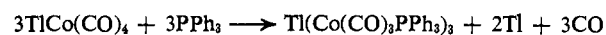


solvents of this study. It is seen that the solvents cover virtually the whole range of the donor numbers. All of the solvents, however, show a donor ability of sufficient strength to bring about the simple T_d ion site structure. Thus, the phenomena of ion site character is not included in the donor number as measured by solvent-SbCl₅ interaction.

The chemistry of a salt in solution is just the sum of the chemistry at the ion sites. What makes this statement nontrivial is an expectation that the chemistry will generally be different at the different ion sites. The nature of an ion site in solution can be expected to have a role in both the quantitative and qualitative aspects of reactions in which it is involved either directly as a reactant or indirectly as a catalyst. The qualitative importance of the solvent surrounded ion

site found for the $\text{Co}(\text{CO})_4^-$ ion in these solvents is demonstrated by the reaction



which, while it takes place in selected nonaqueous solvents, does *not* occur at solvent surrounded ion sites.^{17,23}

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Solution Thermodynamics in Nonideal Mixed Solvents under Endostatic Conditions¹

Ernest Grunwald* and Adan Effio

Contribution from the Chemistry Department, Brandeis University, Waltham, Massachusetts 02154. Received May 7, 1973

Abstract: Thermodynamic functions of solution, reaction, and activation measured in nonideal mixed solvents of constant composition are inherently complex because the addition of a solute under such conditions is attended by changes in the relative partial molal functions of the solvent components. This complexity is avoided if the thermodynamic functions are measured under endostatic conditions, that is, in such a way that the ratio a_1/a_2 of the activities of the solvent components remains constant. Precise definitions are given, and it is shown that functions measured under endostatic conditions in mixed solvents are exactly analogous to corresponding functions in one-component solvents. Thermodynamic equations are derived for transforming data obtained at constant composition to constant a_1/a_2 . Solvent properties required in such transformations are tabulated for common water-organic solvent mixtures. The use of endostatic functions is illustrated for the solvolysis of *tert*-butyl chloride in ethanol-water mixtures.

Equilibrium and rate constants and thermodynamic properties of solutes in binary liquid solvent systems are sometimes inordinately complex when studied as a function of temperature, pressure, solvent composition, or neutral-salt addition. This is particularly true for water-organic mixed solvents, and for those thermodynamic functions for which the solvent system itself shows marked deviations from ideal behavior.^{2,3} For example, in water-organic mixtures, activation energies, activation volumes, and heats of solution as a function of solvent composition often show maxima and/or minima;^{4–7} partial molal heat

capacities of solutes may show several inflections and differ greatly from molar heat capacities in the pure state;^{8,9} and neutral-salt effects may become specific for each salt so that they can no longer be treated as colligative functions of the ionic strength.^{10,11}

Unfortunately, the mixed solvents which display the greatest deviations from ideal thermodynamic behavior are precisely those of the greatest practical utility. This is because there is little advantage in using a mixed solvent (rather than a pure one) unless the solvating actions of the components are genuinely different and complementary. Thus, familiar patterns of behavior associated with solutions in one-component solvents and ideal mixtures often become distorted in common mixed solvents. For example, the hydrolysis of triethyl orthobenzoate almost certainly proceeds with specific hydrogen ion rather than general acid catalysis.¹¹ However, owing to the peculiarities of neutral kinetic

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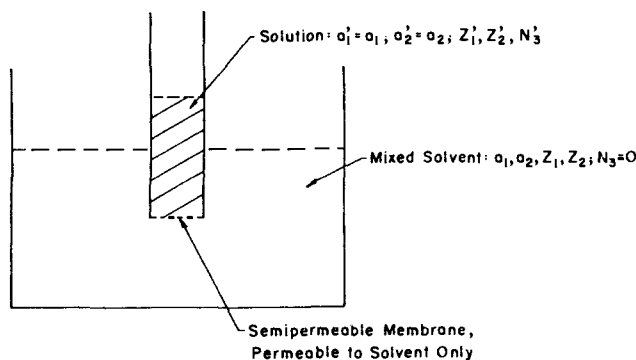


Figure 1. Osmotic equilibrium between a dilute solution and pure mixed solvent. In general, $Z_1'/Z_2' \neq Z_1/Z_2$.

salt effects in mixed solvents, the kinetic data obtained for this reaction in water-organic solvent mixtures can be, and have been, mistaken for general acid catalysis.^{11,12}

In this paper we wish to discuss the reason for the distortion of thermodynamic data in nonideal mixed solvents and show how to avoid it. Basically, the distortion results from our system of chemical thermodynamics, in which we operate with equations that involve partial molal functions evaluated *at constant composition*. When a solute is added to a nonideal binary solvent of constant composition, the addition of the solute may bring about a marked change in the state of the solvent components. There are many manifestations of such a change when it occurs. In particular, there will be a marked increase in the activity of one of the solvent components (per mole of added solute) and a marked decrease in that of the other.¹³ The partial molal functions for the solute are therefore intrinsically complex, since they account not only for the effect of dissolving the solute but also for the coupled change in the state of the solvent components.

Fortunately, the constraint of keeping the composition of the mixed solvent constant, as solute is added, is based on convenience rather than thermodynamic necessity and is in fact quite artificial. To find a more natural relationship it is instructive to consider the classic problem of osmotic equilibrium involving a non-diffusible solute (component 3) and diffusible solvent (components 1 and 2).¹⁴ In Figure 1 and the following, a denotes activity and N denotes mole fraction (*i.e.*, $N_3 = n_3/(n_1 + n_2 + n_3)$, where n denotes mole number). The mixed-solvent composition is expressed conveniently by specifying mole fractions Z_1 and Z_2 , which are computed without counting the solute (*i.e.*, $Z_1 = n_1/(n_1 + n_2)$; $Z_2 = 1 - Z_1$). After osmotic equilibrium is established (Figure 1), the mole ratio (Z_1'/Z_2') of the solvent components in the solution will in general be different from that (Z_1/Z_2) in the original mixed solvent, while the activities of the solvent components are of course equal ($a_1 = a_1'$; $a_2 = a_2'$).

By a straightforward generalization from conditions at osmotic equilibrium it appears that the natural constraint, in the thermodynamic treatment of dilute

solutions in binary solvent systems, is to keep a_1/a_2 (rather than Z_1/Z_2) constant. We shall find that under conditions of constant a_1/a_2 , the activity of each solvent component in dilute solution conforms to Raoult's law. Thus there is a close analogy between binary solvent systems at constant a_1/a_2 , and one-component liquid solvents. In particular, the change in solvent-solvent interaction, as solute is added at constant a_1/a_2 , will be of analogous complexity to that which occurs in one-component solvents. Changes in enthalpy, heat capacity, volume, and most other thermodynamic functions measured at constant a_1/a_2 will be easier to interpret because the relative partial molal functions of the solvent components remain rigorously constant. The effect of dissolving the solute is therefore isolated.

