEG-2000/$(NH_4)_2SO_4$ ABS. The tie line connecting the compositions of the coexisting top and bottom phases becomes longer as the temperature is increased. It is apparent that an increase in temperature produces results which appear to be identical to the addition of salt to PEG solution (19).

At the shorter tie line lengths, close to the binodal curve, increases in temperature cause previously monophasic systems to become biphasic and the binodal curve slowly advances toward lower concentrations of polymer and salt as shown in Fig. 2. Additionally, tie lines show an increase in slope (-1.84 at 25°C and –2.60 at 150 °C), and as a result, tie line length and ΔPEG (the difference in PEG concentration between the phases) increase with increasing temperature. Both an increase in temperature and an increase in the salting-out strength of the salt (by change of salt type) cause an increase in the tie line slope and a shift of the binodal to lower concentrations of PEG and salt. Biphasic formation can thus be expected at much lower salt concentration since the phase separation of PEG-salt ABS is enhanced by temperature (20).

In PEG/salt ABS, the PEG-rich phase is normally the upper, less dense phase, while the salt-rich phase is normally the lower phase. But this is not always the case at elevated temperature (21). At 25 °C, 20% PEG-2000-7% $(NH_4)_2SO_4$ and 20% PEG-2000-8.5% $(NH_4)_2SO_4$ systems are homogeneous solutions. However, at 150 °C they are separated into two phases and the dehydrated, PEG-enriched phase becomes the lower more dense phase. These systems exhibit phase inversion, which can occur either by increasing the system temperature or by changing the concentration of one of the phase-forming components (21). For the other systems, they are biphasic at 25 °C, and PEG remains the predominant upper phase component.

Fig. 3 shows the effect of elevated temperature on phase divergence for PEG-2000/$(NH_4)_2SO_4$ ABS. It is apparent that increases in temperature causes an increase in degree of phase divergence, as measured by the tie line length (TLL), which is defined as in eq. 4 (13-14).

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

Partition of Phthalic Acid at Different Temperatures

Phthalic acid was used as probe for the study of temperature effects on phase partitioning in ABS because it is non-volatile and its behavior is well known in PEG/salt ABS (13). Furthermore, phthalic acid closely resembles the basic aromatic unit which comprises the lignin polymers.

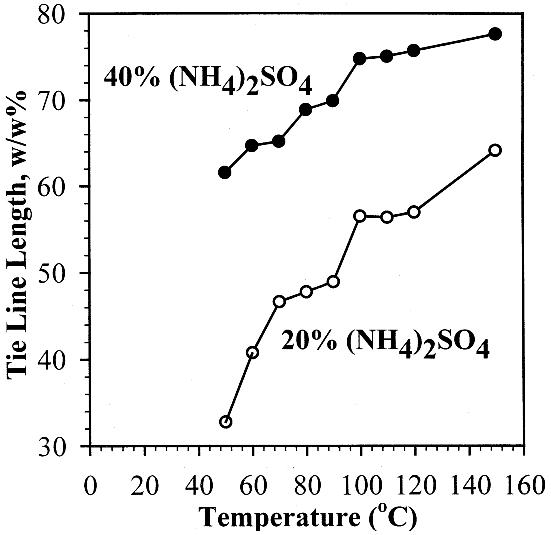


Figure 3. Effect of elevated temperature on phase divergence for PEG-2000/$(NH_4)_2SO_4$ ABS. The open symbols (○) refer to systems prepared by mixing equal aliquots of 40% (w/w) PEG-2000 stock solution and 20% (w/w) $(NH_4)_2SO_4$ stock solution; the closed symbols (•) 40% (w/w) PEG-2000 stock solution and 40% (w/w) $(NH_4)_2SO_4$ stock solution.

Fig. 4 shows the distribution of phthalic acid in the PEG/$(NH_4)_2SO_4$ ABS in relation to increases in temperature. The data were obtained at different starting conditions of PEG and salt prior to raising the temperature, in other words, at different tie line lengths. One system was far from the critical point (ABS prepared by mixing equal aliquots of 40% (w/w) PEG-2000 stock solution and 40%(w/w) $(NH_4)_2SO_4$ stock solution) and the other rather closer to the critical point (40% (w/w) PEG-2000 stock solution mixed with 20% (w/w) $(NH_4)_2SO_4$ stock solution). The distribution ratios increase with increasing concentration of salt and as the temperature of the systems is increased. The principle enthalpic effect is on the phase diagram and the tie line slope, therefore increasing the temperature of the system and salt concentration increases the tie line length (see Fig. 3) and thus phase divergence. As expected then, partitioning of phthalic acid exhibits higher distribution ratios with either increase in salt concentration or temperature.

