Journal of Thermal Analysis, Vol. 54 (1998) 323-332

THERMOCHEMISTRY OF THE BINARY SYSTEM NITROCELLULOSE–s-DIETHYLDIPHENYLUREA

A. Książczak and T. Książczak

Department of Chemistry, Warsaw University of Technology, Noakowskiego 3
00-664 Warsaw, Poland

Abstract

A method of gelation enthalpy determination of nitrocellulose (NC)+s-diethyldiphenylurea (Centralite 1, C1) binary system was elaborated using the change of Centralite 1 melting enthalpy in the mixture. The heats of C1 melting together with gelation and dissolution of NC fibres were determined by DSC calorimetric methods. A sharp maximum of the gelation enthalpy for C1 mole fraction $x_{\mathrm{C1}}^{\mathrm{max}}=0.555$ suggests that the complex is very stable and one partly nitrated anhydroglucose ring is interacting with about 1.25 C1 molecules. The gelatinization enthalpy maximum equals $\overline{H}_{\mathrm{max}}^{\mathrm{M}}=-4.59$ kJ mol^{-1}.

Keywords: gelation, interaction, melting

Introduction

Nitrocellulose is prepared by esterification of cellulose with nitric acid. Physical properties of NC depend on the number of highly polar groups $(\mathrm{OH})_x$ and polar $(\mathrm{ONO_2})_y$ attached to the anhydroglucose ring. The sum of the (x) and (y) parameters is equal to the number of OH groups attached to the anhydroglucose ring of cellulose. Highfield [1] has drawn attention to the fact that having strongly polar (OH) groups and less polar $(\mathrm{ONO_2})$ groups attached to a non-polar ring, nitrocellulose dissolves best either in liquid containing both polar and non-polar group, for instance acetone, esters, acetic acid or in a mixture of two liquids, one of which is polar, the other being non-polar or only weakly polar.

The dimensions of nitrocellulose crystal cell depend on the degree of nitration [2, 3]. Authors [2–5] have established on the basis of X-ray analysis that the addition of small amounts of solvent, e.g. acetone, cyclopentanone to nitrocellulose causes an increase in the distance between the nitrocellulose chains. This distance increases until one molecule of solvent is absorbed in proportion to every anhydroglucose unit after which further addition of solvent does not lead to any further increase in the distance between the two adjacent macromolecules. Finally the fibrous structure disappears completely when one molecule of solvent to one $(\mathrm{ONO_2})$ group – equivalent is added. Before dissolution the polymer

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

undergoes swelling. The swollen nitrocellulose phase can be regarded as a solution of a solvent in the solid phase.

The nature of the interactions between nitrocellulose and different solvents and gelatinizers was investigated by different optical methods. Infrared spectroscopy indicates the existence H bonds in solutions, film and suspension [6]. In the case of nitrocellulose–acetone the most certain mole ratio of the formed adduct is 1:1. The interaction between partly esterified cellulose nitrate and camphor is similar; the molar ratio that is close to 1:1 is a result of one molecule of the solvent interacting three ONO_2 groups [6, 7]. In the case of acetone at this expected value the chains acquire some mobility. In the system of nitrocellulose+s-diethyldiphenylurea (commercial name–Centralite 1, C1) the molar ratio of 1:1 is not found by X-ray investigations, owing to the bulky gelatinizers which can not easily enter the NC lattice [6]. Nitrocellulose forms some aggregates with solvents resulting in an exothermic effect. Heat is developed by the following processes that occurs consecutively wetting of the nitrocellulose fibres, formations of the solvate, swelling and dissolution. These solvents which evolve the greatest heat of wetting and solvation are characterised by a greater ability of swelling and dissolution of nitrocellulose. Centralite 1 (abbreviation–C1) used in NC in small quantities (ca 1%) acts only as a stabiliser, while larger quantities are used when it is required to act also as a gelatinizer.

