Polymer Based ABS in application of regeneration of catalyst

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Aqueous biphasic system (ABS) consists of a tri block copolymer PEG-PPG-PEG and Polyvinylpyrrolidone (PVP) was designed. The phase diagram of the polymer-polymer system was constructed by turbidometric titration method at 298 K. The newly developed ABS was employed for the possible analytical application of separation and recovery of an important catalyst Molybdenum disulfide.

I. INTRODUCTION

There is an increasing demand to explore potentially benign green solvents in extraction and separation technology. Aqueous biphasic systems with reduced hazards to the environment are preferred compared to many aqueous–organic biphasic systems [1]. The aqueous biphasic systems can be formed when a certain water-soluble polymer is dissolved in water together with another kind of hydrophilic polymer or with a given inorganic salt at specific concentrations. The resulting systems are composed of two immiscible phases, which are intrinsically aqueous [2]. It has been shown that the aqueous two-phase partition technique can be suitable for the separation of inorganic compounds and small organic molecules [3]. Aqueous Biphasic Systems (ABS) can be formed above a critical concentration or temperature by mixing aqueous solutions of two polymers (polymer/polymer ABS), for example, polyethylene glycol (PEG) and dextran, [4], a polymer with a water structuring kosmotropic salt (polymer/salt ABS), for example, PEG and K_3PO_4, [5] a chaotropic, water destructuring salt, such as an ionic liquid, and a kosmotropic salt (salt/salt ABS), for example, 1-butyl-3-methylimidazolium chloride and K_3PO_4 [6]. ABS retain all the practical advantages of liquid-liquid extraction and are also possessed of some unique qualities of having nonflammable, nontoxic and nonvolatile properties. They are inexpensive and have favorable phase separation and mass transfer characteristics that are compatible with conventional solvent extraction equipments. Biphase formation in solutions containing hydrophilic polymer mixtures is well established [7]. Different noncovalent interactions of water can occur with the polymer and it increases with the molecular size of the polymers. In such polymer-polymer biphasic systems, phase separation can occur at very low polymer concentrations due to the large size of the polymers and consequently small loss in entropy upon demixing. Phase diagram of such ABS gives useful information about the relative amounts of the two phase forming components needed to maintain a biphasic system, as well as the relative ratios of the two components in either phase. Molybdenum disulfide (MoS_2) is a promising catalyst for electrocatalytic or photoelectrocatalytic hydrogen evolution. It is insoluble in water and most of the organic solvents. Regeneration of the catalyst after its chemical function is very important and a comparative study of catalyst regeneration methods have been reported in the literature [8]. ABS offers a suitable medium for regeneration which may entrap the fine particles of the powdery material inside the micellar matrix of the polymer rich phase. MoS_2 has significant contributions in the field of energy storage and conversion and its composites are also used as electrode materials in Li ion batteries [9]. In this present work aqueous two phase system comprised of two polymers polyvinylpyrrolidone (PVP) and poly(ethyleneglycol) – block - poly(propyleneglycol) – block – poly(ethyleneglycol) (PEG-PPG-PEG) has been characterized. PVP being a biocompatible polymer has the potential to be applied for sustainable extractions and it is also used as drug excipients in pharmaceutical sciences. Phase diagram has been constructed for the polymer-tri block copolymer [PVP (40%) + PEG-PPG-PEG (30%)] ABS and the possibility of its applications in regeneration of MoS_2 has been explored.

II. EXPERIMENTAL

Materials: Polyvinylpyrrolidone (PVP) [$(C_6H_9NO)n$] (MW=40000) (Spectrochem), Poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethyleneglycol) (PEG-PPG-PEG) (MW=5800) (Sigma Aldrich), Molybdenum disulfide (MoS_2) (Loba Chemie, 98%).

Apparatus: The UV visible spectra were obtained using an Agilent 8453 diode array spectrophotometer. Centrifugation was done using Hermle microprocessor controlled universal refrigerated high speed table top centrifuge (model Z 36 K) operated on 230 V/50 Hz with an adjustable speed range of (200 to 30000) rpm. The density was measured using a Mettler Toledo portable density meter (model 30PX). A BOD incubator shaker NOVA model: SHCI 10(D) was used to maintain the temperature at 296 ± 0.5 K. A Mettler Toledo digital balance correct up to fourth decimal place was used for measuring the weights.

