

THERMODYNAMIC PROPERTIES OF POLAR AND NON-POLAR SOLUTES IN AQUEOUS SOLUTION. *

by Sergio Cabani

Istituto di Chimica Fisica, Università di Pisa, Italia.

Important problems of general interest for chemists, chemical engineers and biochemists, as f.i. the effect of the solvent on chemical reactions, the stability of the conformations assumed by biopolymers in solution or association phenomena involving them, the partitioning of a solute between two phases, the structure of liquids and solutions, may receive a fundamental support by the knowledge of the thermodynamic behaviour of ionic and non-ionic compounds in aqueous and in non-aqueous solutions. The development of apparatus for rapid and accurate measurements of heats of solution, heat capacities and densities⁽¹⁾, together with the enormous potentiality of calculus of the actual computers has allowed to collect, in these last two decades, a very noticeable amount of data on the thermodynamic properties of aqueous and non-aqueous solutions and to open new and promising prospects to understanding their structural features at molecular level. Here I will limit myself to consider only the thermodynamic characteristics of binary dilute aqueous solutions of non-charged small molecules.

Thermodynamic data allowing to characterize the state of the solute in dilute aqueous solutions are obtained: (a) by studying the isothermal transfer from gas into the water, in order to calculate the values of the thermodynamic functions of hydration; (b) by measuring some properties of the solution, which allow to calculate partial molar properties such as heat capacity $C_{p,2}$, volume V_2^0 , expansivity and entropic and isothermal compressibility K_j ($j = s$ or T). The experiments are in general carried out at constant pressure and the thermodynamic data are referred to isobaric conditions. The passage from the condition of constant pressure to that of constant volume may be made by using well known thermodynamic relationships. The matter relative to the definition of the thermodynamic functions of hydration and of the partial molar thermodynamic quantities may be found, besides in standard textbooks on chemical thermodynamics, in some monographies on the thermodynamic properties of the aqueous solutions^(2a-2d). Other papers⁽³⁾ report the

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values of the thermodynamic properties in the 1 molar standard state for all the non-charged solutes studied up to 1979 together with extensive bibliographic references.

In these last years much attention has been devoted to obtaining very precise values of the Henry's constants, enthalpies and heat capacities of hydration for hydrocarbons^(4,5), either from measurements of gas solubilities at various temperatures⁽⁴⁾, or from direct calorimetric measurements⁽⁵⁾. In effect very precise values of the thermodynamic functions of hydration of the hydrocarbons are very important since the knowledge of the correct thermodynamic behaviour of these compounds in water is vital for the development of the concepts of hydrophobic hydration and of hydrophobic interactions^(2,6) which are very useful for understanding phenomena of large biological interest. Moreover, to be able to reproduce with the calculus the values of all the thermodynamic standard functions of hydration and their dependence on concentration for a series of hydrocarbons of increasing size is a severe test for the theories on water and the aqueous solutions.

As far as the limiting partial molar thermodynamic quantities are concerned, some papers on the partial molal heat capacities⁽⁷⁻⁹⁾ and volumes⁽⁸⁾ of polyols and sugars, classes of compounds before neglected, should be mentioned.

A lot of recent papers refer to experiments carried out in order to get some insight on the solute-solute interactions. The effects that the solute-solute interactions produce on the free energy, enthalpy, heat capacity and volume in binary, ternary or more complicated aqueous systems have been considered⁽¹⁰⁾. The data have been processed through virial expansion in the solute concentration according to McMillan and Mayer^(11,12) and the pair, triplet and sometimes higher order interaction parameters between solute molecules have been calculated for solutions containing only non-electrolytes⁽¹⁰⁾, but also for aqueous solutions containing electrolytes and non-electrolytes⁽¹³⁾.

I would like finally to remember incidentally that in these last years the thermodynamic studies on aqueous solutions have been addressed to a large part towards more complexes systems bearing importance under technologic aspects or for their likeness with biological or geological aqueous systems. In particular, I wish to quote some papers on aqueous solutions of micelles and microemulsions⁽¹⁴⁾ or on aqueous binary or ternary electrolytes or mixed electrolytes and non-electrolytes aqueous

solutions at high concentrations, temperature and pressures⁽¹⁵⁾.

Solute-solvent and solute-solute interactions in aqueous dilute solutions of non-electrolytes in relation to their molecular structure.

