



Regularities of phase equilibria in the binary uranium tetrachloride systems and their thermodynamic interpretation

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Abstract

The author's phase and thermodynamic studies on the binary salt systems with common anion have shown that there is a quantitative relation between the phase diagram type and the ionic potentials of component cations of the system. The relation may be clearly presented using the binary uranium tetrachloride systems MCl_n-UCl_4 as an example. When all the systems whose phase diagrams are known are listed in sequence of decreasing values of the ionic potentials ratio of both component cations, a certain regularity may be observed: the phase diagram types change suddenly at some precise values of the ratio. Considering the thermodynamic characteristics of the liquid phases of some of the systems, we can observe that the dependence of the excess partial molar Gibbs energy of a component (and molar Gibbs energy of solution as well) on the cation potentials ratio, is linear within the limits of the group of systems of any definite type. © 1997 Elsevier Science B.V.

A relation between the general geometry of the phase diagram of a binary salt system and the physico-chemical properties of the system components were studied by many authors for many decades. The relation has been, however, known to a little extent till now, and almost all the works in this field may be regarded as fragmentary. Consequently, the only reliable method for the investigation of phase equilibria is the experiment. Nevertheless, from the review of research material accumulated in abundance in the literature, it appears that there are some general regularities.

From all proposals of searching for the relations, the most promising are those involving ionic radii (r_i) and/or ionic charges (e_i). A combination of the two quantities is called 'ionic potential' or 'ionic moment' (μ_i) of cation 'i' and is defined as a ratio of cation charge and its radius: $\mu_i = e_i/r_i$, where $e_i = Z_i\varepsilon$ (Z_i = valency, ε = elementary charge). Thus the ionic potential is a measure of the electric field intensity at the cation surface, being consequently a measure of interaction force of the cation with anions. The ratio of two ionic potentials μ_1/μ_2 expresses a comparison of the interaction energies of the two compo-

nent cations with anions in a molten salt mixture regarded as an ionic liquid.

The author's phase and thermodynamic studies on the binary salt systems with common anion have shown that there is a quantitative relation between the phase diagram types and the ionic potentials of component cations of the system [1,2]. The relation may be clearly demonstrated using the binary uranium tetrachloride systems MCl_n-UCl_4 (where M = any metal) as an example.

Table 1 comprises all the MCl_n-UCl_4 systems whose phase diagrams are known. Some of them have been studied by the present author employing thermal analysis, differential thermal analysis, high-temperature cryometry and X-ray diffraction: $AgCl-UCl_4$ [3], $CdCl_2-UCl_4$ [4], $ZnCl_2-UCl_4$ [5], $PbCl_2-UCl_4$ [5], $CuCl-UCl_4$ [6], $ThCl_4-UCl_4$ [7], $HgCl_2-UCl_4$ [8], $LaCl_3-UCl_4$ [9], $InCl_3-UCl_4$ [10], $InCl-UCl_4$ [11] and $SnCl_2-UCl_4$ [2].

The systems in Table 1 are listed in sequence of decreasing values of the ionic potentials ratio μ_1/μ_2 . The ionic potentials of cations have been calculated by using the radii values published in [12–22]. The first component cation radii (r_1) in the table are the arithmetic means of all the values found in the literature for each. The only exception is the stannous cation, the radius of which has been accepted as being 0.122 nm (see Ref. [2]). As it may be immediately observed, all the systems may be divided

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Table 1

Values of ionic potential ratios μ_1/μ_2 of component cations and types of binary uranium tetrachloride-containing systems. The value of the uranium (IV) cation radius is 0.097 nm

No.	Group	r_1 (nm)	μ_1/μ_2	$\pm \Delta$	System	Type of system
1	I'	0.067	1.82	0.10	TaCl ₅ -UCl ₄	eutectic
2		0.039	1.25	0.11	BeCl ₂ -UCl ₄	eutectic
3		0.063	1.15	0.07	FeCl ₃ -UCl ₄	eutectic
4	0	0.102	0.95	0.06	ThCl ₄ -UCl ₄	continuous solid solutions
5		0.082	0.89	0.05	InCl ₃ -UCl ₄	eutectic
6		0.107	0.68	0.05	UCl ₃ -UCl ₄	eutectic
7		0.072	0.67	0.06	MgCl ₂ -UCl ₄	eutectic
8		0.110	0.66	0.04	LaCl ₃ -UCl ₄	eutectic
9	I	0.077	0.63	0.04	ZnCl ₂ -UCl ₄	eutectic
10		0.095	0.51	0.03	CdCl ₂ -UCl ₄	eutectic
11		0.099	0.49	0.03	CaCl ₂ -UCl ₄	eutectic
12		0.106	0.46	0.03	HgCl ₂ -UCl ₄	eutectic
13		0.117	0.42	0.02	SrCl ₂ -UCl ₄	eutectic
14	II	0.122	0.40	0.05	SnCl ₂ -UCl ₄	1 compound 6:1
15		0.122	0.40	0.02	PbCl ₂ -UCl ₄	1 compound 6:1 ^a
16		0.136	0.36	0.02	BaCl ₂ -UCl ₄	1 compound 2:1 ^a
17		0.072	0.34	0.03	LiCl-UCl ₄	1 compound 2:1
18		0.093	0.26	0.03	CuCl-UCl ₄	1 compound 2:1
19		0.100	0.24	0.01	NaCl-UCl ₄	1 compound 2:1
20		0.118	0.21	0.01	AgCl-UCl ₄	1 compound 2:1
21	III	0.118	0.206	0.03	InCl-UCl ₄	4:1 ^a γ 1:1 ^a 1:2 ^a
22		0.134	0.18	0.01	KCl-UCl ₄	2:1 1:1 1:2 ^a 1:3 ^a
23		0.150	0.16	0.01	RbCl-UCl ₄	2:1 3:1 ^a 1:1 1:3 ^a
24		0.169	0.14	0.01	CsCl-UCl ₄	3:1 ^a 2:1 3:2 ^a 1:2 ^a

^a Denotes incongruent melting of the compound.

