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SOLUBILITY STUDIES OF POLYETHYLENE GLYCOLS IN ETHANOL AND WATER

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SUMMARY

A simultaneous TG-DSC method has been used for the determination of ethanol-water solutions containing PEG 4000. The solubility limit increases from approximately 80 weight percent at 40°C to 87 percent at 50°C in a 70/30 weight percent ethanol-water solution.

INTRODUCTION

In powder metallurgy production of cemented carbide products, powders e.g. of metals and carbides are wet milled, dried and compacted to blanks, which later on are sintered. To lower the friction in the pressing operation different lubricants or binders are used. An example is polyethylene glycol (PEG) with a molecular weight from 1500 to 35000.

During milling the PEG is dissolved in the milling liquid, which consists of a solution of ethanol and water, and the wet powder mixture is then spray-dried in nitrogen at 150-180°C. In the beginning of the drying process the suspension of solid particles in a liquid ethanol-water-PEG solution looses ethanol rapidly due to the relatively high vapour pressure and low boiling point. The liquid phase is enriched in water aswell as in PEG. The ethanol/water ratio is thus changed and the amount of solvent decreases until the solubility limit has been reached, see Figure 1. It is thus important to know the solubility of different types of PEGs in ethanol-water solutions of different ratios to be able to predict the mechanism for the drying of the droplets.

The solubility of polyethylene glycols in water has been reported by the manufacturers, e.g. Union Carbide (1) and Hoechst (2). The figures are, however, somewhat inconsistent and the

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temperature dependence is only reported in (1). So far only data from our own laboratory (3) has been found for the solubility of PEG 1000 and PEG 1500 in an ethanol/water solution (88.5/11.5 weight percent). The hypothetic ternary phase diagram in Figure 1 (at 20°C) has been drawn from those data.

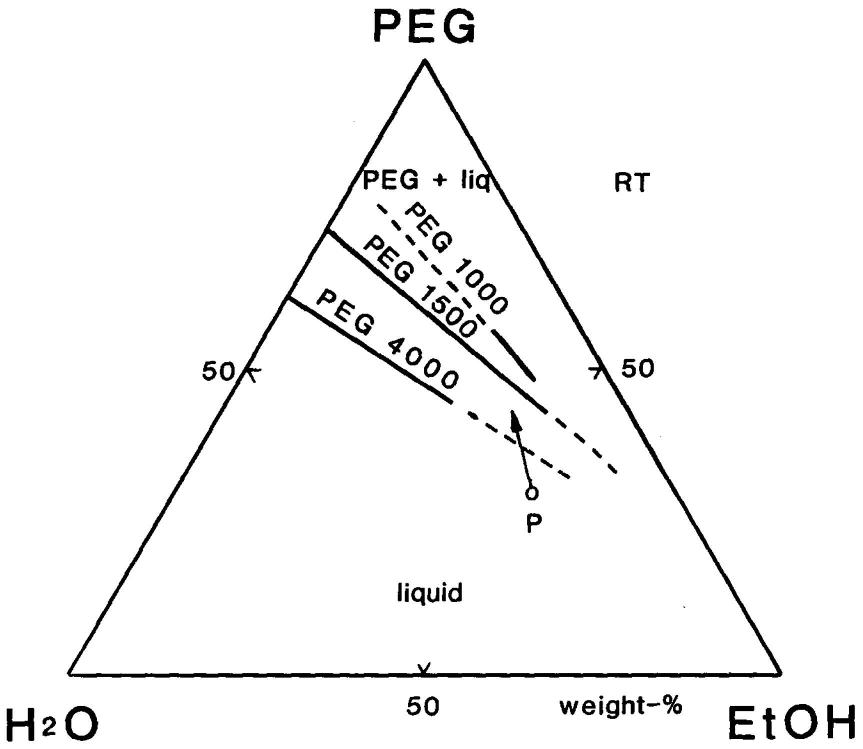

Figure 1. Hypothetic ternary diagram at room temperature for the system polyethylene glycols (with different molecular weights) and ethanol - water solutions

Sources: (1) PEG 1500 and PEG 4000 in water at 20°C
(3) PEG 1000 and PEG 1500 in ethanol/water 88.5/11.5 weight % at 20°C

PRINCIPLE

A simultaneous technique, combining thermogravimetry and differential scanning calorimetry has been used to study the precipitation of PEG from ethanol-water solutions of different concentrations and at different temperatures. The method will not necessarily give a value for the true thermodynamic solubility e.g. due to the possibility for supersaturation or to the influence of high viscosity. The aim of the work is to establish a value for the technical solubility as an aid to understand the solidification mechanism in the spraydrying process.

From the heat of vaporization ΔH^{vap} the ethanol to water ratio and thus also the concentration of PEG in the liquid can be estimated if the PEG in solution is assumed not to influence the heat of vaporization. As long as the ethanol content (and later on also the water content, see point P in Figure 1) monotonously decreases the PEG is anticipated to remain in solution. At the same time the liquid becomes more and more enriched in PEG, see arrow in Figure 1. At the solubility limit the ΔH^{vap} vs weight curve shows a drastic change in its slope.

There are several empirical rules to estimate the heat of vaporization of a liquid. One is the Trouton's rule which says that the molar heat of vaporization of a liquid divided by its absolute boiling point is approximatively constant. For water and ethanol, which both have large dipole moments, this constant is rather high, see Table 1.

