Experimental determination and prediction of solid-liquid phase equilibria for binary (N-(2-acetoxyethyl)-p-nitroaniline (1) + N-ethyle-4-nitroaniline (2)) mixture

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Abstract. The nitrocellulose based materials are degraded in a natural way during their storage; the processes of degradation are accelerated when the temperature or the humidity increases. To prevent this decomposition, these materials include in their composition stabilising agents which retain the nitro groups and avoid the auto-catalytic degradation of nitrocellulose. The aim of the present work is to improve our understanding of the basic mechanisms of the degradation of the nitrocellulose based materials and the way in which their stabilization evolves. Solid–liquid phase equilibrium for the binary system of (N-(2-acetoxyethyl)-p-nitroaniline (1) + N-ethyle-4-nitrooaniline (2)) is determined using DSC technique. The experimental results were correlated using Wilson and UNIQUAC models.

As results, the system studied presents a simple eutectic, where the components are not miscible in the solid phase. Important deviations between experimental and predicted values are observed in the case of ideal model. These deviations can be attributed to the complexity of our system and principally to the presence of intermolecular effects. The best description of SLE was given by the two parameters UNIQUAC.

1 Introduction

Of the methods of measuring SLE, it was shown that differential scanning calorimeter (DSC) is a rapid and sensitive technique, broadly used for the characterisation of any kind of phase change.

Following our systematic study of the thermodynamic properties of organic mixtures [1, 2], it seemed interesting to test the application of DSC to the determination of SLE of complex system including N-(2-acetoxyethyl)-p-nitroaniline and N-ethyle-4-nitrooaniline (2). These components are used as stabilizers of nitrocellulose. Although the behaviour of stabilizers has been the subject of numerous investigations, relatively little is known about the nature of the reactions in the energetic material containing a mixture of stabilizers. The thermodynamic properties and structural details of these mixtures are very scarce. So the study of their phase equilibria will be of great importance in the stability testing of nitrocellulose [3].

The experimental results were correlated using Wilson and UNIQUAC models.

2 Experimental

The chemical of N-ethyle-4-nitrooaniline (NENA) was supplied by Sigma-Aldrich with purity greater than 99%. It was used without further purification.

Their melting temperature and enthalpy of fusion was measured using DSC. The measured melting temperature for this pure compound is in satisfactory agreement with literature data. The N-(2-acetoxyethyl)-p-nitroaniline is synthesized and purified following the methods indicated in the work of Gibson [4]. Its purity was checked by DSC, UV-visible and chromatography analysis and evaluated to be greater than 98%.

The series of binary mixtures were prepared according to the following methodology [5]: an amount of each product was weighed using a high accurate balance ($\pm$ 0.2 mg), thus resulting and uncertainty $\pm$ 0.0002 over the molar fraction with a step of 0.05. The samples weighed were placed in a Pyrex cells and heated very slowly, the liquid obtained is homogenized with continuous agitation, and then cooled abruptly by using liquid nitrogen.

The measurements were carried out at constant heating rate of 2 K.min^{-1} under nitrogen atmosphere (20 ml.min^{-1}). Prior to the analysis, the DSC was calibrated with indium. The processing and data acquisition of enthalpies of fusion of the pure compounds and onsets of the solid-liquid equilibria temperatures were done with Pyris software. The uncertainties of the measurements are estimated to be $\pm$ 0.2 K for the temperature and $\pm$ 0.4 kJ$\cdot$mol^{-1} for the heat of fusion.

3 Results and discussion

A typical DSC curve obtained for N-(2-acetoxyethyl)-p-nitroaniline (1) + N-ethyle-4-nitrooaniline (2) mixture is shown in figure 1. In the case of the system studied, the components are not miscible in the solid phase and all diagrams present a simple eutectic. The experimental values of T_{eu} and x_{1eu} corresponding to the eutectic point of N-(2-acetoxyethyl)-p-nitroaniline (1) + N-ethyle-4-nitrooaniline (2) are T_{eu} = 350.31 K and x_{1eu}= 0.4481.

The activity coefficient γ_i of the component i, in the liquid phase can be calculated according to the following expression:

$$\ln x_i \gamma_i = -\frac{\Delta_{fus} H_i}{RT} \cdot \left(1 - \frac{T}{T_{fus,i}}\right) + \frac{\Delta C_{p,i}}{R}\left(\ln \frac{T}{T_{fus,i}} + \frac{T_{fus,i}}{T} - 1\right) - \frac{\Delta_{tr} H_i}{RT}\left(1 - \frac{T}{T_{tr,i}}\right) \quad (1)$$

where, $\Delta_{fus} H_i$, T_{fus},i , $\Delta C_{p,i}$, $\Delta_{tr} H_i$ and $T_{tr,i}$, are respectively the molar enthalpy of melting in $J \cdot mol^{-1}$, the melting temperature in Kelvin, the molar heat capacity change (assumed to be independent of T) during the melting process in $J \cdot K^{-1} \cdot mol^{-1}$, the enthalpy change corresponding to the transition in $J \cdot mol^{-1}$ and the transition temperature of the pure component i in Kelvin. Because of the lack of appropriate data representing, the related terms in equation (1) was neglected.

Deviations between experimental and predicted value are observed in the case of Wilson, UNIQUAC and ideal models. These deviations can be attributed to the complexity of our systems and principally to the presence of intermolecular effects, especially of the proximity effect. Better results are obtained with UNIQUAC model.
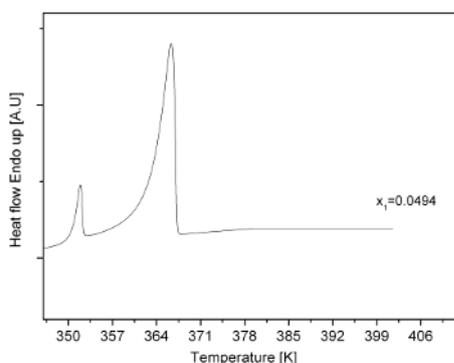
Figure 1. DSC thermogram at composition x_1= 0.0494 for N-(2-acetoxyethyl)-p-nitroaniline (1) + N-ethyle-4-nitrooaniline (2).

References

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