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Modeling Enthalpy and Hydration Properties of Inorganic Compounds

Lionello Pogliani

Dipartimento di Chimica, Università della Calabria, 87030 Rende (CS), Italy

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The method of linear combinations of connectivity indices has been applied to fit the following physicochemical properties of inorganic molecules: the lattice enthalpies of 32 inorganic compounds, the limiting enthalpies of solution of 12 metal halides, the unfrozen water content, the relative humidity and eutectic temperature of metal chlorides and the unfrozen water content of a mixed set of amino acids and metal chlorides. The achieved fit is very satisfactory and it can be normally attained with the help of a single-index linear combination. The obtained fit draws also a validity test for the delta δ^v valence number of the inorganic compounds and for a newly defined D^Z index based on the number of valence electrons and on the principal quantum number. The fit of the unfrozen water content of the mixed set of amino acids and metal chlorides, achieved by means of linear combinations of reciprocal connectivity indices can be seen as a first hint for the construction of a connectivity model encompassing both organic and inorganic compounds.

INTRODUCTION

Recently,[1–3] a molecular connectivity method based on linear combinations of different connectivity indices and known as LCCI has been outlined to encode the maximum number of physicochemical properties of amino acids and different classes of organic molecules. The raw data of the method are the δ cardinal numbers whose electronic meaning has been emphasized in Refs. 4–6.

In this paper, the outlined method will be applied to encode the lattice enthalpies $\Delta H_L^{\varnothing}$ of 32 inorganic compounds divided into three subsets: 8 met-

al oxides and sulfides (MeO and MeS), 20 metal halides (MeHal) and 9 metal chlorides (MeCl), the limiting enthalpies of solution at 298.15 K, $\Delta H^{\varnothing}_{soln}$, of 12 metal halides (apex $\varnothing$ stands for 298.15 K), the unfrozen water content, UWC, the relative humidity, RH%, and the eutectic temperature, ET, of 5 metal chlorides (MeCl') and the UWC of a mixed set of 8 amino acids and 5 metal chlorides (MeCl') at –20 °C and at –15 °C, respectively. Aims of the present study are: i) to test how far molecular connectivity methods[5–8] based on LCCI give a prompt answer to the modeling of physical properties of inorganic compounds, ii) to verify the definition of δ^v (Ref. 5) in inorganic compounds and iii) to check the encoding power of the newly defined D^Z index based on the number of valence electrons, Z^v and on the principal quantum number. Linear combinations of orthogonal molecular connectivity indices (LCOCI) and of reciprocal connectivity indices (LCRCI) will also be used to enhance whenever possible, the modeling of a specific property.

METHOD

Even if a MC model for ionic salts has not yet been defined, we can nevertheless introduce some assumptions that should allow us, for the moment, to use the well-known MC paradigm of Randić, Kier and Hall[5–8] to comprehend inorganic salts.

It will be assumed that electrostatic bonds in salts can be treated as connectivities. They are, thus, field connectivities elaborated by each atom and sensed by other atoms in close proximity. Furthermore, δ(Me) and δ(Anion) values equal the coordination values of the respective ions, while the sums in Eqs. 1 and 2 run, here, over the p electrostatic bonds and over the n number of ions, respectively as it can be deduced from the corresponding chemical formula. The $\{\chi\}=\{D, D^v, {}^0\chi, {}^0\chi^v, {}^1\chi, {}^1\chi^v, \chi_t, \chi_t{}^v\}$ set of connectivity indices will be used to model the different properties of the inorganic compounds. For the given inorganic compounds this set represents a full set of χ indices as no other higher-order indices can be derived for these compounds (in MeHal and $MeHal_2$: $\chi_t = {}^1\chi$ and ${}^2\chi$, respectively). These connectivity values can be calculated using Eqs. (1)–(3).[5,9,10]

$$ {}^{n-1}\chi = \Sigma_p(\delta_1\delta_2....\delta_n)^{-1/2} \tag{1} $$

$$ D = \Sigma_i\, \delta_i \tag{2} $$

$$ \chi_t = (\delta_1\delta_2 \ldots \delta_n)^{-1/2} \tag{3} $$

With these compounds the maximum connectivity order is $m = 2$ ($m = n - 1$), thus subscripts for adjacent atoms in Eqs. (1) and (3) range from 1 to 3.

