

Use of Multivariate Chemometric Techniques in the Thermodynamic Study of Chemical Equilibria in Different Solvents

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Received July 20, 1993

Multivariate chemometric techniques (principal component analysis, factor analysis, feature selection) have been applied to thermodynamic data of equilibria in different solvents. Eight fundamental reactions in various water-cosolvent mixtures have been considered, at 20 °C (63 equilibria in total). Possible advantages deriving from these techniques, in comparison with the use of traditional univariate methods, are briefly examined. In particular, it is shown that two factors account for 97.8% of variance in the data.

INTRODUCTION

The study of the influences of solvents on the stability of complexes aroused greater interest when, in addition to the usual values of Gibbs function, accurate values of enthalpy and entropy became available. It was observed, in fact, that the simple and regular trend of the stability of many complexes, as a function of the dielectric constant of the solvent (which led to assigning the determining role on stability to electrostatic factors), is the result of more complex and not easily explainable variation in enthalpy and entropy.

In addition to the three above mentioned thermodynamic quantities, other variables have begun to get progressively into use in this field of studies. Molar volume (ΔV), specific heat variation (ΔC_p), electrostatic and non-electrostatic components of fundamental thermodynamic quantities¹ can be mentioned among them. Molar expansibility ($\Delta\alpha$) and molar compressibility (ΔK) have also been used in several works on solution equilibria.^{2,3} Also these variables could gradually become useful in these studies.

Thus, it can be concluded that the thermodynamic investigation of solution equilibria is assuming an increasingly marked multivariate character. It is also clear, in this connection, that the usual univariate examination of thermodynamic data can prove to be inadequate, since it required mental synthesis of the simultaneous behaviour of

an increasing number of experimental variables, both in the form of numerical data and of diagrams.

Another question connected with this kind of investigations, which has sometimes been discussed, concerns the actual utility and the significance of some of the above thermodynamic parameters (for example, of the electrostatic and non-electrostatic contributions of the Gibbs function and enthalpy^{4,7}).

As multivariate statistical methods have been formulated with the aim of examining the simultaneous behaviour and the significance of many variables, they could indeed be useful in resolving these problems. Taking into account that multivariate methods have almost always been used to process compositional or structural data, and that in very few cases they have been applied to thermodynamic data,^{8,9} it was thought of interest, in the present investigation, to test their applicability to thermodynamics of complex formation in different solvent mixtures. More particularly, it seems important to evaluate the utility of multivariate methods from two points of view: the ability to extract information from thermodynamic results, and the possibility of selecting the variables with the highest information content.

Thermodynamic data from literature, referring to protonation and complex formation reactions of ligands in various water-organic cosolvent mixtures, have been considered in this study. Although accurate thermodynamic data in different solvents are still scarce in literature, it has been possible to examine a sufficiently wide variety of equilibria as well as of solvent mixtures for the following variables: the three usual thermodynamic quantities (Gibbs function, enthalpy, entropy) and the corresponding electrostatic and non-electrostatic components. It must be pointed out, however, that it does not seem possible, at present, to use other parameters mentioned above (such as molar volume, compressibility, *etc.*) due to insufficient availability of experimental data for statistical treatment.

EXPERIMENTAL DATA AND PARAMETERS

Eight different chemical equilibria, relative to 1:1 association reactions, have been considered. Each equilibrium refers to various water-organic cosolvent mixtures (cosolvents: methanol, ethanol, 1,4-dioxane). Sixty-three combinations of equilibria and solvent mixtures have been studied. The choice of experimental data was made according to the following criteria. (i) A wide variety of the kinds of equilibria. For example, equilibria with and without charge neutralization, or with the simultaneous presence of electrically charged and electrically neutral sites of reaction have been considered, *etc.* An association equilibrium between two neutral molecules (*i.e.* $\text{Hg}(\text{CN})_2$ and thiourea) has also been chosen. (ii) A choice of organic cosolvents with different dielectric properties, such as alcohols and dioxane. The dielectric constants of methanol, ethanol and dioxane are: 32.63, 24.30 and 2.31, respectively, at 25 °C. (iii) Ranges of water-cosolvent percent composition and number of solvent mixtures approximately equal for each equilibrium, in order to extend the possibility of significant comparisons. In particular, five or six mixtures have been considered for each equilibrium and for each cosolvent, while the quantity of cosolvent ranges from zero to a mass fraction of about 65–80%. (iv) Taking into account that large disagreements may be found between the heats obtained from calorimetric measurements and those from the variation of stability with temperature¹⁰ and that the former are generally considered as more reliable,¹¹ only enthalpy values obtained by direct calorimetry have been chosen.

