

THERMODYNAMIC AND KINETIC BEHAVIOUR OF SALICYLSALICYLIC ACID

Calorimetric study

Hermínio P. Digo^{1*}, Susana S. Pinto¹ and Joaquim J. Moura Ramos²

¹Centro de Química Estrutural, Complexo I, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

²Centro de Química-Física Molecular, Complexo I, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

(Received February 17, 2004; in revised form March 8, 2004)

Abstract

The thermal behaviour of salicylsalicylic acid (CAS number 552-94-3) was studied by differential scanning calorimetry (DSC). The endothermic melting peak and the fingerprint of the glass transition were characterised at a heating rate of $10^{\circ}\text{C min}^{-1}$. The melting peak showed an onset at $T_{\text{on}} = 144^{\circ}\text{C}$ (417 K) and a maximum intensity at $T_{\text{max}} = 152^{\circ}\text{C}$ (425 K), while the onset of the glass transition signal was at $T_{\text{on}} = 6^{\circ}\text{C}$. The melting enthalpy was found to be $\Delta_{\text{m}}H = 28.9 \pm 0.3 \text{ kJ mol}^{-1}$, and the heat capacity jump at the glass transition was $\Delta C_{\text{p}} = 108.1 \pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$.

The study of the influence of the heating rate on the temperature location of the glass transition signal by DSC, allowed the determination of the activation energy at the glass transition temperature (245 kJ mol^{-1}), and the calculation of the fragility index of salicyl salicylate ($m = 45$).

Finally, the standard molar enthalpy of formation of crystalline monoclinic salicylsalicylic acid at $T = 298.15 \text{ K}$, was determined as $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{C}_{14}\text{H}_{10}\text{O}_5, \text{cr}) = - (837.6 \pm 3.3) \text{ kJ mol}^{-1}$, by combustion calorimetry.

Keywords: combustion calorimetry, DSC, enthalpy of formation, fragility, glass forming liquid, salsalate, supercooled liquids

Introduction

Salicyl salicylate or salicylsalicylic acid (Fig. 1) is a non-steroidal anti-inflammatory and anti-rheumatic drug with generic name salsalate, that is used to reduce pain and inflammation in conditions such as arthritis or muscle strain [1]. Due to very low solubility in the pH region of acidic gastric fluids media, salicyl salicylate minimises stomach erosion when compared with aspirin [2]. For this reason, salsalate can be used, even at relatively high dosage, with little secondary effects, which is particularly useful in long term therapy of chronic diseases [3, 4].

* Author for correspondence: E-mail: hdiogo@ist.utl.pt

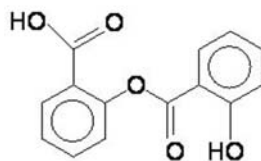


Fig. 1 Chemical structure of salicyl salicylate

In terms of solid state chemistry, salicyl salicylate is reported to be a substance that presents an enormous resistance to crystallisation [5]. In fact, it melts over the range 139–151°C (412–424 K, for a heating rate of 10 K min⁻¹), and it was observed that cooling the melt leads to a high viscosity supercooled liquid that can be moulded and stress-fractured without crystallizing. Furthermore, it was observed that crystallisation in salicyl salicylate could not be induced by any means, including crystal seeding, and that recrystallization could be achieved only by dissolution and reprecipitation [5]. This particular behaviour led us to carry on a calorimetric study of salicyl salicylate, in order to elucidate its thermal behaviour and to determine some of its macroscopic properties. Two calorimetric techniques were used: DSC to characterise the melting process and the glass transition, and Static-Bomb Combustion Calorimetry to determine the enthalpy of combustion. In the study of the melting process we determined the melting temperature range and the melting enthalpy. In the study of the glass transition the DSC fingerprint [6] was analysed in order to determine the glass transition temperature, T_g , and the heat capacity change, ΔC_p , at T_g . Furthermore, the activation enthalpy of structural relaxation at T_g , $E_a(T_g)$, and the fragility index, m , were obtained from the scanning rate dependency of T_g .

