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The Characterisation of Solvents using the Kamlet-Taft Solvatochromic Parameters

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For many years, solvent effects on kinetic and thermodynamic properties and processes were interpreted using single solvent parameters. For example, solvent effects on nonelectrolytes could be studied in terms of the cohesive energy density (CED) of the solvent, as δ_H^2 where δ_H is the so-called Hildebrand solubility parameter. The CED is defined through equation 1,

$$\delta_{\rm H}^2 = (\Delta {\rm Hv- RT})/{\rm V_1} \tag{1}$$

where ΔHv is the enthalpy of vaporisation of the solvent at 298K, and V₁ is the solvent molar volume. Then the Raoults law activity coefficient of a solute, γ_2 , is given by

$$RTln\gamma_2 = V_2(\delta_{H2} - \delta_H)^2$$
⁽²⁾

where V_2 is the solute molar volume and δ_{H2} is the solute solubility parameter.¹ Since the Gibbs energy of transfer of the solute from some standard solvent A to any other solvent B is given by

$$\Delta G_{t}^{o} = RT \ln \gamma_{2}(A) / \gamma_{2}(B)$$
(3)

then equation (2) is equivalent to an equation for the solvent effect on the given nonelectrolyte, cf. equation (3).

For a dipolar solute, Kirkwood² calculated the electrostatic contribution to the Gibbs energy of transfer from a solvent medium of dielectric constant unity to one of dielectric constant Σ , as

$$\Delta G_{\epsilon}^{\circ} = R T \ln \gamma_2 = \frac{\mu_2^2}{r_2^3} \frac{\epsilon \cdot 1}{2\epsilon + 1}$$
(4)

where the dipolar species is considered as a dipole of moment μ_2 in a sphere of radius r_2 . Although the Kirkwood equation (4) has seldom been used to study Gibbs energies of transfer as such, it has been employed from time to time in the study of solvent effects on rate constants.¹

The situation with ionic species is quite different because the Born equation³ has very often been used to analyze solvent effects on the Gibbs energy of ions or of pairs of dissociated ions,

$$\Delta G_{e}^{o} = \frac{Z^{2}}{2} \qquad \frac{1 - 1}{\epsilon r} \qquad (5)$$

Here, ΔG_e° is again the electrostatic contribution to the Gibbs energy of transfer of an ion of charge Z and radius r from a dielectric of ε =1 to a dielectric continuum of ε . Equation(5) as such is not quantitatively very successful and has been amended on numerous occasions in order to obtain agreement with experiment, notably by adjusting the ionic radius r to some arbitrary

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radius (r + Δ). The difficulty, of course, with the Born equation is that it assumes a dielectric constant in the continuum, that is the solvent bulk dielectric constant, ε , up to the surface of the ion. Abraham and Liszi overcame this difficulty by supposing that the solvent round an ion could be represented by a series of concentric layers, each with a different dielectric constant. They solved the system of integrals to obtain an exact solution⁴ and applied this quite successfully to the solvation of gaseous ions in several solvents.⁵⁻⁷ A rather similar approach was taken by Stiles⁸ who constructed an equation for a continuously varying dielectric constant as a function of distance from the ion. Other workers have dealt with problems such as boundary conditions,⁹ nonlocal screening¹⁰ and nonlinear dielectric effects.¹¹ However, practical applications of the various continuum models have nearly always been restricted to the Abraham and Liszi model: for example, Ford and Scribner¹² predicted hydration energies of organic cations, and Meot-Ner¹³ predicted hydration properties of organic ions, using the layer-model.

Of course, a very large number of other single solvent parameters, or descriptors, have been used from time-to-time. Reichardt¹⁴ gives a particularly good account of this area, including the most widely-used descriptor, namely his own E_{τ} parameter, based on solvatochromic shifts.

More recently, attention has switched to the possibility of using several solvent parameters, or descriptors, to analyze solvent effects, the two main methods of analysis being principal component analysis (PCA) and multiple linear regression analysis (MLRA). Very interesting results have been obtained using PCA of solvent effects on nonelectrolytes, with some three¹⁵ or five¹⁵ factors being necessary to account for the observed results. Although these PCA factors cannot be identified with usual solvent descriptors, the observations that several factors, or descriptors, are necessary are important.^{15,16} One might ask how any single solvent parameter can be used successfully to interpret solvent effects when some three to five factors are apparently involved. There are at least two possible situations in which a single parameter can be used, (i) if there is one type of solute-solvent interaction that is quantitatively much larger than any other type, as with ion-solvent interactions, and (ii) if the parameter itself includes various interaction terms that correspond to the solute-solvent interactions taking place in the system. Nevertheless, there is still a need for some type of analysis that will enable specific solute-solvent interactions to be identified and quantified, whether or not there is one dominant interaction or several interactions of the same order of magnitude. It is in this area that MLRA is most suitable.

