large number of solid solutes. Nevertheless, the rather rough agreement does indicate that the modified Polanyi theory is capable of predicting the adsorption, at least approximately, when there are no complications from steric effects. As we have seen, however, severe steric hindrance in the solute can make a considerable difference in the adsorption potential, and one should therefore exercise caution in applying the Polanyi treatment to the adsorption of solutes that show severe steric hindrance to achieving planarity.

Conclusion

Solutes that have steric hindrance to assuming a planar configuration may be expected to show anomalously weak adsorption (by the criteria of the modified Polanyi adsorp-

tion potential theory). When the steric factor is severe, the difference in adsorption can be quite striking. That the effect shown here is a true steric effect of the solute and not simply one of molecular sieving is shown by the essentially similar results on the activated carbon and on an essentially nonporous graphitized carbon black.

Use of the Nonpolar Analog Model in Predicting the Effects of Solvents on Molecular Complex Formation Equilibria

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The nonpolar analog (NPA) model is examined theoretically and methods are developed for using it to predict thermodynamic properties of the transfer of donor, acceptor, and complex molecules from the gas phase into dilute solutions in nonpolar solvents. The general problem of inferring free energies of transfer of polar solutes from experimental values of internal energies of transfer is considered. Thermodynamic results calculated by using the NPA model, in conjunction with solubility parameter theory and with the Prigogine refined average-potential cell model theory, are compared with experimental results for polar components involved in several molecular complex formation equilibria. For individual solutes, including complexes, calculated and experimental free energies of transfer into hexadecane and diphenylmethane generally agree to within 0.1–0.7 kcal/mol.

Introduction

As extensive thermodynamic and spectral information about molecular complexes has become available, numerous investigators have noted the important role played by solvents in modifying the physical and chemical properties of complexes.[1-5] This knowledge has provided the incentive for attempts to obtain accurate experimental results for electron donor-acceptor (EDA) complexes in the vapor phase,[2,3,5] where the complicating effects of solvents are absent, and for which theoretical treatments of the structure and energy of complexes are becoming feasible. Unfortunately, limitations on the volatility and stability of EDA complexes and the unique experimental problems connected with investigations of associating gases have restricted the number and reliability of studies of gaseous complexes.[1-6]

There are two primary reasons, therefore, why methods for predicting the effects of media on complex formation reactions are potentially valuable: (1) comparison with theory will be facilitated if reliable techniques evolve for

converting thermodynamic information about complex formation in condensed phases into information about the corresponding gaseous systems; and (2) an understanding of the role of solvents in altering properties of complexes will be essential in future attempts to provide a molecular explanation of biological and industrial systems in which EDA complexes are important.

Attempts to treat the influence of solvents on the energetics of complex formation have generally fallen into two

(1) W. B. Person and R. S. Mulliken, "Molecular Complexes. A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969, Chapter 7.
(2) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1970, Chapter 7.
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(6) (a) M. Tamres and J. Grundnes, *J. Amer. Chem. Soc.*, 93, 801 (1971), and reports cited therein; (b) J. Grundnes, S. D. Christian, V. Cheam, and S. B. Farnham, *ibid.*, 93, 20 (1971).

classes: methods in which the solvent is treated as a chemical reactant, which forms discrete complexes with donor (D), acceptor (A), or the adduct (DA);[7] and techniques for inferring the effects of non-specific solvent-solute interactions.[5,8] Although it is clear that specific complexes between solvent and solute can be important in condensed phase systems of associating solutes, there appears to be no unique way to determine stoichiometries and specific thermodynamic constants for the solvent-solute complexes which are presumed to exist in dilute solution.[5,8d] Progress has been made in predicting energies and free energies of transfer reactions of the type

X(ideal gas at unit molarity) =

X(ideal dilute solution in solvent S at unit molarity) (1)

for polar solutes involved in representative molecular complex formation reactions.[5,9] It has been observed that the energies and free energies of transfer of a series of polar solutes into a given nonpolar solvent ($\Delta E°_X{}^{v\to s}$ and $\Delta G°_X{}^{v\to s}$) are linearly related; empirical correlations and semiempirical lattice or cell model calculations provide a convenient basis for predicting changes which occur in the equilibrium constants (K_c) and energies (ΔE) of complex formation reactions as various nonpolar and slightly polar solvents are employed.[9a,10]

The general problem of developing a theory of nonelectrolyte solutions involving polar components remains unsolved.[11] Attempts have been made to compare properties of solutions of polar solutes with those of homomorphic nonpolar solutes, i.e., with nonpolar molecules similar in molecular size and structure to the polar solutes.[11-13] The homomorphs have frequently been chosen to have the same molecular volume and polarizability as the polar molecules of interest. Differences between properties of mixtures including a polar component and analogous mixtures in which the polar species is replaced by its homomorph are ascribed to inductive interactions or the formation of molecular complexes involving the polar solute.[13] Estimates have been made of the separate contributions of dispersive and inductive interactions to the solubility parameters of polar liquids, and these parameters have found some utility in treatments of binary mixtures of polar and nonpolar compounds.[14] However, it is apparent that the total effect of interactions between polar and nonpolar molecules, throughout a wide range of concentrations, cannot be rigorously accounted for in terms of a single induction energy density parameter which is concentration independent.[11]

The transfer reactions (eq 1) for the components participating in a molecular complex formation reaction pertain to the formation of infinitely dilute solutions of polar solutes in a given solvent, S. For purposes of the present discussion, S will be taken to be nonpolar. Solute molecules are in contact only with solvent molecules, and the solvent-solute interactions involve only nonspecific dispersion and induction forces. Therefore, it should be much simpler to develop adequate theories for predicting transfer energies and free energies of polar solutes than to formulate theories of pure polar liquids and of concentrated solutions of polar and nonpolar molecules, in which orientation energy and entropy effects must be considered.

