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Equilibrium Diagrams at 27 °C of the Water + Sodium Tungstate + Dodecylamine Chloride System

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Amines are usually used in extracting tungsten from scheelite. Dodecylamine chloride in kerosene and octanol was used as an extracting agent in order to establish the phase diagram at 27 °C for water + sodium tungstate + dodecylamine chloride. Acetone was used to prevent emulsion formation. This procedure made it possible to achieve better partition coefficients; however, there appears to be a saturation region.

Introduction

Tungsten is widely used in industry, and there is a great interest in extracting it from scheelite, since this is the mineral which contains the greatest amount of tungsten.

Amines have been used as extracting agents for this purpose (*1–4*) due to their ability to form water-insoluble aminoorganotungsten complexes, which on the other hand are soluble in their organic phase (*1*). Tungsten (WO_3) extraction from scheelite waste using 1 mass % dodecylamine chloride as an extracting agent can reach up to 90% (*4*). In the present work dodecylamine chloride at 0.19 mass % in kerosene was used as the solvent.

Experimental Section

Chemicals. Sodium tungstate (Merck) and acetone (Merck) had a purity of 99%. Octanol-1 (Merck) and dodecylamine chloride (Merck) had a purity of 98%. The kerosene was obtained from Petrobrás.

Experimental Procedures. The experimental device used was maintained at the constant temperature of 27 ± 0.1 °C in a thermostated vessel. Dodecylamine chloride dissolved in kerosene was used as the solvent and 2 mass % octanol was added with the objective of avoiding formation of an additional liquid layer.

The binodal curve was determined separately from the tie lines during the process of obtainment of the phase diagram. For this purpose various mixtures of water and sodium tungstate of known weight and composition were prepared and titrated with solvent until turbidity was observed. The composition of the obtained solution on the solubility curve was calculated from the amounts of the liquids used. In this manner, points along the water-rich portion of the solubility curve were determined with a relative accuracy of ±1% (*5*). For the solvent-rich portion, it was necessary to titrate known mixtures of sodium tungstate and solvent with water.

The tie lines were determined separately. Mixtures of known composition located on the biphasic region of the diagram were shaken in glass-stoppered separatory funnels for 1 h, and then after standing for 5 min, two layers were formed. The period of 1 h was established as the time in which the equilibrium between the two liquid phases was achieved. It was then observed that after this period of time no alteration of the sodium tungstate concentration took place. A decantation period of 5 min was sufficient to promote separation of the two phases. Sodium tungstate was analytically determined in the aqueous layer by using the thiocyanate method (*6*). The error inherent to the method is less than ±1% (*5*). The concentration of sodium tungstate in the organic phase was determined by difference. The values found were marked over the solubility curve.

Table I. Data from the Ternary Diagram for Water (A) + Sodium Tungstate (B) + (97.81 mass % Kerosene + 2.00 mass % Octanol + 0.19 mass % Dodecylamine Chloride) (C) at 27 °C[a]

(a) Binodal Curve Data

100w_A	100w_B	100w_C	100w_A	100w_B	100w_C
53.31	46.69	00.00	29.49	26.26	44.25
50.30	44.11	05.59	23.78	20.76	55.46
47.38	42.57	10.05	16.75	15.56	67.69
43.66	37.65	18.69	09.18	08.05	82.77
39.18	34.68	26.14	00.00	00.00	100.00
34.56	30.84	34.60			

(b) Tie Line Data

raffinate phase (R)			extract phase (E)			
100w_{AR}	100w_{BR}	100w_{CR}	100w_{AE}	100w_{BE}	100w_{CE}	m
96.62	03.38	–	1.13	0.92	97.05	0.27
88.20	11.80	–	2.99	2.74	94.27	0.23
75.41	24.59	–	3.47	2.82	93.71	0.11
63.42	36.58	–	3.66	3.24	93.10	0.09
57.60	42.40	–	5.14	3.36	91.50	0.08

[a] w is the mass fraction, and m is the partition coefficient.

Solutions of known weight and composition of various concentrations of sodium tungstate in water + acetone, titrated with solvent, were used to determine the solid–liquid saturation curves. At first, three saturated liquid layers are formed. As the titration progresses one of the liquid layers disappears, thus indicating that a point has been achieved over the saturation curve. The composition of the obtained solution was calculated from the amounts of the liquids and solid used.