In order to apply MLRA, solvent parameter or descriptors, are needed that correspond to the various solute-solvent interactions that might take place. Abraham, Kamlet and Taft^{17,18} used a rather simple model of solvation in order to select the necessary descriptors. They viewed solvation of a gaseous solute as taking place in two stages (i) a cavity of suitable size has to be created in the solvent; this involves the endoergic breaking of solvent-solvent bonds, and (ii) the solute is inserted into the cavity, thus setting up various solute-solvent interactions all of which are exoergic. These interactions will include dipole-dipole or dipole-induced dipole effects, as well as two types of hydrogen-bond interactions, viz solute acid-solvent base and solute base-solvent acid. As solvent descriptors for these interactions, the Kamlet-Taft solvatochromic parameters were selected: π_1 the solvent dipolarity/polarisability, α_1 the solvent hydrogen-bond basicity. All three descriptors can be experimentally obtained from rather simple ultraviolet (uv) spectroscopic measurements.

 π_1^* is obtained¹⁹ from the uv absorption maximum of various aromatic indicators in the solvents concerned. Typical indicators are 4-nitro-N,N-diethylaniline, 4-nitro-N, N-dimethylaniline (N1) and 4-nitroanisole (01). Measurements of v_{max} are made in a series of solvents and simply scaled so that $\pi_1^* = 0$ for cyclohexane and $\pi_1^* = 1$ for dimethylsulphoxide. Originally, Kamlet and Taft¹⁹ averaged π_1^* values for several indicators, but later workers have tended to use one particular indicator. Abraham et al²⁰ used (N1) and matched v_{max} to a range of literature values of π_1^* , rather than just to cyclohexane and dimethylsulphoxide, to give,

$$\pi_1^* = 8.006 - 0.2841 \nu_{\text{max}} (N1)$$
 (6)

where v_{max} is in 10³ cm.⁻¹ Then a simple measurement of v_{max} in any other solvent enables π_1^* to be obtained for that solvent.

 β_1 is obtained using the elegant solvatochromic comparison method of Kamlet and Taft.²¹ In this procedure, two indicators are used, for example either 4-nitroanisole(01)and 4-nitrophenol(02) or 4-nitro-N,N-dimethylaniline(N1) and 4-nitroaniline(N2). Then comparison of the v_{max} values for the neutral indicator (N1 or 01) with the acidic indicator (N2 or 02) leads to a measure of the solvent basicity. Again, Kamlet and Taft originally averaged β_1 values from various pairs of indicators,²¹ but Abraham et al²⁰ used just the pair (N1, N2) to obtain β_1 ,

$$\beta_1 = [30.91 - 2.604\pi_1^* - v_{max} (N2)]/3.550$$
⁽⁷⁾

where again v_{max} is in 10³ cm.⁻¹ Hence determination of $v_{max}(N1)$ in any solvent will give π_1^* and then determination of $v_{max}(N2)$ in the same solvent will give β_1 . α_1 is not so easy to obtain,²² because there are no matching pairs of indicators as in the β_1 determinations. However, analysis of Reichardt's E_T values by Kamlet²³ showed that E_T was a combination of π_1^* and α_1 .

$$E_{\rm T} = 30.2 + 12.35\pi_1^* + 15.90\alpha_1 \tag{8}$$

so that now the easiest way to obtain α_1 is through,

$$\alpha_1 = [E_T - 30.2 - 12.35\pi_1^*] / 15.90 \tag{9}$$

where E_T is obtained from measurements of λ_{max} or v_{max} for Reichardt's betaine dye, where λ_{max} is in nm.

