DETERMINATION OF SOLUBILITIES OF ENERGETIC MATERIALS

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Abstract

Five methods to analyse liquid samples regarding to the concentration were compared to determine the solubility curve of RDX in different solvents. Spectroscopy and density measurements provided nearly the same values for all investigated systems. Refractometry and the gravimetric analysis differed in some cases up to 20 % from the other methods. These differences can be explained by an evaporation of solvent during analysis (e.g. tetrahydrofuran) or on the other hand by difficulties during drying the samples due to solvent inclusions in the crystals (low vapour pressure of the solvent like propylene carbonate). The HPLC analysis needs a very high dilution of the samples (otherwise the detector is blind) which can lead to falsification of the results. In conclusion, the best way of measuring the solubility of these systems is the density measurement.

Further experiments with other energetic materials will be carried out to prepare a data pool. With this pool crystallization processes can be designed and the quality of the product can be controlled and improved.

1 Introduction

To control a crystallization process an extensive knowledge about the system (solute and solvent) is necessary. Especially the solubility curve has to be investigated. The type of solubility curve decides about the crystallization process which can be used. If the solubility is more or less independent of the temperature, i.e. the solubility curve is a horizontal line, it is not possible to start the nucleation by cooling down the solution. The system sodium chloride/water shows this type of solubility behaviour therefore sodium chloride is crystallized by evaporation crystallization instead of cooling crystallization.

Also the metastable zone width is an important parameter to analyze the specifications of the products obtained from the industrial crystallization processes, such as product crystal size, crystal size distribution and crystal shape by its contribution to nucleation and crystal growth. The metastable zone width results from the specific characteristics of nucleation in a supersaturated solution of soluble substances. It can be considered as a characteristic property of crystallization for each specific system.

2 Methods and materials

2.1 Materials

Cyclotrimethylene trinitramine (RDX, $C_3H_6N_6O_6$) and cyclotetramethylene tetranitramine (HMX, $C_4H_8N_8O_8$) are energetic materials which are common used in **p**lastic **b**onded e**x**plosives (PBX). In contrast to RDX, HMX crystallizes in four different polymorphic forms. 3-Nitro-1,2,4-triazol-5-one (NTO, $C_2H_2N_4O_3$) is more attractive than RDX, HMX or 2,4,6-trinitrotoluene (TNT) in terms of its insensitivity and stability. The raw RDX and HMX were synthesised and supplied by Dyno Industrier, Norway (purity: 98 %), the NTO by Dynamit Nobel, Germany (purity: 95 %). Aluminium potassium sulphate ($KAl(SO_4)_2$), Merck, Germany, purity: 99 %) was investigated as a reverence material. The used solvents were bought by Merck, Germany with a purity larger than 99 %.

2.2 Experimental procedure

The experiments were carried out in a 50 ml temperature controlled double jacketed vessel. After introducing into the vessel the appropriate solvent and an excess of solid, the vessel was sealed and the slurry was stirred with a blade agitator for one hour at constant temperature. Afterwards the solid was allowed to settle for one hour and liquid samples were collected using a syringe. The samples were analyzed by the different methods at 20 °C so that the samples had to be diluted with pure solvent to avoid precipitation of solid material if the equilibrium temperature was higher than 20 °C. To test when equilibrium is reached we analysed solutions at different times between 10 minutes and 5 hours. We saw that the concentration did not increase if the stirring time was longer than 30 minutes.

2.3 Methods of analysis

The samples were analysed by a gravimetric, chromatographic and spectroscopic method, as well as density measurement and refractometry. For the gravimetric method few millilitres of the solution was dried and the solubility was calculated from the difference in weight between the liquid and the dried samples. The measurement of the refractive index was carried out in a temperature controlled Abbe refractometer at 20 °C. The measuring range is between 1.3 and 1.7 with a scaling of 0.001. The accuracy is specified to 0.0004. The density was measured by the oscillating u-tube method (DMA 4500, Paar) at 20 °C. The measuring range is between 0 and 3 g/cm^3 and the accuracy is 5*10^{-5} g/cm^3. The spectroscopic analysis was carried out in two different spectrometers (Nexus and Magma IR-750, Nicolet Ltd.) by the ATR (Attenuated Total Reflectance) and absorption method in the infra-red spectral region. The data were evaluated according to the PLS (Partial Least Square Regression) method without correction (Otto 1997). This evaluation takes into account five different spectral bands. The lowest solute concentration which can be measured with sufficient accuracy is 2 wt.-% if the absorption method is used and 0.5 wt.-% with the ATR method. In our experiments the results of both methods correspond very good. The HPLC (High Performance Liquid Chromatography) analysis was performed using a HP Series 1100 instrument with a diode array detector and a Nova-Pak C18 (Waters) column (mobile phase: water/acetonitrile 70/30). RDX was detected at its absorption maximum of 234 nm. This method has a high precision but the detector was hypersensitive due to the high concentration of the solute so that a strong dilution of the sample was necessary.

