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Phase diagram and thermodynamic properties of the system $MnCl_2$–UCl_4, prediction and investigation results

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Abstract

The $MnCl_2$–UCl_4 system was studied employing differential thermal analysis, common thermal analysis and high-temperature cryometry. From the results obtained, both the phase diagram and the thermodynamic characteristics of liquid phases of the system have been determined. The results were discussed in terms of regularities found in the phase equilibria of binary salt systems with common anion and compared with those for other systems of the type MCl_n–UCl_4. It appeared that the results confirmed earlier predictions on the title system.

1. Introduction

A series of studies on the binary uranium tetrachloride containing systems performed by the first author resulted in specifying relations [1] that were found to hold between the general geometry of a phase diagram of a binary salt system with common anion and the physicochemical properties of the system components. The relation consisted in the phase equilibrium type depending quantitatively on the ionic potentials ratio (μ_1/μ_2) of both the component cations (1 and 2) of the system [1,2], the ionic potential μ_i of a cation 'i' being defined [3] as a ratio of the cation charge (e_i) and its radius (r_i): $\mu_i = e_i/r_i$. The dependence has been comprehensively demonstrated in [1] using the MCl_n–UCl_4 'family' of systems (where M is any metal) as an example. It appeared that the system types changed in sequence: (0 group of systems) continuous solid solutions (when $\mu_1/\mu_2 \approx 1$) – (I) simple eutectic systems ($0.95 > \mu_1/\mu_2 \geqslant 0.42$), – (II) systems with one compound ($0.40 \geqslant \mu_1/\mu_2 \geqslant 0.21$), – (III) with four compounds ($0.206 \geqslant \mu_1/\mu_2$). Furthermore, the thermodynamic properties of liquid phases in systems of the same group are similar but different as compared to those of another group. Thus, e.g. the excess partial molar Gibbs energies of the first (MCl_n) component (G_1^E), determined at about 90 mol% UCl_4, within group I, amount from −0.68 kJ/mol to +4.8 kJ/mol of the component, while those in group II vary from −18.78 kJ/mol to −48.28 kJ/mol of the first component.

Such a regularity was shown to obey to all binary salt system families with common anion, under the condition that at least one of the system components embodies a strong ionic character. The regularity presented above, enables predictions of high probability to be made for systems where no experimental data are available.

This study was undertaken with the purpose of testing the applicability of this regularity in predicting phase

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and thermodynamic properties of a system that has not yet been studied, as the $MnCl_2$–UCl_4 system has.

The prediction of a system lies in comparison of the ratio $\mu_{M}n+/\mu_{U}4+$ with the μ_1/μ_2 ranges covered by different groups of the MCl_n–UCl_4 systems family. In case of the system $MnCl_2$–UCl_4 the ratio $\mu_{Mn}2+\mu_{U}4+= 0.61$. From the relation it follows that the MCl_n–UCl_4 systems whose μ_1/μ_2 values lie within the range from 0.42 to 0.95, are of the eutectic type. Accordingly, in the manganese(II) chloride–uranium(IV) chloride system, only a simple eutectic should be formed, and the excess partial molar Gibbs energy of the first component at 90 mol% UCl_4 should have a small value.

2. Experimental

In order to verify the above predictions, phase and thermodynamic studies on the title system have been effected employing differential thermal analysis (DTA), common thermal analysis (TA) and high-temperature cryometry.

Pure anhydrous uranium(IV) chloride was obtained by the method described in [4]. Manganese(II) chloride was prepared from commercial $MnCl_2$ (reagent grade, POCh, Gliwice, Poland) by passing a dry hydrogen chloride gas stream through the molten $MnCl_2$ for 24 h to remove both traces of moisture and products of hydrolysis, and then distilling under vacuum at 700 K.

The DTA was applied using the Derivatograph Q-1500 D (MOM, Budapest). This apparatus enabled a rapid preliminary determination of the phase diagram of the system to be performed due to fully automatized temperature measurements. Solid samples (ca. 1 g) of the salt mixtures were placed in quartz ampoules under pure argon (BOC-gazy, Poznań, Poland), then sealed under vacuum. The heating rate was 5 K/min. Because of the relative low accuracy of the method (±6 K, within the temperature range near 800 K), it might be employed as an auxiliary only. The advantages and shortcomings of either the two methods, DTA and TA, including comparison of the results obtained by them, were formerly described in [5].