$$E_{\rm T} = 28591/\lambda_{\rm max} \tag{10}$$

Thus rather simple spectroscopic measurements of λ_{max} or v_{max} of readily available indicator molecules lead to the three solvatochromic solvent parameters of Kamlet and Taft, viz. π_1^* , α_1 and β_1 . These can be used as descriptors for interactions between solute and solvent in MLRA, but the cavity effect that involves solvent-solvent interactions must be separately obtained. Abraham, Kamlet and Taft (AKT) suggested that the Hildebrand cohesive energy density, δ_H^2 in equation (1) could be used as a measure of solvent-solvent interactions and combined all these descriptors into the general AKT solvatochromic equation,

$$Y = c + d\delta + s\pi_1^* + a\alpha_1 + b\beta_1 + h\delta_H^2$$
(11)

where Y can be a thermodynamic property such as ΔG° for an equilibrium reaction, or ΔG° , for the transfer of a solute between various solvents, or Y can be a kinetic property such as ΔG^{\dagger} or logk for a reaction conducted in a number of solvents. However, since $\Delta G^{\circ} = -RTlnK$ it should be noted that use of ΔG° or of logK will not only alter the magnitude of the constants in equation (11), but will also change their sign. Equation (1) contains also a rather trivial polarisability correction parameter, δ , taken as zero except for aromatic solvents (δ =1) and polyhalogenated aliphatic solvents (δ =0.5).

The constants, c, d, s, a, b and b in equation (11) are found by MLRA, using a number of Y values. Care must be taken over application of MLRA. In particular, (i) There must be a sufficient number of data points, i.e. Y-values. In general at least five data points are needed per descriptor. (ii) It is important to check that the descriptors in equation (11) are themselves not collinear. (iii) The number of descriptors used in any application must be regulated by use of students t-test and/or the Fisher F-statistic. Once the constants have been obtained by MLRA, they can then be used to characterise the process under consideration. Suppose Y is ΔG_t° for the transfer of a solute between solvents. Then if the s-constant is large, this will indicate that there is a considerate solute-solvent interaction of a general electrostatic type (in the case of a dipolar solute this will be dipole-dipole and dipole-induced dipole). A large a-constant will show an acid-base interaction of the type solute base-solvent acid, and a large b-constant will reflect solute acid-solvent base interactions. The h-constant is connected to the cavity effect, i.e. the work of creating a cavity in the solvents of a suitable size for the solute. There is in equation (11) no specific term that deals with general interactions. Polarisability effects are to some extent included in the $s\pi_1^*$ term, and general dispersion interactions in the hS_{H}^2 term, it being very difficult to choose some solvent parameter that will reflect only general dispersion effects (and will be independent of the various other parameters or descriptors in the solvatochromic equation).

The solvent parameters used in equation (11) have been listed by Kamlet et al^{24} and by Abraham et $al,^{25}$ and numerous applications of equation (11) have been reviewed.¹⁷ In addition, the solvatochromic parameters themselves have been reviewed in some detail.²⁷

Characterisation of solvents in terms of the solvatochromic parameters is straightforward, with solvents classified, according to generally accepted chemical principles. The π_1^* parameter represents a combination of dipolarity and polarisability. For simple aliphatic solvents, there is a general connection between π_1^* and other measures of polarity such as the bulk dielectric constant, see table 2. As expected, any such connection breaks down for associated solvents such as alcohols or formamide. And naturally, with aromatic solvents there is no simple relationship between π_1^* and dielectric constant, etc., because now the π_1^* parameter includes a very considerable polarisability contribution. The α_1 solvatochromic parameter is a straightforward measure of solvent hydrogen-bond acidity. Within families there are relationships with other measures of acidity. For example, the alcholol α_1 solvatochromic parameter follows reasonably closely both solute pK_a in water and the solute hydrogen-bond α_2^{H} parameter is tetrachloromethane.²⁸ Outside this family, there is not much connection, see for example the α_1 values for carboxylic acids²⁹ in table 2. The numerous scales of basicity have been extensively analysed, ^{30,31} with the general conclusion that relationships between the scales occur only within families of compounds. Thus for non-associated compounds (i.e. leaving out alchols, acids, etc), Abraham et al.²⁰ showed that there was a general connection between β_1 and the solute hydrogen-bond basicity parameter, β_2^{μ} ,

although equation (12) is hardly good enough to calculate β_1 from β_2^H or vice versa. In equation (12), and elsewhere, n is the number of data points, sd is the overal standard deviation, ρ is the overall correlation cofficient, and F is the Fisher F-statistic.

The Kamlet-Taft solvatochromic parameters provide a new and very useful method for the classification of solvents in terms of π_1^* , α_1 and β_1 . Of course, this is not the only classification method of solvents; principal components analysis and cluster analysis have several times been used to classify solvents.^{14, 32, 33} One particular advantage of the Kamlet-Taft system, however, is that the solvent parameters used in the classification system can be incorporated into equations such as the AKT equation (11), in order to correlate and to interpret solvent effects on kinetic and thermodynamic processes. Since much of this work has been reviewed,²⁵ we shall deal only with a recent application to a conformational equilibrium, and then to processes that involve ionic or dipolar species.

