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Phase equilibrium in the ternary system water–ethylene glycol–dimethyl sulfoxide

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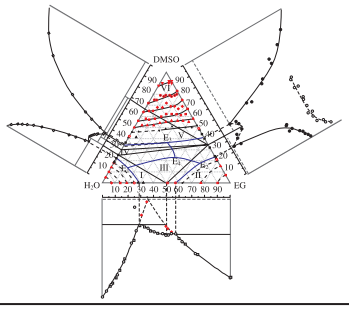
The ternary system water–ethylene glycol–dimethyl sulfoxide (H_2O–EG–DMSO) was investigated by differential scanning calorimetry in the temperature range of 188–298 K. In the concentration range from ~10 to ~50 mol% DMSO, crystallization or glass formation are not observed when the temperature is lowered to 188 K. Significant supercooling of the solution in this composition range is explained by the existence of spatial networks of H_2O and EG.



Keywords: phase equilibria, water, ethylene glycol, dimethyl sulfoxide, supercooled solutions, cryobiology.

Aqueous solutions of dimethyl sulfoxide (DMSO) and ethylene glycol (EG) are prone to significant supercooling of the liquid phase and therefore are widely used in cryobiology to preserve living cells and living organisms.[1–4] The reason for the strong supercooling of the liquid phases of water and EG is that they contain a stable spatial network of hydrogen bonds. The physicochemical properties of binary systems water–DMSO, water–EG and EG–DMSO and phase equilibria in these systems have been studied earlier.[5–11]

Phase diagrams of binary systems indicate that in the H_2O–DMSO system, the compound DMSO·3H_2O is formed, which melts congruently at 210 K. Moreover, it is believed[5] that the compounds DMSO·2.5H_2O and DMSO·0.5H_2O are also formed, which melt incongruently at temperature of about 203 K. The largest supercooling in aqueous DMSO solutions is achieved at 200 K and a DMSO concentration of ~33 mol%.[5]

The results of studying the phase diagram of H_2O–EG, obtained by different research groups, differ in the range of metastable concentrations[6–10] of 25–65 mol% EG. According to some authors,[6] the phase diagram contains a single eutectic with 33 mol% EG. Two laboratories working concurrently[7] have shown that the H_2O·EG hydrate crystallizes at 230 K. It forms eutectics with H_2O at 223 K (28.6 mol% EG) and with EG at 229 K (55.5 mol% EG). The construction of the phase diagram of the H_2O–EG system is complicated by the strong supercooling of solutions that hinders crystallization. The maximum supercooling (223 K) is observed at a concentration of ~28 mol% EG. The supercooling occurs due to the spatial networks of hydrogen bonds formed by both components, H_2O and EG.[12]

Phase states in the EG–DMSO system were studied previously.[11] The formation of DMSO·2EG with a congruent melting temperature of 213 K, close to the temperatures of eutectics with EG (198 K) and DMSO (203 K), is accompanied by strong supercooling of the liquid phase and glass transition at 148 K. Upon rapid cooling and slow heating, stratification is observed in the temperature range of 268–281 K and concentration range of 5–50 mol% DMSO.

The ternary system H_2O–EG–DMSO is a solution of DMSO in a mixed solvent H_2O–EG, characterized by the presence of a spatial mixed network of hydrogen bonds.[13] It was of interest to study the phase diagram of the H_2O–EG–DMSO ternary system and identify the ranges of the liquid state in it upon cooling. These data are required for applications in cryobiology.

The physicochemical properties of the components of the investigated system H_2O–EG–DMSO[14] are presented in Table S1, see Online Supplementary Materials. Table S1 shows that DMSO molecules have a higher dipole moment and a higher electron-donating ability than H_2O or EG molecules. However, although the densities are close, the viscosity of EG is much higher because, like water, it has a spatial network of hydrogen bonds and mixes with H_2O in any ratio.[12] The presence of a spatial network determines the strong supercooling of pure EG and its aqueous solutions. Although water has a more perfect network (fewer defects) than EG,[12] it is less prone to supercooling due to the high mobility of molecules, which follows from the value of the self-diffusion coefficient.[15,16,†]

† Solutions of the H_2O–EG–DMSO system were prepared by the gravimetric method. H_2O (Milli-Q), EG (99%) and DMSO (ACROS, 99.8%) were used for sample preparation. The H_2O–EG–DMSO system samples thermal behaviour was investigated by differential scanning calorimetry on a TA Instruments Q100 differential scanning calorimeter in the cooling–heating mode in the temperature range of 188–298 K at a scanning rate of 3 K min^{-1}. The measurements were carried out in a stream of high-purity argon in aluminum crucibles with sealed lids. The instrumental measurement error is ±1 K for temperature and ±2% for enthalpy. The atmospheric pressure drop in a hermetically sealed constant volume crucible can be roughly estimated based on the ideal gas equation of state. Since the pressure at 200 K is about 0.73 bar, it was considered equal to atmospheric pressure when describing the thermal analysis data and constructing the phase diagram.