In order to determine the solubility of water in the solvent, titration of pure water with solvent was carried out. An inverse operation was used to determine the solubility of the solvent in water.

Results and Discussion

Results are given in Tables I and II. Figures 1 and 2 show the tie lines for the sodium tungstate + dodecylamine chloride systems in octanol + kerosene, in which pure water (Figure 1) or water + acetone (Figure 2) was used. Figure 1 corresponds to the ternary diagrams of type 1 classification proposed by Treybal (*7*), whereas Figure 2 corresponds to type 2 classification. Acetone was responsible for the saturation region formed by the three liquid phases and solid crystals. In both cases the solubility of water in dodecylamine

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Table II. Data from the Pseudoternary Diagram for (67 mass % Water + 33 mass % Acetone) (A) + Sodium Tungstate (B) + (97.81 mass % Kerosene + 2.00 mass % Octanol + 0.19 mass % Dodecylamine Chloride) (C) at 27 °C[a]

$100w_A$	$100w_B$	$100w_C$	$100w_A$	$100w_B$	$100w_C$
		(a) Binodal Curve Data			
87.17	12.83	00.00	40.13	21.36	38.51
76.50	21.12	02.38	32.90	19.06	48.04
67.83	23.52	08.65	24.13	16.87	59.00
67.07	24.00	08.93	17.22	13.65	69.13
58.78	24.27	16.95	08.29	07.86	83.85
52.53	23.69	23.78	00.00	00.00	100.00
45.11	22.89	32.00			
		(b) Mutual Solubility Data			
76.33	23.66	00.01	45.84	36.42	17.74
71.10	23.88	05.02	32.23	53.28	14.49
68.01	23.95	08.94	28.52	64.05	07.43
65.35	24.00	10.65	27.70	67.50	04.80
52.51	31.68	15.81			

(c) Tie Line Data

raffinate phase (R)			extract phase (E)			
$100w_{AR}$	$100w_{BR}$	$100w_{CR}$	$100w_{AE}$	$100w_{BE}$	$100w_{CE}$	m
95.93	04.47	-	00.99	0.80	98.21	0.20
92.41	07.59	-	01.32	1.66	97.02	0.22
86.01	13.99	-	02.97	3.38	93.65	0.24
78.63	19.37	2.00	04.04	5.18	90.78	0.27
67.43	23.57	9.00	11.17	8.61	80.22	0.37

[a] w is the mass fraction, and m is the partition coefficient.

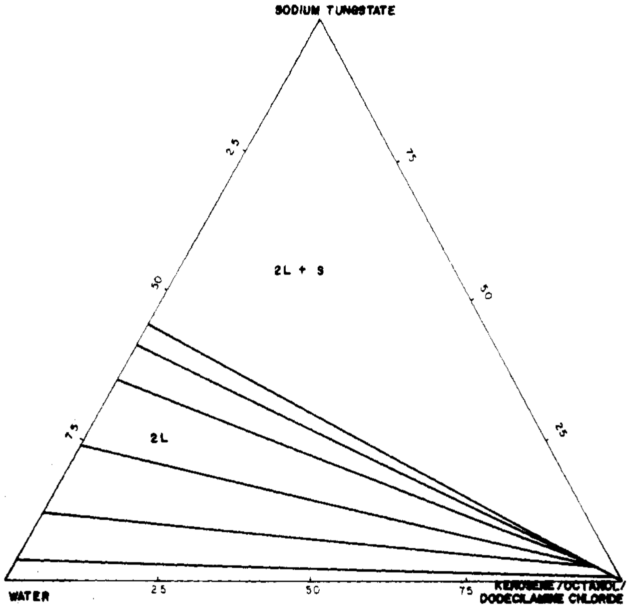

Figure 1. Water + sodium tungstate + (octanol-1 + dodecylamine chloride + kerosene) phase diagram with tie lines at 27 °C (L = liquid, S = solid).

chloride and the solubility of dodecylamine chloride in water remained unchanged; that is to say, the mixture is totally immiscible at 27 °C.

The partition coefficient is defined as the ratio of the WO_3 concentration (mass %) in the organic phase and the WO_3 concentration (mass %) in the aqueous phase. Higher coefficients resulted from using a water + acetone solution, as shown in Table II, part c.