Experimental

General

Salicyl salicylate (CAS number 552-94-3) supplied by Acros (mass fraction >0.99), was used after recrystallisation from water. Fifty grams of the sample was dissolved in boiling distilled and deionised water, filtered into a thermostated double-wall beaker, and then cooled to 275 K at a rate of ca. $1.4 \cdot 10^{-3}$ K s⁻¹, by circulating water from a Julabo F25-EC temperature controller. The precipitated of salicyl salicylate was removed from the mother liquor by vacuum filtration and dried, in an oven for 3 h, at 363 K. Elemental analysis carried out with Fisons Instruments EA1108 apparatus led to the following results for the mass fractions of C and H in C₁₄H₁₀O₅: calcd. C, 0.6512; H, 0.0390; found: C, 0.6509; H, 0.0392 (average of two independent runs). The Fourier-transform infrared spectrum of the sample in KBr determined with a Jasco 430 spectrophotometer calibrated with polystyrene film, is similar to one published in the literature, and do not reveal the water band [7]. The ¹H NMR spectra carried out in CDCl₃ solution for salicylsalicylic acid, at room temperature, on a Varian 300 MHz spectrometer was as follows (chemical shifts, δ , relative to

tetramethylsilane) $\delta / 10^{-6} = 10.24$ (s, COOH, 1H), 8.12 (dd, CH, 1H), 8.05 (dd, CH, 1H), 7.66 (m, CH, 1H), 7.51 (m, CH, 1H), 7.39 (m, CH, 1H), 7.25 (m, CH, 1H), 6.99 (m, CH, 1H), 6.92 (m, CH, 1H), which are in good agreement with the spectra reported in the literature [5, 7]. X-ray powder diffractometry (XRD) was carried out using a Rigaku Geigerflex diffractometer employing $\text{CuK}\alpha$ -radiation, over the range $5^\circ \leq 2\theta \leq 35^\circ$. The powder patterns were indexed as monoclinic, using Checkcell programme [8]. The space group was identified as Cc , with $a = 1307.9(9)$ pm, $b = 1296.4(8)$ pm, $c = 1554.2(6)$ pm, $\beta = 113.81^\circ$. These values are in excellent agreement with those obtained by single crystal X-ray diffraction experiments ($a = 1296.5(4)$ pm, $b = 1298.2(4)$ pm, $c = 1553.0(3)$ pm, $\beta = 114.039^\circ$) [5]. The indexation of the lines is shown in Table 1 where θ represents the diffraction angle and $\Delta 2\theta$ is the difference between the predicted and observed diffraction angle.

Table 1 Powder pattern indexation (space group Cc , with $a=1307.9(9)$ pm, $b=1296.4(8)$ pm, $c=1554.2(6)$ pm, $\beta=113.81^\circ$)

h	k	l	$2\theta/^\circ$	Int. rel./%	$\Delta 2\theta/^\circ$
-1	1	0	9.98	11	-0.074
1	1	3	13.29	100	-0.104
2	0	0	14.81	83	0.031
1	1	6	18.36	15	-0.073
-2	2	0	20.09	18	-0.091
-3	1	5	21.58	100	0.016
1	3	2	22.87	5	0.020
-2	2	9	23.37	43	-0.040
-2	0	12	23.87	4	-0.001
3	1	3	26.52	19	0.057
1	3	6	26.94	14	0.072
-1	3	9	27.16	60	0.031
-2	0	14	27.53	2	-0.013
0	4	2	27.85	19	-0.016
-3	3	7	29.74	3	0.021
0	0	14	29.98	4	0.021
-2	4	2	30.84	2	0.000
0	2	13	31.08	4	0.008

Combustion calorimetry

The combustion calorimetric experiments were performed using a static-bomb combustion calorimeter and an experimental technique previously described [9]. The energy equivalent of the calorimeter and its standard deviation, $\epsilon_0 = (18562.6 \pm 1.8) \text{ J K}^{-1}$, was previously determined from the combustion of benzoic acid (NIST, Standard Reference

