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Determination of salt solubility data for ternary aqueous systems with a quasiisothermic thermometric technique

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Abstract

The purpose of the present work is to study the solid–liquid equilibrium in aqueous multi-electrolyte systems using the quasiisothermic thermometric technique (QTT). The principle of the QTT is based on thermal effects associated with the phase transformations that occur in the system. In order to test the apparatus, salt solubility data at 298.15 K for the aqueous systems $H_2O+NaCl+KCl$, $H_2O+NaCl+Na_2SO_4$, $H_2O+NiCl_2+NiSO_4$ are presented. The data obtained for the three systems are in good agreement with the literature, including solid phase boundaries due to hydration. This agreement indicates the accuracy of the proposed method. Furthermore, the system with nickel salts are now experimentally determined.

Keywords: Phase diagram; Salt solubility; Electrolyte solutions; Thermometry; Solid–liquid equilibrium

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1. Introduction

In the thermodynamic equilibria of polyphase systems, the appearance and disappearance of the phases are related with the change of the mixture composition. These phenomena have been previously used [1–3] to determine solid–liquid diagrams. Among the physical properties, density and conductivity have usually been exploited.

In the present work, an automatic device to study the solid–liquid equilibrium of aqueous multi-electrolyte systems was developed. The technique, known as quasiisothermic thermometric technique (QTT), is based on the thermal effects associated with the phase transformations that occur in the mixture. The QTT is classified as a synthetic method, in which the composition of the system is known during the experiment and temperature is utilized to detect phase equilibrium data. In order to test this technique, salt solubility curves at 298.15 K for the systems $H_2O+NaCl+KCl$, $H_2O+NaCl+Na_2SO_4$ and $H_2O+NiCl_2+NiSO_4$ were determined and compared with the available literature data.

2. Experimental

2.1. Materials

Double distilled water has been used. The salt mixtures were prepared with p.a. grade (Aldrich and Merck) reagents. These reagents present the following purity grades in mass percent, i.e., NaCl 99%,

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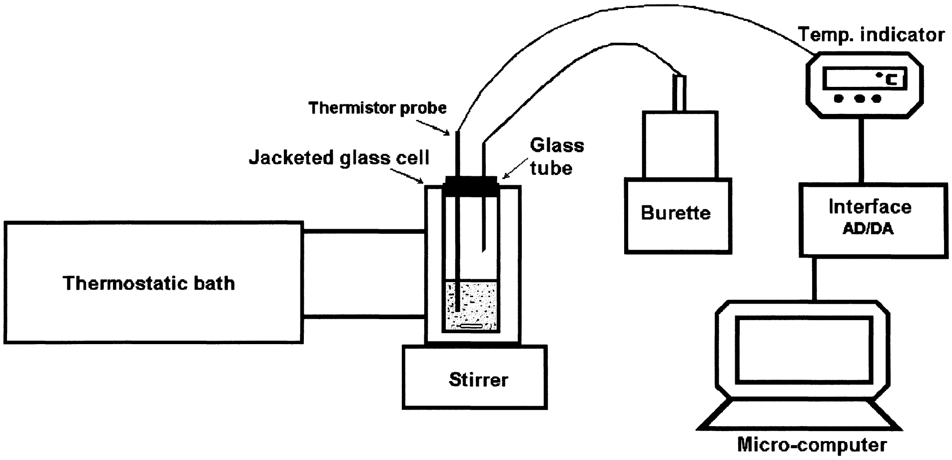

Fig. 1. Experimental setup scheme for determination of solid–liquid equilibrium data using the quasiisothermic thermometric technique.

KCl 99%, Na_2SO_4 99%, $NiCl_2$ 99.999% and $NiSO_4$ 99.999%. The salts have been finely ground and care has been taken to avoid the problem of wetness.

The purity and water contents of the nickel hydrated salts have been checked using thermogravimetry (TG) and differential thermal analysis (DTA), with the aid of the Perck-Elmer (model TGS-7) device.