Exact temperature measurements of phase transitions occurring in the examined samples were made by TA (the cooling curve method) in an apparatus designed for phase and cryometric studies, described in [4,5] (Fig. 1). A container for studied samples (ca. 25 g) was an alumina crucible placed within the quartz cylinder filled with pure argon. The apparatus was hermetically closed with a glass (Thermisil) head. The temperature of the samples was measured by means of a thermopile consisting of three Pt/Pt, Rh thermocouples connected in series, calibrated at freezing points of standards. During the measurements, the liquid samples were vigorously stirred with a quartz stirrer driven electromagnetically, making vertical strokes, the stirring speed being controlled within 10 strokes per second (the stroke length was 10 mm). Successive portions of another component were added to the molten sample through the inlet tube in the countercurrent argon flow. The most important condition to be satisfied in such measurements was the sample of molten salt mixture to be kept in equilibrium, which was accomplished by efficient stirring the salt melts on cooling. The cooling rate was 1–1.5 K/min. The accuracy of the temperature measurements was ±0.2 K.

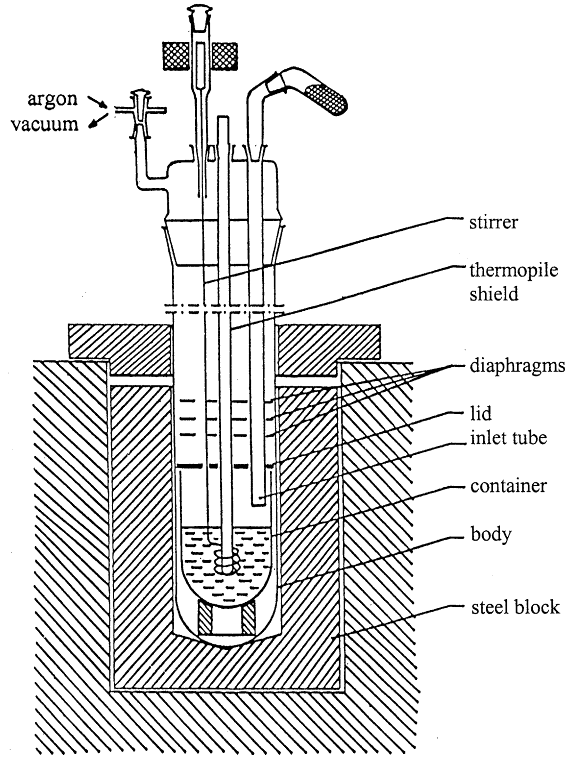

Fig. 1. Apparatus for high-temperature cryometric and phase studies by thermal analysis [4,5].

As no terminal solid solutions were found in the system by TA and X-ray diffraction, the thermodynamic characteristics of the liquid phase might be determined through high-temperature cryometry. The cryometric measurements were effected in the same apparatus.

The compositions of melts were calculated from the taken masses of the components. Nevertheless, because of possible evaporation of any component, the composition was controlled analytically after each measurement series had been completed: uranium and the chloride anion contents were determined by the photometric (calibration curve technique) and potentiometric titration methods, respectively.

Taking into account both the results of analyses and an error in a graphical determination of co-ordinates of the eutetic point, its composition might be given with an accuracy of not less than ±0.5 mol% UCl_4.

3. Results and discussion

The phase diagram of the system manganese(II) chloride – uranium(IV) chloride has been established (Fig. 2) from the results of phase studies by thermal methods, but mainly by common thermal analysis (Table 1). The obtained results confirmed the earlier prediction: it appeared that one eutectic in the system $MnCl_2$–UCl_4 was formed of composition (60.6 ± 0.5) mol% UCl_4 and melting temperature (781.2 ± 0.2) K. This value of the eutectic melting point is an average of several measurement series. The eutectic is richer in UCl_4 than in $MnCl_2$ and this is compatible with a general rule [6] according to which a composition of a eutectic is shifted towards the lower melting component, as is the case with the system under consideration (melting point of $MnCl_2$ is 923.8 K while that of UCl_4 is 863.7 K). The eutectic composition results from both the properties and the behavior of a system components in solution, and this in turn is reflected in its thermodynamic characteristics.