The proposal that the analysis of solution data in mixed solvents be done at constant a_1/a_2 is not new. Scatchard¹⁴ and others¹⁵ have shown that a_1/a_2 must remain constant in molecular weight determinations of macromolecules. Grunwald and Butler^{10a} have made such a proposal the basis for their theory of salt-induced medium effects. Mistura and Cohen¹⁶ have demonstrated that for fluids near the critical point, thermodynamic relationships for binary mixtures become analogous to those for pure substances if the difference in the chemical potentials of the components in the binary mixture (and hence a_1/a_2) is held constant.

To distinguish thermodynamic functions measured at constant a_1/a_2 from conventional partial molal functions, we shall use the following notation. We shall let $a_1/a_2 = \alpha$ and refer to conditions of constant α as *endostatic* conditions (*endo* = internally; *static* = staying constant). Partial derivatives measured at constant α will be called *endostatic molal quantities* and be given an α subscript. For example $(\partial H/\partial n_3)_{\alpha, (n_1+n_2), T, P}$ will be represented by $H_{\alpha,3}$. Conventional partial molal quantities will be denoted in the usual way; *e.g.*, $(\partial H/\partial n_3)_{n_1, n_2, T, P} = \bar{H}_3$. Thermodynamic relationships between partial and endostatic molal functions will be derived.

In determinations of the molecular weight of macromolecules, it is both possible and desirable to work under endostatic conditions.¹⁵ On the other hand, when the solutes are not macromolecular, suitable semipermeable membranes rarely exist. It is then convenient to work at constant Z_1 and to transform the results to endostatic conditions by means of thermodynamic relationships. We shall illustrate this procedure with a familiar reaction, the solvolysis of *tert*-butyl chloride in ethanol-water mixtures, for which highly accurate data exist.^{4,9} We believe that in this case the endostatic functions of activation reveal the solvation of the reactant and transition-state molecules more clearly, or at least more simply, than do the original functions measured at constant Z_1 . Unfortunately we cannot make a strong claim, because the transformation to endostatic conditions, with currently available data, entails a large loss of accuracy.

Addition of Solute at Fixed Solvent Composition. In this section we wish to show that when a small quantity of solute is added to a binary solvent at fixed Z_1 , the activities of the solvent components may vary

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(16) L. Mistura and C. Cohen, *Phys. Rev. A*, **4**, 253 (1971).

markedly. We shall assume that the solute is dilute, so that a_3 is proportional to N_3 . Beginning with the Gibbs–Duhem equation (eq 1), we let $N_1 = Z_1(1 - N_3)$, $N_2 = Z_2(1 - N_3)$, and $N_3 d \ln a_3 = dN_3$. Substitution in (1)

$$N_1 d \ln a_1 + N_2 d \ln a_2 = -N_3 d \ln a_3 \quad (1)$$

and integration at constant Z_1 then leads to (2). Be-

$$Z_1 \delta \ln a_1 + Z_2 \delta \ln a_2 = \delta \ln (1 - N_3) \quad (2)$$

cause the solute is dilute, $\delta \ln (1 - N_3) \approx -\delta N_3$, and its magnitude is very small. However, the individual magnitudes of $Z_1 \delta \ln a_1$ and $Z_2 \delta \ln a_2$ need not be very small, since only the algebraic sum is constrained by eq 2. Indeed, when the solvent system is nonideal, it is common for $Z_1 \delta \ln a_1$ and $Z_2 \delta \ln a_2$ to be of opposite sign and for their absolute magnitudes to be many times greater than that of δN_3 .¹⁷ Since $a_1 = Z_1(1 - N_3)f_1$ and $a_2 = Z_2(1 - N_3)f_2$ (where f denotes the mole-fractional activity coefficient), we see that the addition of a solute may be attended by marked changes in f_1 and f_2 . As a result \bar{G}_3 is inherently complex, since its value reflects not only the effect of adding the solute itself, but also the coupled changes in the partial molal free energies of the solvent components. It can readily be shown that other partial molal functions for dilute solutes in mixed solvents are similarly complex.

Addition of Solute under Endostatic Conditions. To show that the activities of both solvent components obey Raoult's law at constant α , we begin with eq 1. Scatchard¹⁴ has shown that the osmotic pressure of dilute solutions, measured at constant α , conforms to the ideal law: $\Pi = c_3 RT$, at least up to solute concentrations of the same order of magnitude as those at which Henry's law may be applied at constant Z_1 . This means that $-N_3 d \ln a_3$ will reduce to $-dN_3$ in dilute solutions also under endostatic conditions. On making this substitution in eq 1 and introducing the constraints that $d \ln a_1 = d \ln a_2$ and $N_1 + N_2 = 1 - N_3$, we obtain eq 3, which is the desired expression of Raoult's law in differential form.

$$d \ln a_1 = d \ln a_2 = -dN_3/(1 - N_3) \quad (3)$$

In order to keep α constant as solute is added, the solvent composition must vary. If the solute concentration is expressed by the mole fraction N_3 , it is mathematically convenient to let the solvent composition vary in such a manner that the solvent mole number $n_1 + n_2$ remains constant.¹⁸ The process for defining endostatic molal functions is then shown in Figure 2. It consists of the simultaneous transfer to the solution in the mixed solvent of dn_3 moles of pure solute, dn_1 moles of component 1, and $dn_2 = -dn_1$ moles of component 2, such that $d \ln \alpha/dN_3 = 0$. The solvent components are transferred under conditions of constant N_3 .

Let Y denote any extensive thermodynamic function. Let Y_A , Y_B , Y_C , and Y_{soln} denote the values of that function for the respective phases shown in Figure 2, and let dY_A , dY_B , dY_C , and dY_{soln} denote the changes in that function as dn_3 , dn_1 , and dn_2 moles of the respective component are transferred. The endostatic molal

(17) A familiar example in which the changes in a_1 and a_2 are large and of opposite sign is the salting-out effect: when an inorganic salt is added to a water–organic mixture, the activity of the organic component often increases dramatically.

(18) If the solute concentration is expressed by the molality m_3 , it is convenient to keep $n_1 M_1 + n_2 M_2$, the mass of solvent, constant.

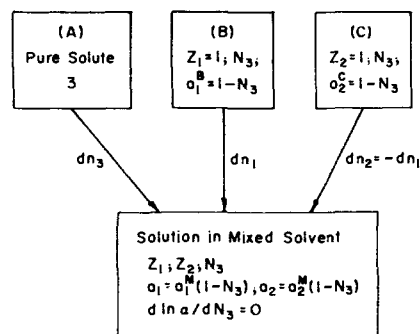


Figure 2. Endostatic addition of solute to a solution in a mixed solvent. The solvent components are transferred simultaneously with the solute so that both α and $n_1 + n_2$ remain constant.

function $Y_{\alpha,3}$ for the solute in the mixed solvent is then defined by eq 4, where Y_3^0 is the value per mole of pure solute.

$$Y_{\alpha,3} - Y_3^0 = \left(\frac{\partial(Y_{\text{soln}} - Y_A - Y_B - Y_C)}{\partial n_3} \right)_{\alpha, n_1 + n_2} \quad (4)$$

Relationship of Endostatic to Partial Molal Functions. We begin with some definitions.