The conformational equilibrium (13) is solvent-dependednt, and the NMR coupling constant, J, between the C-1 and C-2 protons in 1,1,2-trichlorethane has been measured in 32 protic and aprotic solvents covering a wide range of solvatochromic parameters.³⁴

Application of the AKT equation (11) yielded,

$$J/H_{z} = 6.35 + 0.28 \delta - 0.87 \pi_{1}^{*} - 0.33 \beta_{1}$$
(14)
n = 32 sd = 0.10 $\rho = 0.948$

Equation (14) shows that the solvent dependence of J arises because conformer II is more dipolar than conformer I, and because the I-H proton in II is slightly more acidic than is the I-H proton in I. 34



More relevant to the present discussion is work on the correlation of kinetic solvent effects for processes in which the transition state is highly dipolar. For the unimolecular reaction of tbutyl chloride at 298K in a wide range of protic and aprotic solvents, Abraham et al. find,³⁵

$$\Delta G^{\dagger}(t-BuCl) = 7.95 + 1.30 \ \delta \ -6.49 \ \pi_1^* \ -5.45 \ \alpha_1 \ -0.83 \ \beta_1 \ -0.73(\delta_{\rm H}^2)/100 \tag{15}$$

$$n = 30 \qquad {\rm sd} = 0.68 \ \rho = 0.9863$$

The main effects are those of solvent dipolarity/polarisability and solvent hydrogen-bond acidity that help to stabilise the dipolar transition state in dipolar, protic solvents. Interestingly, the effect of solvent hydrogen-bond basicity is small, so that the Me_3C -- entity, although carrying a substantial fractional positive charge, is not stabilised by basic solvents.

A similar effect is found in the Menschutkin reaction of triethylamine and ethyl iodide.

$$Et_3N + EtI \rightarrow Et_4NI$$
 (16)

where rate constants, as ΔG^{\ddagger} values in kcal mol⁻¹, are correlated by the AKT equation,²⁵

$$\Delta G^{\dagger}(Et_3N/EtI) = 5.41 + 1.29 \ \delta -7.31 \ \pi_1^* + 0.54 \ (\delta_H^2)/100$$
(17)

n = 33 sd = 0.35 \rho = 0.980

Although the reaction is accelerated by dipolar/polarisable solvents that lower the energy of the transition state, basic solvents seem to have no effect on the developing Et_3N --Et entity, which carries some 0.40 units of positive charge.

Exactly the same effect was observed³⁶ when the general AKT equation (11) was applied to Gibbs energies of transfer of ion-pairs (R_4NX) and pairs of dissociated ions ($R_4N + X^-$) from methanol to water and a series of aliphatic protic and aprotic solvents. In no case was a term in bB, observed, and the AKT equation was reduced to,

$$\Delta G_t^\circ = c + s\pi_1^* + a\alpha_1 + h\delta_H^2 \tag{18}$$

Values of the constants in equation (18) are collected in Tables 4 and 5, with ΔG_t° in kcal mol⁻¹ on the mol fraction scale.

The constants for the ion-pairs in table 4 all seem reasonable, with s and a becoming more negative along the series I, Br and Cl, as expected for the effect of solvent dipolarity/polarisability and hydrogen-bond acidity in stabilising the ion-pair. The term in δ_{H}^2 , however, does not increase with increase in solute size, as would be the case just for a cavity effect, and probably includes a component due to electrostriction.³⁶

Constants for the dissociated ion regressions are in table 5, again for a selection of aliphatic solvents. The s-constant and the a-constant are much more negative than for the ion-pairs, with still the correct trends. It would be very useful to dissect effects into these for individual ions, and this is carried out now for the case of $(Et_4N^+ + I)$, for which more data exists than for any other ionic combination in table 5. The available data on this pair of ions is given in table 6, and for this slightly wider selection of aliphatic protic and aprotic solvents,

$$\Delta G_{t}^{\circ} = 28.62 - 41.40 \pi_{1}^{*} - 15.47 \alpha_{1} + 5.90 \delta_{H}^{2}/100$$
(19)
n = 17 sd = 1.12 \rho = 0.9838