2.4 Measurement of the metastable zone width by an ultrasonic method

The ultrasonic velocity through a liquid media is a temperature dependent physical property. It depends on the density and the adiabatic compressibility of the medium. The in-situ measurement of the ultrasonic velocity and temperature can be used to characterise the metastable zone of the solution.

The different experimental solutions were prepared in a closed vessel (Volume: 750 ml) and stirred by a magnetic stirrer for one hour at a temperature of 5 °C above the saturation point to ensure the dissolution of all the solid phase. Then the solution is cooled down with a well known cooling rate. The temperature is adjusted to get a certain level of supersaturation. The ultrasonic velocity and temperature of the prepared solutions were measured using the model LiquiSonic Lab immersion sensor connected with a controller, developed by SensoTech GmbH, Magdeburg, Germany. The measuring principle is explained by Omar and Ulrich (1997). This system can measure the velocity of the ultrasonic wave through the liquid media with a precision of ± 0.01 m/s and reports the temperature with a precision of ± 0.01 °C. The sensor sends a very low frequency longitudinal ultrasonic waves (1.5 MHz) which has no cavitation effect in the solution. This gives a guarantee that no enhancement of nucleation will be achieved and the effect of the ultrasonic field on nucleation can be neglected (Mikonsaari et al., 2000).

3 Results

3.1 Solubility of RDX

The solubility of RDX was measured in N,N-dimethyl formamide (DMF), cyclohexanone, γ-butyrolactone, N-methyl pyrrolidone (NMP), tetrahydrofuran and propylene carbonate (PC). Figure 1 shows the solubility curves of RDX in DMF determined by the different analysis methods.

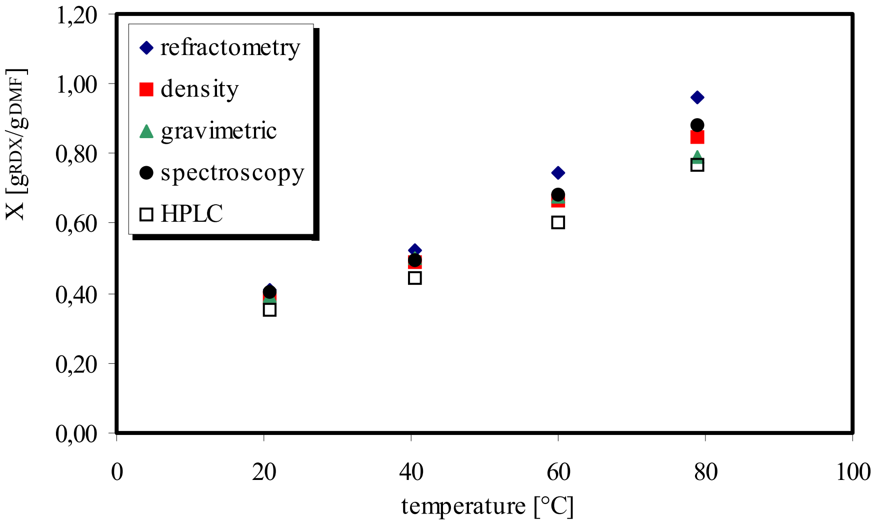

Fig. 1: Solubility curve of RDX in DMF: samples analysed with five different methods

It can be seen that the differences between the curves representing the different analysing methods are in the range between 15 % at lower temperature and 20 % at higher temperature. Over the whole investigated temperature range the refractometry provides the largest value whereas the HPLC analytic results in the lowest value. Determining the solubility by measuring the density gives a mean value of the five methods. The large concentration value obtained from the measurement of the refractive index can be explained by the fact that a few amount of solvent evaporates during the measurement. The vapour pressure of DMF and PC at 20 °C are 377 Pa and 3 Pa, respectively. Figure 2 presents the solubility of RDX in PC as a function of temperature.