A list of the systems studied, together with the references from which the stability and enthalpy values have been taken, is reported in Table I.

TABLE I
Association equilibria (1:1) and water-organic cosolvent mixtures considered
in the present investigation (25 °C)

N.	Reagents	Cosolvent	Symbol used	Mass fraction/% of cosolvent	Ref.
1	H ⁺ , acetate	Ethanol (E)	HAcE	0,20,40,60,80	12
2	H ⁺ , COO ⁻ of α -alaninate	Methanol (M)	HAl(O)M	0,20,40,60,75	13
	<i>id.</i>	Dioxane(D)	HAl(O)D	0,20,35,50,65	13
3	Cu ²⁺ , Cl ⁻	Methanol	CuClM	0,4,16,5,34,6,54,3,70,4	14
	<i>id.</i>	Ethanol	CuClE	0,4,16,5,34,6,54,3,64,9	14
4	H ⁺ , NH ₂ of α -alaninate	Methanol	HAl(N)M	0,20,40,60,75	13
	<i>id.</i>	Dioxane	HAl(N)D	0,20,35,50,65	13
5	H ⁺ , 1,10-phenanthroline	Dioxane	HPhD	0,11,1,20,5,55,1,76,6	15
6	Hg(CN) ₂ , thiourea	Ethanol	HgTuE	0,20,40,60,80,92,3	16
7	Cu ²⁺ , α -alaninate	Methanol	CuAlM	0,20,40,60,75	13
	<i>id.</i>	Dioxane	CuAlD	0,20,35,50,65	13
8	Ni ²⁺ , α -alaninate	Methanol	NiAlM	0,20,40,60,75	13
	<i>id.</i>	Dioxane	NiAlD	0,20,35,50,65	13

As regards the use of the three fundamental thermodynamic quantities (ΔG , ΔH , ΔS) in the case of different solvents, as well as their subdivision into the electrostatic and non-electrostatic components, only a short account will be given here, as the subject has been treated in full detail in previous papers.^{1,4-6,17}

Given a general equilibrium in solution:



the corresponding conventional overall equilibrium constant (K_n) can be expressed in the form¹:

$$K_n = K_n^x M_s^{-n} \quad (2)$$

where K_n^x is the corresponding constant expressed in terms of the mole fraction unit, M_s is the molar concentration of the solvent, and n denotes the amount of reactants minus the amount of products with reference to the solute. The latter part (M_s^{-n}) is then a general contribution, depending only on the solvent and the stoichiometry. It is known as the cratic contribution.¹ The former part (K_n^x), called unitary, depends on all the other factors that are specific for every single equilibrium. Unitary quantities, instead of conventional (or global) quantities, are treated in this study, as the former are unanimously considered more appropriate for correct comparisons between equilibria in different solvents. Only in the case of enthalpy, since its cratic part is zero (*i.e.*, $\Delta H^x = \Delta H^0$), the conventional standard quantity (ΔH^0) has been considered here (superscript symbol ⁰ denotes a conventional standard quantity; when the standard quantity refers to a chemical reaction, symbol $\Delta_r X^0$ is also recommended by IUPAC, where $X = G, H, S$). As all the thermodynamic quantities in the present case refer to chemical reactions, symbol ΔX^0 is equivalent to $\Delta_r X^0$.

The unitary part can be further subdivided into the electrostatic and the non-electrostatic contribution. The electrostatic component represents long-range electrostatic interactions, which are affected by the dielectric nature of the solvent and by the temperature. Therefore, it is determined by solute-solute electrostatic bonds and by long-range solute-solvent interactions. The non-electrostatic part is determined by all short-range factors, independent of the dielectric constant and temperature. They consist of solute-solute covalent bonds and of solute-solvent contact interactions (*i.e.*, solvation interactions).