Data collected on thermodynamic properties of binary aqueous solutions concern some hundreds of compounds^(3b). Their examination allow to recognize some regularities such as f.i.: (i) In the homologous series of monofunctional compounds with normal chains, the values of each thermodynamic property X , no matter what it is, is always linearly related to the number of carbon atoms n_C . By changing the nature of the hydrophilic group, the straight lines X vs. n_C do not change in the slope but only in the intercept⁽¹⁶⁾; (ii) The enthalpy of hydration is linearly related to the entropy of hydration: many straight lines, of the same slope but different intercept, are produced by changing category of compounds⁽¹⁷⁾; (iii) For large molecules constituted by more than one large framework, the property is linearly related to the number of frameworks⁽¹⁸⁾; (iv) The values of the slopes of the straight lines valid for the dependence of the partial molar volumes \bar{V}_2 on concentration in dilute solutions of monofunctional solutes lie on a single curve when plotted against the limiting partial molar volumes \bar{V}_2^0 . A second curve fits the values of these slopes for polyfunctional compounds⁽¹⁹⁾.

The regularities above listed suggest that it is possible to give a systematic organization to the thermodynamic properties of non-electrolytes in water and that is important for both practical and theoretical aspects.

A way this object may be attained is simply to associate to each group constituting the solute molecule proper contributions to the thermodynamic properties. In some cases⁽²⁰⁾ the data were handled so that non-specific effects due to the formation in the solvent of a cavity able to lodge the molecule of the solute were taken into account. In others^(3b,21) instead, no preliminary correction has been made and the experimental data have been fitted by assuming that each group constituting the molecule had its own contribution.

In the first of the approaches, in order to overcome the difficulties for a correct evaluation of the energy required to form the cavity, the hydration functions of ten saturated hydrocarbon ΔX_h^0 ($X = G, H, S, C_p$) corresponding to the isothermal process:

$$R \left\{ \begin{array}{l} \text{ideal gas at} \\ c_g = 1 \text{ mol dm}^{-3} \end{array} \right\} \rightarrow R \left\{ \begin{array}{l} \text{ideal aqueous solution} \\ \text{at } c_s = 1 \text{ mol dm}^{-3} \end{array} \right\} \quad (1)$$

have been fitted with the equation:

$$\Delta X_h^\circ(R) = \alpha_R + \beta_X A(R) \quad (2)$$

where $A(R)$ is the surface area of the hydrocarbon. The hydration functions $\Delta X_h^\circ(RY_1Y_2\dots Y_m)$ for a generic compounds having one or more hydrophilic groups Y_i bonded to an hydrocarbon frame R , are described as:

$$\Delta X_h^\circ(RY_1Y_2\dots Y_m) = \Delta X_h^\circ(R) + \sum_i \Delta X_h^\circ(Y_i) + \delta_{1,2\dots m} (X_h^\circ)_{Y_1Y_2\dots Y_m} \quad (3)$$

Proper choices of compounds allow to obtain first the values of the contributions $\Delta X_h^\circ(Y_i)$ for various functional groups Y_i in the hypothesis of a strict rule of additivity, and successively the values of the effects $\delta_{1,2\dots m} (X_h^\circ)_{Y_1Y_2\dots Y_m}$ arising from the interactions between the functional groups in the polyfunctional compounds. As a result concerning fortytwo saturated monofunctional organic compounds and twentyfour bifunctional saturated compounds it was observed that: (i) The $\Delta G_h^\circ(Y)$ contributions to the free energy of hydration in the monofunctional compounds are always negative and faibly dependent on the nature of Y : except for the $-\text{CONH}_2$ groups having $\Delta G_h^\circ(\text{CONH}_2) = -48 \text{ kJ mol}^{-1}$, the others $\Delta G_h^\circ(Y)$ range from -20 to $-30 \text{ kJoule mol}^{-1}$. The contrary occurs for the $\Delta H_h^\circ(Y)$ quantities which are instead largely dependent on the nature of Y ; (ii) The $\Delta S_h^\circ(Y)$ values are always negative and generally larger in magnitude than the value of the entropy of hydration of the methylene group, $\Delta S_h^\circ(\text{CH}_2) = -13 \text{ Joule mol}^{-1}\text{K}^{-1}$; (iii) The interaction between polar centres produce positive and almost constant values of $\delta G_h^\circ(Y_1Y_2)$. However the $\delta H_h^\circ(Y_1Y_2)$ and the $\delta S_h^\circ(Y_1Y_2)$ terms are strongly dependent on the nature of Y_1 and Y_2 , thus indicating interactions between hydrophilic centres in polyfunctional compounds, which are subject to the enthalpy-entropy compensation rule⁽¹⁷⁾, valid also for the solvation of the single Y group (see point (i)). (iv) The substitution of a part of an hydrocarbon molecule with an hydrophilic group of the same size produces a shrinkage in the volume which may be remarkable: for amide and peptide groups it is equal to about 10 ml mol^{-1} (3a).