The aim of this paper is to determine selected thermochemical properties of binary system nitrocellulose (13.2% N)+s-diethyldiphenylurea and the structure of the formed mixture. This goal has been achieved by measuring of C1 melting enthalpy for different compositions.

Experimental

Nitrocellulose containing 13.2% nitrogen was dried over P_2O_5 under vacuum. The average number of nitrated hydroxyl groups in one anhydroglucose unit was 2.65 (degree of substitution). Molecular mass of anhydroglucose unit ('submole of nitrocellulose') is 281.56 g s-diethyldiphenylurea was crystallised from benzene several times. The purity of the sample determined by the cryometric method was 99.7 mol%. Melting enthalpy of C1 sample was ΔH_m=106.18 J g^{-1}.

The measurements were performed on a heat-flux DSC 605M UNIPAN calorimeter combined with an IBM-AT computer. Calorimetric measurements of the melting processes were carried out using hermetic aluminium pans. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene, and benzoic acid. The metals used were of purity higher than 99.999%, and the organic compounds were more than 99.95% pure. Temperature calibration was made using the melting temperature of the substances determined by cryometric analysis [8, 9].

Samples of nitrocellulose and s-diethyldiphenylurea were grounded separately. Appropriate amounts of these components were mixed and tableted under pressure of ca 3000 atms. C1 melting process was investigated during heating at a rate β=2 K min^{-1} from 300 to the same final temperature 380 K. After the measurement the sample was frozen by placing on the surface of ice. The thermal history of used samples was the same for consecutive measurements performed with the same sample. Samples of (NC+C1) mixture were sealed in hermetic pans under a reduced pressure of about 1.3 kPa [10].

Method background

It was assumed that the penetration of C1 into NC fibres starts at the beginning of the melting processes of C1 during DSC measurements. Endothermic peaks observed in the DSC curves are due to the melting of C1 and the molecular interaction between liquid C1 with NC chains. The contribution of C1 melting enthalpy per 1 g of the mixture can be predicted according to the relation:

$$\Delta H_{\mathrm{mC1}} = \Delta H^{0}_{\mathrm{mC1}} x_{\mathrm{wC1}} \qquad (1)$$

where $\Delta H^{0}_{\mathrm{mC1}}$ is the melting enthalpy per 1 g of pure C1, and x_{wC1} is the weight fraction of C1 in the investigated mixture. The enthalpy corresponding to the interaction of C1 molecules with NC chains is given by:

$$H^{\mathrm{M}} = \Delta H - \Delta H_{\mathrm{mC1}} \qquad (2)$$

where ΔH is the measured enthalpy for C1 melting processes and the gelatinization per 1 g of mixture. When it is assumed that C1 penetrates only amorphous zone of NC fibres Eq. (2) describes adequately mixing processes. For better discussion it is more convenient to express H^{M} per 1 mole of mixture of

$$\overline{H}^{\mathrm{M}} = H^{\mathrm{M}}\left[x_{\mathrm{C1}} M_{\mathrm{C1}} + (1 - x_{\mathrm{C1}}) M_{\mathrm{NC}}\right] \qquad (3)$$

where x_{C1} – mole fraction C1, M_{C1} – molecular mass of C1, M_{NC} – molecular mass of unit (submole nitrocellulose) which is a function of the average number (Y) of the groups attached to one anhydroglucose ring according to the formula: $(C_6H_7O_2)(OH)_{3-Y}(ONO_2)_Y$.

