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HEAT CAPACITIES OF FLUOROANILINE, FLUOROPHENOL AND DIFLUOROBENZENE IN CONDENSED PHASE

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ABSTRACT

Microcalorimetry was used to determine the heat capacities of solid and liquid fluoroaniline, fluorophenol and difluorobenzene as a function of temperature. Capacities were then expressed parametrically.

In the solid state, the contributions of optical and acoustic modes were evaluated by determining vibrational spectra. In the liquid state, the values of discontinuity of heat capacity occurring during melting, $\Delta_{\mathrm{melt}} C^{\theta}_{P,m}$, and those of the increment of heat capacity corresponding to the substitution of a fluorobenzene hydrogen by CH_3, NH_2, OH or F were interpreted by invoking the participation of molecular association.

INTRODUCTION

The thermodynamic properties of benzenes disubstituted with CH_3, NH_2 and OH have been reported and compared [1,2]. This work has been extended to compounds of the same isoelectronic family containing one fluorine atom on the benzene ring interacting with NH_2, OH or F.

The comparison of the present results with published data on the same compounds in the ideal gas state enables the evaluation of the heat capacity of the network associated with the propagation of acoustic modes and elastic vibrations.

EXPERIMENTAL

Experimental methods have been published in detail elsewhere [1]. Only essential features and new refinements are described.

Compounds used in the experiments were obtained from Aldrich, with purity equal to or greater than 99%. They were stored at low temperature in the presence of a desiccant.

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Heat capacities were determined with a SETARAM model DSC 111G microcalorimeter. The stepwise method was used, with the following characteristics: heating rate 2 °C min^{-1}, heating time 240 s, isotherm 400 s. In these conditions, the precision with which heat capacity $C_{p,m}^{\theta}$ is determined is estimated as better than 2% for temperatures higher than −50 °C, while fluctuations of the baseline between −90 °c and −50 °C reduce this precision to ≈ 5%.

RESULTS AND DISCUSSION

In the absence of a solid–solid transition with discontinuity of heat capacity, *ortho, meta* and *para* isomers of the benzene compounds have very similar heat capacities, which cannot be differentiated in the light of the experimental precision described above. This result was confirmed in the series studied by comparing heat capacities of *meta*- and *para*-difluorobenzenes in the liquid state between −50 and +25 °C (Table 2, Fig. 1). Subsequently, the *para* isomer of each compound having the highest melting point was chosen for the determination of heat capacities, since it permits the exploitation of solid state results over the widest temperature range possible.

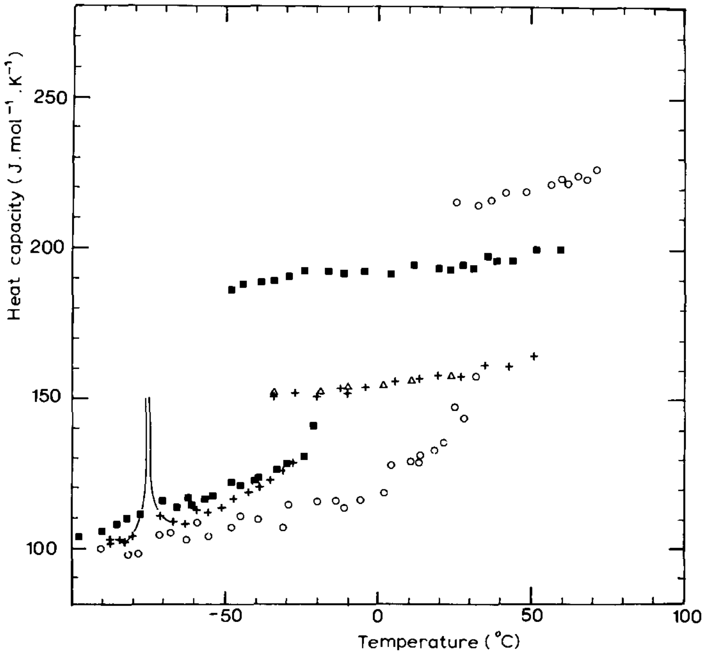

Fig. 1. Variations in the molar heat capacity as a function of temperature. ■ *para*-Fluoroaniline; ○ *para*-fluorophenol; + *para*-difluorobenzene; △ *meta*-difluorobenzene.

