trum.[14] (The primed coordinate system is used in their analysis.) Earlier literature is discussed in reference.[8]

Summary

The DICD technique is seen to yield selection rules that facilitate assignment by simply referring to the DICD spectrum and the relevant table derived from the DICD symmetry rules. The results are qualitative, the calculation of absolute intensities requiring knowledge of all transition moments in the relevant expressions. Usually only a few are known (from oscillator strengths in absorption). When these quantities are determined theoretically, better comparisons with experiment will be possible. As discussed earlier, however, the use of suitable chiral inducing agents should be able to effect a separation of the magnetic and electric dipole allowed transitions and lead to a more definitive assignment of the entire spectrum, even without quantitative estimates of all the transition moments.

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Appendix

DICD-Allowed Symmetries for Various Stereochemistries. In Table III, the possible combinations of $|A^0\rangle$, $|A^s\rangle$, and $|A^t\rangle$ are given for point group symmetries common to Cu(II) complexes. These are the only combinations that lead to DICD activity in the s transition through the magnetic induction mechanism. If more than one symmetry of $|A^t\rangle$ is given for a certain $|A^s\rangle$, then any one of those states is a potential intermediate state for inducing DICD in the s transition. The symmetry of state $|A^r\rangle$ will be denoted Γ_r.

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An Analysis of the Endostatic Transformation of Thermodynamic Functions

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Abstract: The endostatic transformation of the standard state properties of a solute in a mixed solvent system has been analyzed in terms of the hypothetical experiment on which the transformation is based, the relationships between transformed functions, and the behavior of transformed functions for a simple model system. This analysis reveals serious flaws in the structure of endostatic transformations.

In a recent article, Grunwald and Effio proposed a transformation of the thermochemical properties of a solute in a mixed solvent system from the normal condition of fixed solvent composition to a hypothetical condition of fixed activity ratios.[2] This transformation was based on a hypothetical experiment in which the addition of solute to a solution was accompanied by transfer of solvent components between the solution and reservoirs containing the individual solvents and solute at the same solute mole fraction as the solution so that the total number of moles of solvent and the ratio of solvent activities in the solution were unchanged. This transformation was designed to simplify interpretation of the thermodynamic properties of the solute in a mixed solvent by making these functions analogous to corresponding functions in one-component solvents. The utility of considering processes at constant solvent activity ratios cannot be denied. Some processes actually occur under these conditions, i.e., the osmotic experiments designed by Scatchard[3a] and many other processes in biological systems. Treiner[3b] has observed that mixed solvents obey Raoult's law (as it was originally stated) under these conditions. However, these processes have an important distinction from the endostatic process described by Grunwald and Effio (GE) in that the real processes occur in a system in which the chemical potentials of the solvent components are uniform throughout the system, while the endostatic process occurs in a system containing solvent components in different free energy states. One can conceive a reversible process occurring in an osmotic experiment with two solutes in chemical equilibrium. This process could not occur reversibly under endostatic conditions, except in highly specific cases. Because of this difference between endostatic and osmotic conditions we have analyzed the endostatic experiment described by GE on the basis of the definition of the hypothetical experiment, the relationships between transformed functions, and the behavior of transformed functions for a simple model system. We have found that the fundamental concept is flawed in that: (1) the hypothetical experiment cannot be applied to the addition of a finite quantity of solute, (2) the temperature dependence of transformed standard state properties is much more complex than in the normal case, and (3) interpretation of solvent effects on transformed properties is hampered by complexities even in the case of an ideal binary solvent. These flaws appear to arise from the properties of the hypothetical system on which transformations are based, rather than from the properties of the solution formed by addition of solute at constant solvent activity ratio.