Results and discussion

DSC curves of pure naphthalene and binary mixture naphthalene+NC containing 80% of naphthalene are presented in Fig. 1. As predicted on the basis of Eq. (1) the contribution of naphthalene melting enthalpy in this mixture is consistent with the measured melting enthalpy with the accuracy of the measurement (about 1%). Melting enthalpy of the second melting processes is equal to the same enthalpy of the first measurement. The gelation enthalpy predicted with

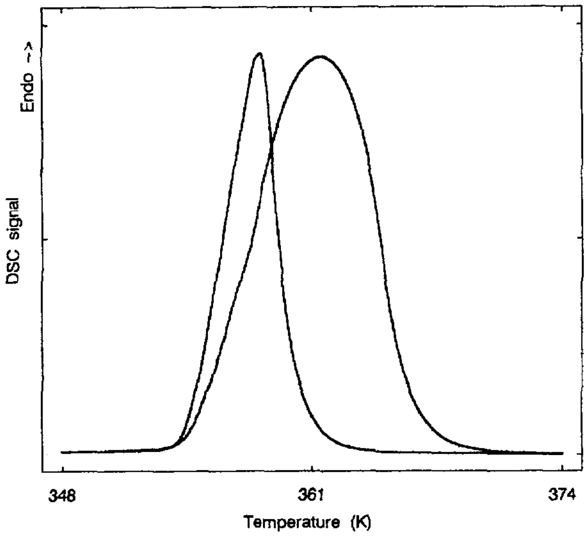

Fig. 1 DSC curves of the melting of pure naphthalene (narrow peak) and its mixture 20% with nitrocellulose (broad peak)

Eq. (2) is equal to zero with the accuracy of the measurements. In agreement with the expectations naphthalene is not a gelatinizer for NC fibres. Naphthalene molecules can not penetrate NC fibres. These results indicate that the proposed method of calculation of the heat of mixing penetration is correct. The change of the peak shapes for pure naphthalene and its mixture with NC results from heat conduction change of investigated samples.

Two consecutive melting processes using the same sample with weight fraction of C1 x_{wC1}= 0.936 are presented in Fig. 2. The shape of first part of the melting peak is due to the overlap of the melting and gelation processes. The measured melting enthalpy of C1 is lower than predicted from Eq. (1). This result indicates that the mixing is an exothermic process. The second melting peak is more regular and similar to the melting peak of pure C1. This observation suggests that the gelation is completed during the first melting process. The second DSC curve exhibits a small exothermic peak before the endothermic melting peak which is generated by the crystallisation of C1 existing in pores of the investigated sample. To confirm this interpretation the following experiments were performed. The second measurement was stopped after the exothermic peak and before the melting peak. The third DSC curve exhibits only the melting peak of C1. The next DSC curve is composed of the exothermic and endothermic peaks again. These parts of DSC curves before the melting peak are collected in Fig. 3.

The first and second DSC curves for a sample with weight fraction of C1 lower than 0.5 are illustrated in Fig. 4. The first DSC curve exhibits an endother-

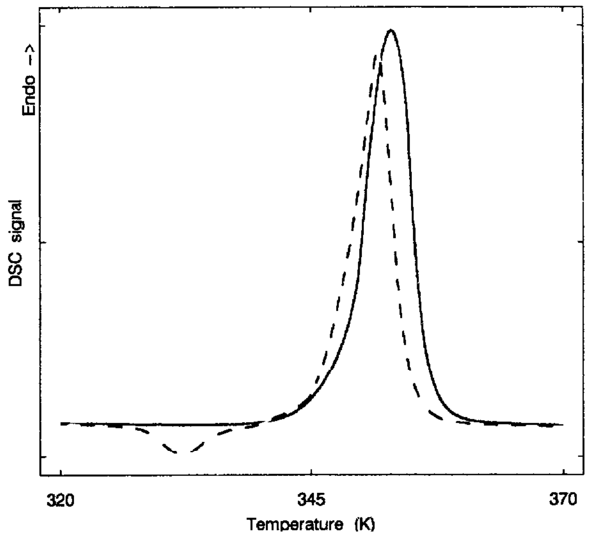

Fig. 2 DSC curves of (NC+C1) mixture performed with the same sample x_{wC1}=0.9363; first (—–) and second (- - -) scans

