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Poly(ethylene glycol)-based aqueous biphasic systems: effect of temperature on phase equilibria and on partitioning of 1,10-phenanthroline–copper(II) sulphate complex

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Abstract

Solvent extraction is a proven technology for the selective removal and recovery of metal ions from aqueous solutions: the use of aqueous biphase systems can be attractive for many separation processes. These systems have usually been used previously at temperatures around 25°C; however it is possible that better separations may be achieved at other temperatures: phase diagrams have been determined for a polyethylene glycol (AMW 3350)–ammonium sulphate–water system over the temperature range 269–343 K and the effect of temperature on partitioning has been determined for 1,10-phenanthroline–copper(II) sulphate complex.

Keywords: Aqueous two-phase systems; Poly(ethylene glycol); 1,10-Phenanthroline–copper(II) sulphate

1. Introduction

Nowadays there is growing interest in the use of aqueous two-phase systems (ATPS) as a powerful but mild separation technique for mixtures of biomolecules [1,2]. A solute added to such a system, partitions between the phases, and its partition coefficient, *D*, is defined as the solute concentration in the upper phase divided by the solute concentration in the lower phase.

The two aqueous phases can be fine-tuned to achieve excellent phase separation characteristics which are often quite similar to widely used oil–water systems [3,4,6,10]. Hard metal ions require a different approach for extraction: in traditional oil–water solvent extraction, complexing ligands are often necessary to coordinate the metal ion and give it a hydrophobic shell before partitioning to an organic solvent. To utilise this approach in PEG–ATPS, water-soluble complexing ligands are required because in the absence of ligands, the distribution ratios are often all very low [5,9].

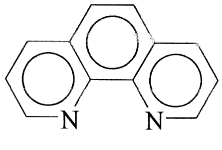
In this work, the most important results obtained in batch tests studying ATPS polyethylene glycol-based are shown and the partitioning of 1,10-phenanthroline–copper(II) sulphate complex is determined and discussed as a function of temperature.

2. Experimental

The salts were ACS reagent grade. PEG-3350 was purchased from Aldrich and used as received.

$H\text{-}(O\text{-}CH_2\text{-}CH_2)_n\text{ - }OH$

Polyethylene Glycol (PEG)



1,10-phenanthroline

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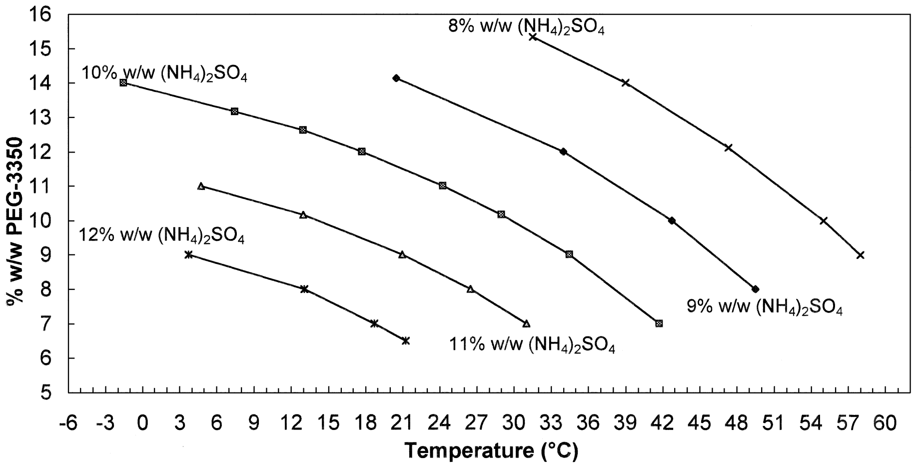

Fig. 1. Observed phase diagram of the PEG3350–ammonium sulphate–water system. The percentages by weight refer to the total composition of systems. In the region below the lines, the composition results in a single phase, above the lines, aqueous biphasic systems are observed.

