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INFLUENCE OF EXPERIMENTAL VARIABLES ON CURVES IN DIFFERENTIAL SCANNING CALORIMETRY. PART III. EFFECTS ON PEAK HEIGHT, PEAK WIDTH, SHAPE INDEX AND BASELINE DISPLACEMENT

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ABSTRACT

The extent to which experimental variables may affect the results of quantitative DSC was investigated in factorial designs. The factors investigated concerned the apparatus, test substance, reference and atmosphere.

The following were used as test substances: adipic acid (melt without noticeable decomposition), naphazoline nitrate (melt with decomposition), potassium nitrate (solid—solid transition) and sodium citrate dihydrate (dehydration).

The apparatus used was a commercial heat-flux DSC equipment. This paper, the third of a series which reports our findings, describes our results on the peak parameters: peak height, peak width, shape index and baseline displacement. We conclude that these parameters can only be averaged with relatively large standard deviations. However, many significant effects could be shown. All variables investigated affected the results, usually in a non-systematic manner which differed with each test substance. It is therefore stated that DSC peaks should preferably not be described in terms of peak height, peak width, shape index and baseline displacement, if quantitative work is required.

INTRODUCTION

In this paper, the results are presented of factorial studies to investigate the main effects and possible interactions of experimental variables on some peak-related parameters in differential scanning calorimetry (DSC). This paper is the third of a series of four [1,2].

Peaks in DSC are sometimes described in terms of peak width, peak height, shape index and baseline displacement. The parameters peak width and peak

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height are used as defined by ICTA [3]. The estimation of shape index follows a suggestion of Kissinger [4]. The baseline displacement, being the difference between the extrapolated baselines before and after the peak, is measured at the line through the peak top vertical to the time axis. It is expected to occur if during a transition the specific heat and/or the mass of the sample changes.

EXPERIMENTAL

A description of the test substances, reference compounds, the apparatus, characterization of the DSC curves, calibration checks and the study design, is given in Part I of this series of papers [1].

RESULTS AND DISCUSSION

Mean values

The mean values for peak height, peak width, shape index and baseline displacement are given in Tables 1 and 2. It can be seen that they are very much dependent on the setting of the experimental variables. It is, therefore, not useful to present one overall mean value. The coefficients of variation vary from 3 to 23% (peak height), 4 to 18% (peak width) and 4 to 22% (shape index).

TABLE 1

Mean values of peak height and peak width per experiment

Compound	Experiment no.	Peak height (μV)			Peak width (K)		
		Mean	*s*	*v*	Mean	*s*	*v*
Adipic acid	1.3	315.33	9.67	29	15.93	0.72	27
	1.4	180.43	11.08	24	14.34	0.55	20
	1.5	217.82	7.29	17	12.88	1.71	17
Naphazoline nitrate	2.3	131.55	11.24	28	18.67	1.52	24
	2.4	62.24	8.06	24	13.41	1.53	28
	2.5	94.57	8.37	27	11.59	1.03	27
Potassium nitrate	3.3	70.44	4.41	28	14.75	1.62	24
	3.4	30.89	3.92	40	14.94	1.58	32
	3.5	46.00	2.67	17	10.21	0.96	17
Sodium citrate dihydrate	4.3	327.90	29.93	16	23.91	1.54	16
	4.4	112.85	26.35	24	21.65	1.90	28
	4.5	174.90	7.90	11	16.21	1.59	16

TABLE 2

Mean values of shape index and baseline displacement per experiment

Compound	Experiment no.	Shape index			Baseline displacement (μV)		
		Mean	*s*	*v*	Mean	*s*	*v*
Adipic acid	1.3	0.537	0.078	29	1.02	1.32	29
	1.4	0.740	0.162	28	1.93	0.43	20
	1.5	0.519	0.106	27	0.01	0.88	17
Naphazoline nitrate	2.3	0.996	0.147	14	−0.88	1.76	24
	2.4	0.671	0.028	20	1.21	0.97	48
	2.5	1.124	0.131	17	0.03	0.50	27
Potassium nitrate	3.3	1.426	0.264	28	−2.32	1.27	28
	3.4	1.792	0.282	40	−0.25	0.23	40
	3.5	1.271	0.150	27	−0.32	0.18	27
Sodium citrate dihydrate	4.3	0.922	0.146	16	1.70	2.32	16
	4.4	1.034	0.111	16	2.44	2.21	28
	4.5	0.787	0.116	16	0.35 *	0.65	16

* Without values for helium and without covers.