From the results of cryometric measurements, the thermodynamic characteristics of the liquid phase of the system has been determined within the whole concentration range. Within the equilibrium region between the pure solid component '*i*' and the molten salt solution, the thermodynamic activities (a_i) of either component '*i*' in the solution at the liquidus temperatures have been calculated employing known equation (as e.g. in [7]):

$$\ln a_i = \Delta_{\rm fus}H/R(1/T_{\rm f} - 1/T) + \Delta C_{\rm p}/R[T_{\rm f}/T - 1 + \ln(T/T_{\rm f})],$$

where $\Delta_{\rm fus}H$ is the enthalpy of fusion of component '*i*', R the gas constant, $T_{\rm f}$ the melting point of component '*i*', T the liquidus temperature, $\Delta C_{\rm p}$ is the difference of molar heat capacities of the component in the liquid and solid states at its melting temperature, assuming independence of the $\Delta C_{\rm p}$ on temperature within the temperature range from $T_{\rm f}$ to T.

The excess partial molar Gibbs energy (G_i^E) of the component '*i*' was calculated from the relation $G_i^E = RT\ln(\gamma_i)$; $\gamma_i = a_i/X_i$, where γ_i is activity coefficient and X_i is the molar fraction of the component.

The G_i^E and then a_i values for the other component within the same equilibrium region were calculated applying the Gibbs–Duhem equation.

Following values of fusion enthalpies of $MnCl_2$, α-UCl_4 and β-UCl_4 have been used in the calculations: 37.7 [8], 61.5 [9,10] and 45.6 [11] kJ/mol, respectively. The heat capacity difference of $MnCl_2$ was 7.0 J/K mol [8] while that of UCl_4 was 15.2 J/K mol [11]. Results of calculations, i.e. the values of activities of $MnCl_2$ (a_1) and UCl_4 (a_2) as well as the excess partial molar Gibbs energies of both the components (G_1^E and G_2^E, respectively) in liquid solutions of different mole fractions (X_2) of UCl_4 at the liquidus temperatures (T), are listed in Table 2. The accuracy of determination

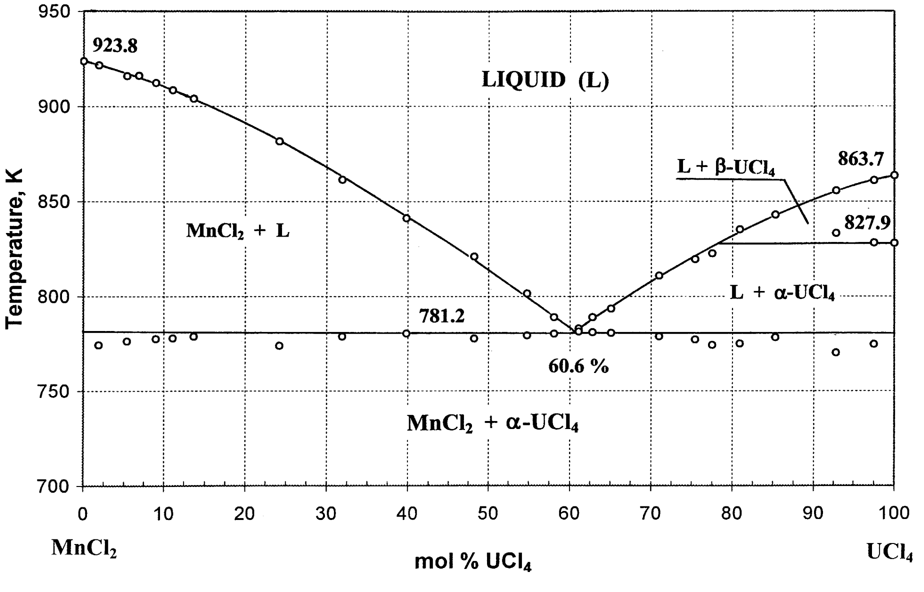

Fig. 2. Phase diagram for the system $MnCl_2$–UCl_4.

Table 1
Results of studies on the system $MnCl_2$–UCl_4 by common thermal analysis

No.	X_2 (mol% UCl_4)	Liquidus temperatures (K)	Solidus temperatures (K)	$\alpha \leftrightarrow \beta$ phase transition temperature (K)
1	0	–	923.8	
2	1.90	921.5	774.3	
3	5.4	916.0	776.3	
4	6.9	916.1	–	
5	9.0	912.3	777.5	
6	11.1	908.6	777.9	
7	13.7	904.0	778.7	
8	24.2	881.6	773.8	
9	31.9	861.5	778.7	
10	39.8	841.2	780.3	
11	48.2	820.9	777.6	
12	54.8	801.4	779.3	
13	58.1	788.9	780.2	
14	61.1	783.0	781.2	
15	62.8	788.8	781.0	
16	65.1	793.5	780.5	
17	71.0	810.7	778.7	
18	75.4	819.4	777.1	
19	77.5	822.5	774.3	
20	80.9	835.3	774.9	
21	85.3	843.1	778.2	
22	92.8	855.7	770.0	833.3
23	97.5	861.1	774.6	828.1
24	100.0	–	863.7	827.9