The *standard state of unit activity* for each solvent component is the pure liquid component. Thermodynamic functions per mole of the component in the standard state are indicated by a superscript 0, e.g., H_1^0 or V_2^0 .

The *reference state of unit activity coefficient* for each solute will be the infinitely dilute state ($N_{\text{solute}} = 0$) in the given binary solvent medium whose composition is specified by Z_1 . Thermodynamic functions for the solvent components in any such reference state are indicated by a superscript M, e.g., a_1^M , α^M or \bar{H}_2^M . Functions such as these vary with Z_1 .

Relative partial molal functions for the solvent components are indicated by a superscript ρ , e.g.; $\bar{V}_1^\rho = \bar{V}_1^M - V_1^0$, $\bar{G}_2^\rho = \bar{G}_2^M - G_2^0$, or $\bar{H}_1^\rho = \bar{H}_1^M - H_1^0$. \bar{H}_1^ρ is identical with Lewis and Randall's relative molal heat content \bar{L}_1 .¹⁹ \bar{V}_1^ρ , \bar{H}_1^ρ , and their derivatives with respect to T or P are sometimes called partial molal *excess* functions.²⁰ On the other hand, $\bar{G}_1^\rho = RT \ln a_1^M$, while the partial molal excess free energy $\bar{G}_1^E = RT \ln f_1^M$.

The partial molal free energy of the solute will be represented by eq 5, where \bar{G}_3^0 is a function of solvent

$$\bar{G}_3 = \bar{G}_3^0 + RT \ln N_3 \quad (5)$$

composition. To indicate the effect of changing the solvent, it is convenient to introduce the operator δ_M . Thus $\delta_M \bar{G}_3^0$ denotes the difference between \bar{G}_3^0 in the given solvent and in a reference solvent (which is usually chosen to be pure water).²¹

In order to derive a general relationship between endostatic and partial molal functions, we shall consider any extensive thermodynamic function Y . Referring to eq 4, the required differentials are then given

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(20) G. L. Bertrand, F. J. Millero, C. H. Wee, and L. G. Hepler, *J. Phys. Chem.*, **70**, 699 (1966).

(21) Some authors prefer to use medium activity coefficients f_3^M rather than a variable \bar{G}_3^0 . The two quantities are related by $\delta_M \bar{G}_3^0 = RT \delta_M \ln f_3^M$.

by eq 6, in which \bar{Y}_1 , \bar{Y}_1^B , and \bar{Y}_2^C denote the partial

$$\begin{aligned} dY_{\text{soln}} &= \bar{Y}_1 dn_1 + \bar{Y}_2 dn_2 + \bar{Y}_3 dn_3 \\ dY_A &= Y_3^0 dn_3 \\ dY_B &= \bar{Y}_1^B dn_1 \\ dY_C &= \bar{Y}_2^C dn_2 \end{aligned} \quad (6)$$

molal function of the indicated component in the solution in the mixed solvent or in liquid B or C, respectively (Figure 2). On substituting in eq 4, recalling that $dn_2 = -dn_1$, and rearranging, we obtain eq 7.

$$Y_{\alpha,3} = \bar{Y}_3 + [(\bar{Y}_1 - \bar{Y}_1^B) - (\bar{Y}_2 - \bar{Y}_2^C)] \left(\frac{\partial n_1}{\partial n_3} \right)_{\alpha, n_1+n_2} \quad (7)$$

To evaluate $\partial n_1 / \partial n_3$, we introduce mole fractions $Z_1 = n_1 / (n_1 + n_2)$ and $N_3 = n_3 / (n_1 + n_2 + n_3)$ in place of mole numbers. The result is (8). The evaluation of

$$\left(\frac{\partial n_1}{\partial n_3} \right)_{\alpha, n_1+n_2} = (1 - N_3)^2 \left(\frac{\partial Z_1}{\partial N_3} \right)_{\alpha} \quad (8)$$

$(\partial Z_1 / \partial N_3)_{\alpha}$ in actual problems will be discussed in the next section.

We now wish to show that $\bar{Y}_1 - \bar{Y}_1^B = \bar{Y}_1^{\rho}$, and that $\bar{Y}_2 - \bar{Y}_2^C = \bar{Y}_2^{\rho}$. The proof is straightforward for the case of the free energy (eq 9; see also Figure 2). Ac-

$$\bar{G}_1 - \bar{G}_1^B = RT \ln a_1^M = \bar{G}_1^{\rho} \quad (9a)$$

$$\bar{G}_2 = \bar{G}_2^C = RT \ln a_2^M = \bar{G}_2^{\rho} \quad (9b)$$

cording to eq 9, $\bar{G}_1 - \bar{G}_1^B$ and $\bar{G}_2 - \bar{G}_2^C$ are independent of the solute mole fraction N_3 . Partial differentiation of eq 9a with respect to P then leads to $\bar{V}_1 - \bar{V}_1^B = \bar{V}_1^{\rho}$; partial differentiation with respect to T leads to $\bar{S}_1 - \bar{S}_1^B = \bar{S}_1^{\rho}$ and $\bar{H}_1 - \bar{H}_1^B = \bar{H}_1^{\rho}$, and so on for further partial differentiation. Analogous results are obtained for the other solvent component by partial differentiation of eq 9b. Thus, when the solute is introduced endostatically, the quantities $\bar{Y}_1 - \bar{Y}_1^B$ and $\bar{Y}_2 - \bar{Y}_2^C$ are rigorously independent of the solute concentration N_3 and simply equal to the relative partial molal function for the given solvent component. On combining eq 7-9 we obtain the desired relationship (eq 10).

$$Y_{\alpha,3} = \bar{Y}_3 + (\bar{Y}_1^{\rho} - \bar{Y}_2^{\rho})(1 - N_3)^2 (\partial Z_1 / \partial N_3)_{\alpha} \quad (10)$$