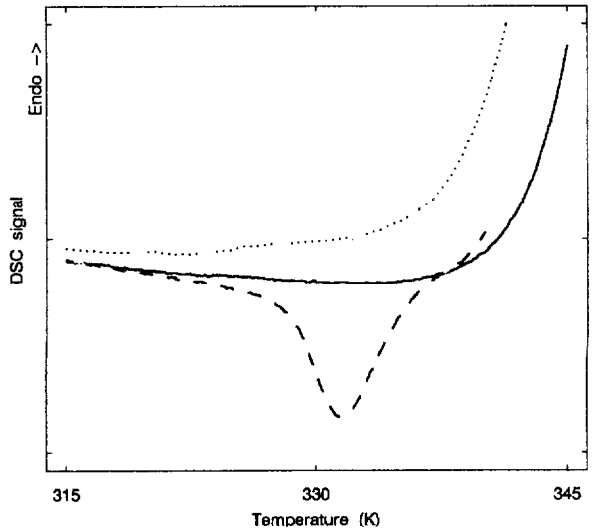

Fig. 3 Part of DSC curves before the C1 melting for the mixture x_{wC1}=0.9363 performed with the same sample; first (—–), second (- - -) and third (· · ·) scans

mic melting processes and partly overlapping exothermic gelation one. In this case the gelation time is longer than C1 melting. The lower rate of gelation results from the lower content of C1 in the investigated sample. The second DSC curves reveal no heat processes. This means that C1 molecules are in the liquid state despite the fact that sample was frozen by placing on the surface of solid

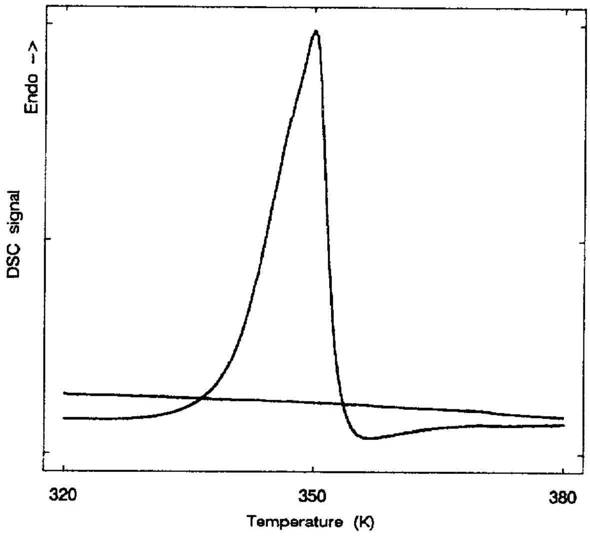

Fig. 4 DSC curves of (NC+C1) mixture, x_{wC1}=0.458 from two measurements performed with the same sample. In the first measurement melting peak appears but in second one it is without this transition

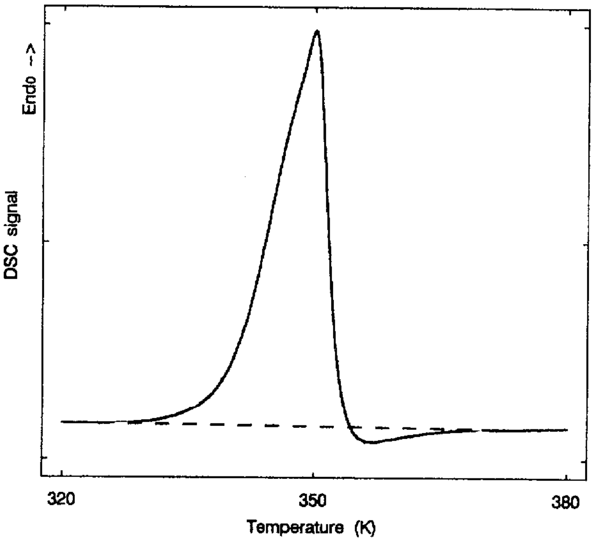

Fig. 5 Peak area determination for the melting and gelatinization processes. Baseline is presented by a dashed line

CO_2. The total heat is estimated from the area between the points indicating the beginning of C1 melting and the point of the gelation end. This method is graphically presented in Fig. 5.