A previous article[9b] introduced a general model for dilute solutions of polar compounds dissolved in nonpolar media. The model involves use of a nonpolar analog (NPA) of the polar solute (P) in place of the polar solute in calculating properties of the solutions; the NPA molecule is chosen to have the same molecular volume and the same total interaction energy with the surrounding solvent molecules as does P. In this model, the NPA molecule must have a value of molecular polarizability, α, large enough to interact as strongly with the solvent as does P, for which both dispersion and inductive interactions are important. It is assumed that not only $\Delta E°_P{}^{v\to s}$, but also $\Delta G°_P{}^{v\to s}$, $\Delta S°_P{}^{v\to s}$, and other thermodynamic constants for the transfer reactions 1 will be the same as the corresponding transfer quantities for the NPA molecule. No attempt is made to utilize or predict properties of the pure polar component in this treatment. The theoretical basis for the NPA model and methods for applying it to predict the effects of solvents on molecular complex formation equilibria are presented here.

Justification for the Nonpolar Analog Model

An isolated polar molecule dissolved in a nonpolar medium may interact with the solvent through several types of forces, including short-range repulsive forces and van der Waals attractive forces of the dipole-induced dipole and dispersive types.[15] The potential energy of interaction between the polar molecule P and the solvent molecules S resulting from dipole-induced dipole forces is

$$V_{ps}(\text{dip}) = -\tfrac{1}{2}\ \hat{\mu}_p \cdot \hat{R}_{ps} \tag{2}$$

Here $\hat{R}_{ps}$ is the reaction field at the polar molecule resulting from the polarization of the solvent molecules by the electric moment of the solute molecule, $\hat{\mu}_p$. If one adopts the dielectric cavity model of a solution (in which the solute molecule is at the center of a cavity whose walls consist of a continuum with dielectric properties identical with the bulk solvent) the reaction field is taken to be proportional to the electric moment; the coefficient of proportionality is given in several standard texts on dielectric theory.[15] The reaction field may be written as a summation over the contributions of each solvent-solute pair

$$V_{ps}(\text{dip}) = \tfrac{1}{2}\hat{\mu}_p{}^2 \sum_s \frac{\alpha_s f_{ps}}{|\hat{r}_{ps}|^6} \tag{3}$$

where $|\hat{r}_{ps}|$ is the magnitude of the vector distance between a solvent molecule and the polar molecule, α_s is the molecular polarizability of a solvent molecule, and f_{ps} is an orientation factor which accounts for the anisotropy of

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(8) (a) H. Buchowski, J. Devaure, P. V. Huong, and J. Lascombe, Bull. Soc. Chim. Fr., 2532 (1966); (b) S. D. Christian, J. R. Johnson, H. E. Affsprung, and P. J. Kilpatrick, J. Phys. Chem., 70, 3376 (1966); (c) P. V. Huong, N. Platzer, and M. L. Josien, J. Amer. Chem. Soc., 91, 6514 (1969); (d) S. D. Christian and E. E. Tucker, J. Phys. Chem., 74, 214 (1970).

(9) (a) J. Grundnes and S. D. Christian, Acta Chem. Scand., 23, 3583 (1969); (b) S. D. Christian, K. O. Yeo, and E. E. Tucker, J. Phys. Chem., 75, 2413 (1971).

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(11) J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand, New York, N. Y., 1970, Chapter 7.

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the interactions.[15,16] The dispersive interaction may be written as

$$V_{ps}(disp) = -\frac{3}{2} I_p \alpha_p \sum_s \frac{I_s \alpha_s}{I_p + I_s} \frac{1}{|\hat{r}_{ps}|^6} \quad (4)$$

where I_p and I_s are the ionization potentials of the solute and solvent, respectively, and α_p is the molecular polarizability of the solute.

The NPA molecule has no permanent dipole moment; it interacts with the solvent molecules solely through dispersive forces.[9b] However, the magnitude of this interaction must be large enough so that the *total* energy of interaction of the NPA molecule with the solvent equals the total energy of interaction of the original polar molecule with the solvent (the sum of eq 3 and 4)

$$V_{NPA} = V_{ps}(dip) + V_{ps}(disp) \quad (5)$$

Since the vector distances between the polar solute and the solvent molecules are the same as those between NPA and S, and since all of the terms in eq 5 have the same distance dependence, the energy compensation required by eq 5 will be achieved whenever

$$-\frac{3}{2} I_{NPA}\alpha_{NPA} \frac{I_s \alpha_s}{I_{NPA} + I_s} = -\frac{1}{2} \mu_p^2 \alpha_s f_{ps} -$$

$$\frac{3}{2} I_p \alpha_p \frac{I_s \alpha_s}{I_p + I_s} \quad (6)$$

for each solute–solvent interaction. For example, if the solvent polarizability is spherical, eq 6 may be satisfied by varying only the molecular polarizability of the solute, while leaving the ionization potential invariant. Any other combination of values of I_{NPA} and α_{NPA} satisfying eq 6 may be chosen for the hypothetical solute molecule NPA.