The Endostatic Process at Finite Concentrations of Solute

In defining the process for endostatic addition of a solute to a mixed solvent, GE consider a system composed of four separate compartments: compartment A containing pure solute (component 3); the solution containing solute at mole fraction N_3 and solvents at compositions $N_1 = (1 - N_3)Z_1$ and $N_2 = (1 - N_3)Z_2$; compartment B containing solute at mole fraction N_3 and solvent component 1 at mole fraction $(1 - N_3)$; and compartment C containing solute at mole fraction N_3 and solvent component 2 at mole fraction $(1 - N_3)$. The process consists of the transfer of $\mathrm{d}n_3$ moles of solute from compartment A to the solution with simultaneous transfer of $\mathrm{d}n_1$ mol of component 1 between the solution and compartment B and $\mathrm{d}n_2 = -\mathrm{d}n_1$ mol of component 2 between the solution and compartment C, the net process occurring so that the ratio of solvent activities ($\alpha = a_1/a_2$) in the solution is not changed. The solvent components are transferred under conditions of constant N_3, and conditions of constant temperature and pressure are implied. The endostatic molal function $Y_{\alpha,3}$ (Y is any extensive thermodynamic function) is apparently defined as the value of Y for 1 mol of pure solute (Y_3^0) plus the partial derivative of the net property Y of the system taken with respect to the number of moles of solute transferred to the solution at constant $(n_1 + n_2)$ and α in the solution and constant temperature and pressure. GE specify that the value of N_3 is the same in the solution and in compartments B and C; they do not specify, however, how this equality is maintained for the transfer of a finite amount of solute. This is an important consideration, since all three values of N_3 change during the differential process: the value in the solution must increase, and the values in compartments A and B increase and decrease depending on whether the quantity $\mathrm{d}n_1^{\mathrm{soln}}$ is positive or negative. The importance of these changes is related to the relative change in composition, rather than to an absolute change (since the chemical potential of component 3 varies with the logarithm of N_3), and thus may become important in the limit as N_3 approaches zero. The process as described cannot be used to go from infinite dilution ($N_3 = 0$) to finite values of N_3 without additional changes occurring within the system, specifically involving addition of solute or withdrawal of solvent from compartments B and C, nor can the process be reversed to approach infinite dilution from finite concentrations of the solute without additional changes occurring.

The endostatic approach to infinite dilution requires that the mole fraction of solute (N_3) be identical with the solution and with compartments B and C for each incremental transfer of solute from the solution to the pure state in compartment A.

$$N_3{}^{\mathrm{S}} = N_3{}^{\mathrm{B}} = N_3{}^{\mathrm{C}} = N_3;\ \mathrm{d}N_3{}^{\mathrm{S}} = \mathrm{d}N_3{}^{\mathrm{B}} = \mathrm{d}N_3{}^{\mathrm{C}} = \mathrm{d}N_3 \quad (1)$$

Relating these equalities to the change in the numbers of moles of the various components gives (at constant $n_1{}^{\mathrm{S}} + n_2{}^{\mathrm{S}}$)

$$\mathrm{d}N_3 = \frac{(1 - N_3)\,\mathrm{d}n_3{}^{\mathrm{S}}}{(n_1{}^{\mathrm{S}} + n_2{}^{\mathrm{S}} + n_3{}^{\mathrm{S}})} = \frac{(1 - N_3)\,\mathrm{d}n_3{}^{\mathrm{B}} + N_3\,\mathrm{d}n_1{}^{\mathrm{B}}}{(n_1{}^{\mathrm{B}} + n_3{}^{\mathrm{B}})} = \frac{(1 - N_3)\,\mathrm{d}n_3{}^{\mathrm{C}} + N_3\,\mathrm{d}n_2{}^{\mathrm{C}}}{(n_2{}^{\mathrm{C}} + n_3{}^{\mathrm{C}})} \quad (2)$$

In their definition of the endostatic process, GE have indicated that

$$\mathrm{d}n_3{}^{\mathrm{B}} = \mathrm{d}n_3{}^{\mathrm{C}} = 0$$

$$-\mathrm{d}n_1{}^{\mathrm{B}} = \mathrm{d}n_1{}^{\mathrm{S}} = -\mathrm{d}n_2{}^{\mathrm{S}} = \mathrm{d}n_2{}^{\mathrm{C}} \quad (3)$$