Evaluation of $(\partial Z_1 / \partial N_3)_{\alpha}$. In practical applications of eq 10, $\partial Z_1 / \partial N_3$ is often the accuracy-limiting factor. It is convenient to introduce $\ln \alpha$ in place of α and to apply the transformation formula (eq 11). Since N_3

$$\left(\frac{\partial Z_1}{\partial N_3} \right)_{\alpha} = \left(\frac{\partial Z_1}{\partial N_3} \right)_{\ln \alpha} = - \frac{(\partial \ln \alpha / \partial N_3)_{Z_1}}{(\partial \ln \alpha / \partial Z_1)_{N_3}} \quad (11)$$

is assumed to be small, we may without appreciable error equate $(\partial \ln \alpha / \partial Z_1)_{N_3}$ to $d \ln \alpha^M / dZ_1$. To evaluate $(\partial \ln \alpha / \partial N_3)_{Z_1}$, we introduce the thermodynamic equation (eq 12) whose derivation (by methods de-

$$RT \left(\frac{\partial \ln \alpha}{\partial N_3} \right)_{Z_1} = \frac{1}{(1 - N_3)^2} \frac{d\bar{G}_3^0}{dZ_1} \quad (12)$$

scribed earlier²²) is outlined in eq 13-15. The derivation makes use of the identity $\partial \bar{G}_3 / \partial n_1 = \partial \bar{G}_1 / \partial n_3$. The

independent variables are Z_1 and N_3 . T and P are constant. On equating (13) and (14), writing a similar

$$\left(\frac{\partial \bar{G}_1}{\partial n_3} \right)_{n_1, n_2} = \left(\frac{\partial \bar{G}_1}{\partial N_3} \right)_{Z_1, n_1 + n_2 + n_3} \quad (13)$$

$$\left(\frac{\partial \bar{G}_3}{\partial n_1} \right)_{n_2, n_3} = \left(\frac{\partial \bar{G}_3}{\partial Z_1} \right)_{N_3, n_1 + n_2} - \left(\frac{\partial \bar{G}_3}{\partial N_3} \right)_{Z_1, n_1 + n_2 + n_3} \quad (14)$$

expression for $\partial \bar{G}_2 / \partial n_3 = \partial \bar{G}_3 / \partial n_2$, and subtracting, we obtain eq 15. Finally, on recalling that $\bar{G}_1 - \bar{G}_2 =$

$$\left(\frac{\partial (\bar{G}_1 - \bar{G}_2)}{\partial N_3} \right)_{Z_1} = \frac{1}{(1 - N_3)^2} \left(\frac{\partial \bar{G}_3}{\partial Z_1} \right)_{N_3} \quad (15)$$

$G_1^0 - G_2^0 + RT \ln \alpha$, and applying eq 5, we obtain the desired result (eq 12).

Standard Endostatic Functions. Equilibrium and Rate Constants. Scatchard has shown that when a_3 is proportional to N_3 at constant Z_1 , a_3 is also proportional to N_3 at constant α .¹⁴ Beginning with eq 5, we may therefore write a similar expression (eq 16) for

$$G_{\alpha,3} = G_{\alpha,3}^0 + RT \ln N_3 \quad (16)$$

$G_{\alpha,3}$. On combining eq 5, 10-12, and 16, we obtain eq 17 for the relationship between the standard partial and

$$G_{\alpha,3}^0 = \bar{G}_3^0 - [(\ln \alpha^M)(d\bar{G}_3^0/dZ_1)/(d \ln \alpha^M/dZ_1)] \quad (17)$$

standard endostatic molal free energy. Analogous relationships for other thermodynamic functions ($H_{\alpha,3}^0$, $V_{\alpha,3}^0$, $Y_{\alpha,3}^0$) are listed in Table I.

Table I. Summary of Transformation Formulas

$G_{\alpha,3}^0 = \bar{G}_3^0 - \left[(\ln \alpha^M) \left(\frac{d\bar{G}_3^0}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$H_{\alpha,3}^0 = \bar{H}_3^0 - \left[(\bar{H}_1^{\rho} - \bar{H}_2^{\rho}) \left(\frac{d\bar{G}_3^0}{dZ_1} \right) / \left(RT \frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$V_{\alpha,3}^0 = \bar{V}_3^0 - \left[(\bar{V}_1^{\rho} - \bar{V}_2^{\rho}) \left(\frac{d\bar{G}_3^0}{dZ_1} \right) / \left(RT \frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\ln K_{\alpha} = \ln K - \left[(\ln \alpha^M) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\Delta G_{\alpha}^0 = \Delta \bar{G}^0 + \left[(RT \ln \alpha^M) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\Delta H_{\alpha}^0 = \Delta \bar{H}^0 + \left[(\bar{H}_1^{\rho} - \bar{H}_2^{\rho}) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\Delta V_{\alpha}^0 = \Delta \bar{V}^0 + \left[(\bar{V}_1^{\rho} - \bar{V}_2^{\rho}) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\Delta C_{p,\alpha}^0 = \Delta \bar{C}_p^0 + \left[(\bar{C}_{p,1}^{\rho} - \bar{C}_{p,2}^{\rho}) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
General Case	
$Y_{\alpha,3}^0 = \bar{Y}_3^0 - \left[(\bar{Y}_1^{\rho} - \bar{Y}_2^{\rho}) \left(\frac{d\bar{G}_3^0}{dZ_1} \right) / \left(RT \frac{d \ln \alpha^M}{dZ_1} \right) \right]$	
$\Delta Y_{\alpha}^0 = \Delta \bar{Y}^0 + \left[(\bar{Y}_1^{\rho} - \bar{Y}_2^{\rho}) \left(\frac{d \ln K}{dZ_1} \right) / \left(\frac{d \ln \alpha^M}{dZ_1} \right) \right]$	

On writing equations of the form 17 for the reactants and products in a chemical reaction and taking the difference, we obtain eq 18. Thus it is possible to

$$\Delta G_{\alpha}^0 = \Delta \bar{G}^0 - [(\ln \alpha^M)(d\Delta \bar{G}^0/dZ_1)/(d \ln \alpha^M/dZ_1)] \quad (18)$$

(22) E. Grunwald and A. L. Bacarella, *J. Amer. Chem. Soc.*, **80**, 3840 (1958).

define an endostatic equilibrium constant K_α according to eq 19, which is analogous to the familiar relation 20

$$\Delta G_\alpha^0 = -RT \ln K_\alpha \quad (19)$$

$$\Delta \bar{G}^0 = -RT \ln K \quad (20)$$

between standard free energy change and equilibrium constant K at constant Z_1 . The transformation equation from K to K_α is then given in (21). Analogous relationships for other thermodynamic functions are listed in Table I.

$$[\ln \alpha^M] (d \ln K / dZ_1) / (d \ln \alpha^M / dZ_1) \quad (21)$$

For reaction rates, similar relationships between endostatic rate constants and activation parameters, and the corresponding quantities measured at constant Z_1 , are readily derived. The results are of the same form as the relationships for chemical reactions which are listed in Table I. Simply write k instead of K and Δ quantities of activation instead of Δ quantities of reaction.

We shall mention in passing that the difference between $Y_{\alpha,3}$ and \bar{Y}_3^0 , and between $\Delta Y_{\alpha,3}^0$ and $\Delta \bar{Y}^0$, always approaches zero as either Z_1 or Z_2 approaches unity.

Interaction of Solutes. The addition of a second solute (subscript 4) to a dilute solution of solute 3 in a mixed solvent in general brings about a change in the activity ratio α of the solvent components. If the nature of the mixed solvent is determined by the value of α , then the addition of the second solute is tantamount to a change in solvent. We expect therefore that \bar{G}_3 will vary with N_4 , even though any direct solute-solute interaction at short range may be quite unimportant.