Figure 3 shows that the system in which acetone was not used is more selective for values of $w_{BR}/(w_{BR} + w_{AR})$ between 0.04 and 0.25 and for values higher than 0.25 the system using acetone is the most selective. For values lower than 0.04 both systems showed close selectivity.

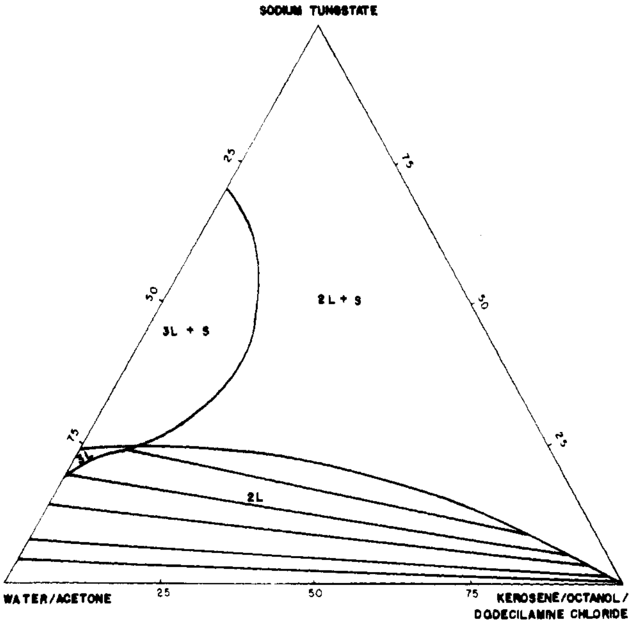

Figure 2. (Water + acetone) + sodium tungstate + (octanol-1 + dodecylamine chloride + kerosene) phase diagram with tie lines at 27 °C (L = liquid, S = solid).

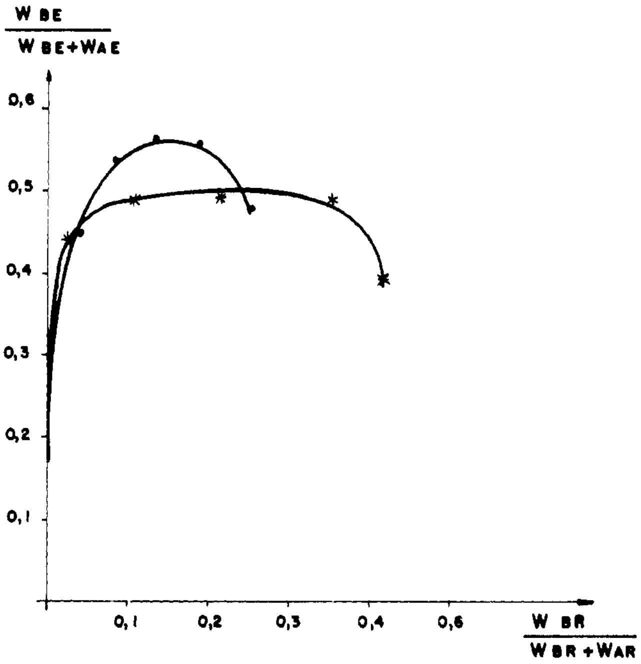

Figure 3. Selectivity diagrams at 27 °C for the systems (●) water + sodium tungstate + (octanol-1 + dodecylamine chloride + kerosene) and (*) (water + acetone) + sodium tungstate + (octanol-1 + dodecylamine chloride + kerosene).

Despite the higher values of the partition coefficients obtained with the use of acetone, the results suggest that the procedure in which acetone was not used should be chosen, since it gives a simpler diagram. Another factor which could be considered in selecting this procedure is the fact that the use of acetone results in higher costs, the need for organic matter destruction, and its recovery as the end product.

Glossary

w_A	mass fraction of water in one phase
w_B	mass fraction of sodium tungstate in one phase
w_C	mass fraction of kerosene, octanol, and dodecylamine chloride in one phase

w_{BR}	mass fraction of sodium tungstate in the raffinate phase
w_{BE}	mass fraction of sodium tungstate in the extract phase
w_{AR}	mass fraction of water or water + acetone in the raffinate phase
w_{AE}	mass fraction of water or water + acetone in the extract phase
m	partition coefficient

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