Equation 2 then becomes

$$\mathrm{d}N_3 = \frac{(1 - N_3)\,\mathrm{d}n_3{}^{\mathrm{S}}}{(n_1{}^{\mathrm{S}} + n_2{}^{\mathrm{S}} + n_3{}^{\mathrm{S}})} = -\frac{N_3\,\mathrm{d}n_1{}^{\mathrm{S}}}{(n_1{}^{\mathrm{B}} + n_3{}^{\mathrm{B}})} = \frac{N_3\,\mathrm{d}n_1{}^{\mathrm{S}}}{(n_2{}^{\mathrm{C}} + n_3{}^{\mathrm{C}})} \quad (4)$$

These equations can be valid only for $N_3 = 0$, not for $N_3 \rightarrow 0$. Therefore, the system of endostatic molal quantities as defined by GE is applicable only at infinite dilution and not in the approach to infinite dilution. The effect of this complication on the applicability of standard state properties depends on the manner of definition of the standard state. The most common method of defining the standard state properties of a solute, while rarely stated explicitly, can be represented as

$$Y_i{}^0 = \lim_{c_i \to 0} [Y_i - \Delta Y_i{}^{\mathrm{theor}}] \quad (5)$$

in which $\Delta Y_i{}^{\mathrm{theor}}$ is calculated from a theoretical expression for the relationship between Y_i and the composition variable (c_i) in the limit as the solute composition approaches infinite dilution. Henry's law and the Debye–Hückel limiting law commonly provide the basis for calculating $\Delta Y_i{}^{\mathrm{theor}}$. This definition of the standard state property implies that Y_i is observed at finite concentrations and that the measured value is corrected for a theoretical effect and extrapolated to infinite dilution with an equation based on the mathematical form of $\Delta Y_i{}^{\mathrm{theor}}$. Since endostatic molal quantities cannot be applied at finite concentrations of solute, this approach to standard state values is not acceptable.

An alternate method of defining standard state properties may be found in the standard thermochemical tabulation of the National Bureau of Standards.[4] The standard state for a solute in an aqueous system is taken as the hypothetical ideal solution of unit molality, and in nonaqueous solutions the standard state of the solute is the hypothetical ideal solution of unit mole fraction of solute. In this state, the partial molal enthalpy and heat capacity (and in some cases, depending on the manner in which standard state pressure is specified, the partial molal volume) are the same as in the infinitely dilute real solution. This definition of standard state properties allows conversion of the normal partial molal enthalpy of the solute at infinite dilution to endostatic conditions. Definition of the behavior of a solute in an "ideal solution for endostatic conditions" as

$$G_{\alpha,3} = G_{\alpha,3}{}^0 + RT \ln N_3;\ G_{\alpha,3}{}^0 = G_{\alpha,3}{}^0(T,\alpha^M) \quad (6)$$

allows definition of the standard endostatic molal Gibbs free energy. Using this definition of the properties of the solute in the endostatic standard state, the transformation formulas given by GE in their Table I are thermodynamically acceptable as individual statements. The relationships between these transformed properties, however, require further definition of the ideal solution for endostatic conditions.

Temperature Dependence of the Standard Endostatic Gibbs Free Energy

The standard free energy of a solute in a binary solvent is normally considered to be a function of temperature and solvent composition,

$$\overline{G}_3{}^0 = \overline{G}_3{}^0(T,Z_1) \quad (7)$$

the standard state pressure being specified as 1 atm. The standard partial molal enthalpy is related to the temperature dependence of the standard free energy

$$[\partial(\overline{G}_3{}^0/T)/\partial T]_{Z_1} = -\overline{H}_3{}^0/T^2 \quad (8)$$

By analogy, one would expect a similar relationship for endostatic molal quantities to apply under some conditions

$$[\partial(G_{\alpha,3}{}^0/T)/\partial T]_{?} = -H_{\alpha,3}{}^0/T^2 \quad (9)$$