Electrostatic and non-electrostatic components of the Gibbs function, enthalpy and entropy (ΔX_{el} and ΔX_{non} , respectively, where $X = G, H, S$), have been calculated by means of the equations published previously.¹⁷ Values of the dielectric constants at various temperatures for the solvent mixtures considered here (which must be used in the calculations) are taken from the works of Åkerlöf and of Herz.¹⁸⁻²⁰

The variables always refer to the association process and to 25 °C. The ionic strength is constant for the measurements relative to each of the eight equilibria listed in Table I, independently of the cosolvent and its concentration. The sign of the thermodynamic quantities has been fixed so that the more favourable they are to complex formation, the more positive they are, and *vice versa*. Moreover, it resulted from the calculations that: (i) $\Delta S_{el}^x = \Delta S^x$; (ii) $-\Delta H_{non} = -\Delta G_{non}^x$. Since obviously, the use of equivalent quantities was avoided, the following six thermodynamic variables were considered in this study: $-\Delta G^x$, $-\Delta H^0$, ΔS^x , $-\Delta G_{non}^x$, $-\Delta S_{el}^x$, ΔH_{el} .

STATISTICAL DATA PROCESSING

Multivariate statistical analysis of experimental data was performed by computer programs included in the package PARVUS.^{21,22} Only a brief account will be given on the techniques used, together with references to specific works for fuller details.

The first processing step involved standardization (or normalization) of the data, in order to avoid misclassification arising, from the span of numerical values (or the corresponding variances) of the parameters considered. This was performed by scaling each variable to the zero mean values and unit variance (autoscaling procedure).²³

The principal component analysis (PCA) was used as a displaying method. This technique has the advantage that, in some cases, just two (or three) new variables, called principal components, are sufficient for a projection of the original hyperspace onto two (or three) dimensions, without excessive loss of information.²³ R-mode PCA gives both the coordinates (or scores) of the objects and the loadings of variables on principal components. The latter allow clustering of variables on the basis of mutual correlations. The rotation of principal components, in accordance with the factor analysis methods (FA), leads to easier determination of the physical factors that control the phenomenon under investigation (association equilibria, in this case). At the same time, the loadings of variables on the rotated principal components give useful indications of the experimental variables associated with each physical factor.²⁴

Selection of variables has also been carried out. It gives a sequence of variables on the basis of their decreasing information content, and, in some instances, it allows one to simplify the original data matrix by eliminating variables at the end of the sequence. Multivariate selection (program SELECT) has been used. It is more significant, from the practical point of view, than the univariate selection, as it decorrelates vari-

ables in the order of decreasing utilities by taking simultaneously into account the discriminant ability and the correlation with other variables. More precisely, the decorrelation method selects the first variable according to the Fisher ratio, then this variable (let it be x_j) is subtracted from the remaining variables: $x_{iv} \rightarrow x_{iv} - \rho x_{ij}$ (where ρ is the correlation between the generic variable v and the first selected variable j). Fisher ratios and correlation coefficients are recalculated for the unselected variables, and a new best variable is obtained, which in turn is subtracted from the remaining variables, and so on, until the best Fisher ratio of the unselected variables is less than a predetermined value.^{25,26}

DISCUSSION

The complete set of experimental data is available on request. For the sake of brevity, the mean value and the standard deviation of each variable for the eight equilibria of Table I are collected in Table II.

TABLE II

Mean values and standard deviations (in parentheses) of thermodynamic variables for the eight equilibria in Table I

N.	Symbol	$\frac{-\Delta G^x}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H^0}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S^x}{\text{JK}^{-1} \text{ mol}^{-1}}$	$\frac{-\Delta G_{\text{non}}^x}{\text{kJ mol}^{-1}}$	$\frac{-\Delta G_{\text{el}}^x}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H_{\text{el}}}{\text{kJ mol}^{-1}}$
1	HAcE	41(4)	-1.7(2.0)	144(19)	15(3)	26.6(0.6)	16.5(5)
2	HA1(O)	26(2)	4.6(1.3)	73(4)	12.8(2.3)	13.5(0.7)	8(1)
3	CuCl	12.7(3)	-12(2)	82(10)	-3.2(2.8)	15.8(1)	9(2)
4	HA1(N)	64.5(1)	47(1)	59(3)	53.5(0.9)	11(1)	6.5(1)
5	HPhD	34(3)	16(4)	61(8)	22.5(3)	12(2)	6.3(0.9)
6	HgTuE	20.3(0.8)	18.4(8)	6(30)	18.6(5)	1.6(6)	0.2(3)
7	CuAl	60(2)	29.5(6)	101(12)	40.7(6)	19(3)	11(1)
8	NiAl	43.8(2)	18.3(2)	86(4)	28(3)	15.9(0.7)	9.6(1)