Material, 39j) [10] whose standard massic energy of combustion under the certificate conditions was $-(26434 \pm 3) \text{ J g}^{-1}$. In a typical calorimetric experiment a pellet of salsalate was placed in a platinum crucible and weighed with an accuracy of $\pm 10^{-5} \text{ g}$ by aid a Mettler AT201 balance. The crucible was adjusted to the sample holder in the bomb head and a platinum wire, with a diameter of 0.05 mm (Johnson Matthey; mass fraction: 0.9995), was connected between the two electrodes. A cotton thread fuse, was weighed with an accuracy of $\pm 10^{-7} \text{ g}$ with a Sartorius 4504 Mp8-1 ultra-micro balance, and tied to the platinum wire. A volume of 1.0 cm^3 of distilled and deionised water from a Millipore system (conductivity, $\leq 0.1 \mu\text{S cm}^{-1}$) was added to the bomb body by using of a volumetric pipette. The stainless-steel bomb (Parr, model 1108) of 340 cm^3 internal volume was assembled and flushed twice by successively charging it with oxygen at a pressure of 1.01 MPa and venting the overpressure. After purging, the bomb was charged with oxygen (ArLiquide N45; mass fraction > 0.9995) at a pressure of 3.04 MPa and a few minutes were allowed for equilibration before closing the inlet valve. The bomb was transferred to the inside of the calorimeter proper, which was, subsequently, filled (on average) with 3751.99 g of distilled water and weighed to $\pm 10^{-2} \text{ g}$ using a Mettler PM6100 balance. The combustion of the sample was initiated by discharge of a 2990 μF capacitor from a potential of ca. 40 V through the platinum wire. Temperature measurements were carried out with a resolution better than $3 \cdot 10^{-5} \text{ K}$, by using a YSI 46047 thermistor of 6.0 K Ω nominal resistance at $T = 298.15 \text{ K}$, connected in a four-wire configuration to a Hewlett-Packard HP 34420A digital multimeter.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) measurements were performed with a 2920 MDSC system from TA Instruments Inc. Dry high purity He gas (ArLiquide; N55) at a flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ was purged through the sample, which was previously encapsulated in an aluminium pan and weighted ($\pm 10^{-7} \text{ g}$) with a Sartorius 4504 Mp8-1 ultra-micro balance. Cooling was accomplished with the liquid nitrogen cooling accessory (LNCA) which provides automatic and continuous programmed sample cooling down to -150°C .

The baseline was calibrated scanning the temperature domain of the experiments with an empty pan. The temperature calibration was performed taking the onset of the endothermic melting peak of several calibration standards: *n*-decane ($T_m = 246.49 \text{ K}$), *n*-octadecane ($T_m = 301.39 \text{ K}$), hexatriacontane ($T_m = 349.09 \text{ K}$), indium ($T_m = 429.75 \text{ K}$) and tin ($T_m = 505.08 \text{ K}$). The organic standards were high purity Fluka products, while the metal standards were supplied by TA Instruments Inc. The temperature calibration for the different heating rates was performed considering the heating rate dependence of the onset temperature of the melting peak of indium and benzoic acid. The enthalpy was also calibrated using indium (enthalpy of fusion: $\Delta_{\text{fus}}H = 28.71 \text{ J g}^{-1}$).

Results and discussion

No scientific papers are found in the literature reporting on the thermal behaviour of salicyl salicylate, and in particular on its phase behaviour. Similarly, important

thermodynamic properties such as the enthalpy of formation have not been determined. However, the values of the enthalpy of formation of chemically related compounds as phenyl benzoate and phenyl salicylate (salol) are reported in the literature [11]. In the following we will report the results obtained in a DSC study on the phase behaviour of salicylsalicylic acid, as well as the results of a combustion calorimetry study that allowed us to determine the enthalpy of combustion and to estimate the enthalpy of formation of this compound as a pure phase.

Combustion calorimetry

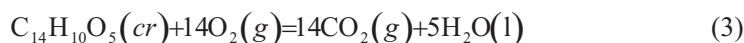
The standard atomic masses recommended by the IUPAC Commission in 2001 [12] were used in the calculation of all molar quantities. The auxiliary values needed for calculating the masses of monoclinic salicyl salicylate and the standard state corrections [13–15] in the combustion are as follows: $\rho = 1.431 \text{ g cm}^{-3}$ [5], $c_p = 1.05 \text{ J K}^{-1} \text{ g}^{-1}$ [16], and $-(\partial u/\partial p)_T = 0.12 \text{ J MPa}^{-1} \text{ g}^{-1}$ [17]. The corrections for formation of nitric acid were based on $-59.7 \text{ kJ mol}^{-1}$ for the molar internal energy of formation of $\text{HNO}_3(aq)$ of concentration 0.1 mol dm^{-3} from $5/4\text{O}_2(g)$, $1/2\text{N}_2(g)$, and $1/2\text{H}_2\text{O}(l)$ [18]. The following standard molar enthalpies of formation were also used in the calculations: $\Delta_f H_m^\circ(\text{CO}_2, g) = -(393.51 \pm 0.13) \text{ kJ mol}^{-1}$, and $\Delta_f H_m^\circ(\text{H}_2\text{O}, l) = -(285.83 \pm 0.04) \text{ kJ mol}^{-1}$ [19].