In order to obtain a relationship between the effects of a second solute at constant Z_1 and at constant α , we shall assume that N_3 is small enough so that, in the absence of the second solute, \bar{G}_3 and $G_{\alpha,3}$ are related to N_3 and to each other according to eq 5, 16, and 17. To simplify the mathematics, we shall assume further that $N_3 = n_3/(n_1 + n_2)$ and $N_4 = n_4/(n_1 + n_2)$, so that our relationship will be strictly valid only in the limit as both N_3 and N_4 approach zero. With these assumptions, the desired relationship takes the form of eq 22,

$$\left(\frac{\partial G_{\alpha,3}}{\partial N_4} \right)_{\alpha, N_3} = \left(\frac{\partial \bar{G}_3}{\partial N_4} \right)_{\alpha, N_3} \quad (22)$$

with both derivatives (at constant T and P) being independent of N_3 .

\bar{G}_3 is normally expressed as a function of Z_1 and N_4 . On changing the independent variables to α and N_4 we obtain (23) which, in view of the stated assumptions and the derivation given in (11)–(15), reduces to (24).

$$\left(\frac{\partial G_{\alpha,3}}{\partial N_4} \right)_{\alpha, N_3} = \left(\frac{\partial \bar{G}_3}{\partial N_4} \right)_{Z_1, N_3} + \left(\frac{\partial \bar{G}_3}{\partial Z_1} \right)_{N_4, N_3} \left(\frac{\partial Z_1}{\partial N_4} \right)_{\alpha, N_3} \quad (23)$$

$$\left(\frac{\partial G_{\alpha,3}}{\partial N_4} \right)_{\alpha, N_3} = \left(\frac{\partial \bar{G}_3}{\partial N_4} \right)_{Z_1, N_3} - \left[\left(\frac{d\bar{G}_3^0}{dZ_1} \right) \left(\frac{d\bar{G}_4^0}{dZ_1} \right) / \left(RT \frac{d \ln \alpha^M}{dZ_1} \right) \right] \quad (24)$$

In order to apply eq 24, the derivatives $d\bar{G}_3^0/dZ_1$ and $d\bar{G}_4^0/dZ_1$ for the given solutes must be available. For nonvolatile solutes, derivatives such as these can be obtained from vapor pressure measurements for the solvent components.²²

A Useful Working Hypothesis. Salt-Induced Medium Effects. In considerations of solute-solute interaction in mixed solvents, the following has been found to be a useful working hypothesis:^{10,11} *the interaction of solutes in a mixed solvent will resemble that in one-component solvents of comparable dielectric constant and chemical type if the interaction in the mixed solvent is studied at constant α .*

An obvious corollary of this hypothesis is that the interaction of solutes in a mixed solvent at constant Z_1 may not resemble that in comparable one-component solvents and may, in view of eq 24, be qualitatively different.

Case I. If solute 3 is a nonelectrolyte and if N_3 is small, we may write eq 25, where g_{34} and $g_{\alpha,34}$ are

$$\bar{G}_3 = \bar{G}_3^0 + RT \ln N_3 + RT g_{34} N_4 \quad (25a)$$

$$G_{\alpha,3} = G_{\alpha,3}^0 + RT \ln N_3 + RT g_{\alpha,34} N_4 \quad (25b)$$

phenomenological "interaction coefficients." Substitution in eq 24 then leads to (26).

$$g_{3,4} = \left(\frac{d\bar{G}_3^0}{dZ_1} \right) \left(\frac{d\bar{G}_4^0}{dZ_1} \right) / \left[(RT)^2 \frac{d \ln \alpha^M}{dZ_1} \right] + g_{\alpha,34} \quad (26)$$

Suppose that for a pair of solutes in comparable one-component solvents, the interaction coefficient $g_{34} \approx 0$. Applying our working hypothesis, we shall therefore assume that $g_{\alpha,34} \approx 0$. However, it then follows from (26) that g_{34} in the mixed solvent is probably *not* equal to zero. Indeed, g_{34} may be substantial in magnitude and will evidently be specific, even though the direct (short-range) interaction of the solutes is relatively unimportant.

Case II. Salt-Induced Medium Effects. Suppose that in a suitable one-component model solvent, neutral-salt effects on the rate or equilibrium constant for a given reaction are simply a colligative function of the ionic strength. We shall assume, therefore, that in the mixed solvent, neutral-salt effects on k_α or K_α are similarly colligative. Neutral-salt effects on k or K , measured at constant Z_1 , will *not* be colligative: on applying eq 19, 20, and 24, we find that the effects on K_α and K are related according to (27), in which N_4 denotes the mole fraction of neutral salt. (Equation 27

$$\frac{d \ln K_\alpha}{dN_4} = \frac{d \ln K}{dN_4} - \left[\left(\frac{d\bar{G}_4^0}{dZ_1} \right) \left(\frac{d \ln K}{dZ_1} \right) / \left(RT \frac{d \ln \alpha^M}{dZ_1} \right) \right] \quad (27)$$

applies also to reaction rates; simply write k instead of K .)

It has been found, for dioxane-water mixtures, that the last term on the right in (27) is of substantial magnitude and highly specific with the salt, since $d\bar{G}_4^0/dZ_1$ is highly specific.^{10b, 13a} This qualitative statement will be true even if neutral-salt effects on K_α or k_α are entirely negligible, in which case the salt effects on $\ln K$ or $\ln k$ will be strictly proportional to $d\bar{G}_4^0/dZ_1$. Since, in the latter case, the salt acts solely by changing α and thus changing the effective solvent medium, neutral-

salt effects of this type have been called salt-induced medium effects.^{10b}

Because the transformation of neutral-salt effects from constant Z_1 to constant α is often large and subject to experimental error, it is rarely advisable to use mixed solvents in order to settle fine points of solute-solute interaction or reaction mechanism. For example, Salomaa and coworkers¹¹ have shown how difficult it is to distinguish between general acid catalysis and specific hydrogen ion catalysis in mixed solvents. It is also possible that some of Sneen's kinetic evidence in favor of ion-pair intermediates in organic reactions,²³ which was obtained mostly in acetone-water mixtures, is distorted by salt-induced medium effects.

Data for Water-Organic Systems. In order to facilitate the transformation from conditions of constant Z_1 to endostatic conditions, we list certain required solvent properties for some common water-organic solvent systems in Tables II-V.