The water was purified using a commercial deionization system. The studied solutions were prepared by dissolution in glass-capped tubes of the appropriate mass of salts and PEG with a weighed aliquot of water.

Phase diagrams were determined by turbidimetry: temperature had been gradually varied until the turbid mixture just cleared.

The distribution experiments were carried out by mixing, for 4 min, the appropriate mass of salts and PEG with the 1,10-phenanthroline–copper(II) sulphate complex 4.7×10^{-3} *M* (the pH was adjusted with NaOH till it reached 11.20) and placing the tubes in a bath at the desired temperature. After 18 h of equilibration, the phases were separated carefully with Pasteur pipettes and analysed.

A Thermo Jarrel Ash “Smith Hieftje 12” A.A.S was used to determine the partition coefficients of copper.

System compositions are defined on a weight/weight basis due to the difficulty of accurate volumetric measurement of the PEG. All distribution

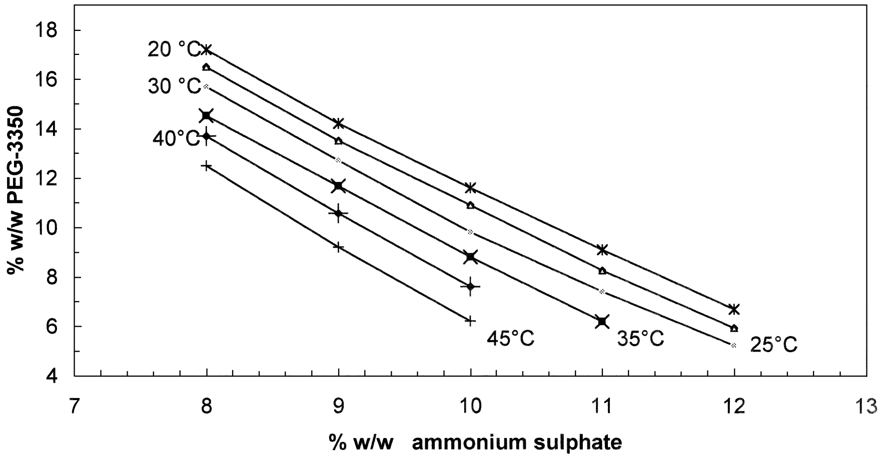

Fig. 2. Observed phase diagram of PEG3350–ammonium sulphate–water system: all compositions represented by points below the curved lines give a one-phase system; all compositions above the curves give a two-phase system.

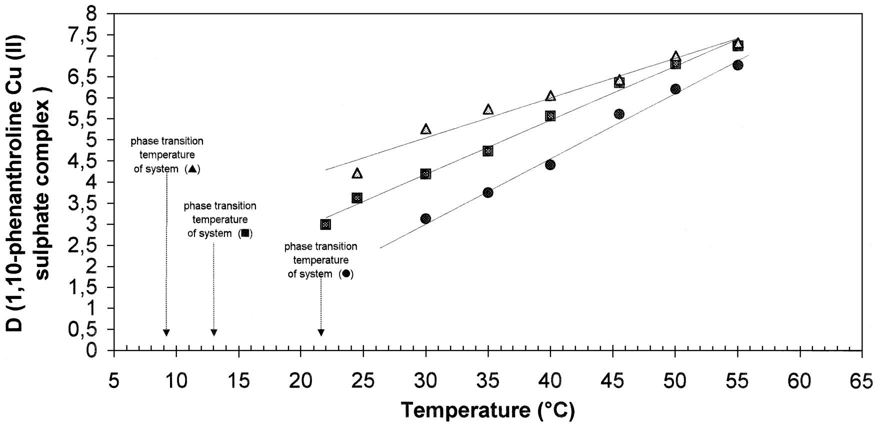

Fig. 3. Measured partition coefficient (D) of 1,10-phenanthroline–copper(II) sulphate complex in the PEG3350–ammonium sulphate–water system versus temperature (°C) after 18 h of equilibration. Total composition of systems: ● 8.4% w/w PEG–1.055 M salt; ■ 10% w/w PEG–1.055 m salt; ▲ 11% w/w PEG–1.055 M salt.

ratios were performed in duplicate as a check on the experimental technique and precision.