The results of the combustion calorimetric experiments are shown in Table 2. On average the ratio of the mass of CO_2 obtained in the analysis to that expected from the mass of sample weighed was (0.999 ± 0.001) . The values of ΔU_{IBP} , the internal energy change associated with the bomb process under isothermal conditions at $T = 298.15 \text{ K}$, and of $\Delta_c u^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5)$, the standard massic energy of combustion of salicylsalicylic acid, were calculated from Eqs (1) and (2), respectively (Table 2).

$$\Delta U_{\text{IBP}} = \left\{ \varepsilon_o + 4.184 \Delta m(\text{H}_2\text{O}) \right\} (T_i - T_f + \Delta T_c) + \varepsilon_i (T_i - 298.15) + \varepsilon_f (298.15 - T_f + \Delta T_c) + \Delta U_{\text{ign}} \quad (1)$$

$$\Delta_c u^\circ = \frac{1}{m} \left\{ \Delta U_{\text{IBP}} + \Delta U_\Sigma - \Delta U(\text{HNO}_3) - \Delta U(\text{fuse}) \right\} \quad (2)$$

The mean value of the standard massic energy of combustion of salicylsalicylic acid indicated in Table 2 is $\Delta_c u^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5) = -(23625.3 \pm 3.9) \text{ J g}^{-1}$, where the uncertainty quoted corresponds to the standard deviation of the mean. This value refer to the reaction:



and leads to $\Delta_c U_m^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5) = \Delta_c H_m^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5) = -(6100.7 \pm 2.7) \text{ kJ mol}^{-1}$, at $T = 298.15 \text{ K}$. The uncertainties quoted represent twice the over-all standard deviation of the mean, and include the contribution from the calibration with benzoic acid. From the values of $\Delta_c H_m^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5)$, $\Delta_f H_m^\circ(\text{CO}_2, g)$, and $\Delta_f H_m^\circ(\text{H}_2\text{O}, l)$ indicated above, the standard enthalpy of formation, $\Delta_f H_m^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5, cr) = -(837.6 \pm 3.3) \text{ kJ mol}^{-1}$ was derived for monoclinic salicylsalicylic acid. To our knowledge no value of the

Table 2 Results of the combustion experiments on monoclinic salicylsalicylic acid ($C_{14}H_{10}O_5$). In this Table $m(C_{14}H_{10}O_5)$ is the mass of salicylsalicylic acid; $m(\text{fuse})$ is the mass of the cotton thread fuse of empirical formula $CH_{1.887}O_{0.902}$ and massic energy of combustion $\Delta_c u(\text{fuse}) = -16565.9 \pm 8.6 \text{ J g}^{-1}$ [9]; $n(\text{HNO}_3)$ is the amount of substance of nitric acid formed in the bomb process; $\Delta m(\text{H}_2\text{O})$ represents the difference between the mass of water inside the calorimeter proper and the average mass of water used in the calibration experiments (3751.99 g); ϵ_i and ϵ_f are the energy equivalents of the bomb contents in the initial and final states of the bomb process, respectively; T_i and T_f represent the initial and final temperatures of the experiment; ΔT_c is the contribution to the observed temperature rise of the calorimeter proper due to the heat exchanged with the surroundings and the heat dissipated by the temperature sensor; ΔU_{ign} is the electrical energy supplied for ignition of the sample; ΔU_{IBP} is the internal energy change associated with the bomb process under isothermal conditions, at $T = 298.15 \text{ K}$; ΔU_{Σ} represents the sum of all corrections necessary to reduce ΔU_{IBP} to the standard state; $\Delta U(\text{HNO}_3)$ is the energy change associated with the formation of nitric acid; $\Delta U(\text{fuse})$ and $\Delta U(C_{14}H_{10}O_5)$, are the contributions of the cotton thread fuse and salicylsalicylic acid to the energy of the isothermal bomb process, respectively; and, finally, $(C_{14}H_{10}O_5)$ is the standard massic energy of combustion of salicylsalicylic acid.

