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Liquid–liquid equilibria for the pseudo-ternary system {aqueous sulfuric acid solution + methyl ethyl ketone or methyl isopropyl ketone + phosphonium-based ionic liquids} at 298.15 K and atmospheric pressure

Sang Hong Shin [a], In-Chan Hwang [a], So-Jin Park [a,*], Young-Yoon Choi [b]

[a] Department of Chemical Engineering, College of Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea
[b] Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Republic of Korea

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ABSTRACT

The extractability of molybdenum in an aqueous phase by methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) and methyl isopropyl ketone (MIPK) were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The pseudo-ternary LLE data are reported for the following systems at 298.15 K: {aqueous sulfuric acid solution (ASAS) + MEK + tri-hexyl tetradecyl phosphonium chloride ([P666,14][Cl])}, {ASAS + MEK + tri-hexyl tetradecyl phosphonium dicyanamide ([P666,14][DCA])}, {ASAS + MEK + tri-hexyl tetradecyl phosphonium bis(2,2,4-tri-methylpentyl) phosphinate ([P666,14][TMPP])}, {ASAS + MIPK + [P666,14][Cl]}, {ASAS + MIPK + [P666,14][DCA]} and {ASAS + MIPK + [P666,14][TMPP]}. The experimental LLE data have been correlated using the non-random two-liquid (NRTL) activity coefficient model.

1. Introduction

Molybdenum (Mo), silvery-white strategic metal [1] is usually obtained from molybdenite, wulfenite ($PbMoO_4$), powellite ($CaMoO_4$) and as a byproduct of mining and processing tungsten and copper. Therefore, Mo should be extracted from the roasted Mo-leaching solution. Solvent recovery in this extraction has become a very important process because recycling is a key component of modern waste reduction. A detailed understanding of the liquid–liquid equilibria (LLE) for the solvents and diluents in the Mo extraction process is therefore necessary, both to analyze solvent capability and to develop recycling processes for these solvents or diluents. Trioctyl amine and acetylacetone are commonly used to extract Mo from aqueous acid leaching solution. In order to find alternative ketone solvent, Mo solubility out of the aqueous phase is studied for some typical ketone solvents: methyl ethyl ketone (MEK), methyl isopropyl ketone (MIPK) and methyl isobutyl ketone (MIBK) using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). MEK and MIPK showed relatively good possibilities for use as selective solvents of Mo compared to MIBK. Therefore, we selected MEK and MIPK as solvents of Mo from the aqueous acid Mo-leaching solution. Solvents are generally used by dilution in proper organic diluents. Most of the diluents and the extracting agents are molecular components, which are volatile, flammable, and harmful to the environment. Thus, a key issue in the field of solvent extraction is to develop safer and environmentally friendly diluents or extracting agents. This problem may be solved by ionic liquids (ILs) as a new type of solvent (or diluent) with negligible vapor pressure. We have reported previously our systematic work on the possibility of using ILs as selective solvents or diluents in the Mo extraction process [2,3].

As a continuation of our work, therefore, the pseudo-ternary LLE data at 298.15 K are reported for the following systems including MEK and MIPK as solvent: {aqueous sulfuric acid solution (ASAS, pH = 1.0) + MEK + tri-hexyl tetradecyl phosphonium chloride ([P666,14][Cl])}, {ASAS + MEK + tri-hexyl tetradecyl phosphonium dicyanamide ([P666,14][DCA])}, {ASAS + MEK + tri-hexyl tetradecyl phosphonium bis(2,2,4-tri-methylpentyl) phosphinate ([P666,14][TMPP])}, {ASAS + MIPK + [P666,14][Cl]}, {ASAS + MIPK + [P666,14][DCA]} and {ASAS + MIPK + [P666,14][TMPP]}. Kim et al. [4] showed that LLE data are not significantly different between pseudo-ternary systems containing ASAS and the same-component system containing pure water instead of ASAS. However, in this study, the LLE

* Corresponding author. Tel.: +82 42 821 5684; fax: +82 42 823 6414.
E-mail address: sjpark@cnu.ac.kr (S.-J. Park).

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Nomenclature

g_{ij}	NRTL energy parameter
N	number of tie lines
OF	objective function
q	UNIQUAC parameter
RMSD	root mean square deviation
R	universal gas constant
r	UNIQUAC parameter
T	temperature (K)
w	weight fraction

Greek letters

a_{ij}	NRTL non-randomness parameter
ρ	density (g/cm^3)

Superscripts

exp	experimental value
cal	calculated value

Subscripts

j	component j
α	phase α
k	tie-line k

determinations have been carried out for pseudo-ternary systems containing ASAS because Mo is leached industrially using ASAS. The experimental LLE data in this study have been correlated using the non-random two-liquid (NRTL) model [5].