Effects of sample mass and heating rate

The parameters investigated are strongly dependent on both sample mass and heating rate. Increases in peak height, peak width and baseline displacement with sample mass were observed. For the solid—liquid transitions, the shape index decreases with sample mass and for the solid—solid transition and the dehydration there is no effect of sample mass on shape index. Peak height, peak width and shape index increase with heating rate in a non-linear manner. A square-root relationship between heating rate and peak height as suggested by Oswald and Wiedemann [5] could not be found.

Interesting effects of heating rate on the peak shape could be seen with potassium nitrate and sodium citrate dihydrate. With KNO$_3$, the peak had a very irregular shape if low heating rates ($\leq$0.04 K sec^{-1}) were used (see Fig. 1). This irregular shape could be due to the concurrent transformation of traces of the metastable phase III into phase I [6,7], but another possible explanation is the presence of thermal lags within the sample, due to which the particles in the sample transform at slightly different temperatures, which at low heating rates is manifested as an irregular peak shape.

The same effect of irregular peak shapes is seen with sodium citrate dihydrate at low heating rates. Here, the effect may also be due to concurrent evaporation and again condensing of the hydrate water.

The effect of the heating rate on baseline displacement depended upon the type of compound. For adipic acid and sodium citrate dihydrate no effect was seen; for naphazoline nitrate, the responses for high heating rates were negative; for KNO$_3$ a decrease with heating rate could be seen.

Fig. 1. KNO_3 peak shape at low heating rates.

Effects of particle size distribution

Peak height

For adipic acid, the influence of the particle size on peak height is inconsistent. In the non-diluted specimens the response of the material with complete spectrum is about 10% higher than in the sieved samples; in the diluted specimens the response of the samples consisting of fines is 10% lower than those of both the unfractionated material and the large particles. An interaction ($P = 0.01$) existed between sieve fractions and method of dilution: when the mixture was prepared by dissolution and recrystallization there was no difference in response between the different size fractions, but when the whirl-mixer- and the pestle-and-mortar-methods were used, the small particle fractions had a lower response than the other fractions. There seems to be no effect of comminuting on the peak height of adipic acid.

For naphazoline nitrate, the peak height responses for the fractions of the smaller particles (both diluted and undiluted) are lower (to an extent of about 30%). The reason for this may be the concurrent oxidation which should give broader and less steep peaks. In the diluted samples of this substance an interaction was seen between sieve fraction and diluting agent ($P = 0.01$), since in carborundum and air the peak height was greater for the small particle size than for the complete spectrum, whereas in aluminium oxide it was the same.

In the case of the solid—solid transition of KNO_3 a decrease in peak height (with an amount of 10—40%) was observed if the particle size was reduced (both by sieving and milling). In the diluted mixtures of KNO_3, however, the effect was reversed: the peak height decreased in the range small particles → complete spectrum → large particles.

For sodium citrate dihydrate a small increase (about 7%) in response ($P = 0.05$) was found if small particles instead of the complete spectrum were used. In the diluted samples there appeared to be no influence of particle size on peak height and also comminution did not show a large effect.

Peak width

Particle size distributions seem to have only a slight effect on the peak width. For adipic acid, the peak width generally decreases with increasing fineness of the particles. With naphazoline nitrate smaller particles gave an increase of approximately 30%. This effect did not occur in the diluted samples. In the case of KNO_3 and sodium citrate dihydrate there were no main effects of particle size. However, statistically significant interactions in which particle sizes play a role, were numerous.