where new values are on the molar scale, and, again, ΔG° , is in kcal mol⁻¹ from methanol solvent. The transfer free energies are all from the original work,³⁷ except for transfer to dimethylsulphoxide taken as -2.7 kcal mol⁻¹ from Johnson and Persson.³⁸ There is good agreement between equations (19) and results (in table 5) bearing in mind the change of standard state and the additional number of solvents. Single-ion Gibbs energies of transfer, based on the Ph₄As⁺/Ph₄B convention, have been collected by Marcus³⁹ and by Gritzer⁴⁰ and can be used to divide up ΔG° , for Et₄N⁺ + I⁻ into single-ion contributions for a number of solvents. Single-ion values are available also for the n-alcohols^{41,42} and nitromethane,⁴³ and the available data are summarised in table 6. There remain seven solvents for which single-ion values are unavailable. In these cases, ionic contributions were evaluated by trial-and-error using equations for ΔG° , (Et₄N⁺) and ΔG° , (I⁻) until the best agreement between observed and calculated values was obtained. This leads to the remaining single-ion values given in table 6, and to the following equations,

$$\Delta G^{\circ}_{t}(Et_{4}N^{+}) = 4.59 - 9.90 \pi^{*}_{1} + 1.06 \delta^{2}_{t}/100$$
(20)
n = 17 sd = 0.54 ρ = 0.9588

$$\Delta G^{\circ}_{\iota}(\Gamma) = 23.75 - 30.98 \pi^{*}_{1} - 15.11 \alpha_{1} + 4.69 \delta^{2}_{H}/100$$
(21)
n = 17 sd = 0.70 p = 0.9907

Equations (20) and (21) add up to equation (19), as required, but show, in addition, that the α_1 term in equation (19) is due entirely to the solvent effect on I. Thus the iodide ion is stabilised by dipolar/polarisable solvents and by solvents that are hydrogen-bond acids. The singleion equation for Et₄N⁺ is very interesting, in that neither hydrogen-bond acids nor hydrogen-bond bases stabilise the ion, but only solvents that are dipolar/polarisable. This is quite in line with kinetic results (above) on the t-butyl chloride reaction and the Menschutkin reaction. The CED term in equations (20) and (21) shows that solvents with large solvent-solvent interactions tend to destabilise both ions. This effect, however, is not very pronounced, and , as explained before, the CED term probably includes an electrostriction effect that makes the "cavity effect" smaller than expected. For cations such as K^* there is, indeed, a term in β_1 , see also ref.44. However, for small cations the coefficients of π_1^* and β_1 , in the AKT equation are much smaller than expected. It is generally acknowledged⁴⁻¹¹ that the high electrostatic field of an ion will lead to restructuring and re-ordering of adjacent solvent molecules. In turn, this will result in the solvent properties within the immediate solvation shell differing from the bulk solvent properties. This effect will be greatest for ions of high charge/radius ratio, and so it is not surprising that the AKT equation, and other equations as well, that contain bulk solvent parameters gives rise to coefficients that do not reflect the properties of small ions.

Finally, it should be pointed out that although the AKT equation, using the Kamlet-Taft solvatochromic parameters, gives a good account of solvent effects on the larger ionic species, the various regression equations cannot be used to predict ΔG°_{t} values outside the range of the parameters. Thus if the methanol to gas phase ΔG°_{t} value for Et₄N⁺ + I is taken as around 100 kmol mol,⁻¹ with standard states in mol dm⁻³ in each case, equation (19) would require a π^*_1 value of -1.7 for the gas phase. An approximate equation for $\Delta G^{\circ}_{t}(K^{++} CI)$ leads in the same way to a π^*_1 value of -4.2 for the gas phase. Such disparate, and very negative, calculated values strongly suggest that AKT equations for ionic species cannot be extrapolated towards solvents less polar than those used to set up the equations.

In general, however, the AKT equation gives a good account of solvent effects on various kinetic and thermodynamic properties, and the Kamlet-Taft solvatochromic parameters lead to chemically reasonable and useful classifications of solvents, and also polymers.⁴⁵ One property not considered here, is that of hardness or softness of solvents, as set out by Gritzner.⁴⁶ Whether or not the softness parameter of Gritzner should be incorporated into the AKT equation when dealing with ions such as Ag⁺ has yet to be investigated.

