

SCALES OF BASICITY BASED ON THERMOCHEMICAL DATA OF ADDUCTS

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Abstract

Using the values of standard molar enthalpy of reaction for dimethylethyleneurea (dmeu), dimethylformamide (dmf), dimethylacetamide (dma), tetramethylurea (tmu), hexamethylphosphoramide (hmpa) and pyridine (py) with the acids BF₃, SbCl₅, ZnCl₂ and AsCl₃, it is shown that, in terms of acid-base behaviour, ZnCl₂ is closer to BF₃, which differs from SbCl₅. Furthermore, the equation $-\Delta_r H_m(\text{ZnCl}_2) = -[1.26 \cdot \Delta_r H_m(\text{BF}_3)] - 56.99$ correlates with the standard molar enthalpy of reaction for the same set of molecules with ZnCl₂ and BF₃. A similar equation was obtained to estimate the enthalpy of reaction with AsCl₃: $-\Delta_r H_m(\text{AsCl}_3) = -[4.12 \cdot \Delta_r H_m(\text{BF}_3)] - 417.82$. It is also shown that, for hmpa and tmu, sterical hindrance is a prominent factor that influences the coordination chemistry of the acidic centres, whose deviation from the linearity can be considered as a measure for the steric contribution to $\Delta_r H_m$.

Keywords: acid-base interaction, adduct, scale of basicity, thermochemistry

Introduction

Basicity is an intrinsic property associated with a given molecule that might even be used as ligand, in many systems. The simple presence of the ligand acting as solvent in a reaction medium not only favours the contact of reagents but also strongly influences the development of the reaction. Many attempts were made to establish general behaviours in order to contemplate the various features connected to the idea of the acid-base interactions. The importance of this statement is certainly related to the general application of the principle saying that the occurrence of any reaction can be interpreted from the point of view of the participation of the basic centre that interacts directly to an available acidic one [1, 2].

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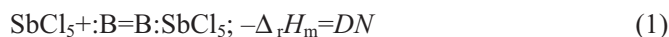
The principle in the establishment of any scale is based on the donor-acceptor complex formation, in which coordinative bonds occurred in solution due to the acid-base interaction. The ligands are electron pair donor species, corresponding to the Lewis base, which bind to the solute molecules, the Lewis acid, to form an adduct [1]. The success of this investigation is dependent on the choice of a suitable acceptor or Lewis acid to establish the basicity scale.

The majority of the proposed scales of basicity was currently obtained from calorimetric measurements due to the easiness and accuracy of the experimental determinations [3, 4]. However, other scales are supported by the shift of the visible absorption band of copper complex in the neat solvent [5], spectrophotometric measurements from nickel octahedral complex in different solvents [6] and softness of solvents applied for a series of nitrile and sulphur donor solvents with hard and soft cation interactions [7]. A scale can be connected to soft-soft interactions where a significant amount of covalency can be formed in the adduct. The donor properties of soft solvents are determined through vibrational spectroscopy. The donor strength scale can be obtained from the difference in the symmetric stretching frequency of the mercury-bromine bond in the gaseous HgBr_2 molecule and in the solvated molecules [8]. Mercury is a soft acid that can form strong bonds, with some covalent character, with other soft donor atoms. The strength parameter D_s in this scale is related to the formation of pseudotetrahedral solvated molecular complexes with monodentate electron-pair donor ligands. The success of this scale is the facility of acid mercury bromide to form a very stable complex with very strong coordinating solvents. Furthermore, steric effects are not expected to influence the final pseudotetrahedral configuration formed [9].

In the course of the interactive process, the basic solvents, classified as hydrogen bond acceptors or available electron pair donors, can interact with the given acidic centres. The net interactive effect is quantitatively expressed by the enthalpic value and defines a sequence of basicity. The idea to follow calorimetrically the ability of the base to donate a free electron pair to the acid was suggested [10] and developed to predict effects in investigations of coordination chemistry [11], thus defining the so-called donor number (DN) [3]. This value represents the force of the interaction, expressed in a quantitative way, and reflects the donor strength of the solvent. The concept of DN was applied to the general basicity scale and spread through various systems, even when a series of reference acids was used. In spite of the vigorous criticisms of either the concept itself or the experimental features related to the measurement of the interaction [3, 4, 12], DN continues to be widely used as an empirical parameter related to the solvent basicity. The application of the acid-base concept was expanded to many systems, in order to explain the course of many important reactions, such as those that take place on inorganic polymeric surfaces [13, 14].

