

## Thermodynamics of Interaction Between $\text{ZnCl}_2$ and N,N-Dimethylacetamide in 1,2-Dichloroethane Solution

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Com o objetivo de se estudar a interação do  $\text{ZnCl}_2$  com a N,N-dimetil-acetamina (dma) em solução de 1,2-dicloroetano (dce), determinou-se uma série de grandezas termodinâmicas a 298,15 K: solubilidade do  $\text{ZnCl}_2$  (s) em dce, igual a  $(5,144 \pm 0,038) \times 10^{-4} \text{ mol dm}^{-3}$ ; entalpia de molhagem e de dissolução do  $\text{ZnCl}_2$  (s) em dce,  $-(17,1 \pm 2,5)$  e  $-(38,1 \pm 6,8) \text{ kJ mol}^{-1}$ , respectivamente; entalpia da dissolução da dma ( $\ell$ ) e do aduto  $\text{ZnCl}_2 \cdot 2\text{dma}(\ell)$  em dce,  $-(3,78 \pm 0,06)$  e  $(12,42 \pm 0,02) \text{ kJ mol}^{-1}$ , respectivamente. Com estes dados e com os obtidos em experimentos de titulação calorimétrica obteve-se as variações de entalpia para as reações (solução de dce a 298,15 K):  $\text{ZnCl}_2(\text{sln}) + \text{dma}(\text{sln}) = \text{ZnCl}_2 \cdot \text{dma}(\text{sln})$  e  $\text{ZnCl}_2(\text{sln}) + 2\text{dma}(\text{sln}) = \text{ZnCl}_2 \cdot 2\text{dma}(\text{sln})$ , sendo respectivamente  $(11,7 \pm 6,8)$  e  $-(26,3 \pm 1,0) \text{ kJ mol}^{-1}$ . Dos dados obtidos conclui-se que estas entalpias de interação em dce, tido como pouco solvatante, não seriam comparáveis com as mesmas entalpias em fase gasosa.

Taking into account the purpose of studying the interaction of  $\text{ZnCl}_2$  with N,N-dimethylacetamide (dma) in 1,2-dichloroethane (dce) solution, a series of thermodynamic values at 298.15 K were determined: solubility of  $\text{ZnCl}_2$  (s) in dce, equal to  $(5.144 \pm 0.038) \times 10^{-4} \text{ mol dm}^{-3}$ ; enthalpy of wetting and  $\text{ZnCl}_2$ (s) dissolution in dce,  $-(17.1 \pm 2.5)$  and  $-(38.1 \pm 6.8) \text{ kJ mol}^{-1}$ , respectively; enthalpy of dissolution of  $\text{dma}(\ell)$  and  $\text{ZnCl}_2 \cdot 2\text{dma}(\ell)$  adduct in dce,  $-(3.78 \pm 0.06)$  and  $(12.42 \pm 0.02) \text{ kJ mol}^{-1}$ , respectively. With these data and with those obtained in the calorimetric titration experiments, the variation in enthalpy for the following reactions (dce solution at 298.15 K) were obtained:  $\text{ZnCl}_2(\text{sln}) + \text{dma}(\text{sln}) = \text{ZnCl}_2 \cdot \text{dma}$  and  $\text{ZnCl}_2(\text{sln}) + 2\text{dma}(\text{sln}) = \text{ZnCl}_2 \cdot 2\text{dma}(\text{sln})$ , given  $(11.7 \pm 6.8)$  and  $-(26.3 \pm 1.0) \text{ kJ mol}^{-1}$ , respectively. From these data it follows that the enthalpies of interaction in dce, which is slightly solvactant, are not comparable with the same enthalpies in the gaseous phase.