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TABLE 1. Some solvent parameters

N	o Solvent	δ	π_1^*	α_1	β_1	$(\delta_{\rm H}^2)_1/100$
55	n-pentane	0.00	-0.08	0.00	0.00	0.499
58	n-hexane	0.00	-0.08	0.00	0.00	0.528
63	n-hentane	0.00	-0.02	0.00	0.00	0.553
72	n-octane	0.00	0.01	0.00	0.00	0.570
86	2 2 4-trimethylpentane	0.00	0.00	0.00	0.00	0.495
126	n-decane	0.00	0.03	0.00	0.00	0.597
102	n-bevadecane	0.00	0.08	0.00	0.00	0.641
207	gyclohevane	0.00	0.00	0.00	0.00	0.672
201	docalin	0.00	0.09	0.00	0.00	0.754
500	dichloromethane	0.00	0.82	0.30	0.00	0.977
552	trichloromethane	0.50	0.52	0.44	0.00	0.887
555	totrachloromethane	0.50	0.28	0.00	0.00	0.738
554	1 1-dichloroothano	0.50	0.20	0.00	0.00	0 794
550	1, 1-dichloroothano	0.50	0.05	0.00	0.00	0 983
557	1,2-dichioroethano	0.50	0.01	0.00	0.00	0.715
558	1,1,1-trichloroothano	0.50	0.49	0.00	0.00	0.968
559	1,1,2-trichioroethane	0.50	. 0.05	0.00	0.00	0.908
560	1,1,2,2-tetrachioroethane	0.50	0.95	0.00	0.00	0.978
584	cis-i, z-dichioroethene	0.50	0.44	0.00	0.00	0.440
586	1,1,2-trichtoroethene	0.50	0.55	0.00	0.00	0.040
587	1,1,2,2-tetrachioroethene	0.50	0.28	0.00	0.00	0.865
616		0.00	0.40	0.00	0.00	0.755
632	1-promoneptane	0.00	0.40	0.00	0.00	0.732
/51	benzene	1.00	0.59	0.00	0.10	0.030
752	toluene	1.00	0.54	0.00	0.11	0.794
753	2-xylene	1.00	0.47	0.00	0.12	0.000
754	3-xylene	1.00	0.47	0.00	0.12	0.770
755	4-Xylene	1.00	0.45	0.00	0.12	0.800
1001	chlarabanzana	1.00	0.40	0.00	0.12	0.772
1001	chioropenzene	1.00	0.71	0.00	0.07	0.930
1201	bromobenzene	1.00	0.79	0.00	0.05	0.974
1251	lodopenzene	1.00	0.81	0.00	0.05	1.000
1352	dietnylether	0.00	0.27	0.00	0.47	0.502
1353	di-n-propytether	0.00	0.27	0.00	0.47	0.576
1354	di - butul ether	0.00	0.2/	0.00	0.47	0.557
1333	al-n-bucylecher	0.00	0.24	0.00	0.40	0.590
1410	1,2-dimethoxyethane	0.00	0.55	0.00	0.41	0.072
1418	dieven	0.00	0.58	0.00	0.55	1 000
1421	uloxall methyl phonyl othor	0.00	0.55	0.00	0.37	1.000
1450	methy ipheny iether	1.00	0.73	0.00	0.22	0.929
1451	echyiphenyiechei	1.00	0.89	0.00	0.20	0.045
1651	propanone	0.00	0.71	0.08	0.40	0.900
1700		0.00	0.07	0.00	0.40	0.000
1708	cyclonexanone	0.00	0.70	0.00	0.55	1 027
1051	acecophenone	1.00	0.90	0.00	0.49	1.037
1051	athul formate	0.00	0.62	0.00	0.37	1.040
1060	mothyl agotato	0.00	0.61	0.00	0.3/	0.0/1
1061	athyl acetate	0.00	0.60	0.00	0.42	0.902
1001	echyr acerate	0.00	0.55	0.00	0.45	0.792
1064	n-propyr acecace	0.00	0.52	0.00	0.45	0.750
1067	n-pontul acotato	0.00	0.50	0.00	0.45	0.749
100/	methyl bonzosto	1.00	0.45	0.00	0.45	1 010
1022	athyl bonzoste	1.00	0.76	0.00	0.39	0.017
1922	echyr Denzoace	T.00	0.74	0.00	0.41	0.91/