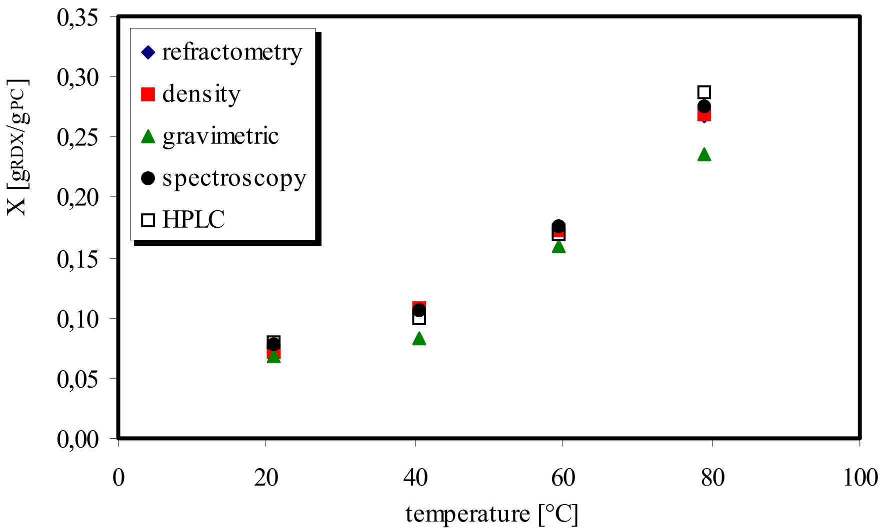

Fig. 2: Solubility curve of RDX in PC: samples analysed with five different methods

The values determined by the spectroscopy, refractometry, chromatography and density measurement are close together. The gravimetric method led to the lowest values and the difference is up to 12 %. During the measurement of the refractive index no evaporation occurs.

The experimental solubility data for each solvent were correlated with the temperature by means of a simple exponential equation:

$$X^{*} = \alpha \cdot \exp(\beta \cdot \vartheta) \qquad (1)$$

In table 1 the coefficients for the different solvents are summarised.

Table 1: Solubility data of RDX in different solvents

Solvent	Method	α [g_{RDX}/g_{solv}]	β [1/°C]
DMF	Density	0.2870	0.0137
PC	Density	0.0437	0.0230
NMP	Density	0.3508	0.0116
γ-butyrolactone	Density	0.0953	0.0196
tetrahydrofuran	Density	0.0203	0.0192
cyclohexanone	Density	0.0813	0.0148

The thermodynamic driving-force for crystallization is taken as the difference of the solute chemical potential in the bulk of solution and in equilibrium conditions. Therefore, from the experimental solubility data, the activity coefficients of RDX in solution were calculated using the equation:

$$\ln\left(\frac{1}{X^*}\right) = \ln\left(\frac{1}{\gamma}\right) + \left(\frac{\Delta H_f}{RT}\right)\cdot\left[1 - \frac{T}{T_m}\right] \qquad (2)$$

The value of ΔH_f (enthalpy of fusion) and T_m (melting temperature), 161 kJ/kg and 477,25 K, were obtained by DSC. Figure 3 presents the calculated activity coefficient of RDX in different solvents as a function of temperature.