**Key words:** N,N-Dimethylacetamide; thermodynamics; zinc chloride.

### Introduction

A knowledge of enthalpies of sublimation,  $\Delta_{\text{sub}}H$ , is of great importance for determination of enthalpies of atomisation and, consequently, of enthalpies of bonding. In a great number of organometallic compounds and metallic complexes, experimental determination of the enthalpy of sublimation is not feasible due to decomposition or other effects associated with the properties of the compounds. Many of these rule industrial and biological reactions and the knowledge of the mean enthalpies of metal atom-ligand bond dissociation,  $\bar{D}(\text{MY})$ , is necessary to understand the processes involved. For compounds of the type  $\text{MX}_2 \cdot n\text{L}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $n = 1, 2, 3$ ;  $\text{L} =$  ligand with CO or PO groups) the approximation,  $\Delta_{\text{sub}}H(\text{MX}_2 \cdot n\text{L}) = \Delta_{\text{cd}}^g H(\text{L})$  ( $\Delta_{\text{cd}}^g H$  is the enthalpy of vaporisation or sublimation), has been used because these compounds do not sublime without decomposition. Recently, was reported<sup>1</sup> one more argument in favour of this approximation, based on a correlation

between the mean enthalpy of the donor atom bonded to metal,  $\bar{D}(\text{MY})$  and  $\Delta_{\text{r}}H$ , i.e.,  $\bar{D}(\text{MY}) = 1/n \Delta_{\text{r}}H + \text{constant}$ , where  $\Delta_{\text{r}}H$  is related to the reaction:  $\text{MCl}_2 \cdot n\text{L}_{(\text{s})} = \text{MX}_{2(\text{g})} + n\text{L}_{(\text{g})}$ , which is experimentally determined and  $n$  is the ligand number bonded to the metal. This correlation showed that, for nearly eighty adducts, the stoichiometries are perfectly reproducible and the differences and variations of  $\bar{D}(\text{MY})$  values for these compounds are correct except for a constant term. Our interest is to search for additional arguments in favour of this approximation and/or to determine the value of the constant term and consequently the actual value of  $\bar{D}(\text{MY})$ . In this publication some thermochemical data obtained within this research program are presented, the solubility of  $\text{ZnCl}_2$  in dce, its enthalpy of such as dissolution, the enthalpy of dissolution of  $\text{ZnCl}_2 \cdot 2\text{dma}$  in the same solvent, and two calorimetric titration experiments to determine the enthalpy of formation of the adducts  $\text{ZnCl}_2 \cdot \text{dma}$  and  $\text{ZnCl}_2 \cdot 2\text{dma}$  in dce. All

thermodynamic functions involved (H, G and S) are molar, standard ( $p^\ominus = 1$  bar) and valid at 298.15 K. For convenience the superscript  $\ominus$  and the subscript m, for standard and molar respectively, will be neglected<sup>2</sup>.

### Experimental

Anhydrous zinc chloride was prepared as described<sup>3</sup>.  $\text{ZnCl}_2 \cdot 2\text{dma}$  adduct was prepared from anhydrous zinc chloride and dma as before<sup>4,5</sup>. Zinc and chloride analyses confirmed the stoichiometry of the adduct; also the infrared spectra was identical to the previous one<sup>3</sup>. Tris (hydroxymethylamino) methane (Aldrich 99.9% m/m), used in the calorimeter calibration, was ground and sublimed *in vacuo*. All these hygroscopic compounds were always manipulated in an anhydrous nitrogen atmosphere.

The liquids of analytical grade were conveniently dried and distilled in a Vigreux column, i.e., ether (for anhydrous zinc chloride preparation) with metallic sodium; dma with calcium oxide; dce, washed with aqueous potassium hydroxide, dried with anhydrous calcium chloride and then with phosphorus pentoxide. In all cases the boiling points were coincident with those indicated in literature.

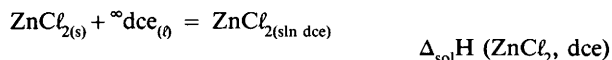
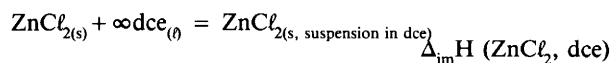
The enthalpies of dissolution were determined by means of a LKB 8700 precision calorimetric system as described<sup>5</sup>, by using the broken ampoule technique, wherein the solid or liquid is introduced into the solvent at (298.15  $\pm$  0.05) K. The performance of the calorimeter was checked through the protonation of tris(hydroxymethylamino)methane in 0.1 mol dm<sup>-3</sup> aqueous HCl solution, giving  $\Delta H = -(29.78 \pm 0.16)$  kJ mol<sup>-1</sup>, which is in agreement with Gunn's value<sup>6</sup> of  $-(29.736 \pm 0.002)$  kJ mol<sup>-1</sup>.