Construction of the phase diagram: The phase diagram of the proposed ABS has been constructed by the turbidometric titration method [7]. Binodal curve was obtained for the biphasic composition of PVP (40%) and PEG-PPG-PEG (30%) system. For the experiment, the initial weight of the blank centrifuge tube was noted. Then experimental sets were prepared with different weight fractions of the polymers keeping the final weight fixed (3g) in each case. Now the mixtures were shaken uniformly for 10 mins in BOD shaker at 298 K and the solutions were then centrifuged for 5 mins at 5000 rpm at the same temperature. Two distinct phases were observed and the weight of the tube was taken. Water was added dropwise into the centrifuge tube until the biphasic system turned into a single phase. The final weight of the centrifuge tube was noted and the amount of water added just prior to single phase formation was noted. The resulting compositions of the polymers were determined considering the amount of water added in different sets. Weight percentages of PVP/PEG-PPG-PEG for variable sets were plotted, and a binodal curve was obtained. By convention, the component predominantly in the bottom phase (PVP) was plotted in the abscissa and the component predominantly in the top phase (PEG-PPG-PEG) was plotted as the ordinate.

Determination of the tie-lines: The experimental binodal curve was further fitted to the following equation proposed by Merchuk et al [10]:

$$Y = Aexp[(BX^{0.5}) - (CX^{3})] \tag{1}$$

Where, Y and X are the mass fraction of the two components respectively. A, B, and C are constants obtained by the regression of the experimental binodal data. The tie-lines associated with the phase diagram were obtained by gravimetric method [11]. Ternary mixture composed of PVP + PEG-PPG-PEG + water at the biphasic region were gravimetrically prepared, shaken uniformly, and allowed to equilibrate for 24 h at (298 ± 0.5) K, for a complete separation of the two polymeric phases. Both phases were then separated and individually weighed.

Each TL was determined by the lever-arm rule through the relationship between the top phase composition and the overall system composition and for which the following system of four equations (equations 2 – 5) and four unknown factors were solved.

$$Y_{\mathrm{T}} = Aexp[(B * X_{\mathrm{T}}{}^{0.5}) - (C * X_{\mathrm{T}}{}^{3})] \tag{2}$$

$$Y_{\mathrm{B}} = Aexp[(B * X_{\mathrm{B}}{}^{0.5}) - (C * X_{\mathrm{B}}{}^{3})] \tag{3}$$

$$Y_{\mathrm{T}} = (\frac{Y_{\mathrm{M}}}{\alpha}) - \frac{1-\alpha}{\alpha} * Y_{\mathrm{B}} \tag{4}$$

$$X_{\mathrm{T}} = (\frac{X_{\mathrm{M}}}{\alpha}) - \frac{1-\alpha}{\alpha} * X_{\mathrm{B}} \tag{5}$$

Where T, B, and M, designate the top phase, the bottom phase and the mixture, respectively; X and Y represent the weight fraction percentage of the phase forming components of PVP/PEG-PPG-PEG and is the ratio between the mass of the top phase and the total mass of the mixture. Each tie-line length (TLL) and slope of the tie-lines (STL) could be obtained using the following equation:

$$TLL = \sqrt{(X_{\mathrm{T}} - X_{\mathrm{B}})^2 + (Y_{\mathrm{T}} - Y_{\mathrm{B}})^2} \tag{6}$$

$$STL = \frac{Y_{\mathrm{T}} - Y_{\mathrm{B}}}{X_{\mathrm{T}} - X_{\mathrm{B}}} \tag{7}$$

Where T, B, and M, represent the top phase, the bottom phase and the mixture, respectively; and X and Y represent the equilibrium weight fraction percentages of the phase forming components.

Application in extraction of molybdenum disulphide: An extraction study of MoS_2 in the proposed PVP/ PEG-PPG-PEG ABS was observed. In both PVP and PEG-PPG-PEG solution, a broad absorption peak was observed for MoS_2 at the wavelength 560 nm. Before extraction study, calibration was done in PVP medium using increasing concentrations of MoS_2. In the proposed ABS, trace amount of MoS_2 was added and extraction was performed in the usual way. The PVP rich phase was separated for absorbance study. The percent extraction was calculated using equation (8).

$$E = \frac{[x]_{\text{top phase}}}{[x]_{\text{bottom phase}}} \tag{8}$$

III. RESULTS AND DISCUSSION

Phase diagram and the tie-lines: Phase diagram of an ABS indicates the biphasic region which can be used for extraction and separation study. Construction of phase diagram is important to know the potential working area for a particular two-phase system. By plotting the weight fractions of the two components a binodal curve is obtained, which acts as a borderline between the zone of component concentrations that will form two immiscible aqueous phases (the region above the curve) from those that will form a homogenous single phase (the region at and below the curve). The phase diagram of the PVP/PEG-PPG-PEG was obtained at 298 K (Figure 1) and the details of system compositions and final compositions are tabulated in Table I.