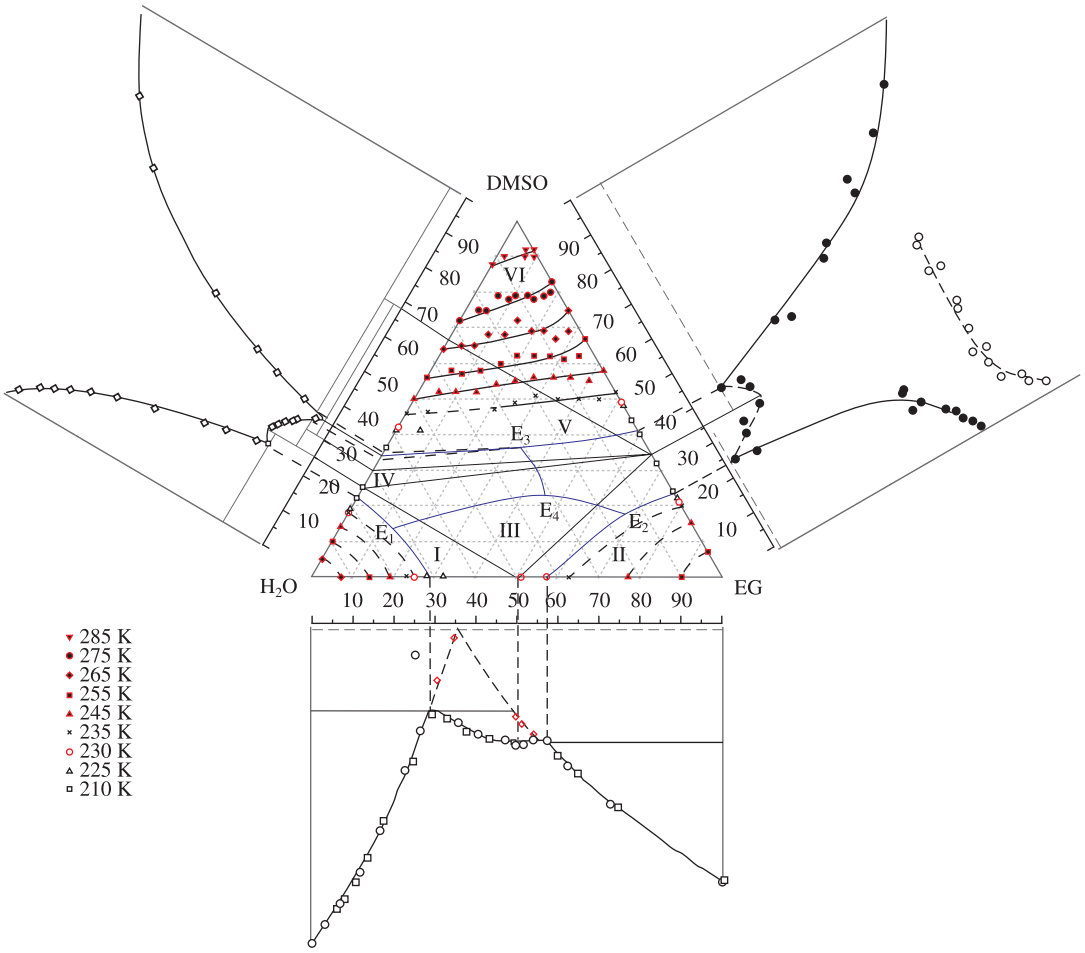


Figure 1 A model of the phase diagram of the H_2O–EG–DMSO system with unfolded diagrams of the binary systems H_2O–EG, H_2O–DMSO and EG–DMSO.

To construct a fragment of the phase diagram for the system (Figure 1), we used compositions with a constant H_2O : EG ratio, to which DMSO was added. The H_2O : EG ratio varied with a step of ~10 mol%, and the DMSO concentration increased by ~10 mol% in each of the sections. In total, ~100 samples were prepared, and thermograms were recorded for all of them. The thermograms manifested exothermic peaks upon cooling the samples at a rate of 3 K min^{-1} and endothermic peaks upon subsequent heating at a rate of 3 K min^{-1}. The thermogram of a sample containing 34.56 mol% H_2O, 4.16 mol% EG and 61.28 mol% DMSO is shown in Figure 2. Figure 3 displays a cross-section of the phase diagram of the ternary system built upon heating the crystallized samples. Phase transition temperatures and enthalpy changes in the H_2O–EG–DMSO system are presented in Table S2, see Online Supplementary Materials.