A saturated solution (0.075 dm<sup>3</sup>) of anhydrous zinc chloride in dce was stirred in a stoppered flask immersed in a thermostat at (298.1  $\pm$  0.1) K. Then, with the aid of a pipette (0.010 dm<sup>3</sup>) supplied with a porous glass filter, five aliquots were withdrawn, each one being added to 0.010 dm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> aqueous HCl. After shaking, the aqueous phase was separated. Another 0.010 dm<sup>3</sup> of aqueous HCl was added, shaken and the aqueous phase separated. This procedure was repeated twice. The aqueous phase was then concentrated on a water-bath and the zinc concentration was determined through EDTA titration<sup>7</sup>.

### Results and Discussion

The value  $(5.144 \pm 0.038) \times 10^{-4}$  mol dm<sup>-3</sup> (mean  $\pm$  standard of the mean), has been found for the solubility,  $\sigma$  ( $\text{ZnCl}_2$ , dce), at 298.1 K. It was observed that the dissolution of zinc chloride in dce is not very rapid, causing certain difficulties in performing the calorimetric measurements, presenting also an appreciable effect in wetting (immersion) similar to that pointed out by Suda and Morimoto for

hydrated zinc oxide in various organic solvents<sup>8</sup>. The problem was overcome considering two parallel reactions.



The variation in enthalpy Q is given by the equation:

$$+ Q = ns \Delta_{\text{sol}} H(\text{ZnCl}_2, \text{dce}) + (nt - ns) \Delta_{\text{im}} H(\text{ZnCl}_2, \text{dce})$$

where nt is the amount of  $\text{ZnCl}_2$  weighed in the ampoule and ns the amount of  $\text{ZnCl}_2$  dissolved in dce, which has been calculated by the  $\sigma$  ( $\text{ZnCl}_2$ , dce) value. These results are listed in Table 1. In all experiments solid is present in the final process. Eq. 1 can be considered in the form  $Q = a(nt - ns) + b$ , and, by a linear regression,  $\Delta_{\text{sol}} H(\text{ZnCl}_2, \text{dce})$  and  $\Delta_{\text{im}} H(\text{ZnCl}_2, \text{dce})$  values, a and b respectively, were determined, which are shown in Table 2. The variation in Gibbs free energy for the dissolution process,  $\Delta_{\text{sol}} G(\text{ZnCl}_2, \text{dce})$ , was calculated by means of the equation:

$$\Delta_{\text{sol}} G(\text{ZnCl}_2, \text{dce}) = -RT \ln[\sigma(\text{ZnCl}_2, \text{dce})/\sigma^\ominus]$$

where R is the gas constant, T the temperature (298,2 K) and  $\sigma^\ominus$  the standard concentration, equal to 1 mol dm<sup>-3</sup>, giving  $\Delta_{\text{sol}} G(\text{ZnCl}_2, \text{dce}) = 19.3$  kJ mol<sup>-1</sup>. The variation in entropy for the same process was also calculated,  $\Delta_{\text{sol}} S(\text{ZnCl}_2, \text{dce})$ , using the expression

$$\Delta_{\text{sol}} S(\text{ZnCl}_2, \text{dce}) = [\Delta_{\text{sol}} H(\text{ZnCl}_2, \text{dce}) - \Delta_{\text{sol}} G(\text{ZnCl}_2, \text{dce})]/T \text{ giving } \Delta_{\text{sol}} S(\text{ZnCl}_2, \text{dce}) = -193 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Notice that the  $\Delta^{\text{sol}} H$  value corresponds to an exothermic process, which is opposite to  $\Delta^{\text{sol}} H(\text{HgCl}_2, \text{dce}) = 13.4$  kJ