Taking into account that studies of correlations, in general, allow one to draw conclusions about the significance and the kind of information given by variables, and also on physical factors which control the phenomena under study, this kind of investigation was carried out first.

Starting from the autoscaled data (initial matrix: 63×6), the correlation matrix was obtained, then a R-mode PCA was carried out. PCA identifies two principal components strongly prevailing over the others as regards the information content. More precisely, the first principal component has a variance of 3.1, the second of 2.8, while the third of only 0.1. The last value is much less than 1, *i.e.*, less than the variance of standardized experimental variables. The first two principal components represent 97.8% of the total variance. This means, in the first place, that bidimensional representations of the scores of objects (*i.e.* of equilibria) or of the loadings of variables on the first two principal components are quite similar to the actual disposition in the six original dimensions. Secondly, it can be concluded that the global structure of experimental data is determined by two main factors. The loadings of the six variables on the two first principal components are shown in Figure 1.

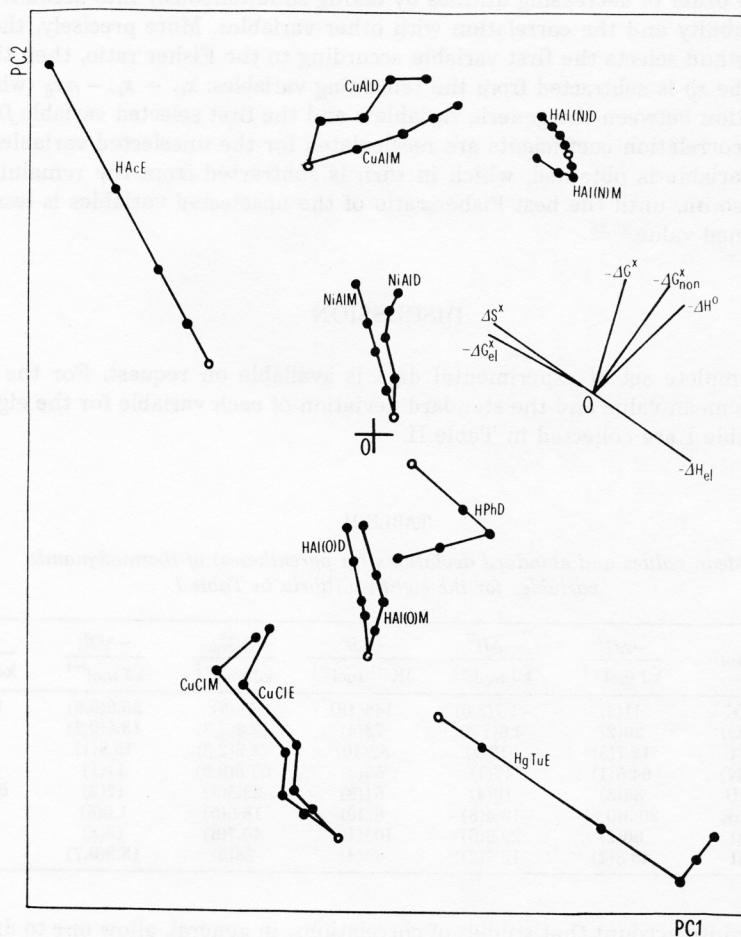


Figure 1. Loadings of six thermodynamics variables and scores of association equilibria in various solvent mixtures, on the two first principal components (PC1 and PC2, accounting for 97.8% of the total variance). The origins of the two-coordinate systems, indicated by 0, must be thought of as coincident. Starting from the white circle (0% of cosolvent), the sequence of the black circles (corresponding to increasing quantities of cosolvent) is indicated for each equilibrium (see Table I).