Shape index

For undiluted samples of adipic acid with large particles, the shape index shows an increase of approximately 23% as compared to samples with complete size spectrum ("tailing" effect). Naphazoline nitrate shows a lower value for the shape index if fine particles instead of the complete size spectrum are used, the value in undiluted samples being 43% lower and in diluted samples 31% lower. This effect is concurrent with the noted decrease in peak height and must be attributed to more degradation in small particles. For KNO_3 the shape index is largest in the case of small particles. The peak height was then at its smallest. For undiluted samples of sodium citrate dihydrate with complete size spectrum the shape index is 29% higher than the values for small particles. In diluted samples no effect was seen.

Baseline displacement

For adipic acid there is an effect of particle size, which is related to weight losses (Table 3). The baseline displacement is smallest if the complete particle size spectrum is used, and largest for the large particles. The effect can also be seen, though less pronounced, in diluted samples. For naphazoline nitrate (Table 3), small particles are more subject to oxidation and therefore the sample with small particles has a positive value for the base-

TABLE 3

Effects of particle sizes on baseline displacements of adipic acid and naphazoline nitrate

Compound/size spectrum	Undiluted		Diluted	
	Baseline displacement (μV)	ΔG(%)	Baseline displacement (μV)	ΔG(%)
Adipic acid				
Small particles	1.07 **	−4.18	1.90 **	−3.99
Complete spectrum	0.01 **	−4.09	1.53 **	−3.96
Large particles	1.97 **	−4.27	2.36 **	−4.48
Naphazoline nitrate				
Small particles	2.77 **	0.00 *	1.84 **	−0.58 **
Complete spectrum	−2.43 **	0.51 *	1.00 **	−0.30 **
Large particles	−2.99 **	0.36 *	0.80 **	−0.48 **

* Significant differences between levels in the same experiment at $P = 0.05$.

** Significant differences between levels in the same experiment at $P = 0.01$.

line displacement. For the other compounds there is no effect of particle size on baseline displacement.

Effects of atmosphere

Peak height

For the solid—liquid transitions, helium gives a 30—45% decrease in peak height, apparently due to an increase in thermal conductivity. In vacuo, the peak height decreases with 10—15%, due to the high thermal resistance which diminishes the apparatus sensitivity by a decrease in heat transfer. For adipic acid there is a considerable decrease in response if holders without lids are used in vacuo. This effect is concurrent with a sharp increase in weight loss and a decrease in peak width and specific enthalpy. For naphazoline nitrate, which melts with oxidation, there is an increase in peak height in vacuo and in nitrogen. Here, an inert atmosphere thus increases peak height and makes the peak sharper. For naphazoline nitrate no significant difference was found between static air and flowing air, although it could have been possible that due to the inability of removal of evolved volatile decomposition products the reaction would have been retarded. For the same substance the value in the case of holders without lids is about 10% higher than the mean value. This effect is concurrent with an increase in specific enthalpy. For KNO_3, if holders without lids were used, a sharper peak was found, together with a decrease in sample weight and increase in peak area. For sodium citrate dihydrate there is no effect of sample holder although it must be said that the experiments with closed lids were not carried out: the tightly closed sample holders are not able to resist the high pressure which is generated by the evolution of water vapour.

Peak width

Helium atmosphere also decreases the peak width, this decrease being approximately 37% in the case of adipic acid and sodium citrate dihydrate, and even approximately 47% for naphazoline nitrate and KNO_3. For naphazoline nitrate, the peak width is increased in oxygen atmosphere and decreased in nitrogen atmosphere (as compared to air). It may therefore be concluded that the solid—liquid transition gives narrower peaks than the oxidation reaction.

Shape index

The influence of atmosphere on the shape indices of the various compounds is inconsistent. For adipic acid, the response in vacuo is higher than in other atmospheres. For naphazoline nitrate the response in helium is lower and in vacuo it is higher than the mean value for other atmospheres; if sample holders are used without covers, the response is lower. For KNO_3 the response in helium is lower again and if sample holders are used without covers, the response is lower. Also, the peak shape in helium is irregular. For sodium citrate dihydrate there is no effect of atmosphere on the shape index.