**Table 1.** Variation of enthalpy observed for  $\text{ZnCl}_{2(s)}$  dissolution in  $\text{dce}_{(\theta)}$ .

$\frac{nt \times 10^4}{\text{mol}}$	$\frac{(nt - ns) \times 10^5}{\text{mol}}$	$-\frac{Q}{\text{J}}$
1.350	0.836	3.200
1.450	0.936	3.654
1.801	1.287	4.041
1.950	1.436	4.735
2.550	2.036	5.309

(see text for definitions of nt and ns)

**Table 2.** Dissolution processes and respective  $\Delta H$  values at 298.15 K.

Processes	$\Delta H/\text{kJ mol}^{-1}$
(1) $\text{ZnCl}_{2(s)} + \infty \text{dce}_{(\theta)} = \text{ZnCl}_{2(s, \text{ dce suspension})}; \Delta_{\text{im}} H(\text{ZnCl}_2, \text{dce})$	-17.1 $\pm$ 2.5
(2) $\text{ZnCl}_{2(s)} + \infty \text{dce}_{(\theta)} = \text{ZnCl}_{2(\text{sln})}; \Delta_{\text{sol}} H(\text{ZnCl}_2, \text{dce})$	-38.1 $\pm$ 6.8
(3) $\text{dma}_{(\theta)} + \infty \text{dce}_{(\theta)} = \text{dma}_{(\text{sln})}; \Delta_{\text{sol}} H(\text{dma}, \text{dce})$	- 3.78 $\pm$ 0.06
(4) $\text{ZnCl}_2 \cdot 2\text{dma}_{(s)} + \infty \text{dce}_{(\theta)} = \text{ZnCl}_2 \cdot 2\text{dma}_{(\text{sln})}; \Delta_{\text{sol}} H(\text{ZnCl}_2 \cdot 2\text{dma})$	12.42 $\pm$ 0.02
(5) $\text{ZnCl}_{2(\text{sln})} + 2\text{dma}_{(\text{sln})} = \text{ZnCl}_2 \cdot 2\text{dma}_{(\text{sln})}; \Delta_a H$	-26.3 $\pm$ 2.0
(6) $\text{ZnCl}_{2(\text{sln})} + \text{dma}_{(\text{sln})} = \text{ZnCl}_2 \cdot \text{dma}_{(\text{sln})}; \Delta_b H$	11.7 $\pm$ 6.8

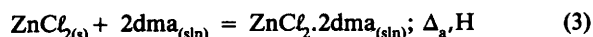
mol<sup>-1</sup> at the same temperature, this chloride being much more soluble than the zinc one<sup>9</sup>. On the other hand,  $\Delta_{\text{sol}}S(\text{ZnCl}_2, \text{dce}) < 0$ , indicates a strong solvation in this non-ionized solvent. For comparison  $\Delta_{\text{sol}}S(\text{I}_2, \text{dce}) = -15.2 \text{ JK}^{-1} \text{ mol}^{-1}$ .<sup>10</sup> Contrary to some assertions, dce does not seem to be such a slightly solvactant solvent<sup>11</sup>.

These substances are soluble enough in dce and do not present the particularities of  $\text{ZnCl}_2$ .  $\Delta_{\text{sol}}H$  values, listed in Table 2, were calculated using the equation

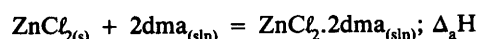
$$Q = n\Delta_{\text{sol}}H \quad (2)$$

where  $Q$  is the observed variation of the enthalpy and  $n$  is the amount of dissolved substance. Notice that this equation gives a straight line which crosses the origin and the experimental points coincide on it. Thus, there is not an association process or appreciable dissociation involving  $\text{dma}$  or  $\text{ZnCl}_2 \cdot 2\text{dma}$  in the solution. The final concentrations of the resulting solutions are smaller than  $2 \times 10^{-5} \text{ mol dm}^{-3}$ .