2.2. Apparatus

A schematic diagram of the QTT apparatus for the measurement of salt solubilities is shown in Fig. 1. The cell is a glass tube (120 cm^3), which is placed in a jacketed glass reactor. The cell temperature is controlled by circulating water in the jacket, with the aid of a thermostatic bath (Heto, ±0.01 K). The titration of the solvent, in this case water, is performed by an automatic burette (Metrohm 665) with a capacity of 50 cm^3 and an accuracy of 0.01 cm^3. The temperature in the cell is measured by a thermistor probe PT100 (Cole-Parmer, 100 Ω Platinum RTD probe with alpha coefficient of 0.00385 Ω/Ω/°C and time constant of 15 s), which is connected to an interface analogical-digital. The experiment is monitored and recorded with a specific computer program (AQDADOS Lynx – version 4.8).

2.3. Procedure

The principle of this method is to measure the thermal effects, associated with the dissolution and mixing processes. The global composition of each mixture is known and changed progressively by the continuous and regular addition of a prefixed volume of water and the temperature evoluted depends on the dissolution and dilution enthalpies of the different phases.

In a typical experiment to determine solid–liquid equilibrium data using QTT the following procedure is to be done. First, a mixture containing, e.g., one or two salts and water is prepared gravimetrically with a composition conveniently chosen, i.e., in the region of the phase diagram where at least one solid phase is present. The tube containing this mixture is then placed in the jacketed glass reactor, which is covered properly with the equipped lid, i.e., temperature probe and filling tube of the burette. The system is submitted to stirring via magnetic stirrer. The size of the initial mixture charged should be ca. 40 g and at least 50% of this mixture should be liquid (water). This restriction is due to the fact that the mixture will give good conditions of stirring and will be properly dissolved and diluted according to the capacity of the utilized burette. The temperature of the cell is controlled and adjusted via the thermostatic bath. Having reached the thermal equilibrium, the experiment may start throughout an initiation of water injected from the automatic burette with a specified addition rate. During the experiment, the temperature in the cell along with the time is monitored and recorded with the aid of the interface and the manager program. Based on the retrieved data, i.e., temperature versus added volume,

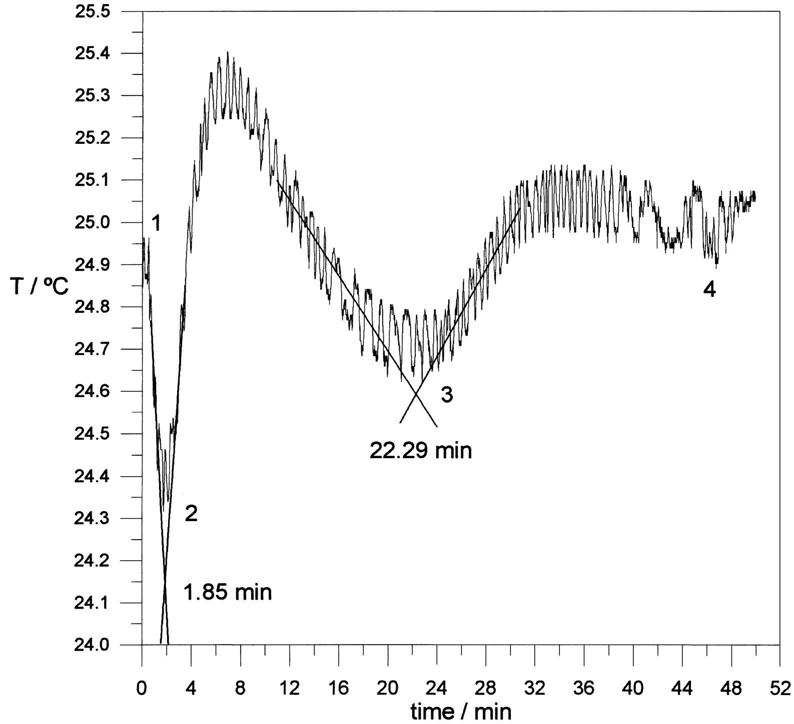

Fig. 2. Experimental curve of the dissolution and dilution processes, to determine solid phase boundary and solubility of $NiSO_4$ in the $NiCl_2$ aqueous solution.

