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PHASE EQULIBRIA IN THE (WATER + 1,4-DIOXANE + MAGNESIUM CHLORIDE) SYSTEM[*]

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ABSTRACT

The solubilities of magnesium chloride in (water+1,4-dioxane) and the corresponding phase diagram at the temperature 298.15 K were determined. To investigate the phase separation Gibbs free energy accompanying the dilution of the saturated two-phase system is given.

INTRODUCTION

Water and 1,4-dioxane are miscible in all proportions. The addition of some salt to (water+1,4-dioxane) causes at certain composition a phase separation, giving two conjugate solutions[1,2,3]. For this phenomenon the Gibbs free energy change[4] has been determined for the system (water+1,4-dioxane+sodium chloride). In this contribution the results of similar investigation are presented for

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[*] Dedicated to Professor Drago Leskovšek on the occasion of his 80th birthday

the (water+1,4-dioxane+magnesium chloride) system. The activities of water, 1,4-dioxane and of magnesium chloride in mixed solvent from the vapour pressure data have been reported[5]. By using of some of these results the Gibbs free energy accompanying the phase separations was obtained.

EXPERIMENTAL

Magnesium chloride, analytical-reagent grade (Kemika Zagreb, Croatia) and spectroscopically pure 1,4-dioxane, $C_4H_8O_2$, (Kemika Zagreb, Croatia) were used without further purification. Distilled water of resistivity greater than 0.3 MΩ· cm was used in all experiments.

To determine the solubility of $MgCl_2$ as a function of the solvent composition the saturated or very concentrated water solution was prepared in the thermostated cell at (298.15±0.05) K. 1,4-dioxane was added until the solid phase was precipitated. The solution was mixed so that the equilibrium was reached. The salt content of the solution was checked by potentiometric titration of Cl^- with $AgNO_3$, using Cl^- ion-selective electrode and a saturated mercury sulphate electrode as the reference. The composition of solvent was determined from a calibration diagram[6], representing the dependence of refractive index on concentration of salt for different mixtures.

To determine the phase diagram, 1,4-dioxane was added to the water solutions of $MgCl_2$ until the phase separation occurs. The composition of solutions, obtained by phase separation, was determined as described above. Some of them were used as stock solution for preparing solutions for vapour-pressure measurements by dynamic gas-saturated method, as described previously[5].

To check the solid phase in equilibrium with saturated solutions or two-phase system, some X-ray powder samples were measured. The solid phase was unambiguously identified as complex $MgCl_2 \cdot C_4H_8O_2 \cdot 6H_2O$, which has been described previously[7].

TREATMENT OF RESULTS

The Gibbs free energy of a homogenous solution consisting of amounts of substance n_1 of H_2O, n_2 of $C_4H_8O_2$, and n_3 of $MgCl_2$, is given by

$$G = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 \ . \qquad 1.$$

μ_1, μ_2 and μ_3 are the corresponding chemical potentials. The chemical potential of component *i* in solution at constant temperature is

$$\mu_i = \mu_i^{\mathrm{o}} + RT \cdot \ln a_i \ , \qquad 2.$$

where μ_i^{o} is the standard chemical potential and a_i the activity of component *i*, obtained from the relation

$$a_i = f_i \big/ f_i^{\mathrm{o}} \ . \qquad 3.$$

f_i is the fugacity of the component in solution and f_i^{o} the fugacity in the standard state. The activity a_3 of the electrolyte is related to the molality *m* by

$$a_3 = a\pm^3 = \left(\frac{m\pm\gamma\pm}{m^{\mathrm{o}}}\right)^3 = 4\frac{m^3}{m^{\mathrm{o}3}}\gamma\pm^3 \ . \qquad 4.$$

$\gamma\pm$ is the activity coefficient of $MgCl_2$ and m^O is the standard molality, 1 mol·kg^{-1}. The fugacities f_1 of H_2O and f_2 of $C_4H_8O_2$ were calculated as[8]

$$f_1 = p_1 \cdot \exp[\{(p - p_1^*)\cdot(B_{11} - V_1^*) + 2\delta_{12}\cdot p \cdot y^2\}/RT] \ , \qquad 5.$$

$$f_2 = p_2 \cdot \exp[\{(p - p_2^*)\cdot(B_{22} - V_2^*) + 2\delta_{12}\cdot p \cdot (1-y)^2\}/RT] \qquad 6.$$

where

$$\delta_{12} = B_{12} - (B_{11} + B_{22})/2 \ . \qquad 7.$$

p_1 is the experimental partial pressure of H_2O, p_2 that of $C_4H_8O_2$ and p the total vapour pressure. p_1^* is the vapour pressure and V_1^* the molar volume of pure liquid water, p_2^* is the vapour pressure and V_2^* the molar volume of pure liquid 1,4-dioxane, and y is the mole fraction of $C_4H_8O_2$ in the vapour. The constants B_{11}, B_{22} and B_{12} are the second virial coefficients, reported in the literature[9,10]

From activities of the components in the mixed solvent the activities of the salt could be obtained by applying of the Gibbs-Duhem theorem as has already been done[5].