Conclusions drawn from the examination of the loadings in Figure 1 can be summarized in the following points. ΔS° and $-\Delta G_{el}^\circ$ are mutually joined by a strict correlation (coefficient correlation $r = 0.98$), while, on the other hand, they are anticorrelated with $-\Delta H_{el}$ ($r: -0.95$ and -0.87 , respectively). The negative correlation between ΔS° and $-\Delta H_{el}$ can be justified by considering that the solvent destructuring processes caused by charge neutralization (*i.e.* ΔS° favourable to complex formation) give rise to electrostatic bond ruptures between the solvent molecules ($-\Delta H_{el}$ unfavourable). Considering

also the nature of these variables, it can be supposed that they define a direction of variance associated with the electrostatic factor. Moreover, this factor seems to be connected with solute-solvent environmental (or external) processes. The direction of the loading of $-\Delta G_{\text{non}}^x$, on the other hand, is likely to define the non-electrostatic, or short-range, factor. The orthogonality of the two directions indicates lack of correlation between the two factors. The higher correlation of $-\Delta G^x$ with $-\Delta G_{\text{non}}^x$ than with $-\Delta G_{\text{el}}^x$ (r : 0.94 and 0.20) shows that the difference in stability of the complexes (and, at the same time, the difference in stability of a given complex in different solvents) is mainly determined by non-electrostatic, rather than by electrostatic factors. Similar conclusions can be drawn by considering the remarkable correlation of $-\Delta H^0$ with the non-electrostatic factor. A Varimax rotation²⁷ of principal components was also performed. The rotation allows one to transform the principal components that have a pure mathematical significance into factors that may have a physical significance. The rotation confirmed the two directions indicated above for the electrostatic and for the non-electrostatic factors. Variable $-\Delta G_{\text{non}}^x$, in particular, in comparison with all the other parameters, shows the highest loading, *i.e.* the highest correlation, with the non-electrostatic factor.

Passing now to simultaneous examination of scores and loadings in Figure 1, it can be noted that the positions of the complexes are roughly distributed along the electrostatic and the non-electrostatic directions of variance. Any shift parallel to one of the two directions (*i.e.* radial shift) corresponds to a merely quantitative variation in one (and one only) factor. For example, passing from HgTuE to HAcE, an increasingly favourable electrostatic factor is obtained (through the influence of ΔS^x and $-\Delta G_{\text{el}}^x$), the non-electrostatic factor being roughly constant. A tangential shift [*e.g.* from HAcE to HAl(N)M], on the other hand, corresponds to a variation in the ratio between factors, and then to a qualitative variation in the forces that cause the complex formation. A relative evaluation of the importance of non-electrostatic and electrostatic forces in an association reaction is also possible, from the coordinates of the complex on the two lines representing the factors. From this point of view, the plane presented in Figure 1 can be subdivided into regions controlled by different ratios between covalent and electrostatic forces. Such a subdivision can be useful for evaluating the discriminant ability of the variables (see below).

As regards the effect of a solvent variation on the position of a given equilibrium in the plane of Figure 1, the following three parameters must be considered: orientation, direction and amplitude, both for a shift along the line corresponding to a water-cosolvent pair and for the translation of the line, passing from one cosolvent to the other. The orientation is in obvious relation with the orientation of the electrostatic and the non-electrostatic factors. This indicates the relative influence on the two factors when the concentration of cosolvent is changed. It must also be noted that the two reacting species of the solute (and then the so-called solute-solute factors) remain unaltered after a change of solvent. Consequently, in this case, any variation in the electrostatic or in the non-electrostatic factor should be only considered as a variation, respectively, in structuring-destructuring processes of the solvent or in solvation-desolvation processes of the solute (see Experimental Data and Parameters). The shift direction for a given orientation indicates in which manner the factor is affected, *i.e.* whether it becomes more or less favourable to complex formation, as well as the amplitude in relation with the intensity of the variation of the factor. The significance of a trans-

lation of the line as a consequence of a change of cosolvent, as well as the significance of a trend represented by a broken line, are easily inferred through considerations analogous to the preceding ones.

