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SHORT COMMUNICATION

A THERMOANALYTIC METHOD FOR THE STUDY OF THE SOLUBILITY OF POLYETHYLENE GLYCOLS IN ETHANOL AND WATER

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A simultaneous TG-DSC method has been used for the determination of the solubility of polyethylene glycols in ethanol-water solutions. As a comparison precipitation was studied in test tubes at cooling to 15 or 20°C as well as dissolution at heating to temperatures between 25 and 60°C. The results are shown in ternary diagrams for polyethylene glycols with molecular weights from 1500 to 35000.

Cemented carbide achieved its technical breakthrough during the 1920s when it was discovered that the combination of tungsten carbide and cobalt produced a highly favourable combination of high wear resistance and high toughness. Through the addition of other hard constituents – primarily titanium and tantalum carbides – cemented carbide has gained increasing industrial application.

Cemented carbide is made by powder metallurgy methods which makes it possible to vary the composition and microstructure. Its properties can be carefully tailored for different applications by varying the relative amount of the components, carbide grain size, sintering technique etc. The appropriate raw materials are weighed out and thoroughly mixed together by wet milling, normally in ethanol or water.

After milling the cemented carbide is spray dried and the milling liquid is evaporated. The dry powder is then pressed into appropriate shapes i.e. inserts for metal cutting and rock drilling tools, wear parts, forming tools etc.

Lubricant and its solubility

In order to facilitate the pressing and to increase the strength of the compacted blank a lubricant is added to the powder before the wet milling.

Among the lubricants used polyethylene glycol (PEG) with molecular weights ranging from 1500 to 35000 may be mentioned [1, 2]. It is im-

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portant to know the solubility of different types of PEGs in ethanol-water solutions in order to be able to predict the precipitation of the lubricant and thus also the mechanism of the drying of the droplets.

Technical solubility

From the technical point of view the macroscopically homogeneous solution is most important even if it is not a completely molecular-dispersed solution [3]. It is evident that such a "technical solubility" cannot be defined by a sharp solubility limit due to high viscosity of the solution and supersaturation. However, the technical solubility can be estimated from the onset of the release of the solution enthalpy, if and when precipitation of solid phase occurs.

Experimental

A simultaneous technique, viz. the combination of 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 experiments were made in a Mettler TA 2000C Thermoanalyzer with the sensitivities: TG 100 mg and DSC 50 μV f. s. d. Heating rate: 4 deg/min. Deoxidized and dried nitrogen was used at a flow rate of 50 ml (NTP) per minute.

When an ethanol-water mixture is evaporated a continuous increase in the heat of vaporization is noted until all liquid has disappeared [4]. On the other hand, when a solution of PEG in ethanol-water is evaporated there is a sudden change from the endothermic heat of vaporization to an exothermic heat of solution when the solubility limit has been passed.

The instantaneous ratio of ethanol to water can be estimated from the heat of vaporization, provided that no interaction with the PEG occurs. Calibration curves have been calculated from the evaporation experiments with pure ethanol-water solutions.

Bench-scale experiments

Two series of experiments were made:

(i) Cooling – precipitation experiments at 15 and 20°
(ii) Heating – dissolution experiments from 25 to 60°

In the first series, clear solutions were prepared at approx. 30°. After soaking at 15 or 20° some PEG was precipitated until the solubility limit was reached. The solvent was evaporated after filtering and the solubility was calculated from the mass of the residues.

In the second series, a number of closed test tubes containing saturated solutions of PEG 4000 and different amounts of solid PEG 4000 were heated to and kept at a chosen temperature up to 60°. The occurrence of test tubes with clear solutions were noted and indicated that the two-phase systems had been transformed to single-phase solutions.

Results

The results are summarized in Figs 1–3. It is evident that somewhat varying results are obtained which can be explained by the facts that precipitation from a supersaturated solution is not complete and further that a complete dissolution from solid PEG needs a long time and a vigorous stirring. The difference is especially evident in the thermoanalytical experiments in which obviously a high degree of oversaturation may occur.