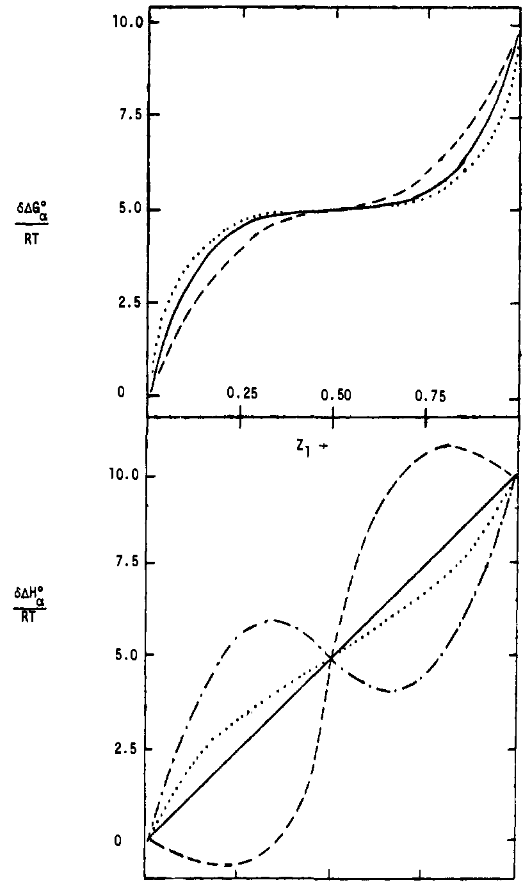

Figure 1. Standard endostatic functions for a reaction in a simple model system (see text, eq 27 and 28). The normal thermodynamic functions are straight lines connecting the values in the pure solvents: (—) $g_{12} = h_{12} = 0$; (• • •) $g_{12} = h_{12} = -1.5RT$; (- - -) $g_{12} = h_{12} = 1.5RT$; (- • -) $g_{12} = RT$, $h_{12} = -2RT$.

By alternately considering the standard partial molar free energy of the solute as a function of (T,Z_1) and then as a function of $(T, \ln \alpha^M)$ and applying the cycle rule

$$(\partial Z_1/\partial T)_{\ln\alpha^M}(\partial T/\partial \ln \alpha^M)_{Z_1}(\partial \ln \alpha^M/\partial Z_1)_T = -1 \quad (10)$$

one obtains

$$[\partial(\overline{G}_3{}^0/T)/\partial T]_{\ln\alpha^M} = [\partial(\overline{G}_3{}^0/T)/\partial T]_{Z_1} - (1/T) \times (\partial\overline{G}_3{}^0/\partial Z_1)_T(\partial \ln \alpha^M/\partial T)_{Z_1}(\partial Z_1/\partial \ln \alpha^M)_T \quad (11)$$

From basic thermodynamic relationships, one obtains in the notation of GE

$$(\partial \ln \alpha^M/\partial T)_{Z_1} = -[(\overline{H}_1 - \overline{H}_1{}^0) - (\overline{H}_2 - \overline{H}_2{}^0)]/RT^2 = -[\overline{H}_1{}^\rho - \overline{H}_2{}^\rho]/RT^2 \quad (12)$$

Combination of (8), (11), and (12) gives

$$[\partial(\overline{G}_3{}^0/T)/\partial T]_{\ln\alpha^M} = -(1/T^2)\left[\overline{H}_3{}^0 - \frac{(\overline{H}_1{}^\rho - \overline{H}_2{}^\rho)(\partial\overline{G}_3{}^0/\partial Z_1)_T}{RT(\partial \ln \alpha^M/\partial Z_1)_T}\right] \quad (13)$$

The rhs of eq 13 is related to the transformation formula for the standard partial molal enthalpy,

$$[\partial(\overline{G}_3{}^0/T)/\partial T]_{\ln\alpha^M} = -H_{\alpha,3}{}^0/T^2 \quad (14)$$

Equation 14 can be used to show that eq 9 cannot be generally valid for conditions of constant α^M or constant solvent composition.

The transformation formula for the standard partial molal free energy can be rearranged to

$$\frac{G_{\alpha,3}{}^0}{T} = \frac{\overline{G}_3{}^0}{T} - \left[(\ln \alpha^M)\left(\partial\frac{\overline{G}_3{}^0}{T}\middle/\partial Z_1\right)_T/(\partial \ln \alpha^M/\partial Z_1)_T\right] \quad (15)$$

and partially differentiated with respect to temperature at constant α^M to give

$$\left(\partial\frac{G_{\alpha,3}{}^0}{T}\middle/\partial T\right)_{\alpha^M} = \left(\partial\frac{\overline{G}_3{}^0}{T}\middle/\partial T\right)_{\alpha^M} - [(\ln \alpha^M)/(\partial \ln \alpha^M/\partial Z_1)_T] \times \left[\frac{\partial}{\partial Z_1}\left(\partial\frac{\overline{G}_3{}^0}{T}\middle/\partial T\right)_{\alpha^M}\right]_T \quad (16)$$

