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Determination of solubility of uranium in liquid sodium

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Abstract An experimental technique has been developed which overcomes the two major problems common to liquid metal solubility measurements, namely, maintaining the integrity of the samples during transfer of the liquid sodium from container to whatever device is used for analysis and detecting solute at very low concentration in liquid sodium. The solubility of uranium in liquid sodium has been measured over the temperature range 150~400°C, by equilibration and sampling technique, the solubility of uranium is approximately 0.00001%.

Key words Solubility, Uranium, Liquid sodium

CLC numbers 0645.12, TL24

1 Introduction

Liquid sodium is used as the coolant in a fast neutron breeder reactor, both in the primary and secondary cycles. Therefore, investigation of the solvent properties of liquid sodium is of considerable scientific and practical interest. Basic solubility data for iron^[1,2], copper^[3], bismuth^[4], tellurium^[4], tin^[5], $cobalt^{[6]}$, nickel^[6], chromium^[6], manganese^[7], oxygen^[8,9] and carbon^[10] in high-purity liquid sodium, as well as chromium sesquioxide^[11] and magnesium^[12] in uranium dioxide fuel were reported. Chemical interactions of sodium with non-irradiated and irradiated uranium-plutonium oxide fuel pins were conducted^[13,14]. Reactions of fission products of the fuel with liquid sodium were carried out^[15], partial-molal enthalpy and entropy of solution of several solutes were calculated^[16]. Thermodynamic stabilities of oxides of transition metals in liquid sodium were studied^[17-21]. Corrosion and creep tests with cladding tubes specimens were performed^[22-25]. The knowledge of physiochemical properties is helpful in understanding diffusion and mass transfer process, corrosion mechanism, and chemical changes of materials in high temperature sodium systems.

Peng et al^[26] proposed in 1997 a new design concept for a nuclear explosion fusion power plant. Current interest in high temperature compact nuclear fuel cycle for a nuclear explosion fusion power plant has emphasized the need for basic information on the nature of liquid metal solutions. Douglas *et al*^[27] estimated that the solubility of uranium in liquid sodium at 97.8°C does not exceed a few hundredth of one percent by weight, and may actually be small by measuring the lowering of the freezing point of liquid when in contact with the solid. In binary sodium-uranium system, there are inherent difficulties. First, the liquid sodium is highly reactive, and analysis of the liquid phase is complicated by high reactivity and extreme sensitivity to the inadvertent entry of impurities from containment material and the atmosphere. A second major problem in sodiumuranium system results from very low solubility of the uranium. Probably the uranium level in liquid sodium is not more than 1×10^{-6} g·g⁻¹. Because of experimental difficulties, the sodium-uranium system was limited to temperature around the melting point and only one point was presented. In this paper, relationships of the

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solubility at 150~400°C, and impurities in sodium are investigated.

2 Experimental

2.1 Reagents

Purified argon was used as cover gas in the experiment. Purification was achieved by passing the gas over a copper catalyst bed (which had been activated by heating to 600 °C for 12 h under a flow of 30 mL·min⁻¹ hydrogen), following by a zirconium-aluminum alloy getter bed (previously activated by heating to 450 °C for 12 h). As revealed by mass spectrometric analysis (GAM 500UT Inprocess Instruments), the purified argon contained negligible (<0.0001%, v/v) oxygen, water vapor, methane and carbon dioxide.

The uranium specimen (in $^{235}\text{U}/^{238}\text{U}$ ratio of 0.003899, measured using Finnigan MAT262 thermal ionization mass spectrometry) was $\Phi 6 \text{ mm} \times 4 \text{ mm}$ in size (approximately 2 g). Before experiment, it was immersed in 8 mol·L⁻¹ HNO₃ for 1 h, washed in a large volume of deionized water, dried and weighed to $W\pm 0.2$ mg.

The sodium was supplied by China Institute of Atomic Energy, with the high-purity grade having impurities (in $10^{-6} \text{ g} \cdot \text{g}^{-1}$) of oxygen, 26.8; carbon, 27.1; nitrogen, 6.8 and calcium 0.6 while the commercial grade having impurities (in $10^{-6} \text{ g} \cdot \text{g}^{-1}$) of oxygen, 72.0; carbon, 81.2; nitrogen, 4.1 and calcium 282.5.