As there is no pure $MgCl_2$ in equilibrium with saturated solutions neither in water nor in mixed solvents, it can not be chosen as an initial state. So we decided to consider the process, where the two-phase system with an average concentration of solvent ($0.677\,H_2O$+$0.323\,C_4H_8O_2$), saturated with $MgCl_2$, is diluted by adding the solvent with the same composition. The reduced Gibbs free energy, accompanying this process is given by

$$\Delta G/RT = n_1^{\ddagger}\ln(f_1/f_1^{\ddagger}) + n_1^{\dagger}\ln(f_1/f_1^{\dagger}) + n_2^{\ddagger}\ln(f_2/f_2^{\ddagger}) + n_2^{\dagger}\ln(f_2/f_2^{\dagger})$$
$$+n_3\{(\Delta\mu_3^{O(m)}-\Delta\mu_3^{\ddagger(m)})/RT+3\ln(m\gamma\pm/(m^{\ddagger}\gamma\pm^{\ddagger}))\}. \qquad 8.$$

The fugacities of H_2O and $C_4H_8O_2$, f_1 and f_2, molality m and the mean activity coefficient $\gamma\pm$ are taken from the literature[5]. The superscript$^{(\ddagger)}$ refers to the saturated solution and the superscript $^{(\dagger)}$ to the solvent without salt. Because the standard chemical potential μ_3^O in initial and final solution is not known, the differences between the standard chemical potential of $MgCl_2$ in mixed solvent and in water $\Delta\mu_3^O$ and $\Delta\mu_3^{\ddagger}$ are applied, giving $\mu_3^{O(m)}-\mu_3^{\ddagger(m)}=\Delta\mu_3^{O(m)}-\Delta\mu_3^{\ddagger(m)}$ in molal scale[5].

RESULTS AND DISCUSSION

Figure 1 shows the dependence of the solubility of $MgCl_2$ on solvent composition. It is evident that the phase separation occurs in the region where the mole fraction of $C_4H_8O_2$ in the solvent is between 0.137 and 0.823. The top phases are rich in $C_4H_8O_2$ and low in salt while the converse is true for the bottom phases.

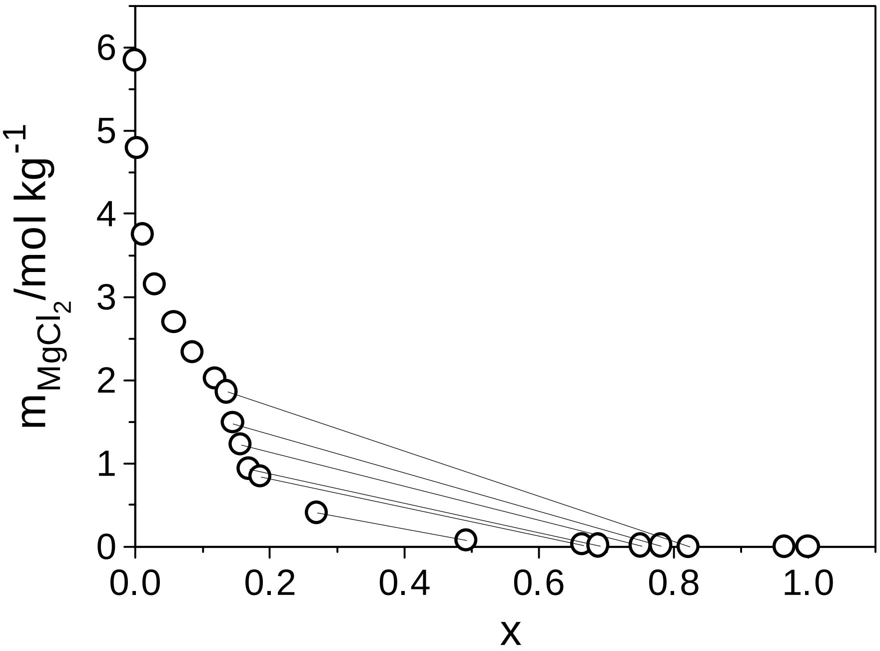

FIGURE 1. The solubility of $MgCl_2$ in $\{(1\text{-}x)\,H_2O + x\,C_4H_8O_2\,)\}$ and the phase diagram at the temperature 298.15K.