No	Solvent	δ	π_1^*	α_1	β_1	$(\delta_{\rm H}^2)_1/100$
1003	propulene carbonate	0.00	0 83	0 00	0 40	1 760
2101	nitromethane	0.00	0.85	0.00	0.40	1.505
2101	nitroethano	0.00	0.00	0.22	0.25	1.365
2102	nitrobenzene	1 00	1 01	0.00	0.25	1.209
2201	acetonitrile	1.00	0.75	0.00	0.30	1 270
2201	propriopitrile	0.00	0.70	0.19	0.37	1 120
2202	benzonitrile	1 00	0.70	0.00	0.37	1.130
2501	formamide	1.00	0.90	0.00	0.37	1.229
2501	N N-dimethylformamide	0.00	0.97	0.71	0.60	1 200
2509	N N-dimethylacetamide	0.00	0.00	0.00	0.09	1 166
2701	nyn dimeenyrdeetamide	1 00	0.00	0.00	0.70	1 112
2854	N-methyl-2-nyrrolidinone	0.00	0.07	0.00	0.04	1 276
2951	formic acid	0.00	0.78	1 88	_	2 772
2952	acetic acid	0.00	0.64	1.12	0.45	2.035
2953	propanoic acid	0.00	0.62	1.06	0.45	1.668
2954	butanoic acid	0.00	. 0.60	1.04	0.45	1.439
3351	water	0.00	1.09	1.17	0.18	5.490
3352	methanol	0.00	0.60	0.93	0.62	2.052
3353	ethanol	0.00	0.54	0.83	0.77	1.621
3354	propan-1-ol	0.00	0.52	0.78	0.83	1.432
3355	propan-2-ol	0.00	0.48	0.76	0.95	1.331
3356	butan-1-ol	0.00	0.47	0.79	0.88	1.295
3359	t-butyl alcohol	0.00	0.41	0.68	1.01	1.119
3360	pentan-1-ol	0.00	0.44	0.70	0.92	1.198
3362	3-methylbutan-1-ol	0.00	0.45	0.78	0.90	1.163
3368	hexan-1-ol	0.00	0.41	0.67	0.94	1.131
3389	heptan-1-ol	0.00	0.39	0.64	0.96	1.084
3405	octan-1-ol	0.00	0.37	0.62	0.97	1.033
3460	ethandiol	0.00	0.92	0.90	0.52	2.740
3495	2-fluoroethanol	0.00	0.76	0.97	-	-
3497	2,2,2-trifluoroethanol	0.00	0.73	1.51	0.00	1.371
3499	hexafluoropropan-2-ol	0.00	0.65	1.96	0.00	0.893
3520	benzyl alcohol	1.00	0.98	0.80	0.50	1.484
3630	dimethylsulphoxide	0.00	1.00	0.00	0.76	1.688
4102	triethyl phosphate	0.00	0.72	0.00	0.77	-
4355	hexamethylphosphotriamide	0.00	0.87	0.00	1.05	0.734

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TABLE 3. Comparison of various acidity parameters.

	π_1^*	З	
Water	1.09	78.36	
Formamide	0.97	109.5	
TFE	0.73	26.1	
Methanol	0.60	32.62	
DMSO	1.00	46.68	
DMF	0.88	36.71	
Nitromethane	0.85	38.6	
PC	0.83	64.5	
Acetonitrile	0.75	36.02	
Propanone	0.71	20.49	
Butanone	0.67	18.01	
Ethyl formate	0.61	7.20	
Ethyl acetate	0.55	6.02	
Butyl acetate	0.50	4.94	
Diethyl ether	0.27	4.22	
Dibutyl ether	0.24	3.10	
Cyclohexane	0.00	2.01	

	Solvent	Solute	
	α_1	$\alpha_2^{\rm H}$	pK _a
HFIP	1.96	0.77	93
TFE	1.51	0.57	12.39
Water	1.17	0.35	14.00
2-Chloroethanol	1.04	0.35	14.31
2-Fluoroethanol	0.97	0.40	14.20
Methanol	0.93	0.37	15.09
Ethanol	0.83	0.33	15.93
Propan-1-ol	0.78	0.33	16.1
Butan-1-ol	0.79	0.33	16.1
Propan-2-ol	0.76	0.32	17.1
t-Butanol	0.68	0.32	19.0
Formic acid	1.88		3.75
Acetic acid	1.12	0.55	4.75
Proprionic acid	1.06	0.54	4.87
Butanoic acid	1.04	0.54	4.81