Equation 6 indicates the molecular requirements for equality of $\Delta E^\circ{}_p{}^{v \to s}$ and $\Delta E^\circ{}_{NPA}{}^{v \to s}$ for homomorphic P and NPA molecules. It can be shown that various cell theories of liquids lead to the result that $\Delta S^\circ{}_p{}^{v \to s} = \Delta S^\circ{}_{NPA}{}^{v \to s}$ and $\Delta G^\circ{}_p{}^{v \to s} = \Delta G^\circ{}_{NPA}{}^{v \to s}$ provided the energy compensation required by eq 6 is achieved.[17] Hence the use of the NPA model under quite general conditions appears warranted.

Application of the Nonpolar Analog Model in Predicting Thermodynamic Properties of Polar Solutes

The NPA model does not by itself provide a basis for predicting thermodynamic properties for the transfer reactions (eq 1) for polar solutes. However, to the extent that the model applies it permits the use of theories and properties of nonpolar liquids and liquid mixtures in predicting properties of dilute solutions of polar solutes in nonpolar solvents.[9b] The model is based on the assumption that $\Delta G^\circ{}_p{}^{v \to s}$ is uniquely determined by $\Delta E^\circ{}_p{}^{v \to s}$ and the molecular volume (more correctly, the molecular geometry) of P. Using the nonpolar analog concept

$$\Delta G^\circ{}_p{}^{v \to s}(\Delta E^\circ{}_p{}^{v \to s}, \bar{V}_p) = \Delta G^\circ{}_{NPA}{}^{v \to s}(\Delta E^\circ{}_{NPA}{}^{v \to s}, \bar{V}_{NPA}) \quad (7)$$

where $\Delta E^\circ{}_p{}^{v \to s} \equiv \Delta E^\circ{}_{NPA}{}^{v \to s}$ and $\bar{V}_p \equiv \bar{V}_{NPA}$.

The NPA model may be most simply tested by comparing experimental values of $\Delta G^\circ{}_X{}^{v \to s}$ and $\Delta E^\circ{}_X{}^{v \to s}$ for various solutes X (polar and nonpolar) of comparable molecular volume dissolved in a given solvent. Previously,[9,10] we observed that the empirical relation

$$\Delta G^\circ{}_X{}^{v \to s \prime} = \beta_S \Delta E^\circ{}_X{}^{v \to s} + 300 \text{ cal/mol} \quad (8)$$

provides a good correlation of results for both polar and nonpolar solutes (without regard for molecular volume) in a given solvent S at 298°K.[18] The parameter β_S is characteristic of the solvent only, and has a value of about 0.6 for many common nonpolar solvents. Correlations of this type demonstrate the feasibility of replacing P by its nonpolar analog in thermodynamic calculations; they also show that moderate variation in molecular volume does not strongly influence the magnitude of $\Delta G^\circ{}_X{}^{v \to s}$ corresponding to a given value of $\Delta E^\circ{}_X{}^{v \to s}$. (Actually, there is a reasonably close correlation between $\Delta E^\circ{}_X{}^{v \to s}$ and the molecular volume of related solutes; hence, the effect of variation in solute volume is largely hidden in the $\Delta G^\circ{}_X{}^{v \to s}$ vs. $\Delta E^\circ{}_X{}^{v \to s}$ correlations.)

At a more fundamental level, it would be desirable to develop theories for predicting $\Delta E^\circ{}_p{}^{v \to s}$ and $\Delta G^\circ{}_p{}^{v \to s}$ from molecular parameters of the P, S, and NPA molecules. In this development, it is convenient to refer to the following conceptual diagram of the energy of P and NPA in various states
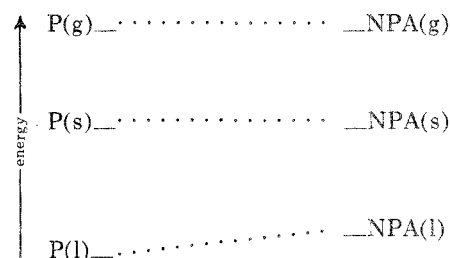
The states P(g) and NPA(g) refer to ideal gaseous states; P(s) and NPA(s) refer to dilute solution states in the nonpolar solvent;[19] and P(l) and NPA(l) represent pure liquid P and NPA. Note that the energy of P(l) will ordinarily be considerably lower than that of NPA(l) and that the energy change for the transfer P(l) → P(s) will be correspondingly greater than that for the transfer NPA(l) → NPA(s); the reason for this is that in the pure liquid state, P molecules interact relatively strongly with each other through orientation forces, which are absent in liquid NPA and in the states P(s) and NPA(s). The model forces P(g) and NPA(g) to be at the same level of energy (and by assumption, free energy); similarly, P(s) and NPA(s) have the same energy (and, presumably, free energy).