3. Results and discussion

Figs. 1 and 2 show the observed phase diagram of PEG3350–ammonium sulphate–water system; the percentages by weight refer to the total composition of systems and the curves represent the monophasic/biphasic boundary. Regions to the right of the line are biphasic. Concentrations of solutes in each phase are independent of phase volume.

The temperature [7,8,11] affects the position of curves in ATPS: higher temperatures increase the salting-out effect. This effect is illustrated in Fig. 2, in which the curves are located at progressively lower salt/PEG concentrations.

Fig. 3 shows the experimentally determined partition coefficient (D) of 1,10-phenanthroline–copper(II) sulphate complex in a PEG3350–ammonium sulphate–water system as a function of the temperature and of the PEG concentration. Results of regressing the best-fitting line through these data are listed in Table 1.

The fact that $D > 1$ indicates that the 1,10-phenanthroline–copper(II) sulphate complex partitions preferentially into the PEG-rich phase (upper phase): increasing the PEG concentration, as expected, the partition coefficient increases.

This result is in agreement with the suggestion in the literature [12–15] that partitioning in ATPS is governed by the relative hydrophobicity of the solute: the large 1,10-phenanthroline–copper(II) sulphate complex, most with aromatic structure, is comparatively hydrophobic and partitions to the less structured PEG-rich phase.

Fig. 4 shows that the formation of further complexes of Cu^{2+} is negligible in the adopted experimental conditions.

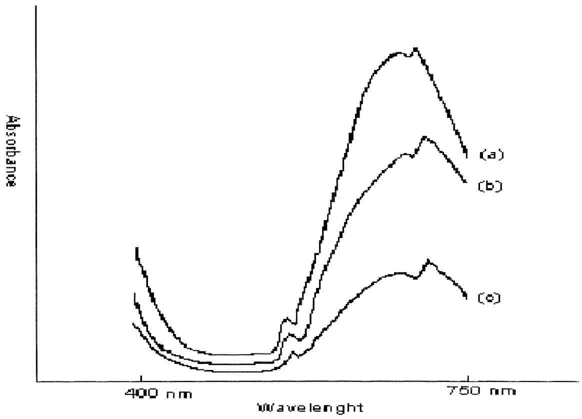

Fig. 4. Qualitative VIS-spectrum of: (a) 1,10-phenanthroline–copper(II) sulphate complex in ATPS upper phase; (b) 1,10-phenanthroline–copper(II) sulphate complex, 4.7×10^{-3} M in water (pH = 11.20); (c) 1,10-phenanthroline–copper(II) sulphate complex in ATPS lower phase.

Table 1
Results of regressing the best-fitting line ($D = aT + b$) through the observed data shown in Fig. 3

ATPS composition	*a*	*b*	Correlation coefficient
8.4% w/w PEG; 1.055 m $(NH_4)_2SO_4$	0.1536	−1.564	0.9909
10% w/w PEG; 1.055 m $(NH_4)_2SO_4$	0.1292	0.303	0.9925
11% w/w PEG; 1.055 m $(NH_4)_2SO_4$	0.0948	2.202	0.9684

4. Conclusions

As it is important in industry to properly design appropriate separation equipment; knowledge of phase equilibria is a prerequisite. In this work we have determined the phase diagram of PEG3350–ammonium sulphate–water system over the temperature range of 269–343 K.

We have also demonstrated that it is possible to modify distribution ratios of 1,10-phenanthroline–copper(II) sulphate complex by modifying the temperature: altering temperature may then serve as an additional and useful tool to modify phase incompatibility and thus shift the partitioning of compounds in aqueous biphasic systems.

Our future research will be aimed at achieving a better understanding of the major factors governing metal ions partitioning (particularly rare earths) in PEG–ATPS.

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