Determination of the enthalpies of dissolution of zinc chloride in solution of  $\text{dma}$  in  $\text{dce}$ ,  $H\Delta_{\text{a,H}}$ , expressed as:



permitted calculation of the enthalpy of donor-acceptor interaction in solution, i.e.,



For each variation of enthalpy observed for the process indicated by eq. 3, a corresponding value was subtracted due to the solubility of zinc chloride in  $\text{dce}$ , which was calculated by means of  $\Delta_{\text{sol}}H(\text{ZnCl}_2, \text{dce})$ . From eq. 2,  $\Delta_{\text{a,H}}$  was calculated. The value is shown in Table 2, where the (mean  $\pm$  deviation of the mean) was obtained for two series of measurements. In each of these series, four samples of  $\text{ZnCl}_2$  were dissolved in a solution of 2.0 and 5.0% v/v in  $\text{dce}$ , respectively, assuring that in the end there was a  $n(\text{dma})/n(\text{ZnCl}_2) \approx 200$  ratio, which permits the formation of only the  $\text{ZnCl}_2 \cdot 2\text{dma}$  species.

In contrast to  $\text{ZnCl}_2 \cdot \text{dmf}$  ( $\text{dmf} = \text{N,N-dimethylformamide}$ )<sup>12</sup>, it was not possible to isolate the adduct  $\text{ZnCl}_2 \cdot \text{dma}$ . However, qualitative evidence shows its existence in solution. To determine its enthalpy ( $\Delta_{\text{b,H}}$ ) and formation constant ( $K$ ) in  $\text{dce}$ , an experiment based on calorimetric titration was performed<sup>13</sup>. Ampoules of  $\text{dma}$  were broken in a saturated solution of zinc chloride in  $\text{dce}$ , so the observed variation of enthalpy,  $Q_{\text{obs}}$ , was observed for each addition of reagent. Three series of experiments were made and Figure 1 represents one of them.  $Q_{\text{sol}}$

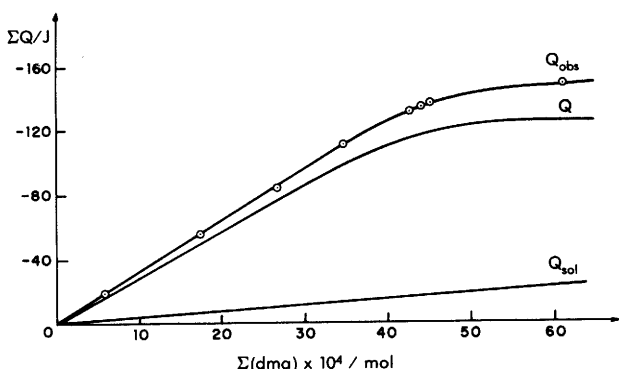
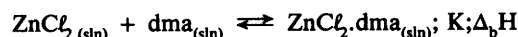
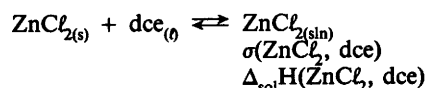


Figure 1. Calorimetric titration of  $\text{ZnCl}_2$  with  $\text{dma}$  in  $\text{dce}$  solution (290.20 mg of  $\text{ZnCl}_2$  in 90.0 cm<sup>3</sup> of  $\text{dce}$ ).

corresponds to the heat of dissolution of  $\text{dma}$  in  $\text{dce}$ , which is calculated from  $\Delta_{\text{sol}}H(\text{dma}, \text{dce})$ , and  $Q = Q_{\text{obs}} - Q_{\text{sol}}$ ; this value is the variation of enthalpy in the studied process and can be displayed as two equilibria.



where  $K = c(\text{ZnCl}_2 \cdot \text{dma})/c(\text{ZnCl}_2) \cdot c(\text{dma})$  and  $c$  is the concentration of the indicated species in equilibrium in solution. With  $\text{dma}$  addition the second equilibrium is displaced to the right, because  $\text{ZnCl}_{2(\text{sln})}$  in solution is consumed to form the adduct, promoting the dissolution of more  $\text{ZnCl}_{2(s)}$ . Thus, considering the material balance and the  $K$  expression, one obtains:

$$c(\text{ZnCl}_2 \cdot \text{dma}) = [n(\text{dma})/V][K\sigma/(K\sigma + 1)] \quad (4)$$