Solid state

The values of $C^{\theta}_{P,m}$ determined every 4 °C were expressed as a function of temperature, using the following polynomial development

$$C^{\theta}_{P,m} = a + bT + cT^2 + dT^3 \qquad \left(C^{\theta}_{P,m} \text{ in J mol}^{-1}\text{ K}^{-1};\ T \text{ in } ^{\circ}\text{C}\right) \tag{1}$$

The coefficients a, b, c and d were calculated by a least squares method. The use of the terms cT^2 and dT^3 takes account of the more rapid increase of the values of $C^{\theta}_{P,m}$ just before melting. On the other hand, if the expression $C^{\theta}_{P,m} = f(T)$ does not include the values corresponding to pre-melting, the law of variation of heat capacity with temperature in the range from $-90\,^{\circ}$C to $(T_{\text{melt}} - 30)\,^{\circ}$C is linear

$$C^{\theta}_{P,m}(\text{s}) = a_1 + b_1 T \qquad \left(C^{\theta}_{P,m} \text{ in J mol}^{-1}\text{ K}^{-1};\ T \text{ in } ^{\circ}\text{C}\right) \tag{2}$$

Tables 1 and 2 list the values of these coefficients, as well as the correlation coefficients R of the two equations.

p-Difluorobenzene undergoes an allotropic transformation at $-75\,^{\circ}$C. This transition occurs without a discontinuity of the heat capacity, $\Delta_{\text{trans}}C^{\theta}_{P,m} \approx 0$. This result enables the same equation (1) or (2) to be used to explain the variations of the heat capacity of the two forms of *p*-difluorobenzene.

The observed experimental values were plotted on the same $C^{\theta}_{P,m} = f(T)$ diagram, along with the results previously obtained with *para*-fluorotoluene [2]. *Meta*- and *para*-difluorobenzene have analogous behavior [3], both presenting a solid–solid transition, at $-86.4\,^{\circ}$C and $-75\,^{\circ}$C, respectively, and $C^{\theta}_{P,m}$ values which are very close, confirming our earlier observations [1].

These results show, as previously pointed out for molecules of the same family (dihydroxybenzene, phenylenediamine, aminophenol, cresol, tolui-

TABLE 1

Coefficients a, b, c and d of the polynomial $C^{\theta}_{P,m} = a + bT + cT^2 + dT^3$ (T in °C; $C^{\theta}_{P,m}$ in J mol^{-1} K^{-1})

Product	a	b	c	d	R
para-Fluoroaniline (s) (18 points) (−98 °C, −21 °C)	172.511	2.190	3.013×10^{-2}	1.535×10^{-4}	0.95
para-Fluorophenol (s) (28 points) (−90 °C, +34 °C)	123.033	0.579	9.573×10^{-3}	7.243×10^{-5}	0.95
para-Difluorobenzene (s) (17 points) (−87 °C, −80 °C) (−70 °C, −28 °C)	175.622	2.346	3.026×10^{-2}	1.496×10^{-4}	0.98

TABLE 2

Coefficients a_1 and b_1 of the polynomial $C^{\theta}_{p,m}(\mathrm{s}) = a_1 + b_1 T$ (T in °C; $C^{\theta}_{p,m}$ in J mol^{-1} K^{-1})

Product	a_1	b_1	R
para-Fluoroaniline (s) (17 points) (−98°C, −24°C)	137.265	0.337	0.96
para-Fluorophenol (s) (21 points) (−90°C, +20°C)	127.259	0.356	0.96
para-Difluorobenzene (s) (15 points) (−88°C, −80°C) (−70°C, −35°C)	135.767	0.391	0.96

dine, xylene), that for a given temperature the heat capacities remain very close but that the sequence $C^{\theta}_{p,m}$ (fluorophenol) < $C^{\theta}_{p,m}$ (difluorobenzene) < $C^{\theta}_{p,m}$ (fluoroaniline) remains significant.