Given the energy level diagram (above) the NPA model requires that

(16) Ordinarily in systems consisting of a polar solute and a nonpolar solvent, orientation effects will not play an important role, and f_{ps} may realistically be taken to be unity. However, interactions between polar molecules capable of donating n electrons and neutral acceptor molecules (e.g., halogens or aromatic hydrocarbons) may be highly specific.[1,2] Donor–acceptor interaction may therefore produce retardation effects even in systems where the solvent has no permanent dipole moment.

(17) A discussion of the relation between the NPA model and various cell theories of liquids will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JPC-73-813.

(18) In ref 9a the constant term in eq 15 was given erroneously as 450 cal/mol. Incorrect terms were utilized to account for the thermal expansion of the solvent, and the reported $\Delta E^{v \to s}$ values are all too small (algebraically) by 200–250 cal/mol.

(19) Gaseous standard states are taken to be the unit molarity ideal gas; the infinitely dilute, unit molarity state is used for all solutes in condensed phases.

$$\Delta E^{\circ}{}_{P}{}^{v \to s} = \Delta E^{\circ}{}_{NPA}{}^{v \to s} = E^{\circ}{}_{NPA(s)} - E^{\circ}{}_{NPA(g)}$$

or

$$\Delta E^{\circ}{}_{P}{}^{v \to s} = \left(E^{\circ}{}_{NPA(s)} - E^{\circ}{}_{NPA(l)} \right) - \left(E^{\circ}{}_{NPA(g)} - E^{\circ}{}_{NPA(l)} \right) \tag{9}$$

and similarly

$$\Delta G^{\circ}{}_{P}{}^{v \to s} = \left(G^{\circ}{}_{NPA(s)} - G^{\circ}{}_{NPA(l)} \right) - \left(G^{\circ}{}_{NPA(g)} - G^{\circ}{}_{NPA(l)} \right) \tag{10}$$

Equations 9 and 10 may be rewritten

$$\Delta E^{\circ}{}_{P}{}^{v \to s} = \Delta E^{\circ}{}_{NPA}{}^{dil} - \Delta E^{\circ}{}_{NPA}{}^{vap}... \tag{11}$$

and

$$\Delta G^{\circ}{}_{P}{}^{v \to s} = \Delta G^{\circ}{}_{NPA}{}^{dil} - \Delta G^{\circ}{}_{NPA}{}^{vap}... \tag{12}$$

where $\Delta E^{\circ}{}_{NPA}{}^{dil}$ and $\Delta E^{\circ}{}_{NPA}{}^{vap}$ are, respectively, the energy of transfer of NPA from pure liquid NPA into the infinitely dilute solution state in solvent S and the energy of vaporization of liquid NPA, and $\Delta G^{\circ}{}_{NPA}{}^{dil}$ and $\Delta G^{\circ}{}_{NPA}{}^{vap}$ are the corresponding free energy changes.

Several current theories of solution provide means for relating $\Delta E^{\circ}{}_{NPA}{}^{dil}$ and $\Delta E^{\circ}{}_{NPA}{}^{vap}$ to parameters characteristic of the NPA and S molecules. For example, solubility parameter theory[11] predicts that

$$\Delta E^{\circ}{}_{NPA}{}^{dil} = \bar{V}_{P}(\delta_{S} - \delta_{NPA})^{2} \tag{13}$$

and

$$\Delta E^{\circ}{}_{NPA}{}^{vap} = \delta_{NPA}{}^{2} \bar{V}_{P} \tag{14}$$

where δ_{S} and δ_{NPA} are the solubility parameters of S and NPA, respectively, and where for convenience we neglect volume changes on mixing NPA with S. The expressions for $\Delta E^{\circ}{}_{NPA}{}^{dil}$ and $\Delta E^{\circ}{}_{NPA}{}^{vap}$ may be substituted into eq 13, which may be rearranged to give

$$\delta_{NPA} = \tfrac{1}{2} \left(\delta_{S} - \Delta E^{\circ}{}_{P}{}^{v \to s}/\delta_{S} \bar{V}_{P} \right) \tag{15}$$

Thus, it is possible to infer the solubility parameter of the nonpolar analog of a given polar solute from the solubility parameter of the solvent and the energy of transfer of P from the ideal gaseous state into the infinitely dilute state in S. The free energy of transfer of NPA from vapor to the infinitely dilute state in solvent S may then be related to δ_{NPA} and the vapor pressure of pure liquid NPA ($P^{\circ}{}_{NPA}$). Equation 12 may be rewritten

$$\Delta G^{\circ}{}_{P}{}^{v \to s} = RT \ln \left(P^{\circ}{}_{NPA}/RT \right) + \bar{V}_{P}(\delta_{S} - \delta_{NPA})^{2} +$$
$$RT \ln \bar{V}_{S} \tag{16}$$

where the first term on the right represents the free energy change for converting NPA vapor at unit molarity into pure liquid NPA under its own vapor pressure; the second term is the free energy of transfer of NPA from the pure liquid state to the ideal dilute solution in S (using the unit mole fraction standard state) and the last term is the free energy change for converting from the mole fraction standard state for the solute to the unit molarity standard state.[9b]