Replacing the cardinal δ numbers by the valence δ^v numbers, the corresponding valence connectivity indices ${}^m\chi^v$, D^v and $\chi_t{}^v$ are obtained. The χ^v values of the given ions are obtained with the help of the following relation:[5]

$$\delta^v = Z^v / (Z - Z^v - 1) \tag{4}$$

where Z^v is the number of valence electrons and Z is the atomic number of the corresponding atom. While the δ value of the atoms of the studied inorganic compounds are just 1 or 2 (Me in $MeCl_2$), the valence δ^v values of the different atoms computed by the aid of Eq. (4) are:

Li	Na	K	Rb	Cs	Be	Mg	Ca	
1	1/9	1/17	1/35	1/53	2	2/9	2/17	
Sr	Ba	Cu	F	Cl	Br	I	O	S
2/35	2/53	2/26	7	7/9	7/27	7/45	6	6/9

The encoding power of the following new index will also be tested

$$D^Z = \Sigma_i(Z_i{}^v / n_i) \tag{5}$$

where Z^v has already been defined and n is the principal quantum number. If the Z^v/n index is regarded as a kind of δ^z number the similarity between Eq. (5) and Eq. (2) becomes evident. With this newly defined index the set of connectivity indices used to model the different properties of the inorganic compounds becomes: $\{\chi\} = \{D, D^v, {}^0\chi, {}^0\chi^v, {}^1\chi, {}^1\chi^v, \chi_t, \chi_t{}^v, D^Z\}$. The δ^z values of the atoms of the studied inorganic compounds are:

Li	Na	K	Rb	Cs	Be	Mg	Ca & Cu
1/2	1/3	1/4	1/5	1/6	2/2	2/3	2/4
Sr	Ba	F	Cl	Br	I	O	S
2/5	2/6	7/2	7/3	7/4	7/5	6/2	6/3

The multivariate regression based on χ indices can be regarded as a linear combination of connectivity indices (LCCI) where the constant term of the regression can be considered to multiply the unitary index $\chi^0 \equiv 1$. This unitary index does not influence the regression but allows to describe a property as a simple dot product $P = \mathbf{C} \cdot \chi$, where P is the encoded property, $\mathbf{C}$ is the correlation row vector (or a matrix, if the properties are more than 1) of the coefficients of the connectivity χ parameters (of the column χ vector), determined by the least-square procedure. Orthogonal molecular connectivity Ω as well as reciprocal $R = 1/\chi$ indices will be used to improve, whenever possible, the description of the given properties. The Ω indices can be ob-

tained with the aid of an orthogonalization procedure recently outlined by Randić.[11]

The unfrozen water UWC content of 8 natural amino acids at –20 °C, the UWC at –15 °C, the relative humidities of saturated solutions, RH% and the eutectic ET temperatures of 5 MeCl' are taken from Ref. 12, an interesting review which describes the methods for obtaining the data and their reproducibility. The enthalpy values of the different inorganic compounds are taken from Ref. 13.

RESULTS

In Table I the lattice enthalpies, $\Delta H_L^{\emptyset}$, at 298.15 K of 9 metal chlorides with their corresponding connectivity index and D^Z values and in Table II the lattice enthalpies at the same temperature of 20 metal halides, 8 metal oxides and sulfides together with their corresponding connectivity index and D^Z values have been collected, and in Table III the limiting enthalpies of solution at 298.15 $\Delta H_{soln}^{\emptyset}$ of 12 metal halides along with their corresponding connectivity index and D^Z values have been collected. In Table IV the unfrozen water content, UWC, at –15 °C, the relative humidity, RH% and the eutectic temperature of 5 metal chlorides together with their respective connectivity index and D^Z values have been collected. This Table also gives the unfrozen water content at –20 °C of 8 amino acids while their corresponding connectivity values have been taken from Table II of Ref. 1. Because indices D, ${}^0\chi$, ${}^1\chi$ and χ_t of MeCl of Table I are colinear (R = 1, colinear indices just duplicate one another; for a colinearity criterion see Ref. 17), ${}^0\chi$, ${}^1\chi$ and χ_t indices have been omitted. The connectivity $\{D, {}^0\chi, {}^1\chi = \chi_t\}$ indices of MeHal of Tables II and III, instead, being meaningless (their value is constant for

TABLE I

Lattice enthalpies, $\Delta H_L^{\emptyset}$ at 298.15 K (kJ mol^{-1}) of 9 metal chlorides (MeCl) and their corresponding molecular connectivity and D^Z index values.

MeCl	$\Delta H_L^{\emptyset}$	D	D^v	${}^0\chi^v$	${}^1\chi^v$	$\chi_t{}^v$	D^Z
LiCl	852	2	1.77778	2.13389	1.13389	1.13389	2.83333
NaCl	786	2	0.88889	4.13389	3.40168	3.40168	2.66667
KCl	717	2	0.83660	5.25700	4.67516	4.67516	2.58333
RbCl	695	2	0.80635	7.04997	6.70820	6.70820	2.53333
CsCl	676	2	0.79664	8.41400	8.25487	8.25487	2.50000
$BeCl_2$	3017	4	3.55556	2.97489	1.60357	0.90914	5.66667
$MgCl_2$	2524	4	1.77778	4.38911	4.81070	2.72741	5.33333
$CaCl_2$	2255	4	1.67320	5.18326	6.61168	3.74847	5.16667
$SrCl_2$	2153	4	1.61270	6.45109	9.48683	5.37853	5.06667

TABLE II

Lattice enthalpies, $\Delta H_L^{\emptyset}$ at 298.15 K (kJ mol^{-1}) of 20 metal halides (MeHal), 4 metal oxides (MeO) and 4 metal sulphides (MeS) and their corresponding molecular connectivity and D^Z index values.

