Investigation of Gallium Partitioning Behavior in Aqueous Two-Phase Systems Containing Polyethylene Glycol and Ammonium Sulfate

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The partitioning behavior of gallium in polyethylene glycol (PEG) (1)–ammonium sulfate $(NH_4)_2SO_4$ (2) aqueous two-phase systems (ATPS) in the presence of 4-(2-pyridylazo) resorcinol (PAR) as an extractant has been investigated. The main factors, such as, pH, PEG molecular weight, PEG concentration, and temperature on the partition coefficient (K) have been discussed. Results show that pH has a significant effect on K. In the 20 % (mass fraction) $PEG_{20000}-30$ % $(NH_4)_2SO_4$ system, K reaches 113.43 at pH = 6.54. With the increases of PEG molecular weight and temperature, K also increases, while an increase of the PEG concentration has a negative effect on gallium partitioning. All results were explained well according to the coordination between the −N and −O of the PAR molecule and the gallium ion and the relationship $\ln K = A\Delta w_1$.

Introduction

Gallium is a metallic element in group IIIA of the periodic table. This metal has been paid great attention since it was discovered that gallium combined with elements of group 15 displayed semiconducting properties. Gallium is assumed to be an indispensable rare metal mainly because of its fast growing demand as gallium arsenide (GaAs) in integrated circuits. Other than digital circuitary, GaAs finds increasing application in opto-electronics: for light emitting diodes (LED), semiconductor lasers, solar cells, optical computing, and analogue microwave devices. All these applications have put great pressure on the availability of pure gallium in large amounts. Unfortunately, gallium exists in most cases with other elements. Hence, the extraction of gallium is an important investigation topic.

Traditional extraction methods for gallium usually are organic−water two-phase systems, which involve volatile, flammable, and explosive organic solvents, such as *n*-hexane, toluene, xylene, benzene, nitrobenzene and kerosene.[1−5] The increasing emphasis on the adoption of clean manufacturing processes stringently requires environmentally benign and smart phase tunable systems to minimize discharges to the environment or to modify chemical processes.[6] So the application of traditional extraction methods has been largely restricted because of the organic solvents used. The reported green method for gallium[7,8] is supercritical fluids extraction (SFE). However, SFE usually requires elevated pressure and high capital investment for equipment. So exploration on environmentally benign and low cost extraction methods is required.

Aqueous two-phase systems (ATPS) are well-known green extraction systems. The extraction mechanism is similar to that of conventional organic systems. However, ATPS have many advantages: quick separation, easy operation, clear phase boundary, and no emulsification and, most importantly, the systems avoid organic solvents which are volatile, flammable, or explosive. So ATPS now have been a widely used extraction and separation technique both in experimental and in industrial applications.[9−11]

This work is focused on the exploration of feasibility of green ATPS for gallium extraction to improve environmental efficiency. Partitioning behavior of gallium in polyethylene glycol (PEG) (1)−ammonium sulfate $(NH_4)_2SO_4$ (2) ATPS in the presence of the organic reagent, 4-(2-pyridylazo) resorcinol (PAR), as an extractant was investigated. Effects of pH, PEG molecular weight, PEG concentration, and temperature on the partition coefficient (K) are discussed, and all the results are explained well according to the coordination between the −N and −O of the PAR molecule and the gallium ion and the relationship $\ln K = A\Delta w_1$.

Experimental Section

Reagents and Apparatus. PEG, average molecular weight 2000, 4000, 6000, and 20000, and $(NH_4)_2SO_4$ were purchased from Shanghai Chemical Reagents Co. and were used without further purification. Gallium stock solutions were prepared by dissolving Ga_2O_3 (Bejing Chemical Reagents Co.) in hydrochloric acid and were diluted to 0.19512 $mol \cdot m^{-3}$ with $6 \cdot 10^3$ $mol \cdot m^{-3}$ hydrochloric acid when they were used. PAR solution was prepared by dissolving 0.0504 g of PAR in ethanol to $w = 2.5 \cdot 10^{-4}$. Buffer solutions were prepared by mixing sodium acetate solution, hydrochloric acid solution, and water at different volume ratios. The high pH was adjusted by sodium hydroxide. All reagents used were of analytical grade. Water was twice distilled.

Gallium was analyzed on a model 722 spectrophotometer (Xiamen, China). A model pHS-3C meter (Shanghai, China) was used for pH measurement.

