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The solid–liquid equilibrium of the binary system H_2O–DMSO and the influence of a salt (NaCl, KCl) on the thermodynamic behavior

Correlations using a revised LIQUAC model

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ABSTRACT

The solid–liquid equilibrium of the binary system water (H_2O)–dimethyl sulfoxide (DMSO) is investigated and the results are compared to experimental values to ensure that the applied measurement procedure provides reliable results. After that, the freezing point depression of water is measured in the presence of different amounts of salt. Furthermore solubility measurements are carried out and compared to published experimental data to show that the apparatus used is also capable to provide reliable results for salt solubilities. Afterwards the ternary system is investigated using this measurement procedure to determine the solubilities of the salt in the mixed solvent system as well as the freezing point depression of the mixed solvents after the addition of salt. Two salts are investigated, sodium chloride (NaCl) and potassium chloride (KCl). Most of the measured ternary data seems to be reported for the first time. A correlation of the experimental results is also carried out using a revised version of the electrolyte model LIQUAC.

1. Introduction

In industrial chemical processes salts play a decisive role when regarding waste water treatment, crystallization and desalination processes. This is why for process design the salt effect for these processes has to be described reliably. The model development to describe the influence of salts on the phase equilibrium behavior was first carried out for highly diluted solutions by Debye and Hückel [1], who developed a theory based on statistical thermodynamics. This model is the only model of this kind not using adjustable parameters but it can only be applied for highly dilute solutions up to an ionic strength of about 0.01 mol/kg. However there are several semi-empirical expansions of this model, for example, the expansions of Bromley [2] and Pitzer [3] to extend the application to higher ionic strengths. Another type of extension to this model is achieved when combining these models with g^E models like NRTL [4], UNIQUAC [5] and UNIFAC [6]. The model which is used in this article is the LIQUAC-model developed by Li et al. [7] and expanded by Kiepe et al. [8]. This model allows describing the mean activity coefficient of the salts, the osmotic coefficient, the vapor–liquid and the solid–liquid equilibrium of aqueous electrolyte solutions. Recently, Huang et al. [9] proposed a set of equations to calculate the solubility of salts also in mixed solvent systems. This procedure was later used in an article of Li et al. [10] to correlate parameters for the LIQUAC model for mixed solvent systems to give an adequate description of the solubilities of these systems. In this article the parameters of the LIQUAC model are revised when necessary and a general model is presented which in the case of molecular groups is identical to the LIFAC model [11].

2. Measurement of the solid–liquid equilibrium H_2O–DMSO–salt

The measurements concerning the freezing point depression and the salt solubilities of the ternary system are carried out in the same apparatus but using different measurement procedures. The apparatus is shown in Fig. 1.

2.1. Apparatus for the measurement

A jacketed cell of about 100 mL is equipped with a resistance Pt100 thermometer (Fluke, Hart Scientific 1560 Black Stack with SPRT module 2560) with an precision of ±0.005 K and kept at a constant temperature by means of a thermostat (Lauda RP1845, ±0.01 K). To avoid further heat loss, the thermostatted cell is surrounded by an additional vacuum jacket. Furthermore, the measurements can be carried out under dry nitrogen atmosphere to avoid condensation of water from the air.

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Table 1
Results of the freezing point measurements with NaCl.

Freezing point temperature [K]	Salt free mole fraction of water (x_{H_2O})	Salt concentration [mol/kg]	Precipitating component	Freezing point temperature [K]	Salt free mole fraction of water (x_{H_2O})	Salt concentration [mol/kg]	Precipitating component
273.117	1.000	0.000	Water	242.859	0.501	0.050	DMSO
269.723	0.973	0.000	Water	258.303	0.404	0.050	DMSO
257.739	0.899	0.000	Water	270.834	0.300	0.050	DMSO
240.369	0.847	0.000	Water	272.757	1.000	0.102	Water
222.417*	0.800	0.000	Water	269.318	0.973	0.100	Water
217.268*	0.751	0.000	Water	256.720	0.899	0.099	Water
217.955*	0.700	0.000	DMSO	240.057	0.847	0.099	Water
221.254*	0.650	0.000	DMSO	221.710*	0.800	0.101	Water
225.730*	0.603	0.000	DMSO	226.249*	0.603	0.101	DMSO
243.806	0.501	0.000	DMSO	242.758	0.501	0.101	DMSO
258.362	0.404	0.000	DMSO	237.593	0.847	0.325	Water
271.071	0.300	0.000	DMSO	271.414	1.000	0.500	Water
279.326	0.200	0.000	DMSO	267.537	0.973	0.502	Water
285.326	0.103	0.000	DMSO	252.359	0.899	0.500	Water
291.661	0.000	0.000	DMSO	257.395	0.899	0.502	Water
272.941	1.000	0.050	Water	236.088	0.848	0.500	Water
269.523	0.973	0.051	Water	269.628	1.000	1.030	Water
240.310	0.847	0.051	Water	265.357	0.973	1.001	Water
221.880*	0.800	0.049	Water	249.125	0.899	0.999	Water
216.220*	0.751	0.050	Water	230.342	0.848	1.000	Water
217.737*	0.700	0.050	DMSO	240.662	0.899	2.001	Water
221.130*	0.650	0.050	DMSO	260.298	0.973	2.201	Water
225.917*	0.603	0.049	DMSO	261.628	1.000	3.003	Water