Me(Hal, O, S)	$\Delta H_L^{\emptyset}$	D^v	$^0\chi^v$	$^1\chi^v$	D^Z
LiF	1037	8	1.37796	0.37796	4
NaF	926	7.11111	3.37796	1.13389	3.83333
KF	821	7.05882	4.50107	1.55839	3.75000
RbF	789	7.02857	6.29404	2.23607	3.70000
CsF	750	7.01887	7.65807	2.75162	3.66667
LiCl	852	1.77778	2.13389	1.13389	2.83333
NaCl	786	0.88889	4.13389	3.40168	2.66667
KCl	717	0.83660	5.25700	4.67516	2.58333
RbCl	695	0.80635	7.04997	6.70820	2.53333
CsCl	678	0.79665	8.41400	8.25487	2.50000
LiBr	815	1.25926	2.96396	1.96396	2.25000
NaBr	752	0.37037	4.96396	5.89188	2.41667
KBr	689	0.31808	6.08707	8.09762	2.00000
RbBr	668	0.28783	7.88004	11.6190	1.95000
CsBr	654	0.27813	9.24407	14.2979	1.91667
LiI	761	1.15556	3.53546	2.53546	1.90000
NaI	705	0.26667	5.53546	7.60639	1.73333
KI	649	0.21438	6.65857	10.4540	1.65000
RbI	632	0.18413	8.45154	15.0000	1.60000
CsI	620	0.17442	9.81557	18.4585	1.56667
MgO	3850	6.22222	2.52957	0.86603	3.66667
CaO	3461	6.11765	3.32372	1.19024	3.50000
SrO	3283	6.05714	4.59155	1.70783	3.40000
BaO	3114	6.03774	5.55606	2.10159	3.33333
MgS	3406	0.88889	3.34607	2.59808	2.66667
CaS	3119	0.78431	4.14022	3.57071	2.50000
SrS	2974	0.72381	5.40805	5.12348	2.40000
BaS	2832	0.70440	6.37256	6.30476	2.33333

all the different compounds) have been omitted together with the χ_t^v index, as $\chi_t^v = {}^1\chi^v$. Non valence molecular connectivity indices of metal MeCl' chlorides of Table IV, $\{D, {}^0\chi, {}^1\chi, \chi_t\}$ are also totally colinear but they have been reported (with the exception of χ_t, not derived for AA) because the colinearity disappears when the mixed set of [AA+MeCl'] is modeled. Summarizing, the $\{\chi\}$ set of molecular connectivity indices used to fit the physical properties of the compounds of Tables I–IV (metal chlorides only) are: $\{D, D^v, {}^0\chi^v, {}^1\chi^v,$

TABLE III

Limiting enthalpies of solution, $\Delta H^{\emptyset}_{soln}$ at 298.15 K (kJ mol^{-1}) of 12 metal halides (MeHal) and their corresponding molecular connectivity and D^Z index as well three orthogonal $^i\Omega$ ($^1\Omega \equiv D^Z$, $^2\Omega - {}^1\chi^v$ and $^3\Omega - D^v$) index values.

MeHal	$\Delta H^{\emptyset}_L$	D^v	$^0\chi^v$	$^1\chi^v$	$D^Z \equiv {}^1\Omega$	$^2\Omega$	$^3\Omega$
LiF	4.9	8	1.37796	0.37796	4.00000	0.90870	0.19634
NaF	1.9	7.11111	3.37796	1.13389	3.83333	0.58785	0.52423
KF	–17.7	7.05882	4.50107	1.55839	3.75000	0.81958	0.64776
LiCl	–37	1.77778	2.13389	1.13389	2.83333	–1.33726	–2.04396
NaCl	3.9	0.88889	4.13389	3.40168	2.66667	–1.65811	–0.20420
KCl	17.2	0.83660	5.25700	4.67516	2.58333	–1.42638	0.76832
LiBr	–48.8	1.25926	2.96396	1.96396	2.25000	0.13236	–3.28682
NaBr	–0.6	0.37037	4.96396	5.89188	2.41667	–1.32457	1.46330
KBr	19.9	0.31808	6.08707	8.09762	2.00000	0.04324	2.11784
LiI	–63.3	1.15556	3.53546	2.53546	1.90000	1.22154	–4.00507
NaI	–7.5	0.26667	5.53546	7.60639	1.73333	0.90069	0.63782
KI	20.3	0.21438	6.65857	10.4540	1.65000	1.13242	3.18445

TABLE IV

Unfrozen water content (UWC) of 8 L–amino acids (AA) at –20 °C (g H_2O/g AA), unfrozen water content UWC (g H_2O/g MeCl'), relative humidities of saturated solutions, RH% and the observed eutectic temperatures ET (in °C) of 5 metal chlorides (MeCl') and their corresponding molecular connectivity and D^Z index values.