Procedure. The extraction system was prepared by mixing equal volumes of PEG solution and salt solution in a glass vessel. Then the gallium standard solution (0.19512 $mol \cdot m^{-3}$), PAR solution and buffer solution were added. The mixture was vigorously stirred for 3 h and then was set in a thermostat at the desired temperature for 24 h for equilibration. Preliminary tests[12] showed that these times were long

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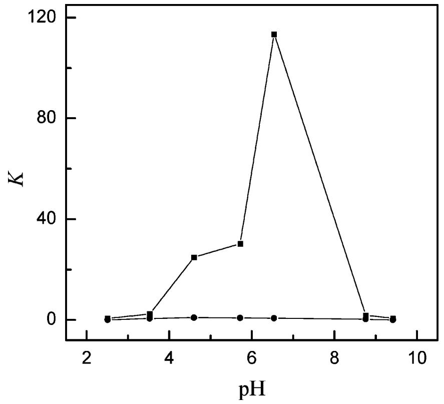

Figure 1. Effect of pH on gallium partitioning behavior in the 20 % PEG−30 % $(NH_4)_2SO_4$ system at $T = 298.15$ K: ■, in the presence of PAR; ●, in the absence of PAR.

Table 1. Gallium Partitioning Behavior in the 20 % PEG_{20000}−30 % $(NH_4)_2SO_4$ System at $T = 298.15$ K at Different pH's

	pH						
	2.51	3.53	4.60	5.72	6.54	8.76	9.42
K in the presence of PAR	0.64	2.50	24.90	30.21	113.43	1.87	0.69
K in the absence of PAR	0.07	0.66	0.91	0.85	0.72	0.32	0.03

enough to achieve equilibrium. The system separated into two transparent liquid phases with a well-defined interface. After separation of the two phases, samples of both phases were collected with a long pinhead syringe and analyzed after being diluted with water.

The concentration of Ga^{3+} was measured by spectrophotometer according to the literature.[13] K was calculated as $K = C_{\text{upper}}/C_{\text{lower}}$, where C_{upper} and C_{lower} are the gallium mole concentrations in the PEG-rich upper phase and salt-rich lower phase, respectively. Acidity was measured on a pHS-3C acidimeter. All experiments were performed in duplicate. The standard deviation of K is ± 0.02.

Results and Discussion

Effect of pH. The effect of pH on gallium partitioning behavior was performed in the 20 % (mass fraction) PEG_{20000}−30 % (mass fraction) $(NH_4)_2SO_4$ system at $T = 298.15$ K. Partition coefficient data are presented in Table 1, and the behavior is shown in Figure 1. In the presence of PAR, pH has a great effect on gallium partitioning, especially near neutral. For example, at pH = 6.54 K reaches 113.43. As the system becomes acidic or basic, K decreases remarkably. The results can be explained according to the coordination between the −N and −O of the PAR molecule and the gallium ion. PAR is a triprotic weak acid. Equilibrium forms of PAR are different at different acidity (Figure 2a).[14] When the system is acid, PAR forms a tridentate 1:1 metal complex with gallium. When pH is around 7, PAR forms the most stable form of metal complex, a 1:2 chelate (Figure 2b).[14] So the maximum K appears at about pH = 7. For comparison, gallium partitioning behavior under the same conditions but in the absence of PAR has also been investigated. Results show that all the K values are less than 1 at different pH's and the maximum is $K = 0.91$ at pH = 4.60. So all the following experiments were performed at pH = 6.54 with the presence of PAR.

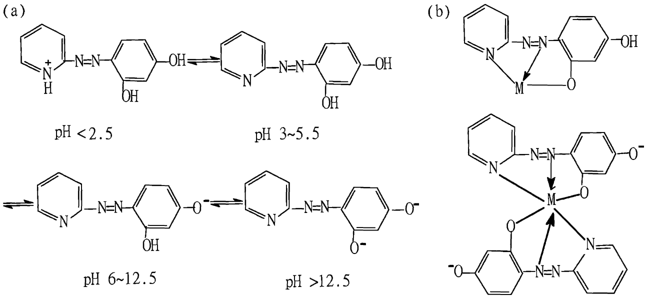

Figure 2. (a) Equilibrium forms of PAR at different pH. (b) Structure of the 1:1 and 1:2 PAR chelates.

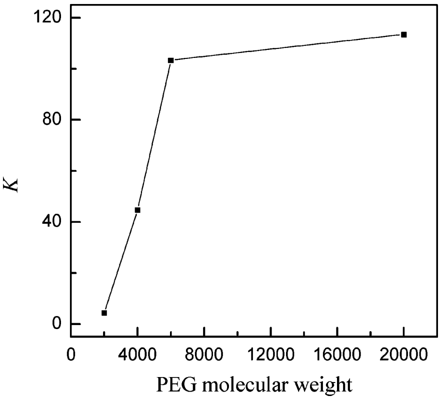

Figure 3. Effect of PEG molecular weight on gallium partitioning behavior in the 20 % PEG−30 % $(NH_4)_2SO_4$ system at $T = 298.15$ K at pH = 6.54.