In order to apply eq 16 to calculate $\Delta G^{\circ}{}_{P}{}^{v \to s}$ it is necessary to obtain the vapor pressure of pure liquid NPA, either from a theory of pure liquids or from experimental measurements on actual nonpolar liquids having approximately the required heat of vaporization and molecular geometry. Fortunately, the vapor pressures of pure low
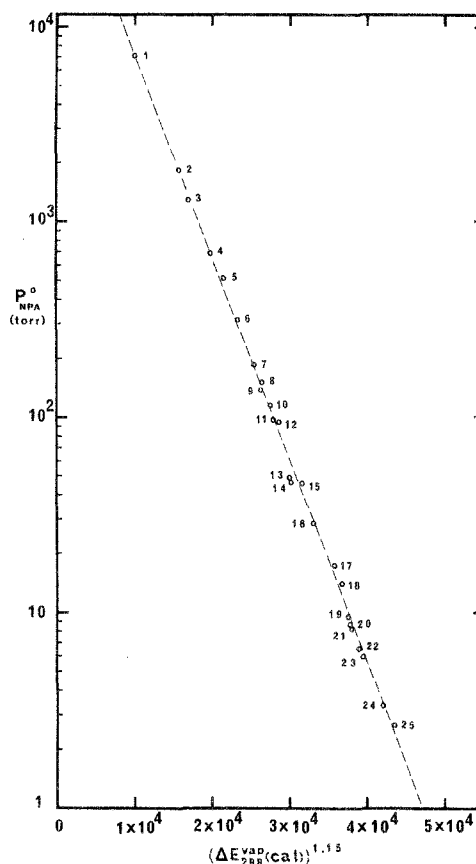
Figure 1. Correlation between vapor pressure and energy of vaporization of nonpolar organic liquids at 25°. All $\Delta E_{298}{}^{vap}$ values were taken from J. H. Hildebrand, J. M. Prausnitz, and R. L. Scott, "Regular and Related Solutions," Van Nostrand-Reinhold, New York, N. Y., 1970, except for propane, butane, and methylcyclopentane, for which $\Delta E_{298}{}^{vap}$ values were found in "Physical Properties of Chemical Substances," The Dow Chemical Company, Midland, Mich., 1952. Vapor pressures were obtained from the latter publication. Numbers refer to compounds as follows: (1) propane, (2) butane, (3) neopentane, (4) isopentane, (5) pentane, (6) cyclopentane, (7) 1-hexene, (8) hexane, (9) methylcyclopentane, (10) carbon tetrachloride, (11) cyclohexane, (12) benzene, (13) isooctane, (14) methylcyclohexane, (15) heptane, (16) toluene, (17) 1-octene, (18) octane, (19) ethylbenzene, (20) p-xylene, (21) m-xylene, (22) o-xylene, (23) stylene, (24) propylbenzene, (25) mesitylene.

molecular weight nonpolar liquids at 25° vary systematically with their energies of vaporization.[20] Figure 1 is a plot of the logarithm of vapor pressure against $\Delta E^{\circ}{}_{298}{}^{vap}$ for a number of common nonpolar liquids (excluding fluorocarbons); the solid curve represents the least-squares equation

$$\log P^{\circ}(\text{Torr}, 298°K) = -1.038 \times 10^{-4}(\Delta E_{298}{}^{vap})^{1.15} +$$
$$4.889 \tag{17}$$

which may be used to calculate vapor pressures of these liquids, with a standard error of about 9%. By employing $\Delta E_{NPA}{}^{vap} = \delta_{NPA}{}^{2} \bar{V}_{P}$ and eq 17 it is possible to obtain a reliable value of $P^{\circ}{}_{NPA}$ to use in eq 16.

Another theory of solutions which may be melded with the NPA model is the average-potential cell model theory of Prigogine,[21] which extends the theorem of correspond-

(20) E. A. Guggenheim, "Thermodynamics," North-Holland, Amsterdam, 1950, pp 142 and 143; ref 11, pp 40 and 41.
(21) I. Prigogine, "Molecular Theory of Solutions," North-Holland, Amsterdam, 1957, Chapters 9 and 10.

ing states to mixtures. In the Prigogine refined average-potential cell model, excess thermodynamic functions for binary mixtures are expressed in terms of parameters σ and ρ defined as

$$\sigma = (\epsilon_B{}^* - \epsilon_A{}^*)/\epsilon_A{}^* \qquad (18)$$

and

$$\rho = (r_B{}^* - r_A{}^*)/r_A{}^* \qquad (19)$$

where r^* and ϵ^* are the distance of separation and internal energy scale factors in the universal potential function, respectively, and the subscripts A and B denote pure components A and B, respectively. Here, A is taken to be the reference component and B is the solute (either P or NPA). When only dispersion forces operate between the two components (e.g., when the solute is the NPA molecule), $\Delta E°$ dil and $\Delta G°$ dil may be expressed in terms of σ, ρ, and the configurational enthalpies and heat capacities of the nonpolar solvent (see ref 21). Then, by using the relations

$$\Delta H°{}^{vap} = 0.678Z\epsilon_A{}^*/RT \qquad (20)$$

and

$$\epsilon_B{}^* = \epsilon_A{}^*(1 + \sigma) \qquad (21)$$

where Z is the number of the nearest neighbors surrounding a cell, one may derive expressions for $\Delta G°$ v→s and $\Delta E°$ v→s for NPA; by the assumptions of the NPA model, these relations will apply as well to P at infinite dilution in S.