AA	UWC	AA	UWC		MeCl'	UWC	RH%	ET
Pro	1.07	Ser	0.48		LiCl	6.5	15	–100
Hyp	0.70	Arg	0.46		NaCl	3.0	75	–30
Glu	0.97	His	0.66		KCl	1.8	85	–15
Lys	0.93				$CaCl_2$	4.0	33	–85
Thr	0.72				$CuCl_2$	4.0	67	–60
MeCl'	D	$^0\chi$	$^1\chi$	D^v	$^0\chi^v$	$^1\chi^v$	$\chi_t{}^v$	D^Z
LiCl	2	2	1	1.7778	2.1339	1.1339	1.1339	2.8333
NaCl	2	2	1	0.8889	4.1339	3.4016	3.4017	2.6667
KCl	2	2	1	0.8366	5.2570	4.6752	4.6752	2.5833
$CaCl_2$	4	2.7071	1.4142	1.6732	5.1832	6.6117	3.7485	5.1667
$CuCl_2$	4	2.7071	1.4142	1.6325	5.8733	8.1777	4.6357	5.1667

$\chi_t{}^v$, D^Z}, {D^v, $^0\chi^v$, $^1\chi^v$, D^Z} and {D, D^v, $^0\chi^v$, $^1\chi^v$, $\chi_t{}^v$, D^Z} respectively, while for the mixed set of [AA+MeCl'] is {D, D^v, $^0\chi$, $^0\chi^v$, $^1\chi$, $^1\chi^v$}.

DISCUSSION

The description of the lattice enthalpies, $\Delta H_L^{\emptyset}$ of the entire set of n = [20(MeHal) + 8(MeO, MeS) + 4($MeCl_2$)] is unsatisfactory and the same can be said for the description of the subset n = [20(MeHal) + 8(MeO, MeS)] compounds. In fact, both fits have a correlation coefficient $r < 0.5$ and a too large standard deviation of the estimates.

The search for a satisfactory description can be achieved by means of segmentation of the entire set of 34 compounds into three homogeneous subsets of inorganic compounds: n = 9 MeCl, n = 20 MeHal and n = 8[MeO + MeS]. Clearly, the practice of segmentation of extended classes of compounds into more homogeneous subclasses, already used with the alkanes,[3] reducing the number of points to be fitted, improves the fit and, for this reason, it should be used with care. The homogeneous segmentation is generally introduced to overcome the inherent limits of the ordinary connectivity indices in describing strong shape-dependent properties. Sometimes, these limits can be overcome by using of supraconnectivity indices or special composite connectivity indices if further properties of the system are known (e.g., self-association, solvation, number of functional groups, *etc*...),[3,14,15,16] but when this information is not at hand, segmentation is a required temporary step for a decent fit till further and more complete data can be obtained.

The set of connectivity indices used to simulate the lattice enthalpies of metal chlorides of Table I has a very low value of the mean correlation coefficient of the interrelation matrix[2,17] $\langle R_{IM}(\Delta H_L^{\emptyset}:\{\chi\})\rangle = 0.565$, the weakest and strongest interrelated indices being: $R_w({}^1\chi v, D^Z) = 0.024$ and $R_s(D, D^Z) = 0.991$. The description of the lattice enthalpies of these n = 9 metal chlorides is already fine with the single D^Z index LCCI ($Q = r/s$ and $F = fr^2/v(1 - r^2)$], r = correlation coefficient, s = standard deviation, f = freedom degrees and v = number of variables)[5,2]

$$\{D^Z\}: Q = 0.007, F = 354.7, r = 0.990, s = 141$$

while the following LCCI, with the contribution of the highly interrelated D and D^z indices, are excellent:

$$\{D, D^Z\}: Q = 0.011, F = 460.3, r = 0.997, s = 88.2$$
$$\{D, {}^0\chi^v, D^Z\}: Q = 0.022, F = 1175, r = 0.9993, s = 45.2.$$

The following $\chi = (D, {}^0\chi^v, D^Z, \chi^0)$ and $\boldsymbol{C}$ = (–1445.99, 59.7100, 1740.31, –1250.53) vectors have been used to fit the lattice enthalpies of the metal chlorides reported in Figure 1. The plot confirms the very good description achieved by the last LCCI, even if the quality of the two- and one-index

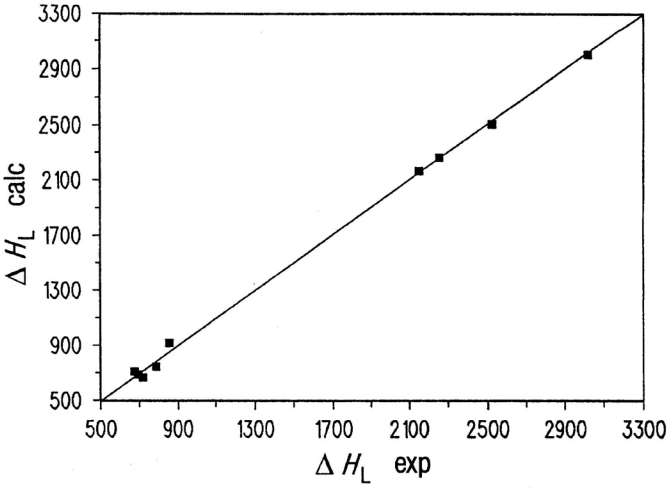

Figure 1. Plot of the calculated *versus* the experimental lattice enthalpies at 298.15 K of n = 9 metal chlorides.