In order to show the benefits obtainable by the use of factor analysis in comparison with the traditional examination of thermodynamic data, the system $\text{Hg}(\text{CN})_2$ -thiourea in water-ethanol mixtures (HgTuE in Figure 1) can be considered as an example. The values of ΔG° , ΔH° and ΔS° for the $\text{Hg}(\text{CN})_2$ -thiourea complex formation in six water-ethanol mixtures (0–92.3% ethanol) had been determined by titration calorimetry in a previous work.¹⁶ A sharp change of thermodynamic behaviour of the system was observed at about 60% ethanol. Considering the values of ΔG° and the corresponding standard deviations, a decreasing stability of the complexes is observed between 0% and 60% ethanol, while stability progressively increases above 60% of cosolvent. This change was attributed to one or both of the following effects: (i) changes in the solvent molecules directly coordinated to the interacting species (*i.e.* a short-range factor, independent of the dielectric constant of the medium); (ii) changes in the structure of the solvent (*i.e.* an electrostatic, long-range factor). However, on the basis of a traditional examination of the thermodynamic data, it was not possible to make further clarify this point. It can now be noted that in Figure 1 the first four points, from 0% to 60% ethanol, are situated parallel with the electrostatic factor, while the other points, from 60% to 92.3% ethanol, are parallel to the short-range factor. Moreover, the experimental points are situated on progressively less favourable positions on the electrostatic factor (in accordance with the decreasing values of complex stability, see above), while an opposite sequence is observed on the axis of the short-range factor. Considering the constancy of the solute-solute direct interactions, Figure 1 gives an immediate indication of the fact that the thermodynamic behaviour of the $\text{Hg}(\text{CN})_2$ -thiourea system is probably caused by a change in the solvent structure (electrostatic factor) below 60% ethanol, while a change in the solvation of the reacting species (*i.e.* a short-range factor) should be the cause of the behaviour of the system above 60%. Analogous discussions can be made for the other equilibria on the basis of the score and the loadings of Figure 1.

Finally, a multivariate selection of variables has been performed. In order to evaluate the discriminant ability of each variable, the 63 equilibria in Figure 1 must be subdivided into categories. The following six zones with different covalent to electrostatic force ratios and the corresponding groups of equilibria can be identified in the plane of Figure 1: the first zone, on the upper left side of the figure (equilibria indicated as HAcE) and the second one [upper right, equilibria $\text{HAl}(\text{N})\text{M}$ and $\text{HAl}(\text{N})\text{D}$], which are characterized by a strong electrostatic and a strong non-electrostatic factor, respectively; another zone, between the preceding ones (CuAlM , CuAlD), with a high contribution from both factors, and, of course, a high complex stability; a wide central zone [NiAlM , NiAlD , HPhD , $\text{HAl}(\text{O})\text{M}$, $\text{HAl}(\text{O})\text{D}$] corresponding to a medium importance of the two factors, and finally, in the region of low stabilities, two further zones, one with a weak non-electrostatic contribution (CuClM , CuClE), the other with a weak contribution from both factors (HgTuE). The order of decorrelation obtained on this basis by the SELECT program is the following: $-\Delta G^x$, $-\Delta G_{\text{el}}^x$, ΔS^x , $-\Delta H_{\text{el}}$, $-\Delta H^\circ$, $-\Delta G_{\text{non}}^x$. A good contribution of information from the electrostatic components is pointed out by this sequence. For enthalpy, in particular, the contribution of the electrostatic part is higher than that obtainable from the conventional parameter.

CONCLUSIONS

Multivariate statistical techniques can give useful information both on thermodynamic parameters, from a general point of view, and on specific complex formation equilibria in solution.

In particular, as regards the equilibria considered in this study, their investigation is made simpler by the fact it is possible to define their position on the axes of two physical factors. Factor analysis, in other words, limits the discussion to only two and »pure« factors (*i.e.* only electrostatic the former and only non-electrostatic the latter), while traditional methods require a mental synthesis of the behaviour of many variables, each of them being affected, to a different extent, by the two factors simultaneously.

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SAŽETAK

**Primjena multivarijatnih kemometričkih tehnika za
proučavanje kemijskih ravnoteža u različitim otapalima***Robert Aruga*

Multivarijatne kemometričke tehnike (analiza glavnih komponenata, faktorska analiza) uspješno su primijenjene na skup termodinamičkih podataka za osam kemijskih procesa u različitim otapalima.