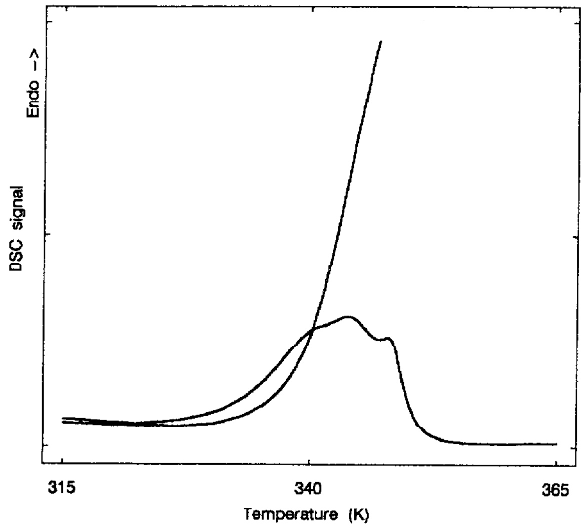

Fig. 6 DSC curves of mixture (NC+C1) with C1 weight fraction $x_{wC1}<0.5$. The first curve presents the change for partly melted sample (about 30%) and the second curve for typical measurement

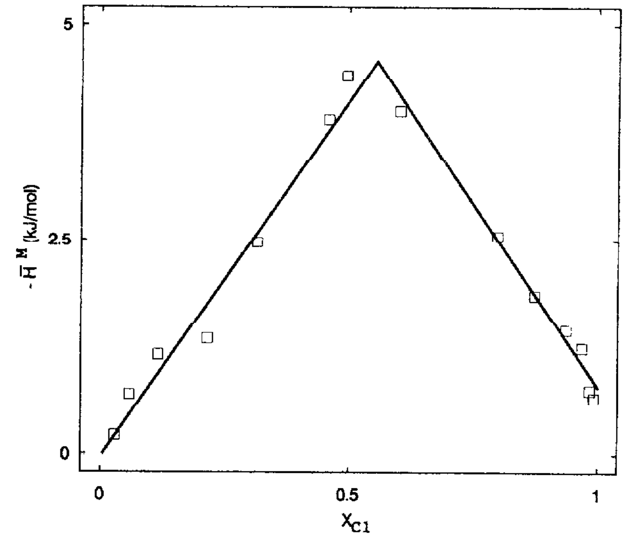

Fig. 7 Gelatinization enthalpy of binary system NC+C1 at the C1 melting temperature (346.15 K); points – experimental data

Table 1 Gelation enthalpy of the binary system nitrocellulose+s-diethyldiphenylurea at the melting temperature of s-diethyldiphenylurea

x_{wC1}	x_{C1}	$-\overline{H}^{\mathrm{M}}$/kJ mol^{-1}	ΔH/J g^{-1}
0.9920	0.9924	0.65	102.91
0.9841	0.9848	0.75	101.72
0.9682	0.9696	1.23	98.21
0.9363	0.9391	1.44	94.05
0.8730	0.8782	1.85	85.84
0.7976	0.8052	2.55	75.26
0.6010	0.6124	4.01	49.15
0.4943	0.5063	4.42	36.41
0.4577	0.4690	3.91	34.40
0.3143	0.3247	2.47	24.44
0.2150	0.2232	1.34	18.03
0.1155	0.1205	1.15	8.15
0.0578	0.0605	0.69	3.67
0.0289	0.0303	0.21	2.33

The sample was partly melted (about 30%) and next the second measurement was performed to prove that in discussed mixture the exothermic peak after C1 melting is caused by the gelation. The DSC curves of these measurements are presented in Fig. 6. Character of the second DSC curve proves that the gelation overlaps only with the first melting process. In addition the DSC curve shows a baseline without an additional peak after the melting.