LCCI are noteworthy. The most remarkable aspect of these LCCI is, surely, the importance of the D^Z index all along this description.

A satisfactory modeling of the lattice enthalpies of the eight MeO and MeS of Table II with the $\{\chi\} = \{D^v, {}^0\chi v, {}^1\chi v, D^Z\}$ set that has : $\langle R_{IM}(\Delta H_L^{\varnothing}: \{\chi\})\rangle = 0.565$ and $R_w(D^v, D^Z) = 0.027$, and $R_s({}^0\chi v, D^Z) = 0.912$, is achieved

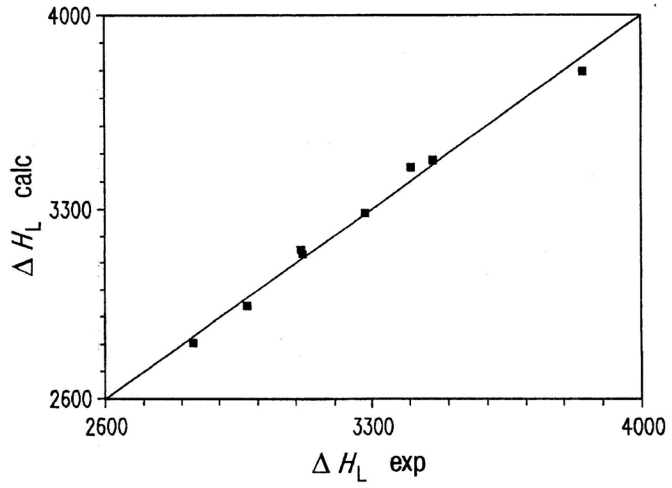

Figure 2. Plot of the calculated *versus* the experimental lattice enthalpies at 298.15 K of n = 8 metal oxides and metal sulphides [4(MeO)+4(MeS)].

by the following one- and two-index LCCI, where the D^Z index plays the primary role and where D^v and D^z are practically orthogonal

$$\{{}^0\chi^v\}: Q = 0.007, F = 37.22, r = 0.928, s = 129$$
$$\{D^v, D^Z\}: Q = 0.024, F = 206.9, r = 0.994, s = 41.4.$$

In Figure 2, obtained using $\chi = (D^v, D^Z, \chi^0)$ and $\mathbf{C} = (-333.285, 2121.75, -1910.16)$, the calculated *versus* experimental lattice enthalpy values are plotted. This figure underlines the admirable score of the two-index simulation.

The four indices of the $\{\chi\} = \{D^v, {}^0\chi v, {}^1\chi v, D^Z\}$ index set with $<R_{IM}(\Delta H_L^{\varnothing}: \{\chi\})> = 0.669$ and $R_w(D^v, {}^0\chi v) = 0.388$, and $R_s(D^v, D^Z) = 0.913$ give rise to the best LCCI for the lattice enthalpy of the 20 metal halides of Table II:

$$\{D^v, {}^0\chi v, {}^1\chi v, D^Z\}: Q = 0.044, F = 101.7, r = 0.982, s = 22.2.$$

Index D^Z appears only in the three- and four-index combinations. In fact, the best one-, two- (poorly interrelated indices) and three-index combinations are:

$$\{{}^0\chi^v\}: Q = 0.0153, F = 45.38, r = 0.846, s = 57.3$$
$$\{D^v, {}^0\chi^v\}: Q = 0.033, F = 115.1, r = 0.965, s = 29.0$$
$$\{{}^0\chi^v, {}^1\chi^v, D^Z\}: Q = 0.043, F = 130.5, r = 0.980, s = 22.6.$$

Vectors $\chi = ({}^0\chi^v, {}^1\chi^v, D^Z, \chi^0)$ and $\mathbf{C} = (-42.1357, 10.5249, 95.9608, 676.913)$ of the three-index combination, due to its better F value, are the vectors that best fit the $n = 20$ enthalpy values, as reported in Figure 3. This figure gives a clear view of the good performance of the three-index simulator although the two-index combination should not be underestimated.

The description of the limiting enthalpies of the solution at 298.15 K, $\Delta H_{soln}^{\varnothing}$ of metal halides of Table III with the $\{\chi\} = \{D^v, {}^0\chi^v, {}^1\chi^v, D^Z\}$ index set, which shows a $<R_{IM}(\Delta H_{soln}^{\varnothing}:\{\chi\})> = 0.790$ and $R_w(D^v, {}^0\chi^v) = 0.564$, and $R_s(D^v, D^Z) = 0.929$, starts with a very poor single-index combination, which unmasks the presence of the dominant orthogonal descriptors for this property and achieves a good description with a three index combination, where the D^Z index is an important component

$$\{{}^0\chi^v\}: Q = 0.021, F = 3.82, r = 0.526, s = 24.5$$
$$\{\mathrm{D^v}, {}^1\chi^{\mathrm{v}}, \mathrm{D^Z}\}: Q = 0.088, F = 21.28, r = 0.943, s = 10.8.$$