In the second full empirical approach to calculate thermodynamic

standard functions of hydration or partial molar properties at infinite dilution the following general equation has been used:

$$Z = A_Z + \sum_j n_j B_Z(j) + C_Z(Y_1Y_2\dots Y_m) \quad (4)$$

where Z indicates any thermodynamic quantity (function of hydration or partial molar property), n_j is the number of times the j^{th} group appears in the molecule under consideration, A_Z is a constant term introduced in order to avoid unjustified high values of contribution of the terminal groups. Moreover this term includes all information concerning standard states, allowing the values of group contribution to the free energy, $B_{\Delta G}$, not to depend on the choice of these states. B_Z is the contribution the j^{th} group gives to the Z thermodynamic property and finally $C_Z(Y_1Y_2\dots Y_m)$ is a correction parameter which taken into account interactions among the hydrophilic groups present in polyfunctional compounds. As a result of a last square treatment, involving some hundreds of non-ionic compounds, for each of the considered properties (ΔG_h° , ΔH_h° , $\Delta C_{p,h}^\circ$, $\bar{C}_{p,2}$, V_2) about twenty values of B_Z and about twenty values of C_Z have been obtained. Fig.1 and 2 reproduce some of these data.

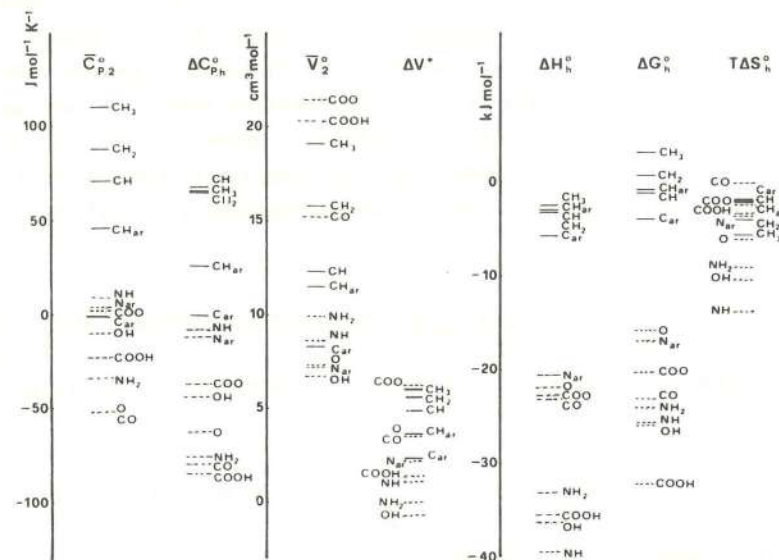


Fig.1 - Selected values of group contributions B_Z , to the thermodynamic properties of non-ionic organic compounds in water at 25°C. (Hydrophobic groups: -----; hydrophilic groups - - - -). (See Ref. 3b)