2. Experimental

2.1. Materials

[P666.14][Cl], [P666.14][DCA], [P666.14][TMPP], MIBK and MIPK were obtained from Sigma Aldrich, and the water was supplied by Baker. MEK was supplied by Samchun Chemical, Korea. Sulfuric acid was supplied by Matsunoen Chemicals Ltd. The purity of the chemicals was confirmed before experimentation using gas chromatographic analyses and by comparisons of the chemicals' physical properties with literature values. All of the chemicals were dried using molecular sieves with a pore diameter of 0.4 nm. The water contents of the MEK, MIPK and MIBK, determined using a Karl-Fischer titrator (Metrohm 684 KF-Coulometer), were less than 2×10^{-5} g/g; the water contents of the ILs were less than 7×10^{-4} g/g. The purities of the above chemicals were periodically confirmed before experimentation, using gas chromatography. The purities and thermo-physical properties are summarized in Table 1 along with the literature values [6–12]. The ASAS (pH = 1.0) was made of a lot of distilled water and a very small amount of sulfuric acid by adding sulfuric acid into water. The pH of ASAS was monitored using a pH meter (Hanna pH-210, Korea) with an accuracy of pH + 0.01. The mole fraction of sulfuric acid in ASAS was less than 0.0009 [13].

2.2. Apparatus and procedure

The solubility of Mo in ketones was checked in an LLE-determination glass vessel specially designed by our group for this purpose. Fig. 1 shows the schematic diagram of this LLE measurement system. For this solubility test, excess amounts of Mo powder introduced into the ASAS and stirred for 12 h at 298.15 K. The insoluble Mo in the ASAS phase was then removed by filtration. From this Mo containing ASAS, Mo was extracted by ketone. This two

Table 1
Properties of used chemicals.

Chemicals	GC analysis (wt%)	ρ (g cm^3) at 298.15 K and atmospheric pressure	
		This work	Reference
Water	>99.9	0.99710	0.99710[a]
MIBK	>99.9	0.79623	0.79622[b]
MEK	>99.9	0.80030	0.80008[c]
MIPK	>99.9	0.80063	0.80135[d]
[P666.14][Cl]	–	0.89023	0.89115[e]
[P666.14][DCA]	–	0.89954	0.89970[e]
[P666.14][TMPP]	–	0.88698	0.88643[f]
Sulfuric acid	–	–	1.8280[g]

The uncertainty of the density was estimated to be less than $\pm 1 \times 10^{-5}$ g cm^{-3} and the accuracy of the temperature was ±0.01 K.

[a] From Ref. [6].
[b] From Ref. [7].
[c] From Ref. [8].
[d] From Ref. [9].
[e] From Ref. [10].
[f] From Ref. [11].
[g] From Ref. [12].

liquid phase was consisted of ca. 3 g of the ketone (solvent phase) and ca. 15 g of Mo-containing ASAS (aqueous phase). They were vigorously stirred for 6 h and settled for more than 12 h at 298.15 K. And then, the partitioned amount of Mo in aqueous phase of each sample was determined using an ICP-AES (Perkin Elmer, OPTIMA 7300 DV, USA). The ICP-AES gave results with an accuracy of 0.1 μg/ml for precious-metal analyses.

The LLE was measured in the same LLE-determination glass vessel containing equal volumes (15 ml) of ASAS (without Mo) and organic phases. The equilibrium vessel was placed in a thermostat (Lauda MD 20, Germany) in which the temperature was regulated to within ±0.02 K. The temperature in the equilibrium vessel was precisely monitored using a digital thermometer (ASL F250, UK). The mixtures in the equilibrium vessel were vigorously stirred using a magnetic stirrer for 6 h and then were settled for more than 12 h at a constant temperature to arrive at an equilibrium state. After both phases reached equilibrium, sampling was carefully performed from the top for the upper phase and from the bottom for the lower phase without contaminating either phase during the sampling procedure. The sample analysis was conducted by gas chromatography for the ASAS and ketones, while ILs was analyzed by mass difference before and after drying the sample. For analyzing of ILs, the equilibrium sample from each phase (approximately

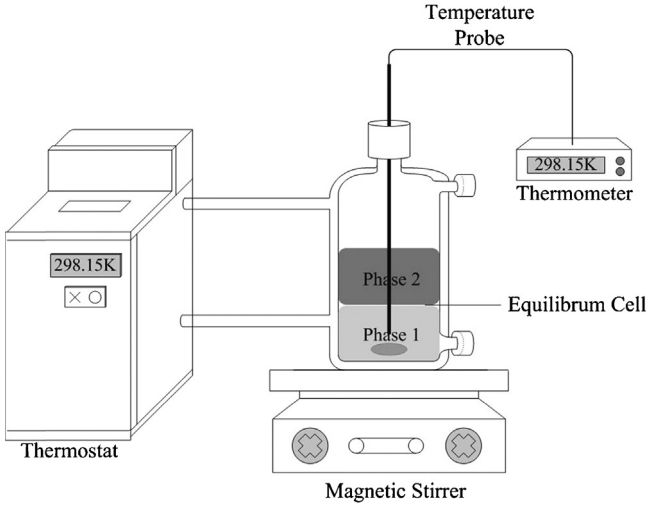

Fig. 1. Schematic diagram of the LLE measurement system.