TABLE 6. Gibbs energies of transfer from methanol,

kcal mol⁻¹, molar scale

Solvent	$\mathtt{Et}_4\mathtt{N}^+$	I	$Et_4N^+ + I^-$
Diethyl ether	2.40	17.70	20.10 a
Ethyl acetate	1.10	11.70	12.80 a
Methyl formate	-0.90	8.70	7.80 a
Butanone	-1.00	6.10	5.10 a
Propanone	-1.50	5.00	3.50
Dimethylformamide	-2.30	3.00	0.70
Acetonitrile	-2.30	2.90	0.60
Nitromethane	-2.50	2.40	-0.10
Dimethylsuphoxide	-3.20	0.50	-2.70
t-Butanol	2.10	6.20	8.30 a
3-Methylbutan-1-ol	1.80	3.90	5.70 a
Propan-2-ol	1.30	3.70	5.00 a
Butan-1-ol	1.00	3.70	4.70
Propan-1-ol	0.70	3.00	3.70
Ethanol	1.30	1.20	2.50
Methanol	0.00	0.00	0.00
Water	-0.10	-1.70	-1.80

a. Ionic contributions this work.

TABLE 4.	Constants	in	the	regression	equation	(18)	for	transfer	of	ion-pairs	from
	methanol,	kca	l mo	l ⁻¹ on the m	ol fraction	scal	e.				

Ion-pair	с	S	а	100h	n	sd	ρ
Me₄NCl	18.3	-20.0	-13.3	2.9	17	0.60	0.997
Me₄NBr	15.4	-18.8	-10.4	2.8	18	0.54	0.996
Me₄NI	10.9	-15.6	-6.2	2.2	18	0.34	0.997
Et ₄ NCl	18.2	-18.9	-14.2	3.1	15	0.59	0.997
Et₄NBr	15.4	-18.0	-11.4	3.1	16	0.52	0.997
Et ₄ NI	10.9	-14.9	-6.8	2.4	18	0.36	0.997

TABLE 5. Constants in the regression equation (18) for transfer of pairs of dissociated ions from methanol kcal mol⁻¹ on the mol fraction scale

Pair of ions	С	S	а	100h	n	sd	ρ
$Me_4N^+ + Cl^-$	36.2	-45.5	-23.9	6.8	13	0.9	0.994
$Me_4N^+ + Br^-$	32.8	-44.5	-20.7	6.7	13	0.9	0.993
$Me_4N^+ + I^-$	28.2	-42.0	-16.4	6.3	14	1.1	0.988
$Et_4N^+ + Cl^-$	34.7	-42.8	-23.7	6.8	13	1.0	0.992
$Et_4N^+ + Br^-$	31.2	-41.9	-20.6	6.7	13	1.1	0.988
$Et_4N^+ + I^-$	26.6	-39.3	-16.3	6.3	14	1.2	0.981

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ADSORPTIVE STRIPPING VOLTAMMETRY

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Abstract

After the impact produced by the introduction of anodic (and cathodic) stripping voltammetry as a very convenient method for the analysis of ultratrace compounds, specially metal ions, alternative methods for the preconcentration step were investigated to extend the field of application of the stripping techniques to non-electroactive species. In adsorptive stripping voltammetry, species with some tendency to be adsorbed at electrode surfaces can be pre-concentrated in this way and then stripped just as in anodic or cathodic stripping voltammetry.

This lecture is sarted with a general view of the methods used in the preconcentration step of stripping voltammatric methods. Afterwards, focus is moved to adsorptive stripping voltammetry: first, some simple theoretical aspects are considered, related with the steps of adsorption and stripping; then, a reference is made to instrumentation, methodology and elimination of interferences; finally, examples of the use of the technique are presented.

Resumo

Depois do impacto causado pela introdução da voltametria de redissolução anódica (e catódica) como um método de análise de ultravestígios de muitos compostos, designadamente iões metálicos, começaram a surgir métodos alternativos de acumulação, que permitiram alargar a espécies não electroactivas o campo de aplicação das técnicas de redissolução. Na voltametria de redissolução com adsorção, as espécies que tenham alguma tendência para serem adsorvidas à superfície de eléctrodos são acumuladas desse modo e depois desalojadas por um processo idêntico ao utilizado na voltametria de redissolução anódica ou catódica.

Esta lição começa com a apresentação geral dos métodos de préconcentração utilizados nas técnicas voltamétricas de redissolução. Segue-se a abordagem da voltametria de redissolução com adsorção: primeiro, referem-se alguns aspectos simples ligados às fases de adsorção e de redissolução; depois, tecem-se algumas considerações sobre a instrumentação, a metodologia e a eliminação de interferências; por fim, são dados alguns exemplos de aplicação da técnica.

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