If the data is expressed in terms of the degree of phase divergence of the systems (tie line length, as shown in Fig. 5), it is apparent that any difference in distribution ratio for the different temperatures of various systems is almost eliminated by this procedure. Fig. 5 shows a nearly linear relationship between the

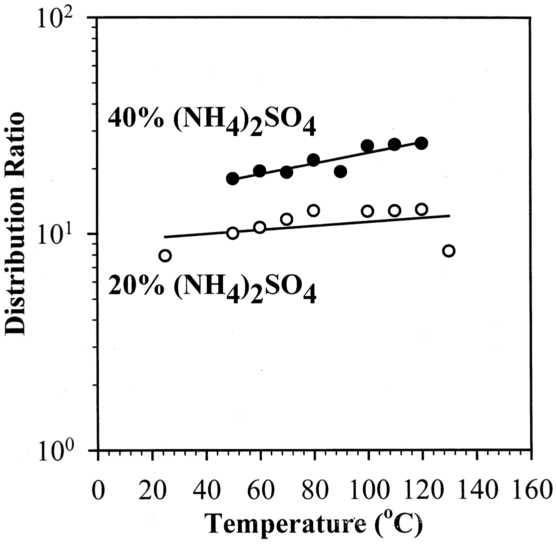


Figure 4. Distribution ratios for phthalic acid in PEG-2000/$(NH_4)_2SO_4$ ABS as a function of temperature. The open symbols (○) refer to systems prepared by mixing equal aliquots of 40% (w/w) PEG-2000 stock solution and 20% (w/w) $(NH_4)_2SO_4$ stock solution; the closed symbols (•) 40% (w/w) PEG-2000 stock solution and 40% (w/w) $(NH_4)_2SO_4$ stock solution.

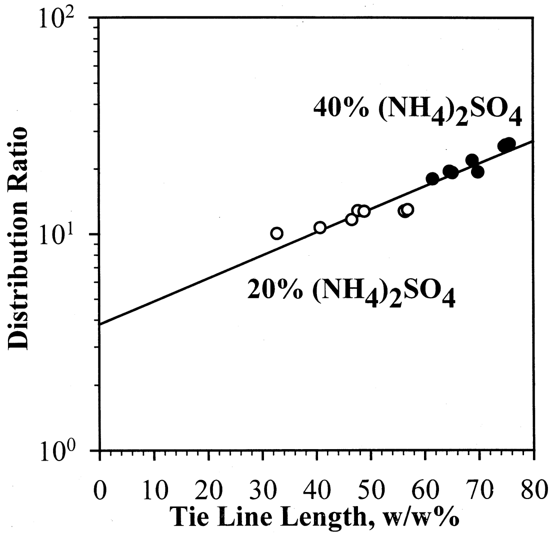


Figure 5. Distribution ratios for phthalic acid versus tie line length. The open symbols (○) refer to 40% (w/w) PEG-2000 stock solution with 20% (w/w) $(NH_4)_2SO_4$ stock solution. The closed symbols (•) refer to 40% (w/w) PEG-2000 stock solution with 40% (w/w) $(NH_4)_2SO_4$ stock solution.

distribution ratios of phthalic acid and tie length in the PEG-2000/$(NH_4)_2SO_4$ ABS.

The relationship between distribution ratio and phase divergence may be affected by partial ionization of phthalic acid ($pK_a1 = 2.89$, $pK_a2 = 5.51$) arising from the effect of increasing pH differences between the phases which we have observed as a function of increasing phase divergence in a PEG/salt ABS. This will be the subject of a separate publication.

CONCLUSIONS

Partitioning of six model lignin species in PEG-2000/NaOH ABS has demonstrated the potential for a wholly aqueous extraction of lignin. Distribution values ranging from 0.5 to more than 40 have been observed. A relationship between the degree of sulfonation and molecular weight of the lignin species and their distribution ratios in a PEG/salt ABS was observed.

The phase diagram for PEG-2000/$(NH_4)_2SO_4$ ABS at higher temperatures indicated that the binodal curve slowly advances toward lower concentrations of polymer and salt and the tie line lengths become longer with increasingly steeper slopes. Increases in either temperature or salt concentration cause an increase in degree of phase divergence for this biphasic system, thus enhancing phase separation. In addition, PEG-2000/$(NH_4)_2SO_4$ exhibits phase inversion. The lower the salt concentration, the more readily the phase inversion occurs with increasing temperature at low salt concentration/high temperature conditions.

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. Increasing the salt concentration of any salt is identical to the effect of increasing temperature on partitioning. Systems composed of different salts and at different temperatures can thus, in principal, all be related through the degree of phase divergence. Here it has been determined that temperature has similar effects on phase behavior and solute partitioning as the type and concentration of salt.

Further research is underway to continue our survey of the practical applicability of various aqueous polymers for use in the alkaline pulping process. A range of polymers will be fully characterized in terms of their room temperature phase diagrams, the partition of organic model species and lignins, and the behavior of the systems at elevated temperatures.

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