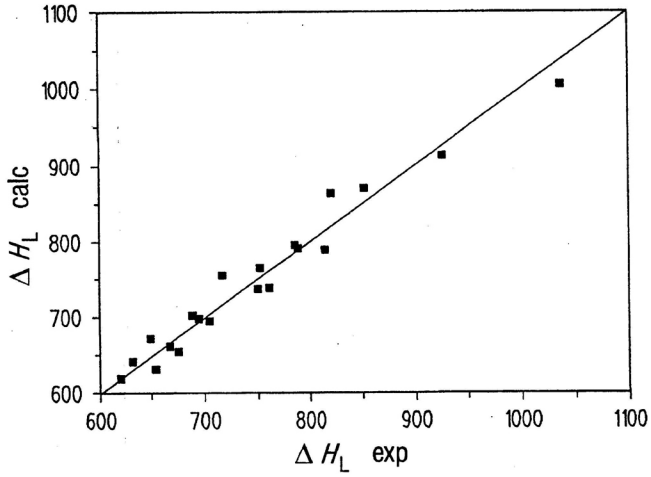

Figure 3. Plot of the calculated *versus* the experimental lattice enthalpies at 298.15 K of n = 20 metal halides.

Use of the orthogonal $\{\Omega\}=\{D^Z \equiv {}^1\Omega, {}^2\Omega, {}^3\Omega\}$ set of Table III, obtained with the aid of Randić's orthogonalization procedure[11] applied sequentially to indices D^Z, ${}^1\chi^v$ and D^v , improves dramatically the fitting power of the single-index LCCI and of the two- and the three-index LCCI, in fact the two-Ω-index is a better combination than the preceding three-χ-index combination

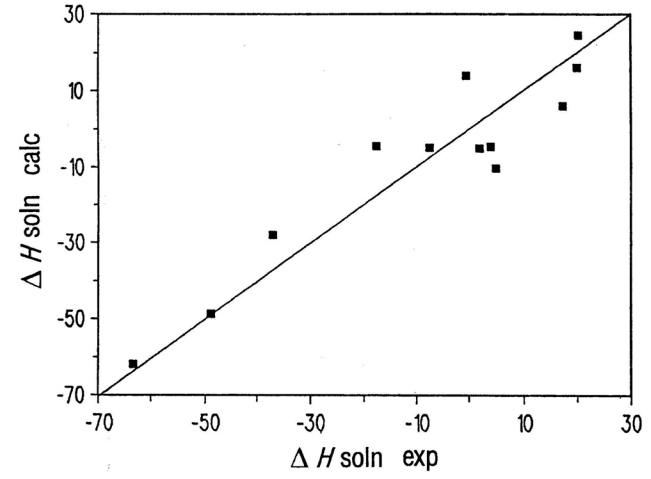

Figure 4. Plot of the calculated *versus* the experimental limiting enthalpies of solution at 298.15 K of n = 12 metal halides.

$\{^3\Omega\}$: $Q = 0.084$, $F = 58.55$, $r = 0.924$, $s = 11.0$

$\{^2\Omega, ^3\Omega\}$: $Q = 0.090$, $F = 33.58$, $r = 0.939$, $s = 10.5$.

The following $\Omega = (^2\Omega, ^3\Omega, \Omega^0)$ and $\boldsymbol{C} = (-4.09101, 11.9769, -8.89999)$ vectors, which best fit the data, have been used to obtain Figure 4. Clearly, this fit is not as good as the preceding ones but the detected improvement achieved by the single-$^3\Omega$-index combination is conspicuous.

We will now try to describe the eutectic temperatures ET, the unfrozen water content UWC (at –15 °C) and the relative humidities RH% of saturated solutions of $n = 5$ metal chlorides (MeCl') of Table IV the $\{\chi\} = \{D, D^v, {}^0\chi^v, {}^1\chi^v, \chi_t{}^v, D^Z\}$ set, where indices D, ${}^0\chi$, ${}^1\chi$ and χ_t due to colinearity are omitted (see the results). These indices have : $\langle R_{IM}(ET, UWC, RH\%:\{\chi\})\rangle = 0.628$ and $R_w(D^v, {}^1\chi^v) = 0.135$, and $R_s(D, D^Z) = 0.998$. The fit of these properties for the five MeCl' will be limited to a two-index LCCI.