By admitting that at the temperatures examined the heat capacity $C^{\theta}_{p,m}(\mathrm{s})$ is due only to vibrational contributions $C^{\theta}_{p,m}$ (E) and those from the network $C^{\theta}_{p,m}$ (D), we have:

$$C^{\theta}_{p,m}(\mathrm{s}) = C^{\theta}_{p,m}(\mathrm{E}) + C^{\theta}_{p,m}(\mathrm{D}) \qquad (3)$$

The terms of this equation have been listed for purposes of comparison in Table 3. The term $C^{\theta}_{p,m}$ (E) given by the Einstein model

$$R\sum_i \frac{x_i^2 e_i^x}{(e^{x_i} - 1)^2}$$

was calculated from the known gaseous state vibrational spectra of *para*-fluorotoluene [4], *para*-fluoroaniline [5], *para*-difluorobenzene [6] and *para*-fluorophenol [7]. The term $C^{\theta}_{p,m}$ (D) corresponding to the contribution from the network (Debye continuum model) was deduced from expression (3), where $C^{\theta}_{p,m}(\mathrm{s})$ is calculated by eqn. (2).

The data in this table clearly show that the increase in heat capacity $C^{\theta}_{p,m}(\mathrm{s})$ with temperature (of the order of 20 J mol^{-1} K^{-1}) is due only to the increased vibrational contribution $C_{p,m}(\mathrm{E})$. The contribution from network modes is practically independent of temperature in the domain studied.

It should also be noted that the term $C^{\theta}_{p,m}$ (D) is relatively insensitive to the nature of the substituent; the corresponding value for fluorophenol, however, is lower ($\approx$ 10 J mol^{-1} K^{-1}). The propagation of acoustic modes along the network of these compounds occurs with parameters whose values are relatively similar, in spite of a very different crystalline cohesion, illustrated, for example, by an 85°C difference between the melting points

TABLE 3

Comparative heat capacities at different temperatures

	−90 °C	−70 °C	−50 °C	−30 °C
para-Fluorotoluene				
$C^{\theta}_{P,m}(\mathrm{s})$	99.2	108.0	–	–
$C^{\theta}_{P,m}(\mathrm{E})$	36.6	43.3	50.2	57.2
$C^{\theta}_{P,m}(\mathrm{D})$	62.6	64.7	–	–
para-Fluoroaniline				
$C^{\theta}_{P,m}(\mathrm{s})$	106.9	113.7	120.4	127.2
$C^{\theta}_{P,m}(\mathrm{E})$	39.2	46.4	53.7	61.3
$C^{\theta}_{P,m}(\mathrm{D})$	67.7	67.3	66.7	65.9
para-Fluorophenol				
$C^{\theta}_{P,m}(\mathrm{s})$	95.2	102.3	109.5	116.6
$C^{\theta}_{P,m}(\mathrm{E})$	40.6	47.7	54.8	61.9
$C^{\theta}_{P,m}(\mathrm{D})$	54.6	54.6	54.7	54.7
para-Difluorobenzene				
$C^{\theta}_{P,m}(\mathrm{s})$	100.6	108.4	116.2	124.0
$C^{\theta}_{P,m}(\mathrm{E})$	35.2	41.9	48.6	55.3
$C^{\theta}_{P,m}(\mathrm{D})$	65.4	66.5	67.6	68.7

of *para*-fluoroaniline and *meta*-fluorotoluene. Nevertheless, if this argument is valid for any compound in the series studied, it must be admitted that the lower $C^{\theta}_{P,m}$ (D) value of fluorophenol is explained uniquely by the existence of molecular association, which is much more important for this compound than, for example, for fluoroaniline.

Liquid state

In order to increase the precision of the calculated curve of $C^{\theta}_{P,m} = f(T)$, samples were heated, then cooled to ≈ 30 °C below their melting point. The temperature range explored was thus considerably extended as a result of the phenomenon of supercooling.

In addition, the maximum temperature to which the sample was subjected did not exceed 60 °C above its melting point. This procedure enables the heat capacity at constant pressure and the heat capacity at saturation to be considered as being the same, by neglecting the term

$$T\left(\frac{\partial V_m}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\mathrm{sat}}$$

a hypothesis which is justified at these relatively low temperatures.