TABLE 1

Boiling points and heats of vaporization

Liquid	Boiling temperature ^{o}C	Heat of vaporization ΔH^{vap} kJ/g	kJ/mole	Trouton's constant $\Delta H^{vap}/T_B$ J/K,mole	Ref
H_2O	100.0	2.256	40.64	108.9	
C_2H_5OH	78.5	0.843	38.82	110.4	(4)

MATERIALS AND MEASUREMENTS

Polyethylene glycol of the brand "Carbowax^R" with molecular weight 4000 was dissolved in 80 % (by volume) ethanol. The solution was pipetted directly into an aluminium crucible in the thermoanalyzer. An empty crucible was used as reference. No lids were used on the crucibles. The mass of the solution sample before the experiment was 20-30 mg and the remaining PEG after the evaporation of the solvent was 7-15 mg.

The experiments were made in a Mettler TA 2000C Thermoanalyzer with simultaneous recording of the TG and DSC signals (sensitivities: 100 mg and 50 or 100 μV f.s.d.). The heating to the desired temperature was made at a rate of 4 K/min. Nitrogen (deoxidized and dried) was used as protective atmosphere at a flow rate of 50 ml (NTP) per minute.

EVALUATION AND CORRECTION OF DATA

From the TG and DSC records the actual heat of vaporization per mass unit is calculated and plotted as a function of total weight loss. Corrections are made for the temperature dependence of the calorimetric sensitivity of the instrument.

Calibration of the sensitivity was made by evaporation of pure water under the same conditions as the other measurements. The temperature dependence of the heat of vaporization $\Delta H_{H_2O}^{vap}$ is known from common steam tables. From these values the corresponding data for Trouton's constant at the temperatures in question were calculated.

The heat of vaporization ΔH_M^{vap} for ethanol-water solutions at their boiling points have been determined by Newsham and Mendez-Lecanda (4) over the whole composition range from water to pure ethanol. The temperature dependence of ΔH_M^{vap} for lower pressures (and corresponding boiling points) is not known. As the vapour pressure of ethanol obeys the same temperature relationship as for water (5) the Clausius-Clapeyron's equation can be used to estimate the ΔH_M^{vap}, or, more simply, the same temperature dependence of the Trouton's constant for the ethanol-water solutions as for pure water can be anticipated. Thus the experimentally determined values of ΔH_M^{vap} can be extrapolated to the boiling points at atmospheric pressure and the actual composition of the liquid phase at any instant of the drying operation can be estimated. As the mass of PEG is determined after each experiment the corresponding composition of the liquid phase can be calculated.

RESULTS AND DISCUSSION

At 40°C the DSC curves show a drastic change when the PEG content (type: PEG 4000) exceeds 80 weight percent. At 50 and 60°C the DSC curves are more difficult to interpret, presumably due to the fact that the PEG is not precipitated as a solid. Possibly a two-phase liquid is formed where the PEG-rich phase has a content of approximately 87 weight percent of PEG at 50°C and the solvent has an ethanol/water weight ratio of 0.7/0.3. From these data Figure 2 is plotted. The solubility limit at 50°C extrapolates fairly well to the data given in (1) for an aqueous solution. At 40°C the extrapolation of the PEG-ethanol data is not in agreement with that obtained for aqueous solutions (1). This seems to indicate that at 40°C the supersaturation in PEG-ethanol solutions before precipitation occurs is higher than at 50°C.

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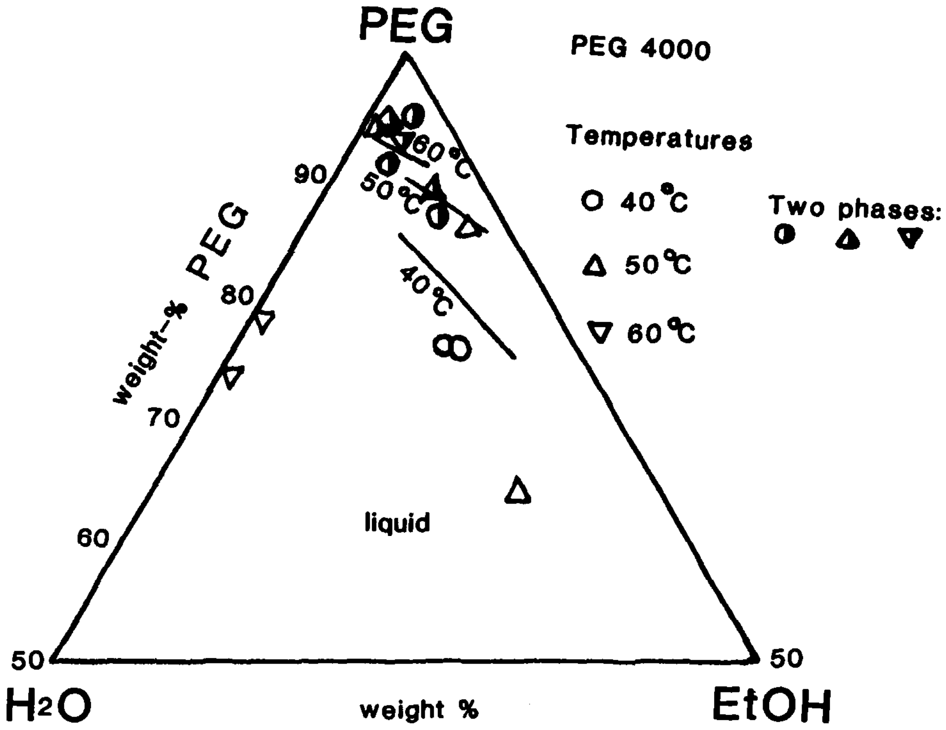

Figure 2. Experimentally determined solubility limits of PEG 4000 in ethanol - water solutions in the temperature range 40 to 60°C

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