ET: $\{D^v\}$: $Q = 0.071$, $F = 25.9$, $r = 0.947$, $s = 13.3$

$\{D^v, \chi_t{}^v\}$: $Q = 0.121$, $F = 37.3$, $r = 0.987$, $s = 8.2$

UWC: $\{D^v\}$: $Q = 0.772$, $F = 7.15$, $r = 0.839$, $s = 1.1$

$\{D, D^Z\}$: $Q = 4.776$, $F = 137$, $r = 0.996$, $s = 0.2$

RH%: $\{D^v\}$: $Q = 0.044$, $F = 6.83$, $r = 0.834$, $s = 18.9$

$\{D, {}^1\chi^v\}$: $Q = 0.113$, $F = 22.4$, $r = 0.978$, $s = 8.7$

Index D^Z and the highly interrelated D index improve conspicuously the description of UWC while the total valence connectivity $\chi_t{}^v$ and the ${}^1\chi^v$ indices improve the description of ET and RH%, respectively. The unfrozen water UWC content is the best described property of this set of MeCl'. The connectivity and correlation vectors used to fit these properties in Figure 5 are:

ET: $\chi = (D^v, \chi_t{}^v, \chi^0)$, $\boldsymbol{C} = (-63.157, 7.70717, 0.88557)$

UWC: $\chi = (D, D^Z, \chi^0)$, $\boldsymbol{C} = (-23.5119, 19.1149, -0.71336)$

RH%: $\chi = (D, {}^1\chi^v, \chi^0)$, $\boldsymbol{C} = (-48.9991, 20.7343, 92.6724)$.

Noteworthy are the single-index descriptions of the three properties made up by the same D^v index, which thus has the features of a dominant descriptor for these three properties.

Now, the possibility to simulate the UWC of the mixed set of [AA+MeCl'] ($n = 13$) of Table IV will be tested. The set of connectivity indices used for this description will be $\{\chi\} = \{D, D^v, {}^0\chi, {}^0\chi^v, {}^1\chi, {}^1\chi^v\}$ (χ_{AA} values are taken

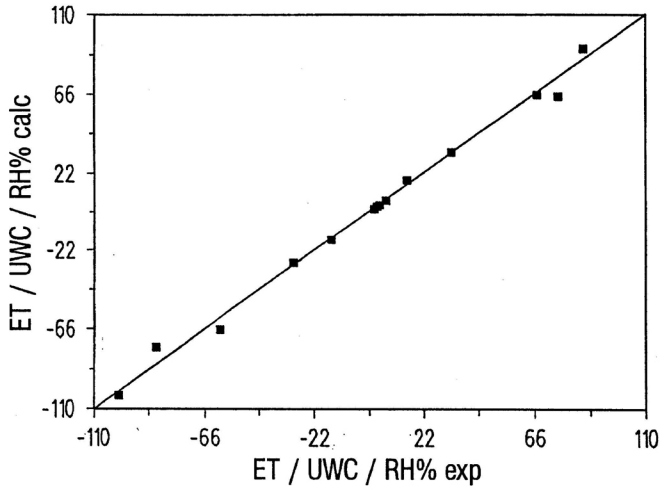

Figure 5. Pot of the calculated *versus* the experimental eutectic temperatures, unfrozen water content, and relative humidity of the saturated solutions of $n = 5$ metal chlorides.

from Ref. 1); clearly the non valence indices of [AA+MeCl'] are no more colinear, thus $\langle R_{IM}(UWC: \{\chi\})\rangle = 0.628$ with $R_w({}^1\chi, {}^1\chi^v) = 0.355$, and $R_s(D, {}^1\chi) = 0.997$.

Estimations with different LCCI show that the best F and Q estimators of UWC of [AA+MeCl'] are:

$$\{D^v\}: Q = 0.71, F = 21, r = 0.81, s = 1.2$$
$$\{D, D^v, {}^0\chi^v, {}^1\chi, {}^1\chi^v\}: Q = 0.92, F = 7.79, r = 0.92, s = 1.0.$$

The fit is in both cases inadequate: the single-index is a rather poor descriptor, and the five-index descriptor, due to the high number of parameters relatively to the number of observations is insufficient. Let us, then, fit the UWC of [AA(–20 °C) +MeCl'(–15 °C)] with the following set of reciprocal connectivity indices ($R = 1/\chi$) as already done for other properties of amino acids:[18,19] $\{R\} = \{{}^DR, {}^DR^v, {}^0R, {}^0R^v, {}^1R, {}^1R^v\}$ with $\langle R_{IM}(UWC: \{R\})\rangle = 0.559$ and $R_w({}^0R, {}^1R^v) = 0.064$, $R_s({}^0R, {}^1R) = 0.999$. The best single-$R$ index description shows no improvement relatively to the single-χ LCCI:

$$\{{}^0R\}: Q = 0.680, F = 19.50, r = 0.800, s = 1.2.$$

But, marked improvements can be detected with the following two- and three-R combinations:

$\{{}^{D}R^{v}, {}^{0}R\}$: Q = 1.340, F = 37.85, r = 0.940, s= 0.7

$\{{}^{D}R^{v}, {}^{1}R, {}^{1}R^{v}\}$: Q = 2.388, F = 80.10, r = 0.982, s = 0.4.

Colinearity of the indices of the last combination is rather low: $R({}^{D}R^{v}, {}^{1}R; {}^{D}R^{v}, {}^{1}R^{v}; {}^{1}R, {}^{1}R^{v})$ = 0.942; 0.203; 0.142. The stimulating plot of Figure 6 has been obtained by means of the following vectors

$\boldsymbol{R}$ = $({}^{D}R^{v}, {}^{1}R, {}^{1}R^{v}, R^{0})$, $\boldsymbol{C}$ = (–12.1241, 19.2811, –5.41956, –1.44850).