The mixtures, saturated with electrolyte, split into two conjugate solutions, connected in the Figure 1 with the upper line. The average concentrations can be obtained from the mass balance as follows

$$\frac{m'-m^*}{m^*-m''}=\frac{D^*-D'}{D''-D^*} \quad , \qquad 9.$$

where m' and m'' denote the molalities of the electrolyte in the bottom and in the top phase respectively. m^* refers to the average concentration of the hypothetical solutions. D', D'' and D^* are the corresponding weight per cent of 1,4-dioxane in the solvent. In Table 1 all for the calculations of the Gibbs free energy demanded quantities are collected[5]. Because the conjugate solutions are in equilibrium only the more precise data for the heavier phases are given.

Table 1. The weight percent of 1,4-dioxane, D´; the molality, m´, the reduced difference of standard chemical potential of $MgCl_2$ in mixed solvent and in water in the molal scale, $\Delta\mu_3^{O(m)}/RT$; the mean activity coefficient of $MgCl_2$, $\gamma\pm$; and the fugacities of water and of the 1,4-dioxane, f_1 and f_2; all in the bottom phase. m^* is the average (hypothetical) molality in the $(0.677\,H_2O + 0.323\,C_4H_8O_2)$ = 70 wt. % solvent.

D´	***m´* / mol kg^{-1}**	**$\Delta\mu_3^{O(m)}$ / *RT***	**$\gamma\pm$**	**f_1 / *Pa***	**f_2 / *Pa***	**m^* / *mol kg*$^{-1}$**
43.8	1.8531	11.947	0.2897	1931	4193	0.922
47.8	1.2187	13.385	0.0403	2197	4074	0.632
52.9	0.8395	15.305	0.0102	2295	3993	0.4653
64.5	0.4086	19.920	0.00313	2411	3907	0.3061
70.0	0.2805	22.075	0.00071	2455	3963	-
70.0	0.2019	22.075	0.00096	2488	3857	-
70.0	0.1084	22.075	0.00176	2530	3743	-
70.0	0.0513	22.075	0.00503	2549	3636	-

In the mixed solvent $(0.677\,H_2O + 0.323\,C_4H_8O_2)$ a binodal point on the phase diagram is almost reached at m($MgCl_2$) ≈ 0.3 mol kg^{-1}, corresponding to $x_3 \approx 0.01$. At this composition a discontinuity in the Gibbs free energy occurs, see Figure 2.

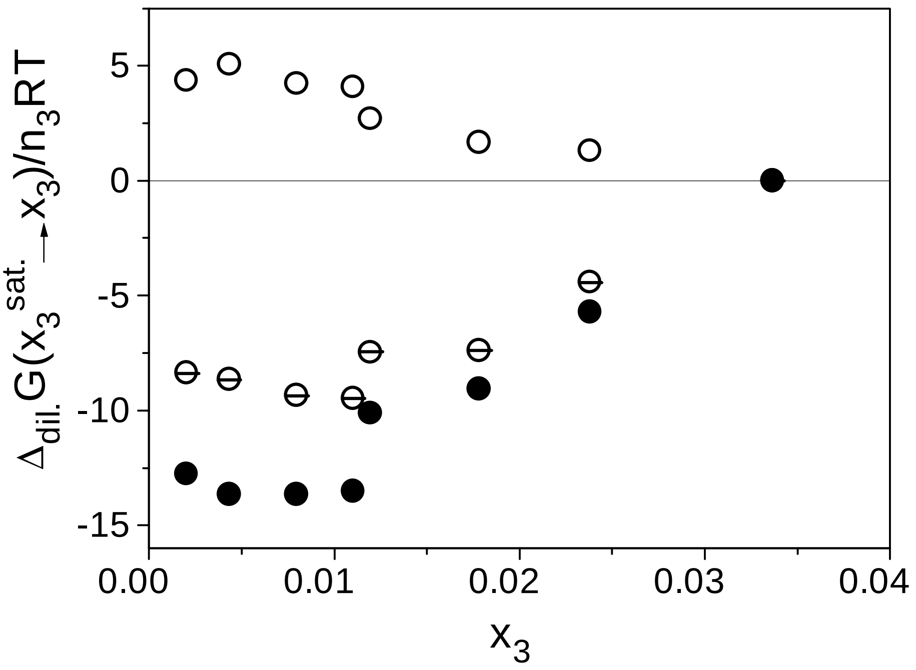

FIGURE 2. $\Delta G / n_3RT$ accompanying the dilution of two-phase system with an average composition of solvent $(0.677H_2O + 0.323C_4H_8O_2)$ saturated with $MgCl_2$, and solvent with the same composition. (O), the contribution of the solvent; (O) the contribution of the electrolyte; and (O) the total change. x_3 is the mole fraction of $MgCl_2$ in the solution.

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POVZETEK

Določili smo topnost in fazni diagram za sistem (voda+1,4-dioxan+$MgCl_2$). Iz podanih vrednosti parnih tlakov komponent v mešanem topilu in aktivnosti $MgCl_2$ smo izračunali Gibbsovo prosto energijo razredčenja nasičenega dvofaznega sistema pri konstantni sestavi topila.