Table 2
Thermodynamic properties of components in the liquid phase of the system $MnCl_2$–UCl_4, indices 1 and 2 at the symbols a and G^E denote 'first component' ($MnCl_2$) and 'second component' (UCl_4), respectively

X_2 (mol% UCl_4)	T (K)	a_1	a_2	G_1^E (kJ/mol)	G_2^E (kJ/mol)
0	923.8				
5.4	916.0	0.959	0.039	0.10	−2.54
9.0	912.3	0.940	0.064	0.25	−2.55
13.7	904.0	0.898	0.097	0.30	−2.56
24.2	881.6	0.792	0.171	0.32	−2.56
31.9	861.5	0.703	0.224	0.23	−2.53
39.8	841.2	0.620	0.278	0.21	−2.52
48.2	820.9	0.544	0.328	0.34	−2.62
54.8	801.4	0.478	0.368	0.37	−2.65
60.6	781.2	0.414	0.407	0.33	−2.59
65.1	793.5	0.352	0.470	0.07	−2.15
71.0	810.7	0.279	0.572	−0.26	−1.46
77.5	822.5	0.206	0.652	−0.61	−1.18
85.3	843.1	0.123	0.857	−1.23	0.03
92.8	855.7	0.055	0.942	−1.86	0.11
97.5	861.1	0.023	0.981	−0.63	0.04
100.0	863.7				

of both the temperatures and the compositions of the melt being kept in mind, the uncertainties of calculation of the thermodynamic functions at the eutectic composition were estimated to amount: a_1 and a_2 – 5% and 0.2%, respectively, G_1^E and G_2^E – 8% and 13%, respectively.

The concentration dependences of activity and excess partial molar Gibbs energy of the components of liquid phase in the $MnCl_2$–UCl_4 system follow approximately the same pattern as those in the systems $InCl_3$–UCl_4 ($\mu_1/\mu_2 = 0.89$) [12], $LaCl_3$–UCl_4 ($\mu_1/\mu_2 = 0.66$) [13] and $CdCl_2$–UCl_4 ($\mu_1/\mu_2 = 0.51$) [14], which belong to the same group I, i.e. to the simple eutectic systems, whose ionic potential ratios of component cations are within the range $0.95 > \mu_1/\mu_2 \geqslant 0.42$ [1]. Accordingly, the predictions made in the introduction of the present paper on the thermodynamic properties of the system under examination have been confirmed.

4. Conclusions

It appears from the thermodynamic data that the $MnCl_2 + UCl_4$ solutions present at the liquidus temperatures, a very small deviation from ideal mixing in the whole concentration range. The values of excess partial molar Gibbs energy of manganese chloride (G_1^E) are small positive in concentrated solutions thereof, while at lower $MnCl_2$ concentrations (i.e. above $X_2 \approx 6$ mol% UCl_4) they change to small negative values. This is an indication of slow dissociation of $MnCl_2$ to give simple ions when it is diluted with uranium chloride. Instead, the excess partial molar Gibbs energies of the latter component (G_2^E) are negative within the almost entire concentration range but are higher than those of the former one. The reason of such behavior is that the Mn^{2+} and U^{4+} cations are strong 'competitors' while interacting with chloride anions. However, the ionic potential of the uranium cation, is higher than that of Mn^{2+}, and this is the reason why UCl_4 exhibits higher (negative) deviations from the ideal behavior than $MnCl_2$. The differences are quite small, accordingly, it may be stated that there is hardly any tendency of the U^{4+} ions to complex formation in the salt solutions. We could presume the complex ions to be formed if the value of G_2^E was lower than −42 kJ/mol UCl_4 [15].

The results of the work reported here provide an evidence that there is a possibility of predicting, with a considerable probability, both the phase diagram shape and the thermodynamic properties of a binary salt system with common anion that was not yet studied. The prediction demands no thermochemical data of pure components. The only condition to be satisfied is the knowledge on the relation between a phase equilibrium type and ionic potentials ratio of component cations within the 'family' of systems to which this system belongs.

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