Substitution of eq 14 into eq 16 gives

$$-T^2\left(\partial\frac{G_{\alpha,3}{}^0}{T}\middle/\partial T\right)_{\alpha^M} = H_{\alpha,3}{}^0 - [(\ln \alpha^M)(\partial H_{\alpha,3}{}^0/\partial Z_1)_T/(\partial \ln \alpha^M/\partial Z_1)_T] \quad (17)$$

Since the square-bracketed term in eq 17 is not generally zero, eq 9 is incorrect for the condition of constant α^M. Equation 9 can also be shown to be incorrect for the condition of constant Z_1 for the specific case of an ideal binary solvent which forms nonideal solutions with the solute. In this case, $\alpha^M = a_1/a_2 = Z_1/Z_2$, the condition of constant α^M also specifies constant Z_1, so that eq 17 can also be written for the condition of constant Z_1. In this case, the square-bracketed term is not necessarily zero, so eq 9 is not generally valid for the condition of constant Z_1. This shows that the endostatic standard molal enthalpy of a solute cannot be obtained directly from the temperature dependence of the standard endostatic molal free energy. A similar treatment can be used to show that the standard endostatic molal heat capacity ($C^0{}_{p\alpha,3}$) cannot be obtained directly from the temperature dependence of the standard endostatic molal enthalpy. This represents a serious departure from the thermodynamic properties of a solute in a one-component solvent or a mixed solvent under the normal conditions of constant composition. By comparison of pressure derivatives of the Gibbs free energy at constant temperature and at infinite dilution, one can show that the standard endostatic molal volume cannot be obtained directly from the pressure dependence of the limiting value (at infinite dilution) of the endostatic molal free energy.

The Relative Complexity of Endostatic Molal Quantities

GE have claimed that "transformed relationships should be easier to interpret, because of the exact analogy of endostatic functions to corresponding functions in one-component systems". The fallacy of this statement can be readily seen by consideration of very simple systems. From a simple model system, Burchfield and Bertrand[5] developed general equations for the excess partial molal properties of a solute at infinite dilution in a binary solvent. Acree and Bertrand[6] have shown that a very simple equation can be used to predict the solubility (and thus the excess partial molal Gibbs free energy near infinite dilution, $(\Delta\overline{G}_3{}^e)^*$) of third components in binary solvents of nonspecific interactions with reasonable success (1-2%) for systems in which the components are of comparable molal volumes. In these simple systems the excess partial molal free energy at infinite dilution can be related to the molal free energy of the pure liquid solute and the standard partial molal free energy (mole fraction as the composition variable in the infinitely dilute reference state) to show

$$\overline{G}_3{}^0 = Z_1(\overline{G}_3{}^0)_1 + Z_2(\overline{G}_3{}^0)_2 - \Delta\overline{G}_{12}{}^e \quad (18)$$

in which $(\overline{G}_3{}^0)_1$ and $(\overline{G}_3{}^0)_2$ represent the standard partial molal free energy of the solute in pure solvents 1 and 2, and $\Delta\overline{G}_{12}{}^e$

is the molal excess free energy of mixing of the solvent pair. We now consider a reaction between two solute components

$$\text{component 3} \rightarrow \text{component 4} \qquad (19)$$

both of which can be described by equations of the type of eq 18. We then have very simple relationships for the normal properties

$$\Delta G^0 = \bar{G}_4{}^0 - \bar{G}_3{}^0 = Z_1(\Delta G^0)_1 + Z_2(\Delta G^0)_2 \qquad (20)$$

$$\Delta H^0 = \bar{H}_4{}^0 - \bar{H}_3{}^0 = Z_1(\Delta H^0)_1 + Z_2(\Delta H^0)_2 \qquad (21)$$