Because all transformations involve $d \ln \alpha^M/dZ_1$, it is unfortunate that this is the least accurate of the solvent

Table II. Smoothed Data for the System Methanol Water, 25°

Z_1	$\ln (f_1/f_2)$	$\frac{\partial \ln (f_1/f_2)}{\partial Z_1}$	$\bar{H}_1^p - \bar{H}_2^p$, cal/mol	$\bar{V}_1^p - \bar{V}_2^p$, ml/mol	$\bar{C}_{p,1}^p - \bar{C}_{p,2}^p$, cal mol ⁻¹ deg ⁻¹
1.00	-0.416	0.47	1756	3.15	-21.0 ^a
0.97	-0.426	0.25	1479	3.14	-14.0
0.94	-0.431	0.05	1229	3.23	-9.6
0.91	-0.429	-0.20	1001	3.32	-7.4
0.88	-0.417	-0.54	796	3.29	-6.0
0.85	-0.398	-0.79	602	3.19	-5.0
0.80	-0.347	-1.17	336	2.65	-2.8
0.70	-0.211	-1.34	18	1.74	-0.9
0.60	-0.079	-1.33	-97	0.83	+0.9
0.50	+0.048	-1.19	-164	-0.15	2.1
0.40	0.157	-0.98	-220	-0.92	2.3
0.30	0.243	-0.74	-290	-1.62	2.7
0.20	0.305	-0.50	-400	-2.29	3.0
0.10	0.343	-0.26	-544	-3.21	2.1
0.05	0.353	-0.13	-630	-3.58	1.7
0.00	0.356	0.00	-719	-3.95	1.4

^a The data in this column are at 27°.

Table III. Smoothed Data for the System Ethanol-Water, 25°

Z_1	$\ln (f_1/f_2)$	$d \ln (f_1/f_2)/dZ_1$	$\bar{H}_1^p - \bar{H}_2^p$, cal/mol	$\bar{V}_1^p - \bar{V}_2^p$, ml/mol	$\bar{C}_{p,1}^p - \bar{C}_{p,2}^p$, cal mol ⁻¹ deg ⁻¹
1.00	-1.324	-1.66	2400	3.87	-39.2
0.97	-1.263	-2.35	2042	4.93	-33.0
0.94	-1.185	-2.80	1536	5.93	-26.6
0.91	-1.097	-3.08	918	5.30	-18.6
0.88	-1.002	-3.24	421	4.54	-11.7
0.85	-0.903	-3.32	96	3.64	-5.7
0.80	-0.736	-3.33	-140	2.39	-2.3
0.70	-0.412	-3.12	-302	0.98	+2.0
0.60	-0.117	-2.78	-282	-0.30	2.8
0.50	+0.143	-2.41	-236	-0.50	4.0
0.40	0.365	-2.03	-174	-1.05	4.4
0.30	0.549	-1.64	-123	-1.67	4.1
0.20	0.694	-1.26	-100	-2.42	5.6
0.10	0.800	-0.87	-167	-3.27	7.0
0.05	0.839	-0.68	-250	-3.72	7.7
0.00	0.868	-0.48	-459	-4.17	8.4

(23) R. A. Sneen, *Accounts Chem. Res.*, 6, 46 (1973).

Table IV. Smoothed Data for the System Dioxane-Water, 25°

Z_1	$\ln (f_1/f_2)$	$d \ln (f_1/f_2)/dZ_1$	$\bar{H}_1^p - \bar{H}_2^p$, cal/mol	$\bar{V}_1^p - \bar{V}_2^p$, ml/mol
1.00	-1.705	-3.26	(1600) ^a	5.91
0.97	-1.607	-3.24	1430	4.81
0.94	-1.511	-3.21	1116	3.86
0.91	-1.414	-3.20	660	3.07
0.88	-1.319	-3.19	206	2.44
0.85	-1.223	-3.18	-170	1.97
0.80	-1.064	-3.18	-390	1.50
0.70	-0.744	-3.22	-500	0.60
0.60	-0.418	-3.32	-500	-0.97
0.50	-0.078	-3.48	-500	-1.56
0.40	+0.281	-3.70	-475	-1.47
0.30	0.664	-3.97	-195	-1.15
0.20	1.077	-4.30	+50	-0.81
0.10	1.526	-4.69	450	-0.59
0.05	1.766	-4.91	436	-0.56
0.00	2.017	-5.14	(400) ^a	-0.57

^a Extrapolated.

Table V. Smoothed Data for the System Dimethyl Sulfoxide-Water, 25°

Z_1	$\ln (f_1/f_2)$	$d \ln (f_1/f_2)/dZ_1$	$\bar{H}_1^p - \bar{H}_2^p$, cal/mol	$\bar{V}_1^p - \bar{V}_2^p$, ml/mol
1.00	3.176	12.22	4328	4.3
0.97	2.821	11.48	4019	3.1
0.94	2.487	10.78	3688	3.0
0.91	2.174	10.10	3335	3.7
0.88	1.881	9.44	2965	3.9
0.85	1.607	8.81	2564	3.0
0.80	1.191	7.83	1854	2.9
0.70	0.499	6.07	656	1.5
0.60	-0.032	4.60	-333	0.1
0.50	-0.430	3.42	-893	-0.9
0.40	-0.725	2.53	-1193	-1.5
0.30	-0.946	1.94	-1286	-1.9
0.20	-1.122	1.63	-1322	-2.1
0.10	-1.283	1.62	-1322	-2.2
0.05	-1.366	1.72	-1300	-2.2
0.00	-1.456	1.90	-1284	-2.3

properties listed in the tables. The Redlich-Kister method²⁴ for smoothing and testing the thermodynamic consistency of vapor pressure data yields an analytical function for the excess molar free energy, $G^E = RT \cdot (Z_1 \ln f_1 + Z_2 \ln f_2)$. Differentiation of this function with respect to Z_1 then yields $\ln (f_1/f_2)$ and hence $\ln \alpha^M$ with fair accuracy. A second differentiation yields $d \ln (f_1/f_2)/dZ_1$ with much reduced accuracy, and thence $d \ln \alpha^M/dZ_1$ via eq 28. (It would be useful if a more

$$\frac{d \ln \alpha^M}{dZ_1} = \frac{d \ln (f_1/f_2)}{dZ_1} + \frac{1}{Z_1 Z_2} \quad (28)$$

direct differential method of measuring $d \ln \alpha^M/dZ_1$ for mixed solvents could be devised.)

When $d \ln (f_1/f_2)/dZ_1$ is negative, a further test of thermodynamic consistency is that $d \ln \alpha^M/dZ_1$ must be positive. This rather stringent test was not met by available data for the system *tert*-butyl alcohol-water.²⁵ However, even when this test is fully met, the accuracy of $d \ln \alpha^M/dZ_1$ is likely to be poor when $d \ln \alpha^M/dZ_1$ is much smaller than $1/Z_1 Z_2$.

The data for the system methanol-water in Table II are based on the following sources: $\ln (f_1/f_2)$ and its

(24) O. Redlich and A. T. Kister, *Ind. Eng. Chem.*, 40, 345 (1948).