The DN concept was initially defined through the thermal effect measured for the interaction of a chosen Lewis acid (SbCl_5) with a series of organic polar molecules ($:B$), the reaction taking place in an apolar solvent 1,2-dichloroethane [3]. From the structural point of view, the acid has only one available coordination centre to receive the lone pair of the Lewis base. For this system, the energetic effect caused by

the rearrangement in the structure of the adduct is assumed to be constant for a selected series of bases. Then, the net energetic effect can be represented by the general equation involved in this process by the reaction:



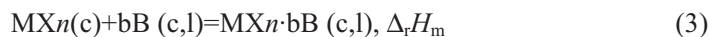
Another feature related to the scale of basicity was established by considering mainly the data collected in the study of a sequence of carbonyl basic compounds interacting with iodine as acidic standard molecule. The approach involved in such a kind of reactions is based on the ease with which the acid iodine accepts the basic lone pair into its available empty antibonding orbital [15]. It was stated that a linear relationship between the basicity of the molecules of solvents can be obtained if the electrostatic/covalent ratio is constant [16]. Another condition in obtaining proportional basicity scales for any interaction, is that the reference acid has a known electrostatic/covalent ratio [17].

Based on the fact that a very fast complexation occurs in a system constituted by dilute solution of boron trifluoride in dichloromethane, then a series of non-protogenic solvents were calorimetrically explored in such a kind of reaction. The suitable thermal effects gave a good linear relationship between the standard molar enthalpic values for a sequence of interactive effect measured in dichloromethane as well as in nitrobenzene [2]. This relationship covered a wide range of reactivity of the Lewis basic molecules to allow the establishment of a basicity scale, as represented by the following general equation:



An identical relative sequence of basicity scale was obtained for both representative acids SbCl_5 and BF_3 , when the same set of Lewis bases was chosen. The calorimetric results produce distinct standard molar enthalpic values, but the sequence follows a similar trend. On the other hand, some inversions in the sequence are observed, as for example, in the couple pyridine and hexamethylphosphoramide, showing that the electronic effect and the steric strain associated with the basic molecule should be taken into account in the Lewis acid-base interactions studies [18].

As part of the interest in improving the knowledge of other features related to the scale of basicity, new input to this study is connected to the adducts formed. Calorimetric determinations were previously performed to obtain reliable thermochemical data, specially those related to the standard molar enthalpy of acid-base reaction in condensed phase, to yield the adducts [19]. In the present case, the general thermochemical data express the basicity through the equation represented as:



The adducts $\text{MX}_n \cdot \text{bB}$ ($M = \text{Zn}, \text{As}, X = \text{Cl}, n = 2, 3$ and $b = 1, 2$) were chosen and a scale of basicity is proposed based on their thermochemical data. These values are now used in an attempt to compare with other proposed scales of basicities, taking into account the adducts formed with antimony and boron halides with a series of selected bases.

Experimental

Dimethylethyleneurea [20] was synthesized by reacting ethyleneurea (Aldrich) with formaldehyde and formic acid (Merck) in stoichiometric amounts. The resulting solution was refluxed for 48 h and then neutralized with a 6.0 mol dm^{-3} sodium hydroxide solution. The purification of the obtained ligand was performed by successive distillations under vacuum.

The adduct $\text{ZnCl}_2 \cdot 2\text{dmeu}$ was prepared by dissolving directly the chloride in a slight excess of dimethylethyleneurea. The solid was immediately formed, and was washed with ether and dried under vacuum for 8 h at 333 K.

Carbon, nitrogen and hydrogen contents were determined using a Perkin Elmer microelemental analyser. The infrared spectra were recorded on a Bomem apparatus in KBr discs, in $4000\text{--}400 \text{ cm}^{-1}$ range, with resolution of 4 cm^{-1} .

The calorimetric measurements were carried out on a Thermometric isoperibolic instrument, model LKB 2250, by using ampoule breaking procedure [21]. All measurements were taken at $298.15 \pm 0.02 \text{ K}$, using a 0.10 dm^3 reaction vessel, charged with ethanol as calorimetric solvent. For each enthalpic determination, at least six individual ampoules were broken and the complete thermal effects were recorded during 240 s. Ampoules of zinc chloride, ligand and adduct were prepared under anhydrous conditions, by using atmosphere of dry nitrogen into a dry box. Uncertainty intervals associated with the variation of the enthalpies of solution are quoted as twice of the standard deviation of the mean.