The experimental values shown in Fig. 1 were described by the expression

$$C^{\theta}_{P,m}(\mathrm{l}) = a_2 + b_2 T \qquad \left(C^{\theta}_{P,m} \text{ in J mol}^{-1}\,\mathrm{K}^{-1};\ T \text{ in } {}^{\circ}\mathrm{C}\right) \tag{4}$$

TABLE 4

Coefficients a_2 and b_2 of the polynomial $C^{\theta}_{P,m}(\mathrm{l}) = a_2 + b_2T$ (T in °C; $C^{\theta}_{P,m}$ in J mol^{-1} K^{-1})

Product	a_2	b_2	R
para-Fluorotoluene [2] (19 points) (−57°C, +25°C)	164.969	0.350	0.95
para-Fluoroaniline (20 points) (−49°C, +60°C)	192.943	0.092	0.82
para-Fluorophenol (12 points) (25°C, 81°C)	209.809	0.212	0.92
para-Difluorobenzene (13 points) (−35°C, 51°C)	155.192	0.158	0.92

where the coefficients a_2 and b_2 (listed in Table 4) were determined by a least squares method.

As the values of the coefficients b_2 indicate, variations in heat capacity with temperature in the liquid state are two to four times lower than in the solid state. In addition, the examination of Fig. 1 or of coefficients a_2 and b_2 shows that the heat capacity of a compound at a given temperature is highly dependent on the nature of the substituent, in contrast to behavior in the solid state. This result is also illustrated by the very different values of the variation of heat capacity at the melting point $\Delta_{\mathrm{melt}}C^{\theta}_{P,m}$ (Table 5) and of the increment of heat capacity $\delta C^{\theta}_{P,m}$ expressed in comparison to fluorobenzene. The values of $\delta C^{\theta}_{P,m}$ correspond to the substitution of a hydrogen on the benzene ring by CH_3 (fluorotoluene), NH_2 (fluoroaniline), OH (fluorophenol) or F (difluorobenzene) group, and are defined by

$$\delta C^{\theta}_{P,m}\left\{\begin{matrix} \mathrm{CH_3} \\ \mathrm{NH_2} \\ \mathrm{OH} \\ \mathrm{F} \end{matrix}\right\} = C^{\theta}_{P,m}(\text{compound}) - C^{\theta}_{P,m}(\text{fluorobenzene})$$

The values in Table 5 call for the following comments: the melting points not referenced are taken from tables of physical constants (Beilstein, Timmermans); the values of heat capacities in the solid, $C^{\theta}_{P,m}(\mathrm{s})$, and liquid states, $C^{\theta}_{P,m}(\mathrm{l})$, are deduced from eqns. (2) and (4), except for those concerning solid fluorotoluene, which are experimental [the temperature range explored in the solid state is too restricted and so a sufficiently precise law of variation $C^{\theta}_{P,m}(\mathrm{s}) = f(T)$ cannot be established]. Finally, for a melting

TABLE 5

Variations of heat capacity at the melting point $\Delta_{\text{melt}}C^{\theta}_{P,m}$ (J mol^{-1} K^{-1})

Product	*ortho*	*meta*	*para*
Fluorotoluene (2)			
T_{fus} (°C)	−62.5	−89.2	−57.6
$C^{\theta}_{P,m}$ (s)	110	100	110
$C^{\theta}_{P,m}$ (l)	143	134	145
$\Delta^{\theta}_{\text{melt}}C_{P,m}$	33	34	35
Fluoroaniline			
T_{fus} (°C)	−29	–	−1.9
$C^{\theta}_{P,m}$ (s)	127.5	–	136.6
$C^{\theta}_{P,m}$ (l)	190.3	–	192.8
$\Delta^{\theta}_{\text{melt}}C_{P,m}$	62.8	–	56.2
Fluorophenol			
T_{fus} (°C)	16.1	13.7	48
$C^{\theta}_{P,m}$ (s)	133.0	132.1	144.3
$C^{\theta}_{P,m}$ (l)	213.2	212.7	220.0
$\Delta^{\theta}_{\text{melt}}C_{P,m}$	80.2	80.6	75.7
Difluorobenzene			
T_{fus} (°C)	−47.1 [8]	−69.1 [4]	−23.7
$C^{\theta}_{P,m}$ (s)	117.4	– [a]	126.5
$C^{\theta}_{P,m}$ (l)	147.8	144.3	151.4
$\Delta^{\theta}_{\text{melt}}C_{P,m}$	30.4	– [a]	24.9