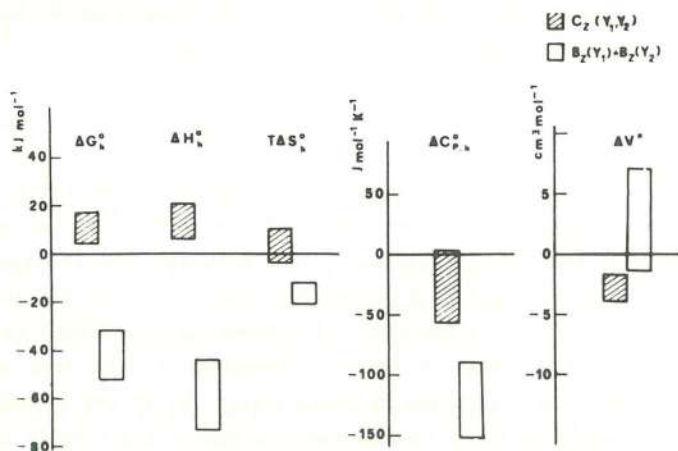


Fig. 2 - Comparison between the ranges of values of correction parameters $C_Z(Y_1, Y_2)$ and the ranges of the sums $B_Z(Y_1) + B_Z(Y_2)$ for bifunctional saturated aliphatic compounds of the type $Y_1-C-C-Y_2$ ($Y_1, Y_2 = O, OH, NH_2$). (See ref. 3b).

The considerations reported in the point (i)...(iv), as a summary of the results of the first approach, may be substantially repeated. In particular it is to be noticed that while the hydrophobic and the hydrophilic contributions to the enthalpy of hydration belong to very well distinguished ranges as far as the entropy of hydration contributions, instead, merge in a unique range. That has some implication relevant to the concepts of hydrophobic hydration and hydrophobic interactions.

As far as the solute-solute interactions are concerned, Savage and Wood^(10b) observed that a simple additivity principle may correlate the thermodynamic pair interaction parameters x which appear in the polynomial:

$$x^E = \sum_{\alpha} \sum_{\beta} x_{\alpha\beta} m_{\alpha} m_{\beta} + \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_{\alpha\beta\gamma} m_{\alpha} m_{\beta} m_{\gamma} + \dots \quad (5)$$

used, for represent the dependence of the experimental excess thermodynamic functions x^E on concentrations $m_{\alpha}, m_{\beta}, \dots$ (in moles for Kg of solvent) of the α, β, \dots solutes. Such additivity principle assumes that every functional group in molecule A interacts with every func-

tional group on molecule B in a way which does not depend from the position of the functional groups present in the molecules A and B or from their number and type.

The total pairwise molecular interaction coefficient x_{AB} may be related to the group contributions x_{ij} by:

$$x_{AB} = \sum_{ij} n_i^A n_j^B x_{ij} \quad (6)$$

where n_i^A and n_j^B are the number of type i functional groups on molecule A and type j groups on molecule B respectively.

The relation (6) has proved to be valid for free energy ($x=g$)^(10a) enthalpy ($x=h$)^(10b) and heat capacity ($x=c_p$)^(10c). For the volumes, the experimental uncertainty in the determination of the volumes in the excess at high dilution prevented to verify the validity of eq. (6), so that for this property no V_{ij} has been at present reported.

The degree of success of the method above summarized may be judged immediately from Fig. 3 where a large amount of experimental enthalpy