By connecting two nodes on the binodal curve tie-lines are obtained. Each points on the tie line represents the final concentrations of the two phase forming components in both top and bottom phases. Any point on the tie-line coordinates represent systems with varying total compositions and volume ratios, but the same final concentration of the phase components in the top

System Composition		**Final Composition**	
x_1	x_2	x_3	x_4
20.0	15.0	15.8	12.0
21.0	14.0	16.0	10.7
22.0	13.5	16.1	9.9
23.0	13.0	16.3	9.0
24.0	12.0	16.5	8.2
25.3	11.0	16.7	7.3
26.0	10.5	17.1	6.8
26.6	10.0	17.4	6.3

TABLE I. Experimental (Liquid + Liquid) Equilibrium Mass Fractions (Binodal Curve Data) for the System PVP (x_1) + PEG-PPG-PEG (x_2) in water at Temperature T = 298 K, Pressure p = 0.1 MPa

Feed Composition		**Top Phase**		**Bottom Phase**		**TLL**	**STL**
x_1	x_2	x_1	x_2	x_1	x_2		
20	12.50	2.50	25.50	28.50	3.50	34.06	-0.84
18.7	13.30	2.60	26.20	27.30	3.65	33.44	-0.91
17.3	14.20	2.65	26.70	26.50	3.90	32.99	-0.99

TABLE II. Experimental (Liquid + Liquid) Equilibrium Data for the system PVP (x_1) + PEG-PPG-PEG (x_2) in water for mass fractions and Tie-line Length (TLL) at the Temperature T=298 K, Pressure p = 0.1 MPa

ABS	**A**	**B**	**$C*10^{-3}$**	**R^2**
PVP + PEG-PPG-PEG	1592.39	-0.5269	4.37	0.996

TABLE III. Fitting parameters of the binodal curves

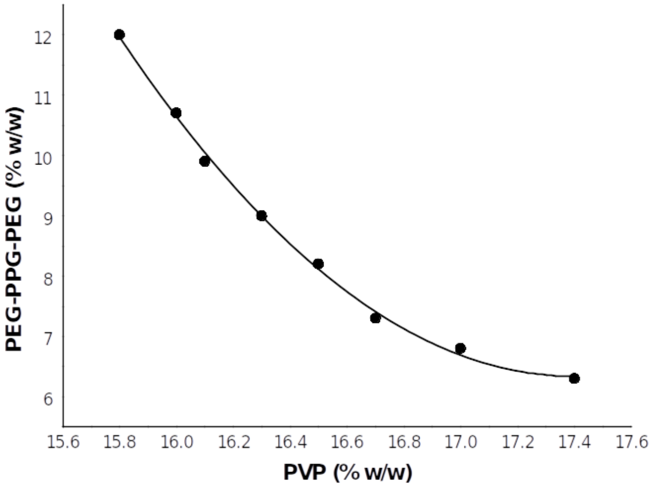

FIG. 1. Phase diagram of PVP + PEG-PPG-PEG aqueous two phase drawn at 298 K. Abscissa shows the weight fraction of PVP and ordinate shows the weight fraction of PEG-PPG-PEG.

and bottom phases. The tie line lengths were calculated using equations (2-5) and are presented in table II for PVP/PEG-PPG-PEG system. Fitting parameters, A, B, C and R2 values are given in table III. Phase diagram is a fingerprint unique to the particular ABS under certain conditions of component concentration, pH and temperature.

Application in extraction of molybdenum disulfide: MoS_2 has a low coefficient of friction due to weak van der Waals interactions between the sheets of sulfide atoms. It is a dry lubricant and used as a cocatalyst for desulfurization in petrochemistry. The effectiveness of the MoS_2 catalysts is enhanced by doping with small amounts of cobalt or nickel. MoS_2 is an efficient catalyst for hydrogen evolution, including the electrolysis of water and useful to produce hydrogen for use in fuel cells. MoS_2 also possesses mechanical strength, electrical conductivity and acts as a component of photoelectrochemical (e.g. for photocatalytic hydrogen production) applications. MoS_2 does not react to most of the acids except aqua-regia and hot concentrated sulfuric acid, hydrochloric acid and nitric acid and also insoluble in most of the organic solvents. Regeneration of this catalyst by using suitable solvent extraction method is quite difficult to carry out. Moreover, another problem is poisoning of heterogeneous catalysts which occur due to the blockage of active sites by the products and side products present in the reaction medium. Therefore regeneration of the catalyst by removing the poisons as completely as possible is a challenging task. H_2 treatment at high temperatures is a common practice to attain this and these reactions are often exothermic [12].