2.2. Freezing point depression

For the measurement of the freezing point depression a known mass of solvent or solvent mixture is filled into the apparatus. The mixture of water (distilled twice, purity: >99.8%) and DMSO (purity: >99.8%) is prepared by using a precision balance (Sartorius CP225D) with an uncertainty of (±0.01 mg). After that, the desired amount of salt (NaCl [purity: >99.8%] or KCl [purity: >99.5%]) is added and the mixture is stirred until the salt is completely dissolved. The mixture is then cooled down with the help of the cryostat and a first initial value for the freezing point is obtained, when the first crystals are observed in the solution. Since this value is too low because of super-cooling effects, a more precise technique is used. After heating the mixture slightly above the melting point, some crystals are generated by adding a few drops of liquid nitrogen to the mixture. After that, a heating program with a heating rate of 2 K/h is used to determine the exact freezing temperature, where all crystals have been dissolved. At the freezing point the temperature curve shows a characteristic kink, which is schematically shown in Fig. 2. This kink is due to the enthalpy of fusion. The measurement is repeated twice to obtain a reliable mean value for the freezing point. The values are listed in Table 1 and Table 2. For temperatures below −40 °C an easier method has been used. The standard procedure is not capable of measuring these points because at these temperatures the cooling medium ethanol formed cords and at the same time the rising viscosity caused mixing problems. Therefore for measurements below −40 °C the mixture is filled in a Dewar vessel and cooled down with liquid nitrogen below the freezing point. After that, the solution is slowly heated up caused by the surrounding room temperature, which is far higher than the mixture in the open Dewar vessel. At the same time the solution is stirred manually. This procedure likewise produces a kink in the heating curve but since the heating rate is a lot higher, the error of this measurement procedure is larger than for the procedure described before. The values measured by this method are indicated by an asterisk in Table 1. The uncertainty of the measured

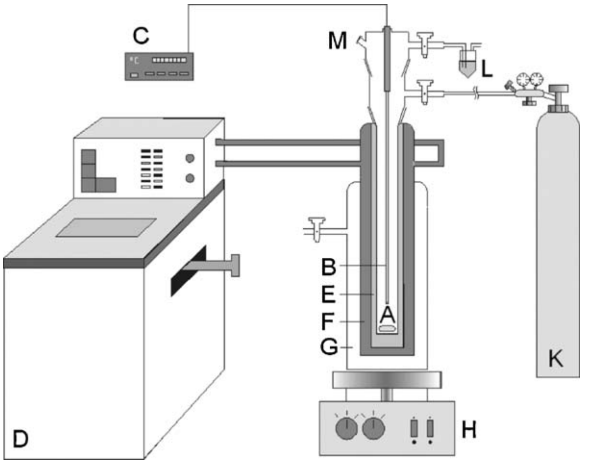

Fig. 1. Apparatus for the measurement of solubilities and freezing points [22], (A) measurement cell with magnetic stirring rod, (B) Pt100 thermometer, (C) temperature device, (D) thermostat, (E) contact fluid (ethanol), (F) thermostattet jacket for the measurement cell, (G) vacuum Jacket, (H) magnetic stirrer, (K) nitrogen, (L) nitrogen outlet, (M) feed inlet.

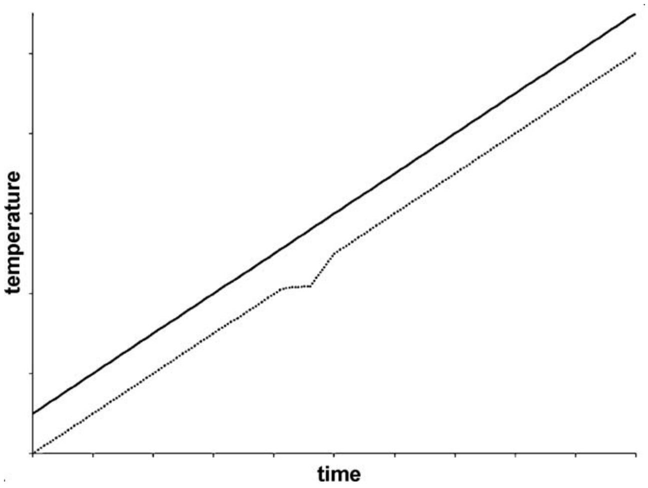

Fig. 2. Typical temperature profile of the freezing point determination, (—) thermostat, (. . .) mixture.