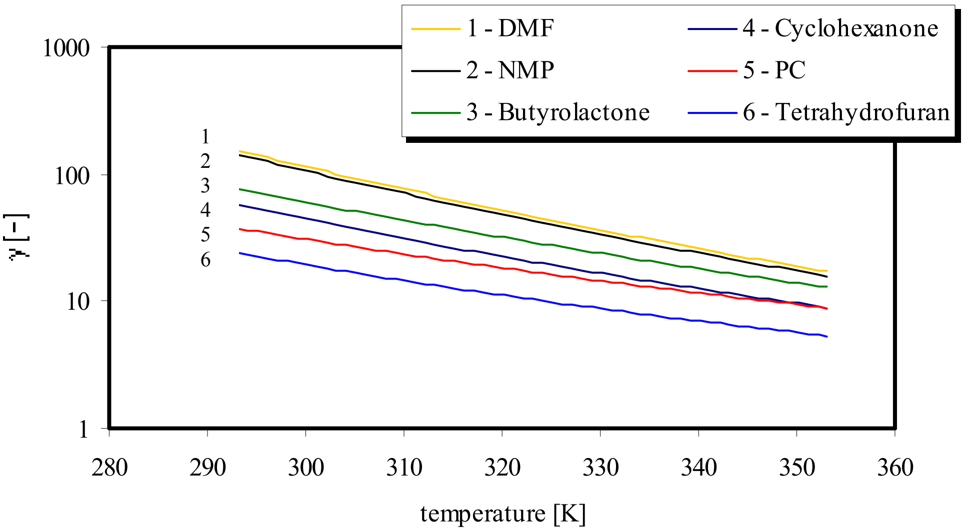

Fig. 3: Activity coefficient of the system RDX + solvent as a function of the temperature

The high activity coefficient points to a non-ideal system. The system RDX/DMF is the most non-ideal system whereas the system RDX/tetrahydrofuran shows the lowest interaction forces. The activity coefficient is larger one so that repelling forces between the solute and solvent molecules occur. With increasing the temperature these forces decrease.

The solubility of HMX was measured in the same solvents as the RDX solubility. During these measurements the formation of a complex between solvent and HMX was found if DMF and NMP was used (Haller et al.., 1983, Haller et al., 1985). Therefore, no solubility data were determined from these systems. Figure 4 presents the solubility of HMX in propylene carbonate, cyclohexanone and γ-butyrolactone. The solubility was determined by measuring of the density.

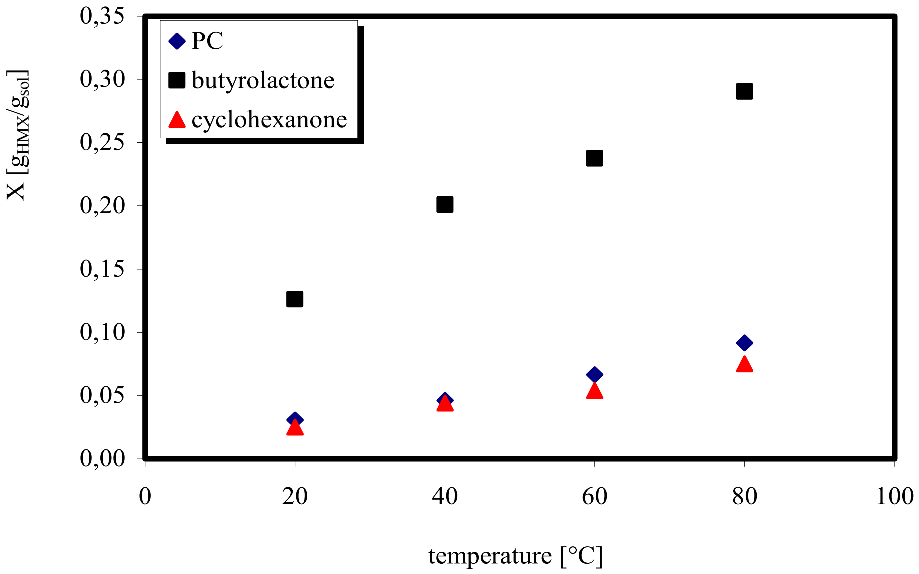

Fig. 4: Solubility curves of HMX in different solvents

NTO was solubilized in water, ethanol, DMF and NMP. The measurements with NMP and DMF were not possible due to the large increase of viscosity in the solution at larger concentrations of NTO. The solubility data of NTO in water and ethanol are summarized in table 2.

Table 2: Solubility data of NTO in water and ethanol

Solvent	Method	X [g_{NTO}/g_{solv}]			
		20 °C	40 °C	60 °C	80 °C
Water	Density	0.021	0.035	0.063	0.120
Ethanol	Density	0.331	0.644	1.143	

From the data it becomes clear that the solubility of NTO in ethanol is much higher than in water. A strong increase of solubility with the temperatures is seen in both solvents. That means that a large amount of material can be recrystallized in a batch crystallization process by cooling.

3.2 Metastable zone width

For the system potassium he measured ultrasonic velocity at three different cooling rates is shown in figure 5. The saturation temperature was in all three experiments 40 °C. The metastable zone can be read from the diagram as the temperature difference between the intersection of the cooling and heating curve (saturation temperature) and the temperature at which the velocity shows the sharp kink (nucleation point). This difference is 7.6 K, 9.3 K and 11.7 K at cooling rates of 0.3 K/min, 0.8 K/min and 1 K/min, respectively.