The high-purity sodium was purified by oxide precipitation, 5 μ m stainless steel porosity filter, and cool trap.

2.2 Solubility measurement apparatus

The experimental apparatus (Fig.1), made of 316 L stainless steel, consist of an argon purification unit, a vacuum unit, a reaction unit with different containers, a by-pass sampling unit, a pre-heating unit and a pressure relief unit. Sodium could be transferred from the material container (5) to the sample container (6), the vessel (7), and the crucible (8). Sodium filled to the tube before the samplers could be transferred to waste container (10) in order to obtain a fresh sample, reaction residue could be transferred from the stainless steel crucible (8) to the waste container (11), by means of vacuum or argon pressure. Temperature of the pre-heating unit, which was made up of furnaces used in the stainless steel containers and flexible heating strap used in tubes, could be controlled to $\pm 1^{\circ}$ C. To the apparatus, solubility tests up to 400°C were performed by equilibrating the solute with the sodium in the crucible (8). Each of the five externally-heated containers, i.e. containers (5), (6), (9), (10) and (11) has a pressure sensor for pressure regulation and a thermocouple for temperature control. Three vertical tubes attached to the top of the containers, had the high temperature bellows-sealed valves.



Fig.1 Solubility measurement apparatus.

(a) Argon purification unit: copper catalyst bed at 420°C (1), Zr-Al alloy getter bed (2), gas filter (3), pressure sensor (4).

(b) Vacuum unit consisting of a rotary pump and a turbo molecular pump.

(c) Reaction unit: material container (5), sample container (6), vessel (7), crucible (8), reactor (9), waste container (10-11).

- (d) By-pass sampling unit with 2 μ m SS porosity filter (12).
- (e) Pre-heating unit with temperature control system (13).
- (f) Pressure relief unit.

2.3 Experimental procedures

The uranium metal was placed in the crucible for solubility determination. After degassing the whole system at 150° C and 10^{-3} Pa for 24 h, approximately 110 g of sodium was introduced into the crucible by means of vacuum or argon pressure. The sodium was melted to contact the uranium metal for 24 h.

To minimize contamination of the sodium by water vapor and oxygen, the apparatus was designed to allow by-pass the sampling liquid metal outside the reactor. A sodium sampler to remove grams of sodium from the reactor consists of a 316L SS tube of Φ 8.3 mm (1/4 inch) ×48 mm (approximately 1 cm³), with high temperature bellows-sealed valves attached to both ends of the tube. Before sampling, the tube between the valves was evacuated and filled with argon to prevent any air from contaminating the sodium.

At completion of the reaction, the sodium was filtered off into the sampler (heated in advance to the equilibrium temperature) by decreasing the pressure to expel gas from the sampler. The filled sampler was allowed to cool, and removed from the bellows-sealed valves during the course of a run, under argon. The sampled sodium was heated to the next equilibration temperature and held for 24 h before a second sample was taken. In this way, filtered liquid metal samples were taken at different temperatures during the heating cycle under a protective atmosphere of purified argon.

The sample was dissolved in absolute alcohol, deionized water and 8 mol·L⁻¹ HNO₃, and a standard volume of the solution was taken prior to analysis. Metal contents of Na, K, Ca, Fe, Ni, Mo and Mn were analyzed using ICP-OES spectrometry (Optima 4300DV, Perkin Elmer).

The uranium separated from the bulk sodium by a wet chemical extraction chromatography technique. 1mL (255.5 ng) of ²³³U was added to each dissolved sample as a diluent. The mixture was heated to dry at **Table 1** Results from tests at 150°C for various equilibrium time $60\sim70$ °C. The remaining was dissolved in 8 mol·L⁻¹ HNO₃, and the solution passed through the TBP-Kel-F column of 7 mm ID ×700 mm. The beaker was washed with 10 mL 8 mol·L⁻¹ HNO₃ for three times to remove residual solution, and the washing solutions passed through the TBP-Kel-F column, too. The column was then eluted with 6 mL 0.1mol·L⁻¹ HNO₃.