Results and discussion

The lack of thermochemical data involving at least two kinds of acid-base determinations restricted the choice of the series of compounds. For this common sequence the data are based on the standard molar enthalpy of reaction involving dimethylformamide (dmf), dimethylacetamide (dma), pyridine (py), hexamethylphosphoramide (hmpa) and tetramethylurea (tmu) with: i) SbCl_5 in 1,2-dichloroethane [3] to yield the donor number (*DN*) values -26.6 ; -32.2 ; -33.1 ; -38.8 and $-31.0 \text{ kJ mol}^{-1}$. ii) the other standard Lewis acid BF_3 in gaseous phase with the solvents [2] that gave -110.5 ; -112.2 ; -128.1 ; -117.5 and $-108.6 \text{ kJ mol}^{-1}$, respectively. Dimethylethyleneurea was only used in the reaction with BF_3 , whose standard molar enthalpy of reaction is $-98.9 \text{ kJ mol}^{-1}$. The sequence of adducts of zinc and arsenic chlorides, used to compare the two previous scales with that proposed here and the respective standard molar enthalpies of reaction in condensed phase, $\Delta_r H_m$, are listed in Table 1.

The sequence of enthalpic values listed in Table 1 should be compared with the values of the respective Lewis bases with both acids [2, 3] SbCl_5 and BF_3 previously presented. There is an agreement among the scales of basicities with respect to the sequence of basicity for the group formed by the Lewis bases dmf, dma and tmu. However, for the basicities of py and hmpa, there is a close agreement between the sequence with the acidic BF_3 , but an inversion occurs for SbCl_5 values, when compared

with the standard molar enthalpic values collected for ZnCl_2 . Then, from these data the sequence of basicity can be identically established for ZnCl_2 and BF_3 as: $\text{py} > \text{hmpa} > \text{dma} > \text{tmu} > \text{dmf}$ [22–26], while the sequence supplied for the proposed donor number, which uses SbCl_5 as acid is: $\text{hmpa} > \text{py} > \text{tmu} > \text{dma} > \text{dmf}$.

Table 1 Standard molar enthalpy of reaction in condensed phase, $\Delta_r H_m^\theta$ for a series of adducts with zinc and arsenic chlorides

Adduct	$-\Delta_r H_m^\theta / \text{kJ mol}^{-1}$	Reference
$\text{ZnCl}_2 \cdot 2\text{dmf}$	81.4	[13]
$\text{ZnCl}_2 \cdot 2\text{dma}$	84.2	[14]
$\text{ZnCl}_2 \cdot 2\text{dmeu}$	67.3	*
$\text{ZnCl}_2 \cdot 2\text{py}$	116.1	[16]
$\text{ZnCl}_2 \cdot 2\text{hmpa}$	113.1	[17]
$\text{ZnCl}_2 \cdot 2\text{tmu}$	83.1	[18]
$\text{AsCl}_3 \cdot \text{dmf}$	39.0	[19]
$\text{AsCl}_3 \cdot \text{dma}$	42.3	[19]
$\text{AsCl}_3 \cdot \text{tmu}$	43.6	[19]
$\text{AsCl}_3 \cdot \text{py}$	110.1	[20]

*this work

These data demonstrate that the basicity sequence for zinc chloride and boron fluoride acids differs from DN values established for antimony chloride acid, showing an inversion between py and hmpa basicities. On the other hand, the sequence of basicity for the acid AsCl_3 [27, 28] is in close agreement with the values obtained for the donor number. This seems to be quite reasonable, due to the fact that arsenic and antimony belong to the same group of the periodic table, then it is expected a similar interactive chemical behaviour for both elements. From these values, it can be concluded that, at least from the point of view of acid-base behaviour, ZnCl_2 resembles much more BF_3 than SbCl_5 .

Figures 1a, 1b, 1c present three distinct sets of the standard molar enthalpies of reaction of ZnCl_2 with the chosen molecules, as a function of the standard molar enthalpies of reaction of the same molecules with BF_3 . In Fig. 1a only the standard molar enthalpies of reaction involving dmeu , dmf and dma are considered. The respective coefficient of correlation (r) for this straight line is 0.999.