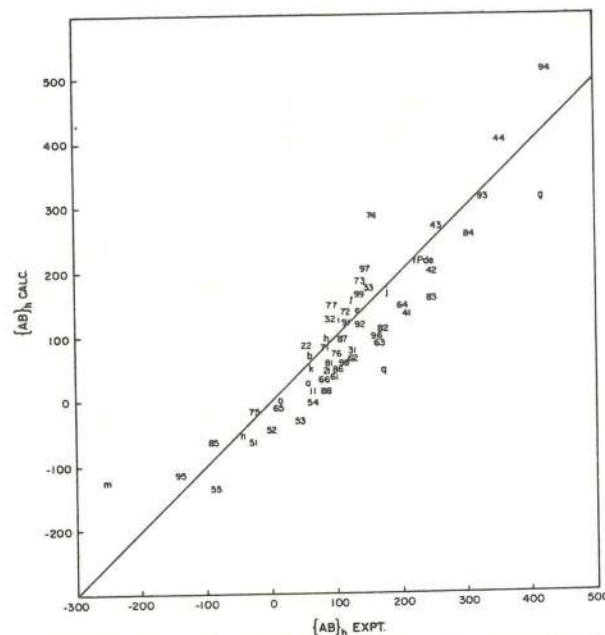


Fig. 3. Plot of $(AB)_h$ (calc.) versus $(AB)_h$ (exp.) for all the compounds in Tables II and III. Calculated values are from Ep. (8) and the coefficients in Table IV. Each digit indicates a molecule: (1) *N*-methylformamide; (2) *N*-methylacetamide; (3) *N*-methylpropionamide; (4) *N*-butylacetamide; (5) urea; (6) ethylene glycol; (7) pentaerythritol; (8) glucose; (9) sucrose. Letters denote the following molecules interacting with themselves: (a) methanol; (b) ethanol; (c) *n*-propanol; (d) *i*-butanol; (e) *n*-butanol; (f) 2-butanol; (g) *i*-pentanol; (k) glycerol; (l) lactose; (m) diketopiperazine; (n) glycolamide; (o) acetamide; (p) dimethylacetamide. Letters also denote the following interactions: (h) ethanol-*n*-propanol; (i) ethanol-*n*-butanol; (j) *n*-propanol-*n*-butanol; (q) urea-*i*-butanol.

(From ref. 10b)

bond) involve an endothermic effect; (ii) A similar endothermic effect is produced also from the interaction of the CH_2 group with polar groups such as CHOH and CONH ; (iii) The interaction between peptide groups $\text{CONH}\dots\text{CONH}$ on the contrary is associated with a large exothermic effect; (iv) The entropy term acts as stabilizing hydrophobic bonding and it is higher than the destabilizing enthalpic term; (v) The contrary occurs for the association propensity related to peptide groups, in which case the negative free energy of interaction arises from the prevalence of the negative enthalpic term on the negative entropic one; (vi) The temperature seems to increase the enthalpy of hydrophobic interaction.

Of course what has been above exposed does not tell us what happens at molecular level, but in spite of that in order to have more insight into this problem the description through the additive group approach is more suitable than to limit to consider only the experimental x_{AB} quantities. These are in effect a balance of many interactions often different for magnitude and also from sign.

The additivity schemes either those relative to the infinitely dilute solutions where only solute-solvent interactions are considered, or those relative to dilute solutions, where only pairwise solute-solute interactions, other than solute-solvent interactions, have to be considered, are certainly useful for the possibility they offer to predict the thermodynamic behaviour of a large number of compounds alone or in mixtures, by using only a small number of parameters. But another aspect of the usefulness of the additivity rules has to be reminded. I refer to the cases where strong differences are found between experimental values and values calculated by means of group contribution methods. Such differences may arise from causes not foreseen in the adopted scheme of simple additivity of group as f.i.: electronic internal interactions between hydrophilic groups with consequent change in the solute-solvent interactions with respect to the case they were present singly; interaction between hydrophilic centres due to their reciprocal position and distance which may favour particular organization of the solvent⁽²²⁾; steric effect which may mask or on the contrary expose to the solvent a particular group; cooperative effects arising when the dimension of the single molecule or of the aggregates of more molecules attain some critical size and so on.

As far as the interpretation of the data in terms of events which occur at molecular level is concerned, much attention continues⁽²³⁾ to be devoted to the problem of the hydrophobic hydration and hydrophobic interactions for which a satisfactory solution has been not yet attained.

From a phenomenological point of view it is a matter of fact that the introduction of a non polar solute into water involves positive values of the standard free energy of hydration due to large and negative values of the standard entropy of hydration (standard states: unitary concentration in both the ideal gas phase and the ideal aqueous solution) which overcome the negative values of the enthalpy of hydration. Other characteristics of the hydrophobic hydration is the very high values of the partial molar heat capacity of the non-polar solutes in the infinitely dilute solution. As to the dependence on concentration of the thermodynamic properties of non-polar solutes, it is still matter of fact that, as already observed, the solute-solute interaction involves endothermic effects and an increase of entropy. The balance of the enthalpic and entropic terms produce a negative value of the free energy of interaction (hydrophobic bonds). Additional characteristics are the decrease of the partial molar volumes as the concentration of the dilute solution is increased and the increase in the dilute solution of the partial molar heat capacities with concentration. For both volumes and heat capacities the trend is inverted as the concentration is increased over certain values.

The negative values of the entropy of hydration and the positive values of the entropy of hydrophobic interaction, have been considered for a long time^(6a-6d) as the more distinctive features of the dilute aqueous solutions of non-polar compounds and were attributed to the organization of the water around the non-polar solutes. In infinitely dilute solution the water forms around the non-polar molecules an hydration shell where it is more structured, i.e. organized in a ice-like way, than in the bulk. When the concentration of the solute is finite but the solution is yet dilute, there is the formation of hydrophobic bonds for a direct contact between the non-polar surfaces of two molecules of the solute or possibly through an indirect contact mediated with interposition of water molecules⁽²⁴⁾. This process of formation of the hydrophobic bonding gives freedom to a part of the water involved in the hydration shells surrounding the two separated molecules of the so-

lute. That determines a gain of entropy and a loss in the heat capacity.