MoS_2 forms a suspension in the micellar medium of polymeric solution at tracer concentrations. If the catalytic reaction occurs in aqueous medium, the poisons can be washed off from the catalyst surface and it can be extract in the PVP rich phase of ABS. MoS_2 was dissolved in PVP solution at milimolar concentration and extracted it using PVP/PEG-PPG-PEG ABS. Absorbance spectrum of MoS_2 in polymeric solution shows a double humped broad spectrum which has gradually increasing absorbance value with increasing concentration of the catalyst. This pattern of spectrum is also supported by the literature report for crystalline MoS_2 [13].

However, the typical broad humped nature and slight changes in the peak positions of the spectrum may be due to the particle size distribution of MoS_2 in the dispersed state in micellar environment of the polymer matrix. As reported in literature, the spectra consists of a well-defined shoulder at 530 nm, and a low-intensity longer wavelength absorption peak at $\lambda_{\max} > 600$ nm. In case of PVP/PEG-PPG-PEG system it was observed that MoS_2 was exclusively extracted in PVP medium which was confirmed by absorbance measurement. Although both the polymeric solution can offer micellar matrix, the preference of MoS_2 for PVP over the tri block copolymer PEG-PPG-PEG may be due to the weak nitrogen-sulphur non-bonding interactions which drives the catalyst to get extracted in the PVP rich phase. However, if the ABS containing MoS_2 is allowed to settle for some time, it aggregates as dust particles at the PVP/ PEG-PPG-PEG biphasic interface and from there the catalyst can be easily separated out for further application.

IV. CONCLUSION

Polymer based aqueous biphasic system was designed with PVP and block copolymer, PEG-PPG-PEG. Well defined phase diagram with suitable tie lines were obtained for two-phase system consisting of polymer-salt [PVP (40%) + PEG-PPG-PEG (30%)] at 298 K. The proposed polymer based ABS was found to be suitable for regeneration of catalyst MoS_2 and this method will be immensely beneficial to the field of catalysis relevant to chemical synthesis.

[1] H. D. Willauer, J. G. Huddleston, and R. D. Rogers, Solvent properties of aqueous biphasic systems composed of polyethylene glycol and salt characterized by the free energy of transfer of a methylene group between the phases and by a linear solvation energy relationship, Industrial & engineering chemistry research **41**, 2591 (2002).

[2] M. Shibukawa, K. Matsuura, Y. Shinozuka, S. MIZUNO, and K. OGUMA, Effects of phase-forming cations and anions on the partition of ionic solutes in aqueous polyethylene glycol-inorganic salt two-phase systems, Analytical sciences **16**, 1039 (2000).

[3] X. Chen, G. Li, and Z. Hu, Determination of microamounts of palladium (ii) by extraction method without usual organic solvents, Microchimica Acta **122**, 143 (1996).

[4] P. A. Albertsson, *Partition of Cell Particles and Macromolecules* (Wiley, New York, 1986).

[5] R. D. Rogers and M. A. Eiteman, *Aqueous biphasic separations* (Springer, 1995).

[6] N. J. Bridges, K. E. Gutowski, and R. D. Rogers, Investigation of aqueous biphasic systems formed from solutions of chaotropic salts with kosmotropic salts (salt–salt abs), Green Chemistry **9**, 177 (2007).

[7] R. Sadeghi, Aqueous two-phase systems of poly (vinylpyrrolidone) and potassium citrate at different temperatures—experimental results and modeling of liquid–liquid equilibrium data, Fluid phase equilibria **246**, 89 (2006).

[8] M. Sheintuch and Y. I. Matatov-Meytal, Comparison of catalytic processes with other regeneration methods of activated carbon, Catalysis Today **53**, 73 (1999).

[9] Y. Zhao, Y. Zhang, Z. Yang, Y. Yan, and K. Sun, Synthesis of mos2 and moo2 for their applications in h2 generation and lithium ion batteries: a review, Science and technology of advanced materials (2013).

[10] J. C. Merchuk, B. A. Andrews, and J. A. Asenjo, Aqueous two-phase systems for protein separation: Studies on phase inversion, Journal of Chromatography B: Biomedical Sciences and Applications **711**, 285 (1998).

[11] K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey, and R. D. Rogers, Controlling the aqueous miscibility of ionic liquids: aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations, Journal of the American Chemical Society **125**, 6632 (2003).

[12] U. Gupta and C. Rao, Hydrogen generation by water splitting using mos2 and other transition metal dichalcogenides, Nano Energy **41**, 49 (2017).

[13] I. Klimenko, A. Golub, T. Zhuravleva, N. Lenenko, and Y. N. Novikov, Solvent effects on the formation and absorption spectra of nanodisperse molybdenum disulfide, Russian Journal of Physical Chemistry A **83**, 276 (2009).