$m(C_{14}H_{10}O_5)/\text{g}$	1.37396	1.22286	1.32628	0.98046	1.07791	1.07484
$m(\text{fuse})/\text{g}$	0.0019776	0.0019128	0.0015817	0.0017956	0.0018092	0.0021854
$n(\text{HNO}_3) \cdot 10^5/\text{mol}$	2.9	2.1	1.1	0.9	1.2	1.1
$\Delta m(\text{H}_2\text{O})/\text{g}$	+2.57	+0.02	-0.92	+0.47	+0.47	-0.03
$\epsilon^i/\text{J mol}^{-1}\text{K}^{-1}$	15.93	15.77	15.88	15.50	15.61	15.60
$\epsilon^f/\text{J mol}^{-1}\text{K}^{-1}$	17.07	16.78	16.99	16.32	16.51	16.50
T_i/K	298.0358	298.0179	298.0661	298.1156	298.0399	298.0497
T_f/K	299.8093	299.6125	299.7845	299.4116	299.4571	299.4608
$\Delta T_c \cdot 10^2/\text{K}$	2.41	3.63	2.88	4.58	4.36	4.21
$\Delta U_{\text{ign}}/\text{J}$	0.89	0.58	0.65	0.31	0.67	0.46
$-\Delta U_{\text{IBP}}/\text{J}$	32535.31	28950.54	26853.69	23223.27	25518.92	25434.31
$\Delta U_{\Sigma}/\text{J}$	29.36	25.66	28.17	19.96	22.22	22.15
$\Delta U(\text{HNO}_3)/\text{J}$	1.73	1.25	0.66	0.54	0.69	0.69
$-\Delta U(\text{fuse})/\text{J}$	32.76	31.69	26.20	29.75	29.97	36.20
$-\Delta U(C_{14}H_{10}O_5)/\text{J}$	32471.46	28891.94	31330.90	23173.02	25466.04	25375.27
$-\Delta U(C_{14}H_{10}O_5)/\text{Jg}^{-1}$	23633.48	23626.53	23623.14	23634.84	23625.39	23608.42

enthalpy of formation of salicyl salicylate, in the condensed phase, was reported in the literature. The obtained result enables us to make a comparison with the corresponding data published for two other molecules which share similar structural features: phenyl salicylate and phenyl benzoate. Thermochemical data are often discussed in terms of an energy/structure analysis. Due to the failure in obtaining a reliable experimental value for the enthalpy of sublimation of salicyl salicylate, and then to calculate a value for the enthalpy of formation in the gas phase, our analysis shall be restricted to the condensed phase. The structural difference between phenyl

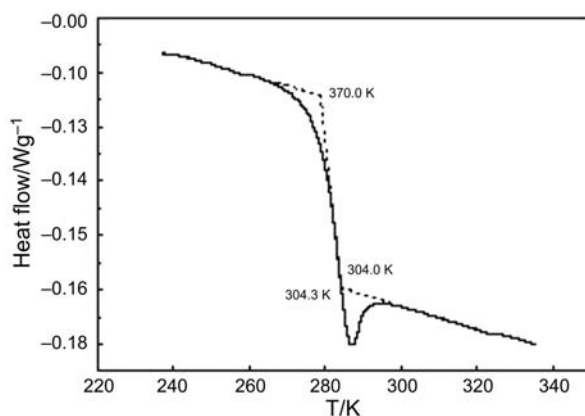


Fig. 2 DSC heating curve for salicyl salicylate obtained at a heating rate of $q = 10$ K min^{-1}