$\pm \Delta$ is the accuracy of calculation of the μ_1/μ_2 ratio.

into four groups: 0 – continuous solid solutions, I and I' – simple eutectic systems, II – systems with one chemical compound (mainly of component molar ratio 2:1 and mostly congruently melting), III – systems with four compounds.

From Table 1 it appears that the tendency to compound formation increases with the decrease in the μ_1/μ_2 ratio: the phase diagrams are getting more complex. This is the

result of stronger and stronger interaction of the U⁴⁺ cation with chloride anions compared with 'competitive' interaction of the first component cation of lower ionic potential.

Applying the table we can predict with considerable probability the general features of a system that has not yet been studied at all. Let us take, for example, two systems whose phase diagrams are quite unknown: CoCl₂-UCl₄

Table 2

Thermodynamic properties of some liquid solutions in the MCl_n-UCl₄ systems

No.	Group	System	μ_1/μ_2	$x_2 = 0.9$		$x_2 = 0.5$	
				G_1^E (kJ/mol)	T (K)	G^E (kJ/mol)	T (K)
1	0	ThCl ₄ -UCl ₄	0.95	-8.0	890	-2.6	961
2		InCl ₃ -UCl ₄	0.89	+4.8	850	+2.2	816
3	I	LaCl ₃ -UCl ₄	0.66	+4.0	832	-2.6	1040
4		CdCl ₂ -UCl ₄	0.51	-0.6	846	-1.0	765
5		LiCl-UCl ₄	0.34	-31.1	851	-13.8	716
6	II	CuCl-UCl ₄	0.26	-18.7	840	-12.5	613
7		NaCl-UCl ₄	0.24	-48.2	845	-22.7	663
8		AgCl-UCl ₄	0.21	-38.7	841	-22.7	705

and $\text{TiCl}_4\text{--UCl}_4$. Their μ_1/μ_2 ratios are: 0.66 and 0.17, respectively. Comparing the two figures with the μ_1/μ_2 values in the table, we can find that the first of the systems should belong to group I (i.e., simple eutectic type) and in the latter four compounds should be formed (group III).

In the $\text{MCl}_n\text{--UCl}_4$ ‘family’ of systems, the changes of the phase equilibrium type occur suddenly at any definite ‘critical’ value of μ_1/μ_2 ratio, not smoothly. Why? The solution of the question may be given by thermodynamics.

The thermodynamic properties of the liquid phase of some of the uranium tetrachloride binary systems have been determined by the cryometric method employing the apparatus described in [3]. The phase transition temperature measurements (with an accuracy of $\pm 0.2^\circ$) have been effected using a thermopile consisted of four thermocouples Pt/Pt, Rh connected in series, calibrated at freezing points of standards. The method, however, cannot be employed in studying systems with limited solid solutions, with an incongruently melting compound and with two or more compounds. Consequently, the determination of the thermodynamic properties was possible for few systems only.

From among the thermodynamic functions, the most sensitive to interactions in molten mixtures is the excess partial molar Gibbs energy (G_i^E) of component ‘i’ and the excess molar Gibbs energy of solution (G^E) as well.

The main disadvantage of the cryometric method is that the values of a component activity may be determined along the liquidus line, i.e., at different temperatures. On the other hand, for comparison we need the function values at the same temperature and this is impossible. Fortunately, all the UCl_4 binary systems have one common point: the melting temperature of pure UCl_4 . So, the G_1^E values of the first component ‘1’ in the solution rich in UCl_4 (at the UCl_4 mole fraction $x_2 = 0.9$) must be taken. They have been determined at this point with reasonable accuracy and still at similar temperatures (Table 2).

Table 2 comprises the G_1^E values for eight systems only, but it is enough to observe that the values are, in general, quite different for these three groups of systems. The same conclusion can be drawn for the excess molar Gibbs energy of solution G^E at $x_2 = 0.5$, but this time, at different temperatures. Unfortunately, the 0 group includes but one system (as yet) $\text{ThCl}_4\text{--UCl}_4$, accordingly, we have only one point, which is less useful in further discussion.

G_1^E and G^E values of systems with one compound are much higher than those of simple eutectic ones. It should be noticed that the statement is valid approximately at both the same temperature (G_1^E) and at quite different temperatures (G^E) as well.

The relation would be more explicit on the graphs of G_1^E and G^E versus the μ_1/μ_2 ratio. Although the points do not lie exactly on straight lines, the number is sufficient to state that the relation has a linear character within the limits of each of the two groups. What more, both pairs (for two groups of systems) of the lines have their intersection points at the μ_1/μ_2 value which is near to the limiting value 0.40 of the two groups I and II.

In such a way, the thermodynamic evidence has been obtained for the stepwise changes of the phase equilibrium type when passing from one group of the systems to another.

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