which is estimated from the time and rate of injection utilized, the phase boundaries and solubility limits can be determined. This is possible due to the differences between dissolution and mixing enthalpies. In practice, the phase boundary, or the solubility limit, is determined by the intersection of the two segments, which represent the two processes involved in the transformation, see an experimental curve in Fig. 2. In order to study a ternary aqueous system with two salts, it is necessary to first measure the binary solubilities, determine the optimum addition rate of solvent, respectively. The rates of water injection have been fixed to 0.5 cm^3 min^{-1} for the aqueous systems with NaCl+KCl and NaCl+Na_2SO_4, and 1.0 cm^3 min^{-1} for the system with nickel salts. This difference is due to the higher heat of dissolution presented by the nickel salts. It is noteworthy that the rate of injection has been determined based on the shape of the experimental curve, i.e., temperature versus time, representing the processes of dissolution and mixture of the binary systems separately, i.e., one salt and water. Based on the rate conditions of the two salts obtained separately, the ternary mixture rate is easily found.

3. Results and discussion

This work presents solid–liquid equilibrium data for three ternary systems. The first two systems, i.e., H_2O+NaCl+KCl and H_2O+NaCl+Na_2SO_4, were studied to perform a validation of the QTT. The third one, i.e., H_2O+$NiCl_2$+$NiSO_4$, had not been studied in the literature and presents particular interest in hydrometallurgy processes. Sections 3.1–3.3 present and discuss the data obtained from each system, both in graphical and tabular form.

3.1. System H_2O+NaCl+KCl

The experimental solubility values obtained using QTT are presented in Fig. 3, where the literature [4] values were also plotted. The concentration scale used is the ionized mole fraction basis and the correlation

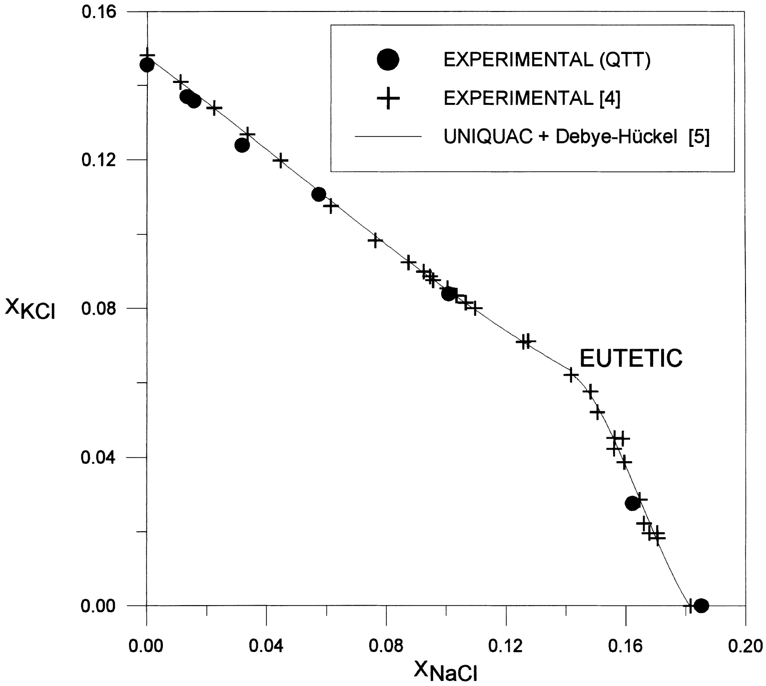

Fig. 3. Solid–liquid diagram for the ternary system KCl+NaCl+H_2O at 298.15 K. Axes are in ionized mole fraction basis.

Table 1
Solubility data observed (obsd) via QTT versus literature (lit)

System (298.15 K)	Experimental solubility[a]		Deviation[b] (%)	Solid phase
	Observed	Literature [4]		
KCl+H_2O	0.1455	0.1472	1.15	KCl
NaCl+KCl+H_2O	0.0838[c]	0.0854[d]	1.87	KCl
NaCl+KCl+H_2O	0.0275[e]	0.0286[f]	3.84	NaCl
NaCl+H_2O	0.1853	0.1816	2.03	NaCl

[a] Data on the ionized mole fraction basis.
[b] Deviation $= |x_{\text{obsd}} - x_{\text{lit}}|/x_{\text{lit}} \times 100$.
[c] x_{obsd} (NaCl)=0.1010.
[d] x_{lit} (NaCl)=0.1004.
[e] x_{obsd} (KCl)=0.1623.
[f] x_{lit} (KCl)=0.1646.

were made by the UNIQUAC+Debye–Hückel model [5]. Table 1 shows the agreement between the observed and literature data for some selected experimental points, numerically. The measured binary solubilities are within 2% deviation from the literature and comparisons for two ternary mixtures could also be made. These deviations may be considered small, regarding that the data present significant scattering [4].