Because of the strong supercooling of the samples, we were unable to obtain the complete phase diagram of the H_2O–EG–DMSO system from the experimental data (188 K is the temperature limit for the TA Instruments Q100 differential scanning calorimeter); therefore, Figure 1 shows a model of the phase state diagram of the H_2O–EG–DMSO system based on the diagrams of binary systems. Thin straight lines show the triangulation of the H_2O–EG–DMSO concentration triangle, which allows describing six subsolidus phase equilibria in the ternary system: ice (H_2O)–H_2O·EG–DMSO·3H_2O (I), EG–H_2O·EG–DMSO·2EG (II), H_2O·EG–DMSO·3H_2O–DMSO·2EG (III), DMSO·3H_2O–DMSO·2.5H_2O–DMSO·2EG (IV), DMSO·2.5H_2O–DMSO·0.5H_2O–DMSO·2EG (V) and DMSO·0.5H_2O–DMSO·2EG–DMSO (VI).

The existence of DMSO·2.5H_2O and DMSO·0.5H_2O remains an open issue, and the last three equilibria between crystalline

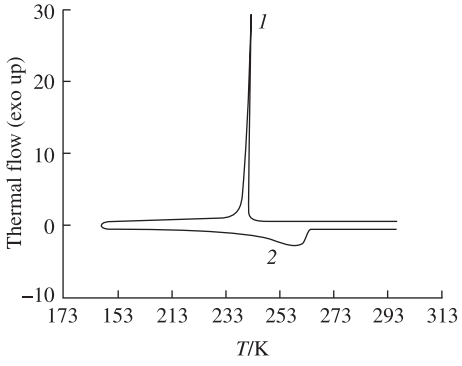


Figure 2 Thermogram of a sample containing 34.56 mol% H_2O, 4.16 mol% EG and 61.28 mol% DMSO, showing (*1*) exothermic and (*2*) endothermic peaks corresponding to crystallization and melting of the sample, respectively.

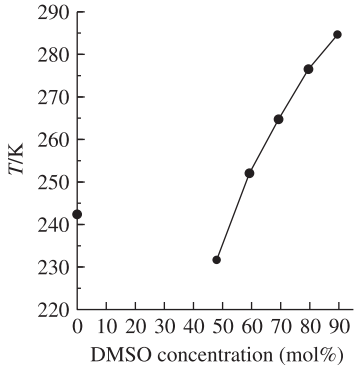


Figure 3 Section of the phase diagram (30.39 mol% H_2O + 69.61 mol% EG)–DMSO.

phases can be reduced to one stable equilibrium DMSO·3H_2O–DMSO·2EG–DMSO. The liquidus surface of the H_2O–EG–DMSO system is represented by isothermal sections from 210 to 285 K, and simulation based on diagrams of binary systems was carried out for the region of supercooled solutions (see Figure 1, thin curved lines). Peritectic melting of DMSO·2.5H_2O and DMSO·0.5H_2O is not considered, and four ternary eutectics E_1–E_4 with melting below 200 K are presented for the system. Accordingly, the liquidus surface is formed by six surfaces of primary crystallization of H_2O, EG, DMSO, DMSO·3H_2O, H_2O·EG and DMSO·2EG. If peritectics with DMSO·2.5H_2O and DMSO·0.5H_2O are realized, then DMSO·2.5H_2O, DMSO·0.5H_2O and DMSO·2EG would melt in the E_3 eutectic (DMSO·3H_2O–DMSO·2EG–DMSO), and two peritectoid equilibrium points, melt–DMSO·3H_2O–DMSO·2.5H_2O–DMSO·2EG and melt–DMSO·0.5H_2O–DMSO–DMSO·2EG, would be located near E_3 (see Figure 1, dashed lines near E_3). Moreover, with a high probability, the following will be realized in the system: metastable states, in which the lowest-temperature metastable eutectic will correspond to ice–EG–DMSO melting; the glass formation region, which can range from H_2O–DMSO[5] to EG–DMSO;[11] and the delamination region, which begins in the EG–DMSO system.[11]

Thus, thermograms demonstrate no thermal effects observed in the H_2O–EG–DMSO system (see Figure 1) in the composition range from 10 to ~50 mol% DMSO upon cooling to 188 K, which indicates the existence of a broad region of supercooled solutions. Keeping for 60 min did not lead to the formation of a crystalline phase. The effect of lowering the low-temperature limit of the existence of solutions can be explained by the formation of mixed networks of hydrogen bonds of water and ethylene glycol with a noticeable strengthening of intermolecular interactions, which create an energy barrier that prevents the crystallization of solution components.

The studied three-component system H_2O–EG–DMSO can be attributed to systems that exist as solutions in a wide range at low temperatures and can be used in cryobiology.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.041.

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