Concentration of ²³⁸U in the eluent was calculated by isotope dilution using ²³⁸U/²³³U and ²³⁵U/²³⁸U ratios (measured using Finnigan MAT262 thermal ionization mass spectrometry). Uranium content in the liquid sodium can be expressed by

$$W_{8} = R_{83}(238/233)W_{3}$$

$$W_{8K} = W_{8} - W_{8C}$$

$$W_{5K} = W_{8} R_{58}(235/238) - W_{8C} R_{58C}(235/238)$$

$$R_{58K} = W_{5K}/W_{8}(238/235)$$

$$W_{8S} = W_{8K} [(R_{58K} - R_{58n})/(R_{58} - R_{58n})]$$

$$S_{U} = W_{8S}/W_{Na}$$

where $S_{\rm U}$ is solubility of uranium, $W_{\rm Na}$ is sodium content in the sample, W_3 is ²³³U content (255.5 ng) in the diluent added to the sample, W_8 is ²³⁸U content in the sample, $W_{8\rm S}$ is ²³⁸U content in the sodium, $W_{8\rm C}$ is ²³⁸U content (0.803 ng) of the chemical procedure blank, $W_{8\rm K} = W_8 - W_{8\rm C}$, $W_{5\rm K}$ is ²³⁵U content subtracting the chemical procedure blank, R_{83} and R_{58} are respectively ²³⁸U/²³³U and ²³⁵U/²³⁸U ratio of the sample, $R_{58\rm C}$ is ²³⁵U/²³⁸U ratio of the chemical procedure blank (0.01767), and $R_{58\rm n}$ is ²³⁵U/²³⁸U ratio of natural background (0.007252).

3 Results and discussion

The solubility at different equilibrium time was investigated. Uranium was added to high purity sodium. The system was equilibrated at 150°C for 5.5~24 h. The results (Table 1) indicated that 24 h was needed for the uranium to dissolve in sodium and equilibrium was attained.

Time / h	R ₅₈	<i>R</i> ₈₃	$W_{8\rm S}$ / ng	$W_{\rm Na}$ / g	$S_{\rm U}$ / 10 ⁻⁷ g·g ⁻¹	
5.5	0.004670	0.07821	91.059	0.694	1.31	
12	0.005172	0.04758	50.998	0.750	0.68	
17	0.005554	0.03594	36.226	0.750	0.48	
24	0.004769	0.06941	79.530	0.737	1.08	

(1)

Experiments were conducted in high-purity sodium at 150~400°C. The uranium was held at each of the temperatures for 24 h before sampling. As shown in Table 2, no temperature dependence of the uranium solubility was observed over the temperature

range. The same experiments were conducted in commercial grade sodium at $180 \sim 400$ °C (Table 3). Compared with the results with Table 2, the solubility is not affected by the oxygen and carbon impurities in the sodium.

Table 2	Solubility	of ur	anium	in	high-	purity	liquid	sodium	for 24	h
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Temperature / °C	R ₅₈	<i>R</i> ₈₃	$W_{8\rm S}$ / ng	$W_{\rm Na}/{ m g}$	$S_{\rm U} / 10^{-7} {\rm g} \cdot {\rm g}^{-1}$
150	0.004769	0.06941	79.530	0.737	1.08
200	0.005816	0.02785	28.038	0.762	0.37
250	0.006026	0.02629	25.018	0.725	0.34
300	0.006083	0.03991	30.880	0.712	0.43
350	0.005859	0.02916	28.283	0.762	0.37
400	0.005686	0.03173	31.811	0.794	0.40

 Table 3
 The solubility of uranium in commercial grade liquid sodium for 24 h

Temperature / °C	R ₅₈	<i>R</i> ₈₃	$W_{8\rm S}/{ m ng}$	$W_{\rm Na}/{ m g}$	$S_{\rm U} / 10^{-7} {\rm g \cdot g^{-1}}$
180	0.005773	0.02516	26.956	0.781	0.35
230	0.004716	0.06206	73.738	0.731	1.01
280	0.005193	0.03525	40.722	0.238	1.71
360	0.005206	0.0342	39.476	0.762	0.52
400	0.004926	0.04215	50.629	0.585	0.87

The uranium solubility in liquid sodium is in distinct contrast to that of transition metals in liquid sodium. The experiments with Sn, Bi and Te in liquid sodium showed that they were completely converted into an intermetallic compounds, and were crystallized, of Na₃Bi^[4], Na₂Te^[4] and Na₄Sn^[5].