Figures 3 and 4 show typical DSC curves for high and low content of C1 in mixture respectively. The gelation (mixing) enthalpies are predicted for a whole range of C1 concentrations on the basis of measured total enthalpy change (ΔH) and Eqs (1)–(3). The results are listed in Table 1 and graphically presented in Fig. 7.

The relation between the gelatinization enthalpy and the mole fraction is described by the broken line. Gelation enthalpy for mixtures containing low concentration of C1 is represented by the equation:

$$\overline{H}^{\mathrm{M}} = -0.040155 + 8.3408x_{\mathrm{C1}} \tag{4}$$

where x_{C1} is the C1 mole fraction. With good approximation the mixing enthalpy tends to zero ($\overline{H}^{\mathrm{M}} \rightarrow 0$) when $x_{\mathrm{C1}} \rightarrow 0$. For compositions rich in C1 the gelation enthalpy can be described by the equation:

$$\overline{H}^{\mathrm{M}} = 9.3314 - 8.5493x_{\mathrm{C1}} \tag{5}$$

In this case the linear extrapolation for the condition $x_{C1} \rightarrow 0$ does not tend to zero. This result proves that the latter relation for diluted solution of NC is more complicated. Probably it is caused by gelation and dissolution to form a typical liquid solution. Sharp change in the relation between the gelation (mixing) enthalpy and the mole fraction of C1 suggests that C1 molecules form strong complexes with NC chains. The maximum of gelation enthalpy equals $\overline{H}^{M}_{max}$=–4.59 kJ mol^{-1} for the mole fraction x^{max}_{C1}=0.555. This value is obtained by the intersection of the lines calculated from Eqs (4) and (5). In this case the intersection point determines composition of the strong complex. At this mole fraction (x^{max}_{C1}) one anhydroglucose ring is interacting with n=1.25 C1 molecules. In the investigated NC containing 13.2% N the average number of nitrated hydroxyl groups in one anhydroglucose unit was equal to 2.65. Assuming that one molecule of C1 is interacting with hydroxyl groups and one anhydroglucose unit the average number of C1 molecules connected with one anhydroglucose amounts to n=1.35. Good agreement between the average number (n) predicted from the calorimetric measurements (1.25) and calculated on the basis of the model mentioned above (1.35) proves that C1 molecules are connected to both anhydroglucose ring and free hydroxyl groups. Comparison of these parameters (n) indicates that only 71% of hydroxyl groups form specific interactions with C1 molecules.

Conclusions

The method of heat of NC gelation by measuring of C1 melting enthalpy is elaborated. It was assumed that the peak observed in the DSC curves are due to the melting of C1 and the molecular interaction between liquid C1 with NC chains. Sharp change in the relation between the gelation (mixing) enthalpy and C1 mole fraction suggest that C1 molecules form strong complexes with NC chains. At the maximum of gelation heat one anhydroglucose unit is connected with one C1 molecules and additionally 71% of hydroxyl group form specific interactions with molecules.

* * *

This work was partly supported by the State Committee for Scientific Research, grant No. 3 T09B 091 08.

References

1 A. Highfield, Trans. Faraday Soc., 22 (1926) 57.
2 M. Mathieu, Trans. Faraday Soc., 29 (1933) 122.
3 F. D. Miles, Cellulose Nitrate. Oliver and Boyd, London - Edinburgh 1955.
4 T. Petitaps and M. Mathieu, Trans. Faraday Soc., 42B (1946) 17.
5 T. Petitaps, J. Chim. Phys., 37 (1940) 6.

6 G. Cherubin, J. Chim. Phys., 57 (1960) 361.
7 K. Hess, T. Tomonari and C. Trogus, Z. Physik Chim., 7(B) (1930) 17, 16(B) (1932) 351.
8 A. Książczak and T. Książczak, Thermochim. Acta, 254 (1995) 19.
9 A. Książczak and I. Nagata, Thermochim. Acta, 254 (1995) 31.
10 A. Książczak and T. Książczak, J. Thermal Anal., 41 (1994) 1153.