To relate $\Delta E°_P{}^{v\to s}$ and $\Delta G°_P{}^{v\to s}$, σ_{NPA} may be calculated explicitly for a given value of $\Delta E°_P{}^{v\to s}$ and a chosen value of ρ, whereupon σ_{NPA} and ρ may be used to calculate $\Delta G°_P{}^{v\to s}$. The parameter ρ may be evaluated from molecular volumes of the solute and the solvent.[22] Alternatively, it is convenient to construct plots of $\Delta G°_P{}^{v\to s}$ vs. $\Delta E°_P{}^{v\to s}$ by using arbitrarily chosen σ values and a fixed value of ρ. Knowing ρ, for a given solute and solvent, $\Delta G°_P{}^{v\to s}$ is estimated from $\Delta E°_P{}^{v\to s}$ by using the curve corresponding most nearly to the correct ρ value. Figure 2 shows standard $\Delta G°_P{}^{v\to s}$ vs. $\Delta E°_P{}^{v\to s}$ curves constructed for ρ values of zero and ±0.2; it may be noted that the plots are not very sensitive to variation in ρ. The predictions based on the theory of Prigogine are seen to be nearly the same as those derived from solubility parameter theory; moreover, the results in Figure 2 are in reasonable agreement with transfer free energy value calculated from empirical eq 8, using a value of β_s equal to 0.60. The calculated intercept ($\Delta G°_P{}^{v\to s}$ corresponding to $\Delta E°_P{}^{v\to s} = 0$) equals 241 cal based on solubility parameter calculations (eq 16) and 284 cal using Prigogine's theory with $\rho = -0.27$ and physical properties of heptane at 298°K. (The value $\rho = -0.27$ is computed for a hypothetical solute having a molar volume intermediate between those of Ar and Kr, for which $\Delta E°$ v→HPT is nearly zero at 298°K.)

Table I illustrates a test of eq 14–17, which are based on the NPA model and solubility parameter theory. Values of $-\Delta E°_P{}^{v\to s}$ given in column 3 are the experimental ones, and column 4 lists $-\Delta E°_P{}^{v\to s}$ values calculated with the quasi-lattice model of Stevens, et al.,[10,23] which utilizes energy parameters characteristic of interactions between specific atomic and submolecular groups of the solute and solvent molecules. In the fifth and sixth columns are listed values of $-\Delta G°_P{}^{v\to s}$ computed from eq 13–17, using the values of $\Delta E°_P{}^{v\to s}$ listed in columns 3 and 4, respectively. Both sets of calculated $\Delta G°_P{}^{v\to s}$ values are in reasonable agreement with the experimental results, and
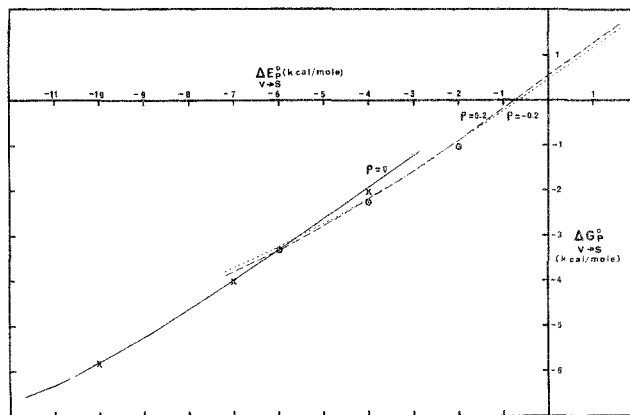

Figure 2. Correlation of transfer free energies and internal energies for the solvent heptane. Calculated curves ($\Delta E°_P{}^{v\to s}$ vs. $\Delta G°_P{}^{v\to s}$) are obtained using the Prigogine refined average-potential cell model theory. Points (X) are calculated from the Hildebrand–Scott solubility parameter theory for the solvent heptane, using $\rho = 0$; points (O) are calculated in the same way using $\rho = -0.2$.

there is apparently nearly random deviation on the order of several tenths kcal between the experimental and calculated free energy values. Similar calculations based on Prigogine's cell model lead to results which are nearly equivalent to those in Table I.

A related useful application of the nonpolar analog model is the calculation of limiting activity coefficients of polar solutes (P) in nonpolar solvents, based on the pure liquid P standard state. $\Delta G°_P{}^{v\to s}$ for the unit molarity solute state in S may be calculated for polar solutes from the value of $\Delta E°_P{}^{v\to s}$ for a given solute (vide supra). But the mole fraction of P (in S) in equilibrium with P vapor at the vapor pressure of pure liquid P may be calculated from the equation

$$X_P{}^{(s)} = (P°_P \bar{V}_s/RT) \exp(-\Delta G°_P{}^{v\to s}/RT) \qquad (22)$$

provided $P°_P$ (the vapor pressure of pure liquid P) is known. Since the activity of P is unity under these conditions, the limiting activity coefficient of P in S can be calculated from

$$\gamma_P{}^\infty = 1/X_P{}^{(s)} = (RT/P°_P \bar{V}_s) \exp(\Delta G°_P{}^{v\to s}/RT) \quad (23)$$

By using the calculated value $\Delta G°(H_2O)^{v\to s} = -1890$ cal for water dissolved in diphenylmethane (see Table I) and the known vapor pressure of H_2O at 25° (23.7 Torr) one may calculate the value $\gamma(H_2O)^\infty = 192$, whereas the experimental value is $\gamma(H_2O^\infty = 227$.