salicylate and phenyl benzoate is similar to that between benzoic acid and ortho-hydroxybenzoic acid. In both cases an intramolecular hydrogen bond is formed between the oxygen of the carboxyl group and the OH group connected to the adjacent carbon of the benzene ring. A value of 195 kJ mol^{-1} is obtained for the difference between the enthalpies of formation of phenyl salicylate ($-\Delta_f H_m^\circ(\text{C}_{13}\text{H}_{10}\text{O}_3, cr) = 436.6 \pm 4.6 \text{ kJ mol}^{-1}$) and phenyl benzoate ($-\Delta_f H_m^\circ(\text{C}_{13}\text{H}_{10}\text{O}_2, cr) = 241.6 \pm 2.1 \text{ kJ mol}^{-1}$)[11]. The corresponding value for the ortho-hydroxybenzoic acid/benzoic acid pair, calculated from the experimental values of enthalpy of formation, is $204.5 \text{ kJ mol}^{-1}$. A similar exercise could be done for the pair salicyl salicylate/phenyl salicylate. Here the structural peculiarity can be looked in two ways: a carboxylic group is added to a benzene ring forming a benzoic acid molecule; or a carboxylic group is connected to a phenol molecule, in the adjacent carbon of benzene ring, giving the ortho-hydroxybenzoic acid molecule. For the first case the difference, in terms of the enthalpy of formation in the crystalline phases, is $424.3 \text{ kJ mol}^{-1}$, and the corresponding difference for the ortho-hydroxybenzoic acid/phenol pair is $424.6 \text{ kJ mol}^{-1}$. A value of the same order (401 kJ mol^{-1}), but probably not strictly comparable, is found for the difference between the enthalpy of formation of salicyl salicylate obtained in this work (single phase – monoclinic) and the corresponding value reported in the literature for phenyl salicylate whose phase purity is not specified.

Differential scanning calorimetry

Our sample of salicyl salicylate was characterised by DSC using a heating rate of $10^\circ\text{C min}^{-1}$. In these conditions, the endothermic melting peak showed an onset at $T_{\text{on}} = 144^\circ\text{C}$ (417 K) and a maximum intensity at $T_{\text{max}} = 152^\circ\text{C}$ (425 K). The DSC signature of the glass transition is a sigmoidal change in the heat flux (Fig. 2), that arises

from a change in heat capacity, ΔC_p , when the sample is heated from the glassy state to the metastable supercooled liquid.

At the same heating rate conditions, the calorimetric glass transition temperature, considered as the onset temperature of the sigmoidal signal, was determined as $T_g = 5.7^\circ\text{C} = 278.85\text{ K}$ at 10 K min^{-1} .

On the other hand, and independently of the heating rate, the enthalpy of fusion was found to be $\Delta_{\text{fus}}H = 112.0 \pm 1.2\text{ J g}^{-1} = 28.9 \pm 0.3\text{ kJ mol}^{-1}$, and the heat capacity jump at the glass transition was obtained as $\Delta C_p = 0.410 \pm 0.004\text{ J K}^{-1}\text{ g}^{-1} = 108.1 \pm 0.1\text{ J K}^{-1}\text{ mol}^{-1}$. This high value of ΔC_p indicates that many degrees of freedom are released on heating above T_g . Indeed, values of ΔC_p of $23\text{ J K}^{-1}\text{ mol}^{-1}$ and $53\text{ J K}^{-1}\text{ mol}^{-1}$ are reported respectively for glycerol ($T_g = 185\text{ K}$) and toluene ($T_g = 113\text{ K}$) [20], while for polymeric systems we have $\Delta C_p = 10\text{ J K}^{-1}\text{ mol}^{-1}$ for polyethylene ($T_g = 140\text{ K}$) and $\Delta C_p = 36\text{ J K}^{-1}\text{ mol}^{-1}$ for poly(vinyl acetate) ($T_g = 302\text{ K}$) [21]. Note that values of the order of $\Delta C_p = 150\text{ J K}^{-1}\text{ mol}^{-1}$ for heat capacity jump at the glass transition have been recently reported for some ionic liquids [22].

The methods of thermal analysis allowing the determination of glass-former fragility have been recently reviewed [23]. One of them is based on the scanning rate

Table 3 Onset temperature, T_{on} , and midpoint temperature, T_{mid} , of the DSC signature of the glass transition of salicyl salicylate as a function of the experimental heating rate, q . The repeated values correspond to newly prepared sample

$q/\text{K s}^{-1}$	T_{on}/K	T_{mid}/K
0.06667	277.0	280.7
0.06667	277.2	281.6
0.08333	277.4	281.9
0.10000	278.1	282.5
0.11667	278.1	283.1
0.13333	278.5	283.1
0.16667	278.8	283.6
0.16667	278.6	283.8
0.16667	278.8	283.4
0.16667	278.7	283.9
0.16667	278.8	283.3
0.18333	278.7	283.8
0.20000	279.1	284.0
0.23333	279.6	284.6
0.25000	279.8	284.6
0.26667	280.0	285.1
0.30000	280.8	285.4
0.33333	280.9	285.7

Table 3 continued

$q/\text{K s}^{-1}$	T_{on}/K	T_{mid}/K
0.33333	281.0	285.8
0.33333	280.9	285.8
0.33333	280.9	285.8
0.36667	281.0	286.0
0.36667	281.1	286.0

dependency of T_g . In the present work we use the DSC technique in order to estimate the activation enthalpy of structural relaxation at T_g , $E_a(T_g)$, and the fragility index, m , of salicyl salicylate.