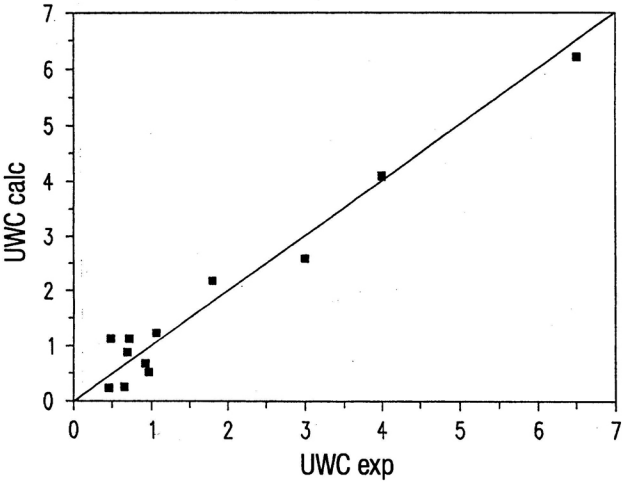

Figure 6. Plot of the calculated *versus* the experimental unfrozen water content of n = 13 amino acids and metal chlorides [8(AA)+5(MeCl')].

Recently, Randić[20] clarified the distinction between the validity of the prediction of equations and their uselessness for (coefficient) interpretation. One of the critical points of predictive equations are the standard errors of the coefficients, which normally become greater than the coefficients themselves with the number of parameters used in the model. All along our best LCCI used to model the given properties the ratio of the coefficients to their standard errors was normally greater than 4 and up to 16, while only for a coefficient in three different estimations it was around 2 and for the constant term of ET it was 0.042 (very poor indeed) but if we take the good single-index LCCI for the ET estimate this ratio becomes 2.1. This overall result seems quite satisfactory and it can be surely ascribed to the rather low $\langle R_{IM}(P:\{\chi\})\rangle$ value of our estimations and to the choice of the F-best LCCI instead of the Q-best LCCI (for rather similar Q values) like for the

description of the lattice enthalpy of the $n = 20$ metal halides. Anyway, this is, here, a rather secondary problem as a satisfactory fit of the given properties is normally achieved by a single-index LCCI or LCOCI.

CONCLUSION

The description of the lattice enthalpies of 32 inorganic compounds, of the limiting solution enthalpies of 12 metal halides and the description of ET, UWC and RH% of five metal chlorides plus the description of UWC of the mixed set {AA+MeCl} is an interesting achievement that underlines the effectiveness of the employed method to model the properties of inorganic compounds. The modeling of these inorganic compounds constitutes also a positive test for the suggested δ^v cardinal number.[5] The introduction of the D^Z index, formally similar to the D index, seems to be a good choice as it contributes to the modeling of the lattice enthalpies, the limiting solution enthalpies and of the UWC of inorganic compounds. The partitioning of the molecular set of inorganic compounds for the modeling of the lattice enthalpies is a required choice for good modeling, as already tried with the melting points of alkanes.[3] The modeling of the UWC of the mixed set of amino acids and metal chlorides with LCRCI underlines again the importance of reciprocal connectivity indices[18,19] and stresses the importance of special constructions of connectivity indices, which have been recently expanded and refined.[14,15] This last modeling could be read as a first hint for the construction of a MC model encompassing both inorganic and organic molecules.

Clearly, the definition of a connectivity model for ionic compounds is far from being achieved, since the conventional molecular connectivity paradigm based on chemical graphs of organic compounds cannot easily be adapted to situations where linkages take the form of fields. Nevertheless, modifications of the model are possible and it seems that they are substantiated by optimistic results. At this level of conclusion, the fact that for every single simulated property a single-index LCCI is sufficient should not be overlooked.

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SAŽETAK

Modeliranje entalpije i hidratacijskih svojstava anorganskih spojeva

Lionello Pogliani

S pomoću linearnih kombinacija indeksa povezanosti opisana su slijedeća svojstva anorganskih molekula: entalpije kristalne rešetke za 32 anorganska spoja, granične entalpije otapanja za 12 metalnih halogenida, sadržaj vode, relativna vlažnost i eutektička temperatura metalnih klorida, te sadržaj vode miješanog skupa aminokiselina i metalnih klorida. Eksperimentalne vrijednosti reproducirane su veoma dobro, obično uz pomoć samo jednog indeksa. Dobiveni rezultati potvrđuju vrijednost δ^v valencijskog broja za anorganske spojeve kao i novog indeksa D^Z, definiranog preko broja valentnih elektrona i glavnoga kvantnog broja. Na primjeru sadržaja vode za aminokiseline i metalne kloride po prvi put je primijenjen model zasnovan na indeksima povezanosti koji obuhvaća i organske i anorganske spojeve.