For simplicity, we consider this reaction occurring in a binary solvent with simple excess properties

$$\Delta\bar{G}_{12}{}^e = Z_1Z_2RTg_{12};\ \Delta\bar{H}_{12}{}^e = Z_1Z_2RTh_{12} \qquad (22)$$

$$\ln \alpha^M = \ln (Z_1/Z_2) + (Z_2 - Z_1)g_{12} \qquad (23)$$

$$(\partial \ln \alpha^M/\partial Z_1)_T = (Z_1Z_2)^{-1}(1 - 2g_{12}Z_1Z_2) \qquad (24)$$

$$\bar{H}_1{}^p - \bar{H}_2{}^p = RT(Z_2 - Z_1)h_{12} \qquad (25)$$

From eq 20 we have

$$(\partial\Delta G^0/\partial Z_1)_T = (\Delta G^0)_1 - (\Delta G^0)_2 \qquad (26)$$

Application of the transformation formulas of GE yields

$$\Delta G_\alpha{}^0 = Z_1(\Delta G^0)_1 + Z_2(\Delta G^0)_2 - \frac{Z_1Z_2[\ln (Z_1/Z_2) + (Z_2 - Z_1)g_{12}][(\Delta G^0)_1 - (\Delta G^0)_2]}{(1 - 2Z_1Z_2g_{12})} \qquad (27)$$

$$\Delta H_\alpha{}^0 = Z_1(\Delta H^0)_1 + Z_2(\Delta H^0)_2 - \frac{Z_1Z_2RT(Z_2 - Z_1)h_{12}[(\Delta G^0)_1 - (\Delta G^0)_2]}{(1 - 2Z_1Z_2g_{12})} \qquad (28)$$

These equations clearly show that the transformed functions for this system cannot be simpler than the ordinary functions which are simply linear in Z_1. Some possible transformations are shown in Figure 1 for various values of the excess mixing parameters of the binary solvent. The ordinary thermodynamic property of the reaction is represented by a straight line between the values in the pure solvents. The endostatic standard enthalpy may take a variety of shapes, depending on the excess properties of the solvent pair. For a broad range of excess properties of the solvent pair the endostatic standard free energy of reaction retains its sigmoidal character, which derives from the ideal mixing term for the free energy of the solvent pair. The difficulty of interpreting endostatic functions is quite apparent. The sigmoidal character of the endostatic free energy of activation of *tert*-butyl chloride in ethanol-water mixtures was interpreted by GE as indicative of a changeover in the medium effect, from dominance by the ground state to dominance by the transition state. While this changeover in medium effects may actually occur, the sigmoidal shape of the endostatic free energy of activation is more likely related to the ideal mixing term in the free energy of the solvent pair.

Conclusions

From this analysis of endostatic transformations, we conclude that the basic definition of the endostatic experiment is flawed by the inclusion of nonequilibrium states within the system and by the inclusion of a condition (transfer at constant solute composition) which cannot be maintained over the addition of a finite amount of solute unless other unaccounted for changes occur within the system. The experiment may be valid at infinite dilution of the solute, and judicious choice of definitions may allow definition of standard state properties. These standard state properties, however, do not interrelate through simple temperature and pressure derivatives under any obvious conditions in the manner of normal thermodynamic properties in one- or multi-component solvents. This flaw may be traced to the temperature and pressure dependence of an essential component of the transformation formulas, the limiting value of the partial derivative of solvent composition with respect to solute concentration at constant activity ratio of the solvents.

$$\lim_{N_3 \to 0} (\partial Z_1/\partial N_3)_\alpha = f(Z_1,T,P) = g(\alpha^M,T,P) \qquad (29)$$

Even with these fundamental flaws, the endostatic transformation might retain some validity if, as GE claim, it simplified the interpretation of solvation phenomena and removed the "distortion" of the normal treatment. However, when applied to a simple model system based on the most elementary type of solvation, tremendous distortions occur.

We wish to emphasize that the difficulties of the endostatic approach as defined by GE do not arise from the condition of constant solvent activity ratio but rather from the manner in which this condition is imposed. Perhaps more rigorous adherence to the conditions of the osmotic experiment with mixed solvents could remove these difficulties, but this modification is almost certain to change the transformation formulas given by GE. At the present time, however, the endostatic transformation of standard state properties of solutes in mixed solvents should be applied with caution.

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