TABLE 4

Adipic acid: influence of atmospheres on baseline displacement (experiment 1.5)

	Baseline displacement (μV) mean value		ΔG in vacuo (%)	ΔH_s in vacuo (J g^{-1})
	All atmospheres	In vacuo		
Tightly closed	−0.39	−1.00	−3.11	264.42
Without lids	−0.19	−1.20	−99.73	107.93
Pierced lids	+0.61	+4.16	−99.88	247.78

Baseline displacement

With adipic acid, an effect ($P = 0.05$) of sample holders can be seen, which is shown in Table 4. It must be concluded that if no lids are used, sublimation is the prime reason for weight loss; if the lids are pierced, the evaporation of the molten compound is the predominant process. If adipic acid was placed in a sample cup without a lid in vacuo, the curve had a shape as shown in Fig. 2. The weight loss after the peak appeared to be 99.7%. It is therefore clear that the jump after the peak must be attributed to the completeness of evaporation of the sample. For naphazoline nitrate, the presence of oxygen atmosphere gave rise to a sharp increase in the baseline displacement (see Fig. 3) together with an increase in sample mass. An increase in the mass of the substance should give a negative value of the baseline displacement. Therefore it must be concluded that the specific heat of the oxidized material is lower than that of naphazoline nitrate itself.

Dilution

Dilution also has an effect on the peak parameters. Aluminium oxide, in particular, reduces peak height and peak width and generally enlarges the shape index, which may be due to its masking effect (by a decrease of the

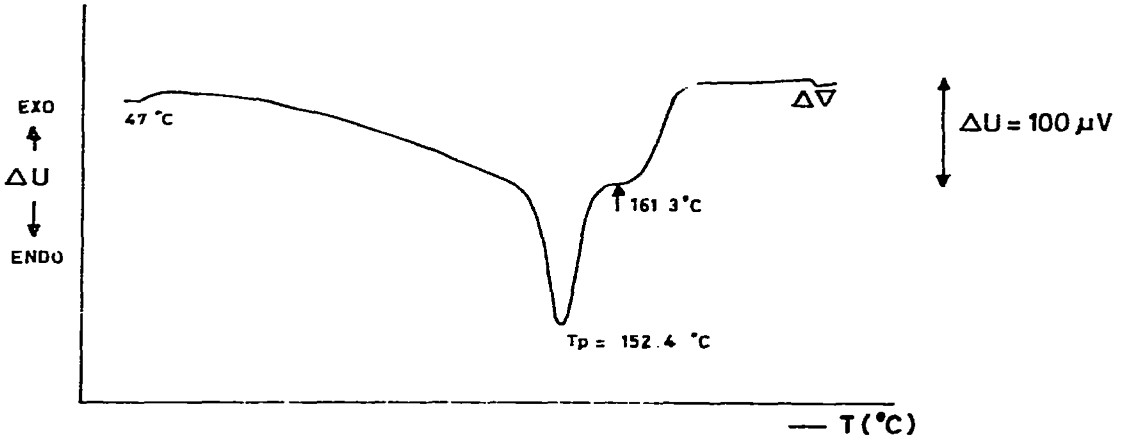

Fig. 2. DSC curve of adipic acid in vacuo.