These largely diffused and well accepted viewpoints have been recently questioned⁽²⁵⁾. As a matter of fact the large negative values of the entropy of hydration are not peculiar of the hydrophobic hydration. In fact the distinction between polar and non-polar solutes has to be founded on the enthalpy of hydration which is largely dependent on the nature of the solutes and not on the entropy of hydration which depends more on the size of the molecules than from their chemical nature (see fig. 1).

Interesting to this purpose is the comparison that Wertz^(25d) made among the enthalpies and entropies of hydration of NH_3 ($\Delta S_h^\circ = -14.2$ e.u.; $\Delta H_h^\circ = -8.54$ Kcal mol⁻¹), CH_4 ($\Delta S_h^\circ = -13.1$ e.u.; $\Delta H_h^\circ = -1.95$ Kcal mol⁻¹) and H_2O ($\Delta S_h^\circ = -14.1$ e.u.; $\Delta H_h^\circ = -10.48$ Kcal mol⁻¹). While the entropies of hydration are almost identical, the enthalpies of hydration are very different. The hypothesis have been put forward that the entropies of hydration are almost independent solute-solvent interactions and that in the transfer of gas into water the same fraction of entropy is lost independently of the nature of the molecules.

Abrahams^(25e), from an analysis of the values of the thermodynamic functions of solution for gaseous non-polar non-electrolytes in water and in non-aqueous solvents, deduced that no special hydrophobic effect has to be invoked in order to justify the thermodynamic behaviour of rare gases in water. The hydrophilic effect for the hydrocarbon compounds is thus calculated as an excess quantity with respect to a hypothetical rare gas of the same dimension. This procedure produces a positive value for the free energy to be associated to the hydrophobic effect of the methylene group ($\Delta G_h^\circ = 0.54$ Kcal mol⁻¹) which is due mainly to the enthalpic term ($\Delta H_h^\circ = 0.44$ Kcal mol⁻¹). The contrary would occur for the methyl group, here the positive free energy of hydration ($\Delta G_h^\circ = 0.33$ Kcal mol⁻¹) is totally determined from the entropy term ($T \Delta S_h^\circ = -0.40$ Kcal mol⁻¹).

These different ways of interpreting the thermodynamic behaviour of non-polar solutes in water are simply the expression of the fact that the thermodynamic data "per se" do not give an unambiguous picture of the molecular events which produce the macroscopic quantities observed. In spite of that, the stimulus to collect new data in order to test some hypothesis on water and its solutions has not to be neglected. On the other hand, the uncertainty in establishing the structure of aqueous

solutions is found also when spectroscopic data are discussed or when the results of Monte Carlo or Molecular Dynamics simulations are considered. Further developments of all these thermodynamic, spectroscopic (i.r., N.M.R.), scattering and theoretical methods, are still necessary in order to arrive at a better understanding of such complicated systems as the aqueous solutions.

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ESTUDO COMPARATIVO DA ELECTROCRISTALIZAÇÃO DO SnS EM
ELÉCTRODOS DE AMÁLGAMA E ESTANHO SÓLIDO

M. Isabel S. Pereira, M.F.G. Silva, M.J.B.V. Melo e
F.M.A. da Costa
CECUL e C.Q.F.R., Faculdade de Ciências
R. Escola Politécnica, 58
1294 LISBOA CODEX - PORTUGAL

ABSTRACT

A comparative study of the electrodeposition of tin(II) sulphide on tin and tin amalgam, has been done in bicarbonate solutions using a potentiodynamic technique. The influence of sweep rate and sulphide concentration, on the peak current has been studied.

The results show, that in the early stages, the deposition takes place by a different mechanism in each substrate. However the thickening of the film seems to occur by diffusion through the solid phase, in both substrates, for high sulphide concentrations, while for low concentrations the rate determining step is the diffusion in solution.

RESUMO

É feito um estudo comparativo da Electrodeposição do sulfureto de estanho II, em eléctrodos de estanho metálico e amálgama, em soluções bicarbonatadas de sulfureto de sódio.