3.2. System H_2O+NaCl+Na_2SO_4

This system has been studied to provide the test that the solid phase transformation is properly detected by the QTT. Fig. 4 illustrates good agreement with the literature of the observed data in determining the transition between the sodium sulfate and sodium sulfate decahydrated. Table 2 presents some experimental solubility values observed (QTT) and from the

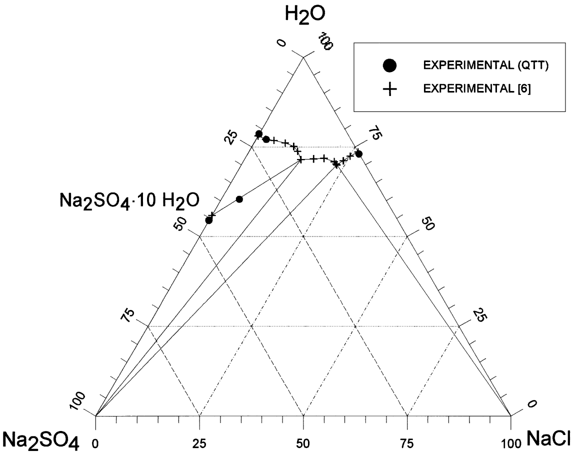

Fig. 4. Solid–liquid diagram for H_2O+Na_2SO_4+NaCl at 298.15 K. Axes are in mass percent.

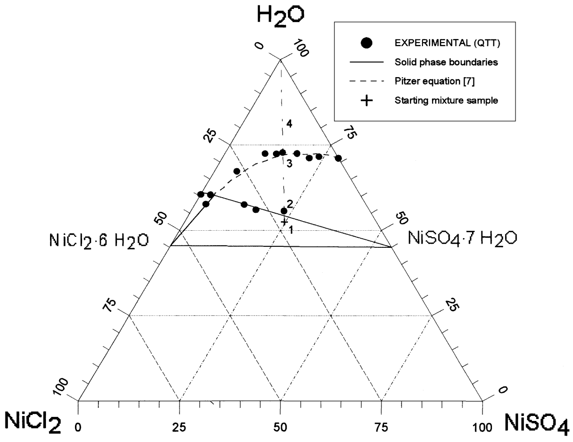

Fig. 5. Solid–liquid diagram for H_2O+$NiCl_2$+$NiSO_4$ at 298.15 K. Axe are in mass percent.

literature [6]. The deviations between these values indicate the performance and the accuracy of the QTT for the determination of solid–liquid equilibria.

3.3. System H_2O+$NiCl_2$+$NiSO_4$

The solid–liquid equilibrium behavior of this ternary system has been properly determined using QTT. The crystallization fields of both salts, including hydrated forms, have also been defined. Fig. 2 gives an illustration of the experimental data obtained from QTT, where the temperature is plotted versus time for the ternary mixture with a starting composition located at point 1, see also Fig. 5, which gives the triangular solid–liquid diagram for the nickel salts system. Three steps of the experiment may be pointed out in Fig. 2. The first one, corresponding to the path 1–2, represents the simultaneous dissolution of $NiCl_2 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$. During this process the composition of the liquid phase is unchanged, i.e., the eutetic composition. The second step (2–3) represents the progressive dissolution of nickel sulfate heptahydrate, where the liquid phase composition containing both nickel salts is continuously varied from the eutetic to point 3, which is the solubility limit of $NiSO_4 \cdot 7H_2O$ in the corresponding nickel chloride aqueous solution. It should be noted that the peak present during steps 2–3 represents just the exothermic effect of the nickel chloride dissolution and does not indicate a phase transformation. Steps 3–4 gives the dilution process of the solution, where at point 3 the last crystal of nickel sulfate heptahydrate was dissolved. Based on these experimental curves, the endothermic and exothermic character of each studied process may be identified. It has been observed from the binary mixture experiments that nickel chlor-