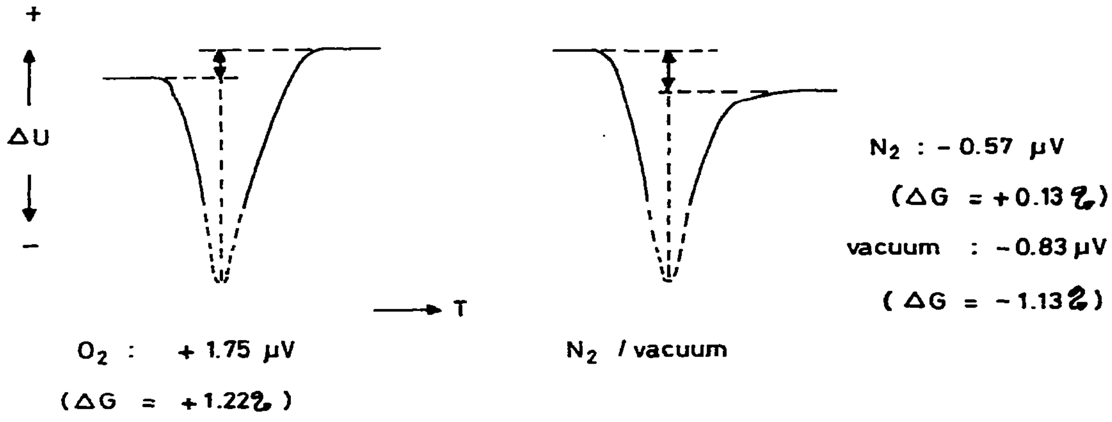

Fig. 3. Baseline displacement, naphazoline nitrate (experiment 2.5).

TABLE 5

Effects of dilution on peak height (µV)[a]

Factor	Compound			
	Adipic acid (s = 11.08)	Naphazoline nitrate (s = 8.06)	KNO_3 (s = 3.92)	Sodium citrate dihydrate (s = 26.35)
Concentration in dilution				
C_1 10%	[b]	48.50 **	27.11 **	111.96
C_2 30%	166.23 **	65.82 **	32.28 **	119.26
C_3 50%	194.64 **	72.41 **	33.28 **	107.32
Diluting agent				
D_1 carborundum	219.52 **	61.19 **	30.86 **	112.33 **
D_2 alum. oxide	91.09 **	38.73 **	23.32 **	91.93 **
D_3 air (i.e. no diluting agent)	230.68 **	86.81 **	38.48 **	134.28 **
Method of dilution				
V_1 whirl mixer	182.56	66.32 **	44.51 **	158.87 **
V_2 pestle/mortar	181.52	60.71 **	22.63 **	66.83 **
V_3 dissolution and recrystallization	117.23	59.71 **	25.52 **	[c]
Particle sizes				
Z_1 small particles	168.15 **	49.07 **	32.40 *	116.12
Z_2 complete spectrum	186.16 **	66.91 **	31.11 *	111.61
Z_3 large particles	187.00 **	70.75 **	29.15 *	110.82

* Significant differences between levels at $P = 0.05$.

** Significant differences between levels at $P = 0.01$.

[a] For the sake of brevity, the significant interactions are not given; their contributions to the main effects were generally slight.

[b] Due to inadequacy of some raw data, mean values cannot be calculated.

[c] Lack of a suitable solvent prevented the dissolution of sodium citrate dihydrate.

thermal effect because of a chemical reaction, complexation or hydrogen bonding with the diluent). The results furthermore indicate that the lower the concentration in dilution the lower the peak height and that the mixing procedure with the whirl mixer generally gives higher peak heights (see Table 5). The influences of concentration and mixing procedures on peak width are difficult to interpret. For the solid—liquid transitions the preparation procedure with the whirl mixer gives higher responses, for the other two compounds the trituration with pestle and mortar gives the highest responses.

The effects of dilution on shape index and baseline displacement are even more complicated.

SUMMARY AND CONCLUSIONS

Factorial experiments were carried out to investigate the influence of some experimental variables on the results of quantitative DSC. The apparatus used was a commercial heat-flux DSC equipment, and the following compounds were studied: adipic acid (melts without noticeable decomposition), naphazoline nitrate (melts with decomposition), potassium nitrate (solid—solid transformation) and sodium citrate dihydrate (dehydration).

The variables investigated concerned the apparatus adjustment, the sample, the reference material and the atmosphere. Significant main effects and interactions were detected by analysis of variance.

From the DSC curves the following peak-related parameters were determined: peak height, peak width, shape index and baseline displacement, which could only be averaged with relatively large standard deviations. They were affected by many variables, particularly heating rate and sample mass, but also comminution, sieve size distribution, dilution and the applied atmosphere. Simple relationships however, could not be found. The results were rather inconsistent and highly dependent on the nature of the transition.

It is concluded that DSC peaks should preferably not be described in terms of peak height, peak width, shape index and baseline displacement, if quantitative work is required.

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