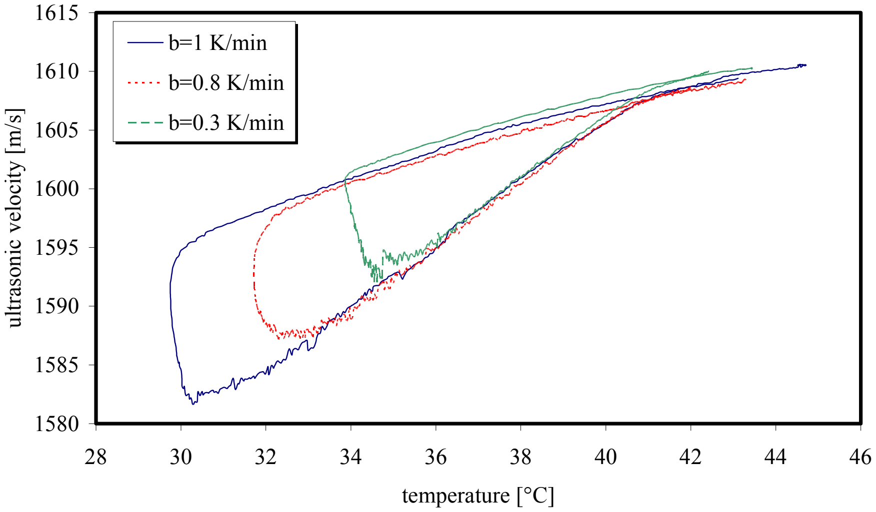

Fig. 5: Influence of the cooling rate on the metastable zone width for $KAl(SO_4)_2/H_2O$

This system shows a very large metastable zone width so that this measurement system seems to be suitable for detecting the metastable zone of this system. The same curve for the system RDX/DMF is described in figure 6.

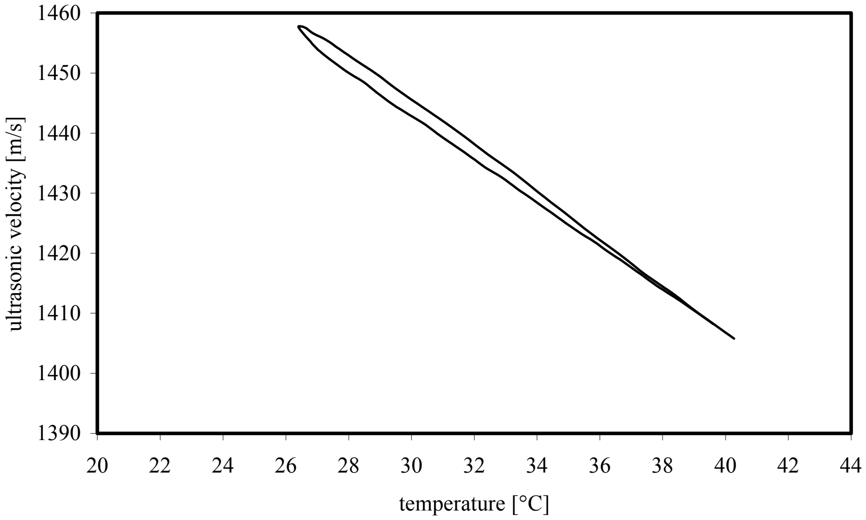

Fig. 6: Metastable zone of RDX/DMF at a cooling rate of 1 K/min

The cooling rate was 1 K/min and the saturation temperature was 40 °C. The determined temperature difference can be read to 13.5 K.

In contrast to the aluminium potassium sulphate/water system the difference between the cooling and heating curve is very small so that an interpretation of the temperature difference is not clear. Experiments with higher and lower solute concentrations (corresponding with higher and lower saturation temperatures) showed the same small region. At a saturation temperature of 20 °C a metastable zone width of 9.1 K and at 60 °C a metastable zone of 7.4 K was detected, respectively. The measurement of the metastable zone of nitramines in organic solvents by the ultrasonic method seems to be very difficult. The explanation for the different behaviour of such substances will be the motivation of further experiments.

4 References

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