It is well known that the DSC results obtained on heating depend on the thermal treatments used to produce the glass (namely on the cooling rate), present the so-called overshoot peak in the heat capacity, and are influenced by ageing effects [24]. The overshoot peak, that arises from the structural relaxation, appears in Fig. 2 as an endothermic peak, in the right-hand side of the heat flow jump. Since the DSC results obtained from experiments carried out in the cooling mode do not present the overshoot peak, and are not influenced by ageing, it should be advisable to develop our analysis based on results obtained in the cooling mode. However, most of the DSC studies of the glass transition are carried out on heating, which is due to the difficulty of obtaining reliable curves under cooling conditions [24]. One of the reasons is probably that the accurate control of the temperature variation is most difficult on cooling than on heating. The calibration of the temperature-scale during cooling is also reported to be problematic. In this context, we carried out all the DSC

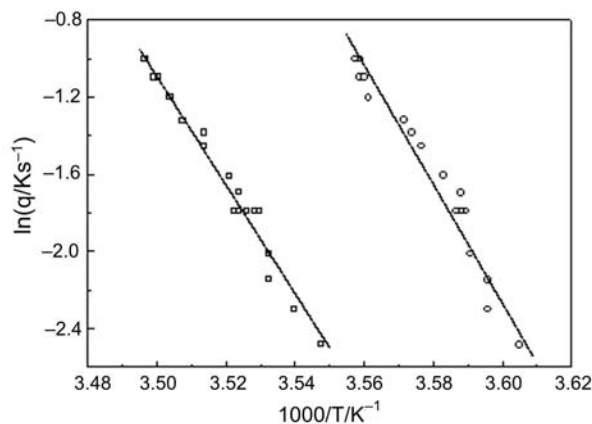


Fig. 3 'Arrhenius plot' for the onset temperature, T_{on} (open circles), and for the mid-point temperature, T_{mid} (open squares), of the glass transition of salicyl salicylate. The data was obtained with heating rates between 22 and 4 K min^{-1} (0.367 and 0.067 K s^{-1}) and is presented on Table III

experiments in the heating mode. Figure 2 shows the three characteristic temperatures in the DSC curve: the onset and endset temperatures, respectively T_{on} and T_{e} , and the midpoint of the heat capacity jump, T_{mid} . Since the presence of the overshoot peak in the DSC curve obtained on heating prevents the accurate determination of the endset temperature, in the following we will analyse the influence of the heating rate on the onset temperature, T_{on} , and on the midpoint temperature, T_{mid} , of the glass transition signal.

The fragility index, m , of a substance was defined as the slope of the $\log \tau(T)$ vs. T_{g}/T line at the glass transition temperature, i.e. at $T = T_{\text{g}}$ [25, 26],

$$m = \left[\frac{d \log_{10} \tau(T)}{d(T_{\text{g}}/T)} \right]_{T=T_{\text{g}}} \quad (4)$$

where τ is the structural relaxation time which slows down to ~ 100 s at T_{g} . Equation (4) can be expressed in terms of the apparent activation energy, E_{a} , as

$$m = \frac{1}{2.303} \left[\frac{E_{\text{a}}(T_{\text{g}})}{RT_{\text{g}}} \right] \quad (5)$$

Any experimental technique which allows the determination of the activation energy of a motional process from the rough experimental data is useful for obtaining the fragility index of a glass-forming system. One of these techniques is DSC. In fact, it was shown [27] that the dependence of the glass transition temperature, T_{g} , on the heating or cooling rate, $|q|$, of a conventional DSC experiment is given by

$$\frac{d \ln |q|}{d(1/T_{\text{g}})} = -\frac{E_{\text{a}}}{R} \quad (6)$$

where E_{a} is the activation energy for the relaxation times controlling the structural enthalpy relaxation. The value of E_{a} obtained from Eq. (6) can thus be used to calculate the fragility index of a glass forming system according to Eq. (5).