By comparing Figs 1a to 1c one can verify that dmeu , dmf and dma present a highly linear behaviour. The straight line presented in Fig. 1b correlated the plot of standard molar enthalpies of the reactions involving the ZnCl_2 and BF_3 acids, where py is also included. For this linear behaviour a coefficient of correlation of 0.989 decreases slightly as compared with the previous one. It is observed that, when the standard molar enthalpy of reaction with the same bases tmu and hmpa are included, as shown in Fig. 1c, a linear behaviour occurred, but the coefficient of correlation de-

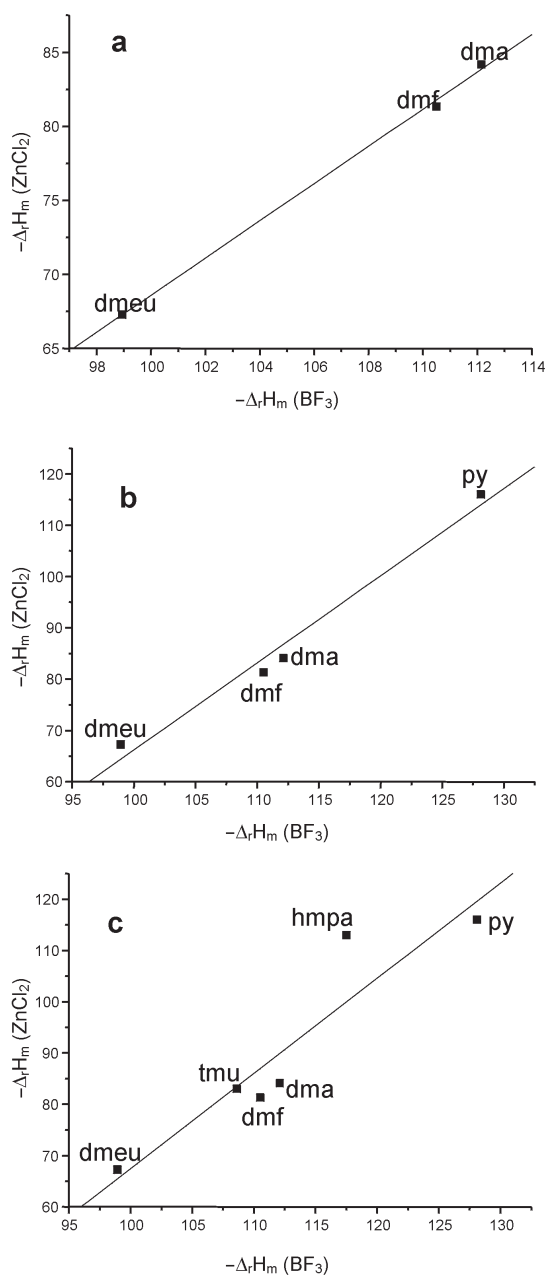


Fig. 1 Standard molar enthalpy of reaction in condensed phase for ZnCl₂ with dimethylformamide, dimethylacetamide and dimethylethyleneurea (a). For the same previous sequence of molecules and including pyridine (b), and tetramethylurea and hexamethylphosphoramide (c). The coefficients of correlation obtained are 0.999, 0.989 and 0.930, respectively

creases significantly to a value of 0.930. Thus, it can be verified that py, tmu and hmpa, mainly these two last molecules, deviated from the linear behaviour presented by dmu, dmf and dma molecules. Although tmu and hmpa have identical basic centres, these are the bulkiest molecules among those in the selected set. The methyl groups attached to carbon or phosphorus can cause the largest hindrance to the basic oxygen atoms to bond the acidic centres. On the other hand, py has nitrogen as donor atom, differing from the other oxygen basic molecules, which can also be a possible explanation. Thus, the deviation from the linearity can be used as a clear indication of the contribution of the steric hindrance to $\Delta_r H_m$ values.