$n(\text{dma})$  being the amount of added  $\text{dma}$ ,  $V$  the volume of solution and  $\sigma = \sigma(\text{ZnCl}_2, \text{dce})$ .  $Q$  is the sum of variation of the enthalpies corresponding to the two equilibria, which is given by:

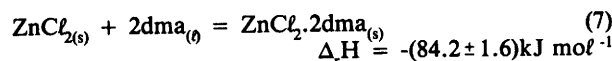
$$Q = n(\text{ZnCl}_2)\Delta_{\text{sol}}H(\text{ZnCl}_2, \text{dce}) + n(\text{dma})[K\sigma/(K\sigma + 1)]\Delta_{\text{b,H}} \quad (5)$$

where  $n(\text{ZnCl}_2)$  is the dissolved amount of  $\text{ZnCl}_{2(s)}$ . This experiment was performed while fulfilling the following conditions: (1) In starting the titration all  $\text{dma}$  is bonded to  $\text{ZnCl}_2$  to form the adduct, e.g.,  $n(\text{dma}) \approx c(\text{ZnCl}_2 \cdot \text{dma})$ .  $V$  and  $c(\text{dma}) \approx 0$ ; (2) Consequently, the amount of  $\text{ZnCl}_2$  which will be dissolved due to adduct formation will be equal to the amount formed giving,  $n(\text{ZnCl}_2) \approx c(\text{ZnCl}_2 \cdot \text{dma}) \cdot V \approx n(\text{dma})$ . Both assumptions are equivalent to considering that  $K$  has a large value and (5) reduces to:

$$Q = n(\text{dma})[\Delta_{\text{sol}}H(\text{ZnCl}_2, \text{dce}) + \Delta_{\text{b,H}}] \quad (6)$$

The validity of this equation can be confirmed by the graph shown in Figure 1 which is approximately linear up to  $\Sigma n(\text{dma}) \approx 35 \times 10^{-4} \text{ mol}$ . Then, from equation (6),  $\Delta_{\text{b,H}}$  is calculated, whose value is listed in Table 2 and, by means of (5),  $K$  is also calculated, giving  $1.9 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ . As before, the variations of the Gibbs energy and entropy were calculated, for the formation of the  $\text{ZnCl}_2 \cdot \text{dma}$  adduct in  $\text{dce}$  solution, giving  $\Delta_{\text{b,G}} = -19 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{b,S}} = 1.0 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1}$ . A  $\Delta_{\text{b,S}} > 0$  value is in agreement with an appreciable  $\text{ZnCl}_2$  solvation on the part of  $\text{dce}$ , larger than that found in  $\text{dma}$  and adduct.

Taking into account the results obtained here and previous ones<sup>5</sup>, it was possible to calculate  $\Delta_{\text{a,H}}$  with the experimental value obtained.



From the processes 1, 3 and 4 indicated in Table 2 and (7), together with Hess' law

$$\Delta_{\text{a,H}} = \Delta_{\text{r,H}} - \Delta_{\text{sol}}H(\text{ZnCl}_2, \text{dce}) - \Delta_{\text{sol}}H(\text{dma}, \text{dce}) - \Delta_{\text{sol}}H(\text{ZnCl}_2 \cdot 2\text{dma})$$

one obtains  $\Delta_{\text{a,H}} = -(26.1 \pm 7.0) \text{ kJ mol}^{-1}$ . This value coincide with the experimental one (see Table 2, process 5).

Many investigators in the donor-acceptor compound field consider that the enthalpies of interaction obtained in poor solvactant solvents are close to those of the gas phase<sup>14,15</sup>. Taking into account this assumption, the value of the enthalpy of interaction of  $\text{ZnCl}_2$  with dma in a specific poor solvactant solvent such as dce was determined. From these results some features can be emphasized: 1.  $\text{ZnCl}_2$ .2dma adduct should present a high constant of formation in dce. 2. it is difficult to admit that the interaction values found in this process are close to those obtained in gas phase, due to the behaviour of  $\text{ZnCl}_2$  in this solvent.

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