The results of our experiments on the influence of the heating rate on the onset temperature, T_{on} , and on the midpoint temperature, T_{mid} , of the glass transition signal are shown in Table 3. Figure 3 shows the representation of $\ln |q|$ as a function of $1/T$, for the data presented on Table 3, and it can be seen that the data points display a linear variation, and that the slope of this linear variation is similar for the onset temperature and for the midpoint temperature. From the linear regression analysis of the data in Table 3 relative to the onset temperature, we obtain activation energy of 256 kJ mol^{-1} (standard deviation of $\pm 11 \text{ kJ mol}^{-1}$, regression coefficient 0.98). The calculated fragility index is $m = 48$. Similar results are obtained if we consider the effect of the heating rate on the midpoint temperature of the glass transition signal: activation energy of 235 kJ mol^{-1} (standard deviation $\pm 8 \text{ kJ mol}^{-1}$, regression coefficient 0.99), fragility index $m = 44$. Note that in the calculation of the fragility index we consid-

ered that the glass transition temperature was $T_g = 278.65$ K, that of the onset of the glass transition signal obtained at a heating rate of 10 K min^{-1} . From these results we can conclude that salicyl salicylate is a relatively strong liquid with a fragility index comparable to that of glycerol ($m = 50$).

The fragility index of a glass forming liquid is a central parameter in glassy state physics that reflects the stability of the structure (short- and intermediate-range order) to thermal degradation [20, 26]. When heated across the glass transition, the structure tends to persist in the case of strong glasses. In contrast, in fragile systems, any traces of structure that is trapped below T_g rapidly disappear upon heating above T_g . In general there is a consistent trend towards larger heat capacity changes, ΔC_p , at T_g as the liquid behaviour tends to increased fragility [20]. Alcohols however are known as a notable exception since they exhibit a large heat capacity jump, yet fall in the middle of the strong-fragile spectrum. Salicyl salicylate seems to share with alcohols a similar anomalous behaviour: high heat capacity jump and low fragility. The proposed qualitative interpretation for this anomaly involves the potential energy hypersurface of a macroscopic system. As a consequence of their rigid structure, strong liquids have configurational constraints such that they have low density of potential energy minima. Fragile liquids, at the other extreme, show a proliferation of possible configurations (lack of rigid structure) so that they have a much higher density of potential energy minima. Salicyl salicylate is thought to have a fragilelike (high) density of local energy minima, but stronglike (large) energy barriers between the minima. A substance with such behaviour is said to be thermodynamically fragile but kinetically strong [26]. In the case of salicyl salicylate and alcohols, the kinetic strength is ascribed to the cost of breaking hydrogen bonds in order to sample different configurations. In this context it is instructive to compare the behaviour of salicyl salicylate with that of phenyl salicylate (salol). The only molecular difference between those two compounds is that, in the later, the carboxylic acid group is absent. This difference is however at the origin of a strongly different kinetic and thermal behaviour, which is expressed by the fact that salol is a much more fragile glass former ($m = 76$) when compared with salsalate.

Conclusions

Our combustion calorimetric study allowed the estimation of the standard enthalpy of formation of monoclinic salicylsalicylic acid: $\Delta_f H_m^\circ(\text{C}_{14}\text{H}_{10}\text{O}_5, cr) = -(837.6 \pm 3.3) \text{ kJ mol}^{-1}$. This value seems reasonable on the basis of a discussion in terms of an energy/structure analysis, comparing with other thermochemical data for molecules which share similar structural features.

The study by DSC confirmed the extremely strong resistance of this substance to crystallise: the liquid supercools without any difficulty, and it easily vitrifies on further cooling. This glass-forming system shows an anomalous behaviour characterised by a high heat capacity jump at the glass transition and a low fragility index. Otherwise stated, it appears as to be thermodynamically fragile but kinetically strong glass forming system.

Part of this work was supported by Fundação para a Ciência e a Tecnologia (Project POCTI/199/QUI/35406). A grant from Fundação para a Ciência e a Tecnologia is also gratefully acknowledged by S. S. Pinto.

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