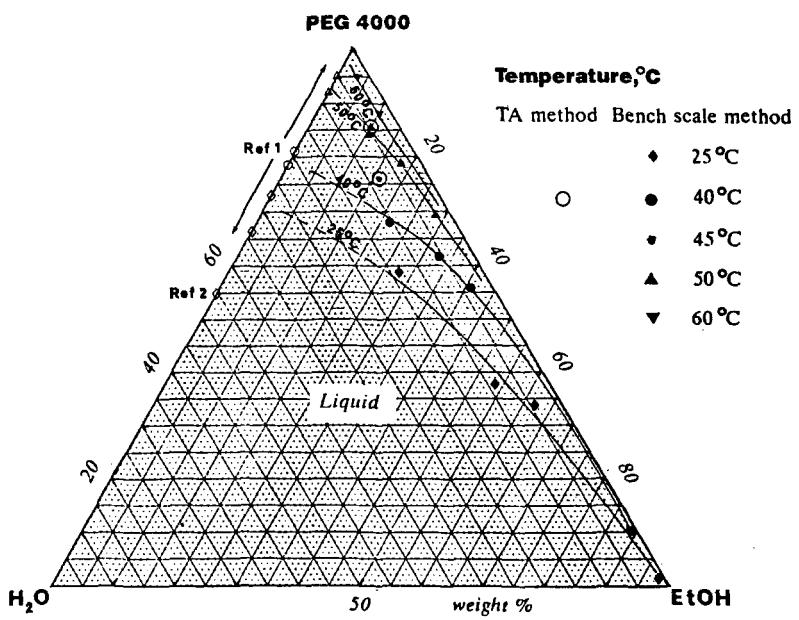

Fig. 1 Solubility limits of PEG 4000 in ethanol-water mixtures. Solid dots are from bench-scale experiments, large open circles are from thermoanalytical experiments

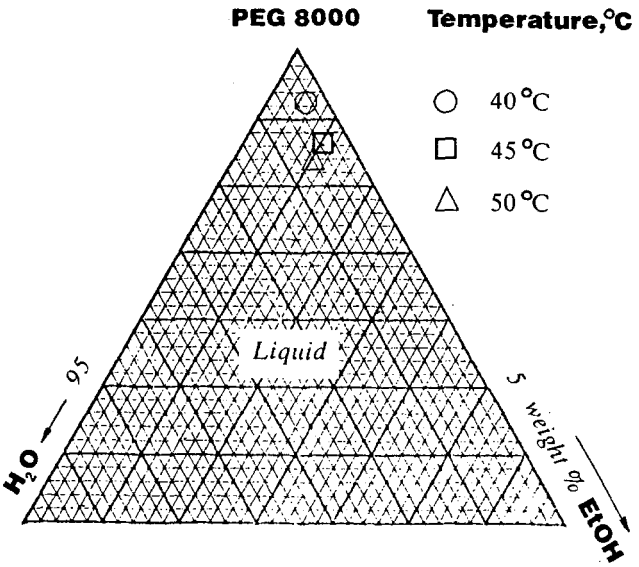

Fig. 2 Solubility limits of PEG 8000 in ethanol-water mixtures. Results from thermoanalytical experiments

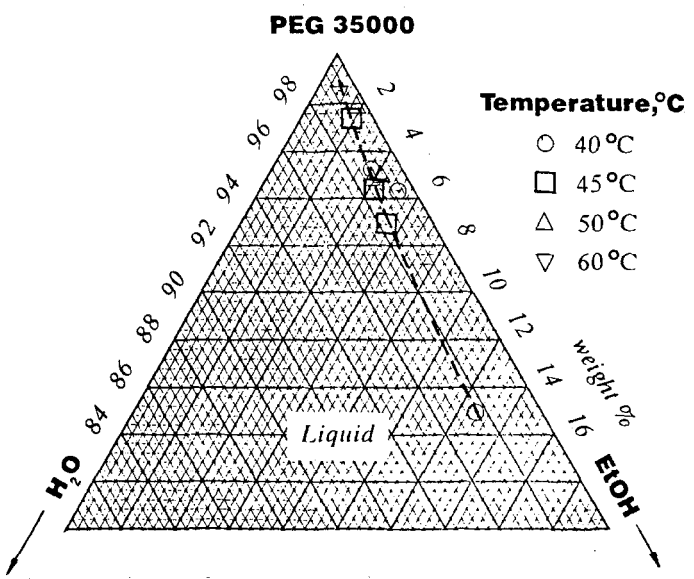

Fig. 3 Solubility limits of PEG 35000 in ethanol-water mixtures. Results from thermoanalytical experiments

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Zusammenfassung – Mittels einem simultanen TG-DSC Verfahren wurde die Löslichkeit von Polyäthylenglykolen in Äthanol-Wasser-Gemischen untersucht. Zum Vergleich wurde die Präzipitation in Reagenzgläsern beim Abkühlen auf 15 order 20°C und auch das Auflösen beim Erhitzen auf 25 und 60°C untersucht. Die Ergebnisse sind für Polyäthylenglykole mit einer Molekülmasse von 1500 bis 35000 in Dreieckphasendiagrammen dargestellt.

Резюме – Совмещенный метод ТГ и ДСК был использован для определения растворимости полиэтиленгликолей в водно-спиртовых смесях. Для сравнения было изучено осаждение этих растворов в испытательных трубках при охлаждении до 15 или 20°, наряду с растворением полиэтиленгликолей при нагревании до температуры 25–60°. Результаты представлены в виде тройных диаграмм для полиэтиленгликолей с молекулярным весом от 1500 до 35000.