Figure 1 illustrates the linear relationship between the standard molar enthalpies for zinc and boron halides. From this relationship the following correlation can be expressed:

$$-\Delta_r H_m(\text{ZnCl}_2) = -[1.26 \cdot \Delta_r H_m(\text{BF}_3)] - 56.99 \quad (4)$$

This equation establishes that the standard molar enthalpy of reaction of a certain molecule with ZnCl_2 can be calculated when the standard molar enthalpy of reaction with BF_3 is already known or vice versa. The values estimated through Eq. (4), will be more reliable as the molecules involved in the set are similar in terms of volume. The resemblance in structure of dmeu, dmf and dma molecules illustrates this statement.

Figures 2a and 2b present the standard molar enthalpies of reaction of dmf, dma, tmu and py with AsCl_3 , as a function of the same enthalpic values for the acid BF_3 . As verified for ZnCl_2 , the introduction of the standard molar enthalpic values for tmu, decreases the coefficient of correlation from 0.999 to 0.983. Again, the deviation of the linearity verified for this molecule can be interpreted in terms of steric hindrance. Even so, differently from the observed sequence for the preceding behaviour, pyridine does not exhibit deviation from the linearity for AsCl_3 . Since arsenic(III) is a harder acid than zinc(II) and nitrogen is a harder base than oxygen [1], it is expected that in the reaction with AsCl_3 , pyridine does not exhibit any deviation, as was observed for the equivalent reaction with ZnCl_2 .

The linear correlation obtained in Fig. 4, might be derived to the equation:

$$-\Delta_r H_m(\text{AsCl}_3) = -[4.12 \cdot \Delta_r H_m(\text{BF}_3)] - 417.82 \quad (5)$$

The application of this equation will be more reproducible as similar are the volume of the considered molecules as dma, dmf and py.

The basicity values for dimethyl-, diethylformamides and acetamide in SbCl_5 [3], BF_3 [2], ZnCl_2 [22, 23] and HgBr_2 [9] scales are listed in Table 2. The spectroscopic scales are used for HgBr_2 acid and all other the basicity values were obtained through thermochemical data. As observed, the thermochemical scales provide the same sequence of basicity, represented by: dea>def>dma>dmf. These values contrasted with the spectroscopic scale, where the four molecules gave identical values for the basicity. These examples illustrate that the thermochemical scales are more precise than the spectroscopic scale considered and consequently, the validity of the use of thermochemical data to establish basicity sequences is reinforced.

Table 2 Basicity values for dimethylformamide (dmf), dimethylacetamide (dma), diethylformamide (def) and diethylacetamide (dea) in the SbCl_5 , BF_3 , ZnCl_2 and HgBr_2 basicity scales

Compound/scale	SbCl_5	BF_3	ZnCl_2	HgBr_2
dmf	26.6	110.49	81.4	24
dma	27.8	112.14	84.2	24
def	30.9	113.20	–	24
dea	32.2	113.61	–	24

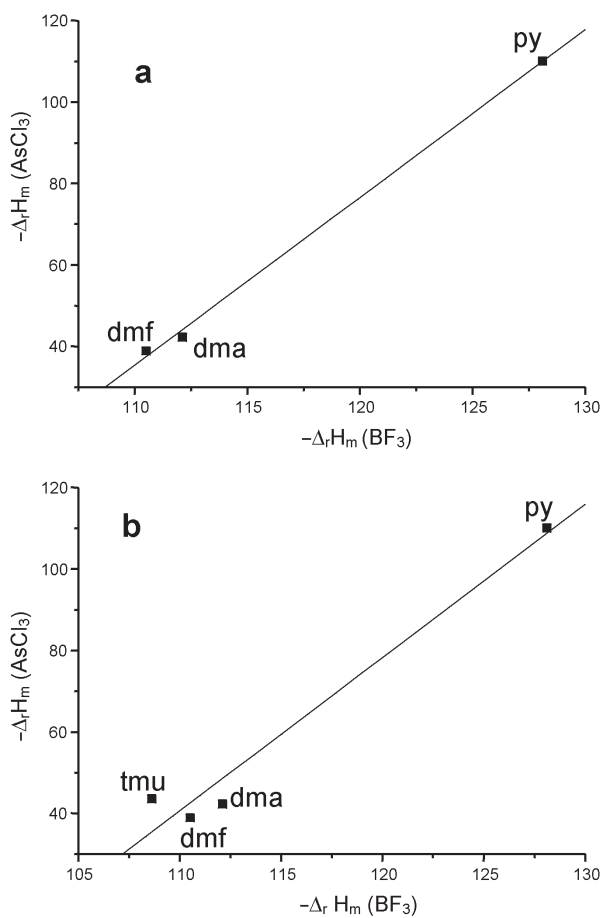


Fig. 2 Standard molar enthalpy of reaction in condensed phase for AsCl_3 with dimethylformamide, dimethylacetamide and pyridine as function of standard molar enthalpy of reaction in condensed phase of the same sequence of molecules with BF_3 (a) and for the same previous sequence of molecules and tetramethylurea (b). The coefficients of correlation are 0.999 and 0.983, respectively