[a] The heat capacity of solid *meta*-difluorobenzene cannot be determined from the relationship $C^{\theta}_{P,m} = 135.767 + 0.391T$ established for the *para* isomer, since a solid–solid transition with discontinuity of the heat capacity $\Delta_{\text{trans}}C^{\theta}_{P,m} = 9.73$ J mol^{-1} K^{-1} occurs at −86.38 °C [3].

point difference of ≈ 30 °C between the *para* and *meta* isomers, there is a relatively small difference $\Delta_{\text{melt}}C^{\theta}_{P,m}(\textit{para}) - \Delta_{\text{melt}}C^{\theta}_{P,m}(\textit{meta})$ (at most, equal to 6.6 J mol^{-1} K^{-1} in the case of difluoroaniline). This result shows that the values of $\Delta_{\text{melt}}C^{\theta}_{P,m}$ depend primarily on the nature of the compound and only slightly on the value of T_{melt}.

Table 6 lists the values of $\delta C^{\theta}_{P,m}$ calculated at 50 °C from eqn. (4) for each compound and from the value of 150.2 J mol^{-1} K^{-1} corresponding to fluorotoluene [9].

Examination of Tables 5 and 6 shows that the parameters $\Delta_{\text{melt}}C_{P,m}$ and $\delta C_{P,m}$ depend strongly on the nature of the compound, and that their value

TABLE 6

Increment of heat capacity $\delta C^{\theta}_{P,m}$ (J mol^{-1} K^{-1}) at 50 °C

L to R	Fluorotoluene	Fluoroaniline	Fluorophenol	Difluorobenzene
$C^{\theta}_{P,m}$	182.5	197.5	220.4	163.1
$\delta C^{\theta}_{P,m}$	32.3	47.3	70.2	12.9

renders the sequence difluorobenzene (F) < fluorotoluene (CH_3) < fluoroaniline (NH_2) < fluorophenol (OH) significant. This result confirms that obtained with the analogous toluene-derivative series [2].

The involvement of higher amplitude movements in the liquid state contributes to a heat capacity which is more sensitive to the structure of the liquid. Thus, the sequence of values observed for the parameters $\Delta_{\text{melt}}C_{P,m}$ and $\delta C_{P,m}$ must be correlated with different structures, which involve a phenomenon of molecular association when the benzene ring includes an OH or NH_2 substituent; this phenomenon was more important for OH than for NH_2.

CONCLUSION

The heat capacities of four fluorinated benzene derivatives of a homogeneous and isoelectronic family in the condensed phase were studied as a function of temperature and were rendered parametrically.

In the solid state, the contribution of optical modes calculated with the Einstein model explains the thermal variation of the experimental heat capacity. The contribution of acoustic modes is relatively insensitive to the nature of the substituent interacting with the fluorine atom on the benzene ring. Nevertheless, the phenomenon of molecular association present in fluorophenol is apparently responsible for the lower value of the Debye term.

In the liquid state, the variation of the heat capacity with temperature is lower than in the solid state. At a given temperature, on the other hand, such variation is highly dependent on the nature of the substituent, suggesting a much more clearcut influence of molecular structure than in the solid state. Thus, the increase of the values of the discontinuity of heat capacity at melting and of the increment of heat capacity in comparison to fluorobenzene from one compound to another is correlated with the importance of molecular association.

REFERENCES

1 P. Bret-Dibat and A. Lichanot, Thermochim. Acta, 174 (1989) 261.
2 L. Mbaze Meva'a and A. Lichanot, Thermochim. Acta, 158 (1990) 335.
3 J.F. Messerly and H.L. Finke, J. Chem. Thermodyn., 2 (1970) 867.
4 J.H.S. Green, Spectrochim. Acta, Part A, 26 (1970) 1503.
5 A.P. Hussein, J. Lielmezs and H. Aleman, Thermochim. Acta, 86 (1985) 209.
6 J.H.S. Green, W. Kynaston and H.M. Paisley, J. Chem. Soc., (1963) 473.
7 J.H.S. Green, D.H. Harrison and W. Kynaston, Spectrochim. Acta, Part A, 27 (1971) 2199.
8 D.W. Scott, J.F. Messerly, S.S. Todd, I.A. Hossen-Lopp, A. Osborn and J.P. McCullough, J. Chem. Phys., 38 (1963) 532.
9 R. Jadot and M. Fraiha, Int. J. Refrig., 12 (1989) 198.