Other, more elaborate theories of nonpolar binary mixtures (such as the recent theory of Flory,[24] which employs a reduced partition function, formulated in terms of segment volumes and segment interaction energies) may be utilized to calculate $\Delta E°$ dil and $\Delta G°$ dil in terms of mo-

(22) The expressions used here in obtaining transfer energies and free energies apply, strictly speaking, only at zero pressure; however, in applications involving pressures not greater than 1 atm, the pressure dependence of energy or free energy may ordinarily be ignored. The parameter ρ should be evaluated from the critical volumes of A and the solute, but for the present calculations it is satisfactory to estimate from the molar volumes of the pure components at 298°K.

(23) T. L. Stevens, Ph.D. Dissertation, The University of Oklahoma, 1968; J. R. Johnson, P. J. Kilpatrick, S. D. Christian, and H. E. Affsprung, J. Phys. Chem., **72**, 3223 (1968).

(24) P. J. Flory, R. A. Orwoll, and A. Vrij, J. Amer. Chem. Soc., **86**, 3507, 3515 (1964); P. J. Flory, ibid., **87**, 1833 (1965); P. J. Flory, Disc. Faraday Soc., **49**, 7 (1970), and references cited therein.

TABLE I: Experimental and Calculated Transfer Energies and Free Energies of Polar Solutes from Vapor into Nonpolar Solvents

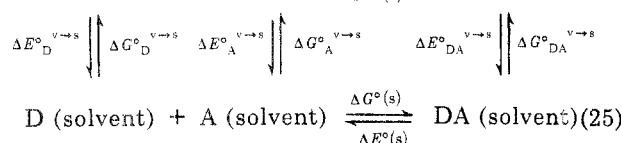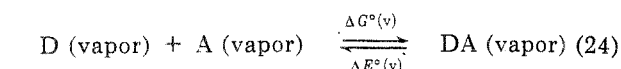| System		$-\Delta E^\circ_P{}^{v\to s}$, kcal/mol (exptl)	$-\Delta E^\circ_P{}^{v\to s}$, kcal/mol[b] (calcd)	$-\Delta G^\circ_P{}^{v\to s}$, kcal/mol[c] (calcd)	$-\Delta G^\circ_P{}^{v\to s}$, kcal/mol[d] (calcd)	$-\Delta G^\circ_P{}^{v\to s}$, kcal/mol (exptl)
Solute	Solvent[a]					
H_2O	HXD	1.98[f]	2.60	0.72	0.87	0.45[f]
CH_3OH	HXD	2.75[f]	2.80	1.16	1.19	1.25[f]
$(C_2H_5)_2NH$	HXD	5.45[f]	(5.45)[e]	2.66	(2.66)	3.16[f]
$(C_2H_5)_2NH\cdot H_2O$	HXD	7.50[f]	6.80	3.93	3.49	3.80[f]
$(C_2H_5)_2NH\cdot CH_3OH$	HXD	5.98[f]	7.00	2.89	3.57	4.15[f]
H_2O	DPM	4.02[f]	5.57	1.89	2.19	1.79[f]
CH_3OH	DPM	5.11[f]	4.78	2.79	2.62	2.34[f]
$(C_2H_5)_2NH$	DPM	6.14[f]	(6.14)[e]	3.27	(3.27)	3.36[f]
$(C_2H_5)_2NH\cdot H_2O$	DPM	8.62[f]	8.26	4.88	4.63	5.20[f]
$(C_2H_5)_2NH\cdot CH_3OH$	DPM	8.11[f]	7.46	4.40	4.38	5.08[f]
$(CH_3)_3N$	HPT	4.60[g]		2.60		2.57[g]
SO_2	HPT	3.60[g]		1.98		1.40[g]
$(CH_3)_3N\cdot SO_2$	HPT	10.10[g]		5.92		5.15[g]

[a] HXD = hexadecane, DPM = diphenylmethane, HPT = heptane. [b] Calculated from the lattice model of Stevens, et al.[23] [c] Calculated from experimental $\cdot\Delta E^\circ_P{}^{v\to s}$ values, using the NPA model and solubility perameter theory. [d] Calculated from $\Delta E^\circ_P{}^{v\to s}$ values derived from the lattice model, using the NPA method in conjunction with solubility parameter theory. [e] Experimental $\Delta E^\circ_P{}^{v\to s}$ for diethylamine used in calculating lattice parameters for N···HXD and N···DPM interaction energy. [f] Data from E. E. Tucker, Ph.D. Dissertation, the University of Oklahoma, 1969. [g] Data from J. Grundnes and S. D. Christian, *J. Amer. Chem. Soc.*, **90**, 2239 (1968).

lecular parameters of the solvent and the nonpolar analog of P. However, since the differences between ΔE° dil and ΔG° dil obtained from various statistical theories are small compared with uncertainties in these quantities for most polar solutes, the equations which can be derived for utilizing these theories with the NPA model are not given here.