The uranium content in liquid sodium was approximately 1×10^{-7} g·g⁻¹ in the above experiments. However, from the solubility data, no relationships could be found with the temperature, time and impurities, owing to the fact that no shaking or stirring was used. In fact, some lacking of mixing of the liquid may have contributed to all the experiments; but it is felt that the degree of consistency of the points of each sample with the corresponding condition is such that this source of error is not serious or else constant from sample to sample within the precision experienced.

Another possible source of error that needs consideration is the solubility in liquid sodium of stainless steel from the container. According to measurements (Table 4) by ICP-OES spectrometry (Optima 4300DV, Perkin Elmer), at these temperatures, iron is soluble in liquid sodium to the extent of $<1\times10^{-4}$ g·g⁻¹, and other transition metals, to the extent of $<1\times10^{-5}$ g·g⁻¹. This would produce an effect on the

solubility of uranium in liquid sodium, but the impurities dependence of the results is unknown.

A detailed explanation of the results observed for the uranium in sodium in this investigation can be obtained by considering the entire process. Uranium has been found to react rapidly with oxygen dissolved in sodium to form UO₂. In all the experiments, surface of the uranium specimen appeared to the naked eye to have irregularities. The oxide formed adhered to the uranium and affords no protection to the uranium. Part of the product formed under the cited conditions sloughed off and was not weighed with the specimen. This is given support by the fact that the rate of removal of oxygen by uranium was proportional to the concentration of oxygen in the sodium^[28]. Carbon was another element which could possibly react with uranium in sodium. The presence of carbon in the sodium was indicated by black deposits which formed on the uranium specimen. So a considerable part of oxygen and carbon elements was somehow removed from the sodium by the surface of the uranium.

Our results is two order of magnitude lower than the results by Douglas^[27]. He estimated a very small solubility of a solid in a liquid by measuring the freezing point of the liquid in contact with the solid. The sodium containing bulk form uranium was found to have an average freezing point lower than without uranium by 0.001 to 0.003 degree, corresponding to approximately 0.007 per cent by weight of uranium in solution. It is concluded that if solubility equilibrium was obtained in those experiments, the solubility of uranium in liquid sodium at 97.8°C would not have exceeded a few hundredth of one per cent by weight, and might have been actually many times smaller. If highly constant and uniform temperature environment is established, if impurities in unknown amount are not present and if miscibility of the solids is negligibly small, his result is reliable. In fact, this is very difficult.

Table 4Solubility of impurities metal elements in liquid sodium / 10^{-4} g·g⁻¹

Sodium	Temperature / °C	Time / h	$S_{\rm K}$	S _{Ca}	$S_{\rm Fe}$	$S_{ m Ni}$	$S_{\rm Mo}$	S _{Mn}
High-purity grade	150	5.5	4.27	2.92	0.576	0.0576	0.0765	0.0251
	150	12.0	3.40	2.85	0.772	0.1750	0.1290	0.0210
	150	17.0	3.30	2.41	0.765	0.1080	0.0800	0.0217
	150	24.0	3.68	3.85	1.200	0.0525	0.0861	0.0341
	200	24.0	3.55	2.70	0.428	0.0488		0.0144
	250	24.0	3.77	6.64	0.600	0.0651	0.0547	0.0231
	300	24.0	3.41	2.44	0.469		0.0095	0.0118
	350	24.0	3.37	3.01	0.378	0.0056	0.1070	0.0114
	400	24.0	3.43	2.96	0.839	0.0630	0.1120	0.0170
Commercial grade	180	24.0	2.36	2.78	0.442	0.0772	0.0198	0.0119
	230	24.0	2.17	3.09	0.559	0.0641	0.0302	0.0150
	280	24.0	2.71	9.30	1.090	0.1380	0.0168	0.0372
	360	24.0	1.87	3.17	0.307	_	_	0.0097
	400	24.0	2.19	4.22	0.575	0.0921	0.1410	0.0149

4 Conclusions

The experimental technique described above overcomes the difficulty of ensuring that the integrity of the samples during transfer of the liquid sodium has been maintained. Furthermore, sampling at high temperature does not present any difficulties by means of vacuum or argon pressure. The apparatus is applicable to solubility measurements ranging from a fraction of 1×10^{-7} g·g⁻¹ to several per cent, provided the uranium for which the solubility is to be determined has a thermal ionization mass spectrometry with diluent ²³³U. Thus, these measures should provide a means of determining solubilities of uranium in liquid sodium for systems whose range of compositions are so low that ordinary methods for their measurement are impracticable.

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