(25) J. Kenttämää, E. Tommila, and M. Martii, *Ann. Acad. Sci. Fenn., Ser. A2*, 93, 1 (1958).

derivative with respect to Z_1 , from the compilation of Katayama;²⁶ enthalpy data, from Bertrand, *et al.*;²⁰ relative molar volumes, from densities reported by Carr and Riddick;²⁷ heat capacities, from concordant specific heats reported in the International Critical Tables (ICT) and by Ivin and Sukhatme.²⁸

The data for the system ethanol–water in Table III are based on the following sources: $\ln(f_1/f_2)$ and its derivative with respect to Z_1 , from Hansen and Miller;²⁹ enthalpy data from Bertrand, *et al.*;²⁰ densities and heat capacities from the ICT. For both methanol–water and ethanol–water, \bar{H}_2^p and $\bar{C}_{p,2}^p$ have been measured directly at $Z_1 = 1.00$ by Arnett, *et al.*³⁰ Values obtained in that work are in satisfactory agreement with values listed in Tables II and III.

The data for the system dioxane–water in Table IV are based on the following sources: $\ln f_1/f_2$, its derivative with respect to Z_1 , and enthalpy data, from Goates and Sullivan;³¹ partial molar volumes, from Hovorka, *et al.*³²

The data for the system dimethyl sulfoxide–water in Table V are based on the following sources: $\ln(f_1/f_2)$, its derivative with respect to Z_1 , and molar volumes, from Kenttämää and Lindberg;³³ enthalpy data from Rallo, *et al.*³⁴

Thermodynamic calculations¹⁹ and interpolations, when required, were made by standard methods.

Solvolysis of *tert*-Butyl Chloride. To illustrate the transformation of solvent effects to endostatic conditions, we shall examine kinetic data for the solvolysis of *tert*-butyl chloride in ethanol–water mixtures. The transformation of neutral-salt effects to endostatic conditions has already been described.^{10,11}

The solvolysis of *tert*-butyl chloride in water–ethanol mixtures provides a classic example of nonideal mixed-solvent effects. Accurate rate constants and activation enthalpies were reported by Winstein and Fainberg (WF)^{4b} in 1957 and have served as the basis for many subsequent discussions. However, WF did not measure ΔH^\ddagger at a uniform temperature. Some of their values (for $Z_1 > 0.76$) refer to 12.5°, others ($0.76 > Z_1 > 0.26$ and $Z_1 = 0$) refer to 37.5°, while still others ($Z_1 = 0.146$ and $Z_1 = 0.062$) refer to 62.5°. In 1969, Robertson and Sugamori (RS)⁹ reported new data for the water-rich range ($Z_1 > 0.7$), with the aim of evaluating not only ΔH^\ddagger but also ΔC_p^\ddagger . They found that ΔH^\ddagger is quite temperature dependent: ΔC_p^\ddagger is consistently negative and reaches an extreme value of -136 cal/mole deg at $Z_1 = 0.925$. It is clear that ΔH^\ddagger should be examined at a uniform temperature.

The data to be analyzed are listed in Table VI. The upper part of the table lists the data of RS at a uniform temperature of 25°. The lower part lists complementary data by WF: $\ln k$ is at 25° and ΔH^\ddagger is measured at, or corrected to, 37.5°. (Required values of

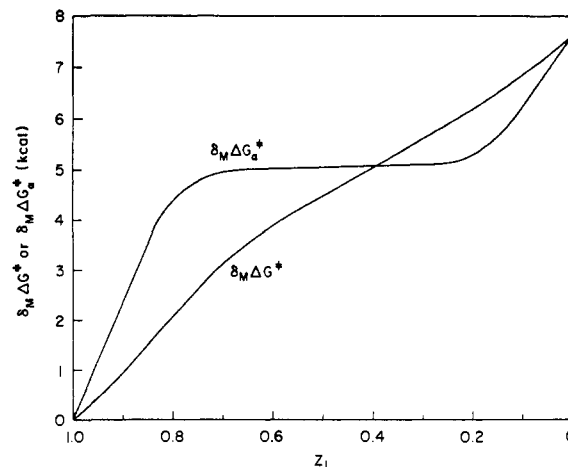


Figure 3. $\delta_M \Delta G^\ddagger$ and $\delta_M \Delta G_\alpha^\ddagger$ for solvolysis of *tert*-butyl chloride in ethanol–water mixtures at 25°.

Table VI. Solvolysis of *tert*-Butyl Chloride in Ethanol–Water Mixtures at 25°^a

Z_1	$d \ln k / dZ_1$	$-\ln k$	$-\ln k_\alpha$	ΔH^\ddagger ^b	ΔH_α^\ddagger ^b	ΔC_p^\ddagger ^c	$\Delta C_{p,\alpha}^\ddagger$ ^c
1.000	14.4	3.514	3.514	22.58	22.58	-83	-83
0.925 ^d	15.1	4.618	6.43 ^e	20.01	21.61	-136	-166
0.899 ^d	17.3	5.023	7.50	19.47	21.05	-116	-151
0.846 ^d	19.9	6.145	9.87	19.36	19.65	-49	-72
0.750 ^d	14.9	7.824	11.61	21.04	19.07	-34	-32
0.765	15.2	7.796	11.52	20.76	19.17		
0.684	12.0	9.002	12.16	21.67	19.47		
0.582	10.0	10.218	12.11	21.90	20.24		
0.448	10.0	11.590	11.89	22.34	21.50		
0.265	10.0	13.309	12.16	22.75	22.62		
0.146	10.6	14.552	13.02	24.08	24.01		
0.062	11.6	15.461	14.13	24.96	24.87		
0.000	13	16.269	16.27	26.13	26.13		

^a Data in upper half of table due to RS;⁹ data in lower half of table due to WF.^{4b} ^b kcal/mol; data in lower half of table refer to 37.5°. ^c cal mol⁻¹ deg⁻¹. ^d Computed from the density of the mixed solvent. ^e Sample calculation: $\ln k_\alpha = \ln k - [\ln \alpha^M \cdot (d \ln k / dZ_1) / (d \ln \alpha^M / dZ_1)]$. $\ln \alpha^M = 1.372$; $d \ln k / dZ_1 = 15.14$ (by numerical differentiation of data in column 3); $d \ln \alpha^M / dZ_1 = 11.48$ [eq 28]. Value of $d \ln(f_1/f_2) / dZ_1$ by interpolation of data in Table III.

ΔC_p^\ddagger are taken from, or extrapolated from, the work of RS.) The transformations to endostatic conditions ($\ln k_\alpha$ and ΔH_α^\ddagger) were made using formulas listed in Table I. Required data for the ethanol–water system were obtained by interpolation from Table III. A sample calculation is given in a footnote to Table VI. The free-energy functions $\delta_M \Delta G^\ddagger$ and $\delta_M \Delta G_\alpha^\ddagger$ are based on water as the reference solvent (definitions are given in eq 29) and are shown graphically in Figure 3.

$$\delta_M \Delta G^\ddagger = -RT \ln(k^M/k^W) \quad (29a)$$

$$\delta_M \Delta G_\alpha^\ddagger = -RT \ln(k_\alpha^M/k_\alpha^W) \quad (29b)$$

ΔH^\ddagger and ΔH_α^\ddagger are compared in Figure 4.