Conclusions

In conclusion, the scale of basicity was established based on thermochemical data obtained from the standard molar enthalpies, whose values derived from acid-base reaction in condensed phase to yield the respective adducts, where $ZnCl_2$ can be successfully employed as a standard acid. The proposed approach is very close to the classical scales, where the most common standard acids were used.

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References

- 1 W. B. Jensen, *The Lewis Acid-Base Concept*, John Wiley & Sons, New York, 1980.
- 2 P.-C. Maria and J.-F. Gal, *J. Phys. Chem.*, 89 (1985) 1296.
- 3 V. Gutmann, *The Donor-Acceptor Approach Molecular to Interactions*, Plenum Press, New York, 1978.
- 4 R. S. Drago, *Coord. Chem. Rev.*, 33 (1980) 251.
- 5 Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, 45 (1972) 465.
- 6 M. Munakata, S. Kitagawa and M. Miyazima, *Inorg. Chem.*, 24 (1985) 1638.
- 7 G. Gritzner, *Pure Appl. Chem.*, 60 (1988) 1743.
- 8 I. Persson, M. Sandström and P. L. Goggin, *Inorg. Chim. Acta*, 129 (1987) 183.
- 9 M. Sandström, I. Persson and P. Persson, *Acta Chem. Scand.*, 44 (1990) 653.
- 10 I. Lindqvist and M. Zackrisson, *Acta Chem. Scand.*, 14 (1960) 453.
- 11 V. Gutmann and E. Wyckera, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 257.
- 12 R. S. Drago, *Pure Appl. Chem.*, 52 (1980) 2261.
- 13 D. J. Parrillo, R. J. Gorte and W. E. Farneth, *J. Am. Chem. Soc.*, 115 (1993) 12441.
- 14 C. Airoidi and L. S. Santos Jr., *Thermochim. Acta*, 104 (1986) 111.
- 15 R. S. Drago, J. A. Nusz and R. C. Courtright, *J. Am. Chem. Soc.*, 96 (1974) 2082.
- 16 R. W. Taft, N. J. Pienta, M. J. Kamlet and E. M. Arnet, *J. Org. Chem.*, 46 (1981) 661.
- 17 C. Laurence and G. Wojtkowiak, *J. Am. Chem. Soc.*, 101 (1979) 4793.
- 18 H. C. Brown, *J. Chem. Soc.*, (1956) 1248.
- 19 C. Airoidi and A. P. Chagas, *Coord. Chem. Rev.*, 119 (1992) 29.
- 20 R. F. de Farias and O. A. de Oliveira, *Quím. Nova*, 19 (1996) 100.
- 21 R. F. de Farias, O. A. de Oliveira, J. V. de Medeiros and C. Airoidi, *Thermochim. Acta*, 328 (1999) 241.
- 22 O. A. de Oliveira, A. P. Chagas and C. Airoidi, *Inorg. Chem.*, 22 (1983) 136.
- 23 J. de A. Simoni, C. Airoidi and A. P. Chagas, *J. Chem. Soc. Dalton Trans.*, (1980) 156.
- 24 C. Airoidi, M. L. C. P. Silva and A. P. Chagas, *J. Chem. Soc. Dalton Trans.*, (1986) 1913.
- 25 J. C. de Queiroz, C. Airoidi and A. P. Chagas, *J. Chem. Soc. Dalton Trans.*, (1985) 1103.
- 26 C. Airoidi, A. P. Chagas and F. P. Assunção, *J. Chem. Soc. Dalton Trans.*, (1980) 1823.
- 27 L. C. R. Santos, A. G. de Souza and C. Airoidi, *Thermochim. Acta*, 317 (1998) 99.
- 28 P. O. Dunstan and C. Airoidi, *J. Chem. Eng. Data*, 33 (1988) 93.