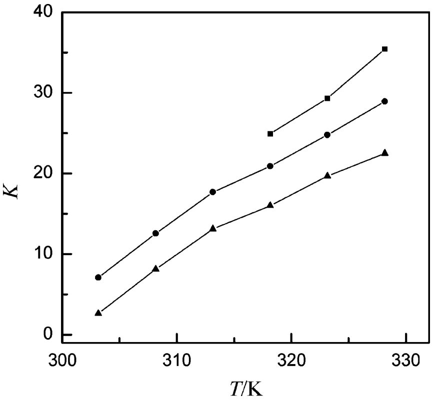

Figure 4. Effect of temperature on gallium partitioning behavior in the PEG_{2000}−30 % $(NH_4)_2SO_4$ system at pH = 6.54: ■, 10 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system; ●, 20 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system; ▲, 30 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system.

Table 2. Gallium Partitioning Behavior in the 20 % PEG−30 % $(NH_4)_2SO_4$ System at $T = 298.15$ K at pH = 6.54 with Different PEG Molecular Weights

	PEG mol wt			
	2000	4000	6000	20000
K	4.42	44.73	103.39	113.43

Effect of PEG Molecular Weight. The effect of PEG molecular weight on gallium partitioning behavior is illustrated in Table 2 and Figure 3. From Figure 3, it can be seen that K increases with an increase of PEG molecular weight. In the 20 % PEG−30 % $(NH_4)_2SO_4$ system, K is 4.42, while in the 20 % PEG_{6000}−30 % $(NH_4)_2SO_4$ system K reaches 103.39 and 98 % of the gallium is extracted to the PEG-rich phase. So K increases slowly again as the molecular weight of PEG increases more. The literature[15,16] points out that the K of a substance in ATPS follows the following relationship: $\ln K = A\Delta w_1$, where K is

Table 3. Gallium Partitioning Behavior in the PEG_{2000}−30 % $(NH_4)_2SO_4$ System at pH = 6.54

	T/K					
	303.15	308.15	313.15	318.15	323.15	328.15
K in 10 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system	a	a	a	24.91	29.30	35.42
K in 20 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system	7.09	12.56	17.67	20.89	24.78	28.91
K in 30 % PEG_{2000}−30 % $(NH_4)_2SO_4$ system	2.61	8.12	13.11	16.00	19.67	22.50

[a] The system is homogeneous.

the partition coefficient, A is a constant and Δw_1 is the difference in PEG mass fraction between the upper phase and the lower phase. According to the ATPS phase diagram,[17] the greater the PEG molecular weight, the greater the difference in concentration of the phase forming substance between the upper and lower phases. So K increases with the increase of the PEG molecular weight.

Effect of Temperature. The effect of temperature (T = (303.15 to 328.15) K) on gallium partitioning behavior was conducted in PEG_{2000}−30 % $(NH_4)_2SO_4$ system at pH = 6.54 and results are shown in Table 3 (as shown in Figure 4). From Figure 4, it can be seen that a temperature increase is favorable to gallium partitioning. For PEG−$(NH_4)_2SO_4$ ATPS, there is a lower critical temperature.[17] A temperature increase reduces the mutual solubility of the two phases and results in an increase of PEG concentration in the upper phase and of volume in the lower phase, which all make Δw_1 increase. Thus, ascending temperature leads to ascending K.

Effect of PEG Concentration. Figure 4 and Table 3 also show the effect of PEG concentration (10 %, 20 %, and 30 %) on gallium partitioning behavior. Results show that a PEG concentration increase has a negative effect on gallium partitioning. An increase in PEG concentration will make both the PEG concentration and volume in the upper phase increase. A volume increase is not favorable to partitioning of gallium, since K is the ratio of gallium concentration in the upper phase to that in the lower phase. Thus, K decreases with an increase of PEG concentration. It is worth pointing out that although K is low, the extraction rate of gallium is increased with a PEG concentration increase since the total quantity of gallium in the upper phase is the product of the concentration of gallium and volume of the upper phase.

Conclusion

The present work confirmed the feasibility of the use of environmentally benign PEG-based ATPS for gallium extraction. Effects of pH, PEG molecular weight, temperature and PEG concentration on K have been investigated. Results show that pH has a significant effect on gallium partitioning and the optimum pH is near neutral. At pH = 6.54 K is as high as 113.43 in the 20 % PEG_{20000}−30 % $(NH_4)_2SO_4$ system. Increases of PEG molecular weight and temperature are favorable to the K of gallium. However, an increase of PEG concentration is not favorable to K. All the results were explained well according to the coordination between the −N and −O of the PAR molecule and the gallium ion and the relationship: $\ln K = A\Delta w_1$.

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