The solvolysis of *tert*-butyl chloride in ethanol–water mixtures is usually thought to proceed by an S_N1 or ionization mechanism^{35,36} with a transition state, $(\text{CH}_3)_3\text{C}^\delta+ \cdots \text{X}^\delta-$, resembling a tight ion pair. Hughes, Ingold, and coworkers³⁵ explain the striking

(35) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

(36) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 70, 846 (1948).

- (26) T. Katayama, *Kagaku Kogaku*, 26, 490 (1962).
 (27) C. Carr and J. A. Riddick, *Ind. Eng. Chem.*, 43, 692 (1951).
 (28) A. A. Ivin and S. P. Sukhatme, *Indian J. Technol.*, 5, 249 (1967).
 (29) S. Hansen and F. A. Miller, *J. Phys. Chem.*, 58, 193 (1954).
 (30) E. M. Arnett, W. B. Kover, and J. V. Carter, *J. Amer. Chem. Soc.*, 91, 4028 (1969).
 (31) J. R. Goates and R. J. Sullivan, *J. Phys. Chem.*, 62, 188 (1958).
 (32) F. Hovorka, R. A. Schaefer, and D. Dreisbach, *J. Amer. Chem. Soc.*, 58, 2264 (1936).
 (33) (a) J. Kenttämää and J. J. Lindberg, *Suom. Kemistilehti B*, 33, 98 (1960); (b) *ibid.*, 33, 32 (1960).
 (34) F. Rallo, F. Rodante, and P. Silvestroni, *Thermochim. Acta*, 1, 311 (1970).

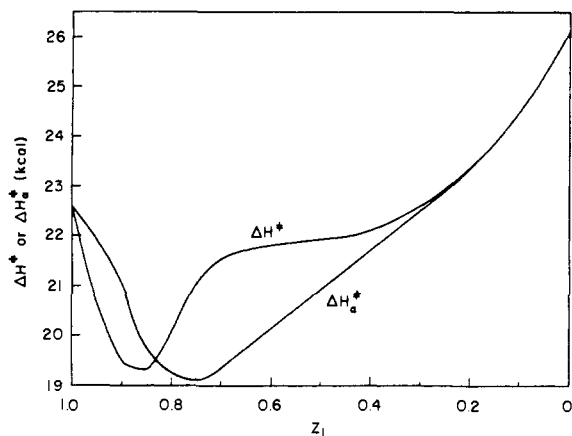


Figure 4. ΔH^\ddagger and ΔH_α^\ddagger for solvolysis of *tert*-butyl chloride in ethanol-water mixtures at 25° ($Z_1 > 0.75$) and 37.5° ($Z_1 < 0.75$).

increase of $\ln k$ with Z_1 by an essentially electrostatic theory in which the charge separation in the transition state is promoted by the change to a more polar solvent medium. However, analysis of Henry's law constants³⁶ and heats of solution³⁷ of *tert*-butyl chloride showed that this is only a partial explanation. In water-rich mixtures ($Z_1 > 0.7$) the characteristic medium effects on ΔG^\ddagger and ΔH^\ddagger are due largely to medium effects in the $(\text{CH}_3)_3\text{CCl}$ ground state, rather than in the transition state.^{36, 37a} On the other hand, in alcohol-rich mixtures ($Z_1 < 0.2$), the characteristic medium effects on ΔG^\ddagger and ΔH^\ddagger are due largely to medium effects in the transition state,^{36, 37c} and it has even been suggested that there is a change in reaction mechanism.^{37c}

Our thesis in this paper is that quantities measured at

(37) (a) E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Amer. Chem. Soc.*, **85**, 1350 (1963); (b) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *ibid.*, **87**, 1541 (1965); (c) E. M. Arnett, W. G. Bentrude, and P. M. Duggleby, *ibid.*, **87**, 2048 (1965).

constant Z_1 , such as $\delta_M \Delta G^\ddagger$ and ΔH^\ddagger , are inherently complex because they include changes in the relative partial molal functions of the solvent components, and that their variation with Z_1 gives accordingly a distorted picture of the underlying solvent effects. The distortion is removed by transforming the functions to endostatic conditions.

Returning to the solvolysis of *tert*-butyl chloride, the plot of $\delta_M \Delta G^\ddagger$ vs. Z_1 (Figure 3) is an approximately straight line which gives no obvious indication of the changeover in the medium effect, from being dominated by the ground state to being dominated by the transition state. On the other hand, $\delta_M \Delta G_\alpha^\ddagger$ is a sigmoid function which shows marked changes in both water-rich and alcohol-rich mixtures and only minor changes in between. The plot of ΔH^\ddagger vs. Z_1 (Figure 4) is quite complicated, with a marked hump near $Z_1 \approx 0.87$; the plot of ΔH_α^\ddagger vs. Z_1 is simpler, with the hump being transformed into a broader minimum.

Data for ΔC_p^\ddagger are available only for water-rich mixtures and are a complex function of Z_1 . Transformation to $\Delta C_{p,\alpha}^\ddagger$ (Table VI) does not lead to any obvious reduction in complexity.

Concluding Remarks

It is clear from the preceding examples that transformation to endostatic conditions causes some functions of Z_1 to become simpler, while others (such as $\delta_M \Delta G^\ddagger$ in Figure 3) become more complicated. However, in each case the transformed relationship should be easier to interpret, because of the exact analogy of endostatic functions to corresponding functions in one-component solvents. With more experience, and with the availability of more accurate data for the required transformations, one may hope that the analysis of endostatic relationships will give a sharper insight into solvation effects.

Orientation in Base-Promoted β -Elimination Reactions. Effects of Base Strength and Size

Richard A. Bartsch,^{*1} Karl E. Wieggers,² and Donna M. Guritz

Contribution from the Department of Chemistry, Washington State University, Pullman, Washington 99163. Received July 27, 1973

Abstract: Orientation in β -eliminations from 2-iodobutane promoted by a wide variety of oxygen, nitrogen, and carbon bases in dimethyl sulfoxide has been determined. By the use of linear free energy relationships, a fundamental control of orientation by base strength and the level of base complexity necessary for the onset of steric effects are demonstrated. Sensitivity of orientation to base strength is dependent upon the first atom of the base, decreasing in the order, oxygen > nitrogen > carbon.

A long-standing controversy concerning the relative importance of base strength and size in determining orientation for olefin-forming elimination re-

(1) Address correspondence to this author at the Department of Research Grants and Awards, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036.

(2) National Science Foundation Undergraduate Research Participant, 1972.

actions has recently been resolved.^{3,4} Fundamental

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(4) Froemsdorf and Robbins have earlier reported a qualitative relationship between orientation observed in eliminations from 2-butyl tosylate induced by six oxyanion bases in DMSO and the pK_a 's of the oxyanion bases in water which suggested that orientation could be significantly affected by base strength alone: D. H. Froemsdorf and M. D. Robbins, *J. Amer. Chem. Soc.*, **89**, 1737 (1967).