Table 2
Solubility data observed (obsd) via QTT versus literature (lit)

System (298.15 K)	Experimental solubility[a]		Deviation[b] (%)	Solid Phase
	Observed	Literature [6]		
Na_2SO_4+H_2O	0.093	0.094	1.06	$Na_2SO_4 \cdot 10H_2O$
Na_2SO_4+NaCl+H_2O	0.089[c]	0.088[d]	1.14	$Na_2SO_4 \cdot 10H_2O$
NaCl+H_2O	0.185	0.181	2.20	NaCl

[a] Data on the ionized mole fraction basis.
[b] Deviation $= |x_{\mathrm{obsd}} - x_{\mathrm{lit}}|/x_{\mathrm{lit}} \times 100$.
[c] x_{obsd} (NaCl)=0.018.
[d] x_{lit} (NaCl)=0.019.

Table 3
Solubility and solid phase transition data[a] for the H_2O+$NiCl_2$+$NiSO_4$ system at 298.15 K observed (obsd) via QTT

w_{NiCl_2}	w_{NiSO_4}	Solid phase
39.46[b]	0	$NiCl_2 \cdot 6H_2O$
37.12	2.48	$NiCl_2 \cdot 6H_2O$
39.61	2.67	$NiCl_2.6H_2O+NiSO_4 \cdot 7H_2O$[d,f]
30.17	12.26	$NiCl_2 \cdot 6H_2O+NiSO_4 \cdot 7H_2O$[e,f]
28.07	15.91	$NiCl_2 \cdot 6H_2O+NiSO_4 \cdot 7H_2O$[e,f]
21.26	23.08	$NiCl_2 \cdot 6H_2O+NiSO_4 \cdot 7H_2O$[e,f]
27.11	5.56	$NiSO_4 \cdot 7H_2O$
14.77	12.84	$NiSO_4 \cdot 7H_2O$
13.04	14.16	$NiSO_4 \cdot 7H_2O$
9.59	17.89	$NiSO_4 \cdot 7H_2O$
7.2	21.59	$NiSO_4 \cdot 7H_2O$
4.6	23.77	$NiSO_4 \cdot 7H_2O$
0	28.84[c]	$NiSO_4 \cdot 7H_2O$

[a] w_{salt}=experimental data in mass fraction percent.

[b] Literature (lit) value [6] is 39.58%; $|w_{obsd} - w_{lit}|/w_{lit} \times 100 = 0.30\%$.

[c] Literature (lit) value [6] is 28.97%; $|w_{obsd} - w_{lit}|/w_{lit} \times 100 = 0.45\%$.

[d] Solid phase transition data between $NiCl_2 \cdot 6H_2O+NiSO_4 \cdot 7H_2O$ and $NiCl_2 \cdot 6H_2O$.

[e] Solid phase transition data between $NiCl_2 \cdot 6H_2O+NiSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 7H_2O$.

[f] Utilizing the solid phase transition data, the eutetic point was estimated through the intersection of the two boundary fitted lines, i.e.: $w_{NiCl_2} = 29.51\%$ and $w_{NiSO_4} = 5.80\%$.

ide dissolution is exothermic and nickel sulfate endothermic. The axis at about 45% water showed in Fig. 5, represents the boundary between the region of anhydrous and hydrated nickel salts. It is noteworthy that no experimental information was available for this ternary system. However, Pitzer correlation [7] may be applied. Finally, the new experimental data for this system are reported in Table 3, where the estimated eutetic point is also reported using the measurements of solid phase transition.

4. Conclusions

It has been shown that the QTT can be applied to study solid–liquid equilibria. The experiments indicate that the rate of solvent addition for the ternary mixtures should be determined from the binary systems. However, in the case where the dissolution enthalpy of one salt is exothermic and the other one is endothermic, the phase transformations might be difficult to identify when they compensate each other. The QTT has been properly tested for the measurement of salt solubilities and solid phase transitions. The apparatus is of simple construction and can be easily operated with the aid of the computer interface, giving accurate data. The burette should also be monitored via interface and computer. The QTT has been applied for the measurement of new salt solubility and solid phase transition data for the system $NiCl_2$+$NiSO_4$+H_2O at 298.15 K.

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