Prediction of the Effects of Solvents on Free Energies of Formation of Molecular Complexes

Applications of the nonpolar analog model method for calculating $\Delta G^\circ{}^{v\to s}$ from $\Delta E^\circ{}^{v\to s}$ for components which participate in complex formation reactions should be useful in predicting solvent effects on the complex formation constants. Consider the equilibrium cycle shown in scheme I where D is an electron donor molecule, A is an

Scheme I

$$D\ (\text{vapor})\ +\ A\ (\text{vapor})\ \underset{\Delta E^\circ(v)}{\overset{\Delta G^\circ(v)}{\rightleftharpoons}}\ DA\ (\text{vapor})\quad (24)$$

$$\Delta E^\circ_D{}^{v\to s}\ \Big\|\ \Delta G^\circ_D{}^{v\to s}\quad \Delta E^\circ_A{}^{v\to s}\ \Big\|\ \Delta G^\circ_A{}^{v\to s}\quad \Delta E^\circ_{DA}{}^{v\to s}\ \Big\|\ \Delta G^\circ_{DA}{}^{v\to s}$$

$$D\ (\text{solvent})\ +\ A\ (\text{solvent})\ \underset{\Delta E^\circ(s)}{\overset{\Delta G^\circ(s)}{\rightleftharpoons}}\ DA\ (\text{solvent})\ (25)$$

electron acceptor molecule, and DA is an EDA complex. The changes in standard free energies (ΔG°) and internal energies (ΔE°) for the steps in the cycle are interrelated by the equations

$$\Delta E^\circ(s)\ =\ \Delta E^\circ(v)\ +\ \Delta E^\circ_{DA}{}^{v\to s}\ -\ \Delta E^\circ_D{}^{v\to s}\ -\ \Delta E^\circ_A{}^{v\to s}\quad (26)$$

and

$$\Delta G^\circ(s)\ =\ \Delta G^\circ(v)\ +\ \Delta G^\circ_{DA}{}^{v\to s}\ -\ \Delta G^\circ_D{}^{v\to s}\ -\ \Delta G^\circ_A{}^{v\to s}\quad (27)$$

However, the values $\Delta G^\circ(s)$ and $\Delta G^\circ(v)$ may be related to the complex formation equilibrium constants in s and v by $\Delta G^\circ = -RT \ln K_c$ so that eq 27 may be rearranged to give

$$K_c(v)/K_c(s)\ =\ \exp[(\Delta G^\circ_{DA}{}^{v\to s}\ -\ \Delta G^\circ_D{}^{v\to s}\ -\ \Delta G^\circ_A{}^{v\to s})/RT]$$

TABLE II: Effects of Media on Molecular Complex Formation Equilibria (Comparison of Experimental and Calculated Gibbs Free Energy Values for Formation of Complexes from Monomers)

Complex	$-\Delta G^\circ$, kcal/mol	Medium			
		Vapor	Hexa-decane	Di-phenyl-meth-ane	Hep-tane
$(C_2H_5)_2NH\cdot H_2O$	Calcd[a]		1.77	0.94	
	Calcd[b]		1.18	0.39	
	Exptl[c]	1.22	1.41	1.27	
$CH_3OH\cdot H_2O$	Calcd[a]		0.61	-0.12	
	Calcd[b]		1.26	0.03	
	Exptl[c]	1.54	1.28	0.92	
$(CH_3)_3N\cdot SO_2$	Calcd[a]				4.74
	Exptl[d]	3.40			4.58

[a] Free energy of formation of complex predicted from experimental $\Delta E^\circ{}^{v\to s}$ values. [b] Free energy of formation predicted from values of $\Delta E^\circ{}^{v\to s}$ obtained from the lattice model. [c] Table I, footnote f. [d] Table I, footnote g.

The ratio of K_c values may therefore be predicted by using methods described in the preceding section to calculate $\Delta G^\circ{}^{v\to s}$ for D, A, and DA individually.

The results of application of the nonpolar analog model method to actual EDA complex formation reactions are given in the Table II. The predicted values of changes in ΔG° for complex formation reactions generally agree with experimental values to within a few hundred calories, although for the MeOH·DEA formation reaction in DPM, the discrepancy is about 1 kcal. The agreement is probably satisfactory, considering the fact that several experimental $\Delta E^\circ{}^{v\to s}$ values, each of which is uncertain by several tenths of a kilocalorie, are involved in calculating a single $\Delta G^\circ(s)$ value. When the quasi-lattice model method is employed for calculation of ΔE° for the complex DA, no energy of stabilization is introduced to account for the interaction between the excess dipole moment of the complex and the solvent. This effect has been discussed in rationalizing the abnormally large (negative) value of the energy and free energy of solvation of $(CH_3)_3N\cdot SO_2$. One

would, therefore, expect the lattice model to lead to values of $\Delta G°$ smaller than experimental values because of the complex dipole–solvent interaction; the effect is apparently most important in the case of methanol-diethylamine in diphenylmethane, where the calculated $\Delta G°$ is about 1 kcal less than the observed value. It is known that complexes of aliphatic amines with water and alcohols possess dipole moments which are significantly greater than the vector sums of the dipole moments of the monomers. Also, the possibility exist that retardation effects are not insignificant in systems where highly polar molecules, with exposed n-electron pairs, interact with an aromatic solvent.[1,2]

Conclusion

The nonpolar analog model, combined with various theories of nonpolar liquids, may be used to calculate thermodynamic properties of polar solutes in nonpolar solvents. Theoretically, the NPA model should apply under a wide range of conditions. The methods developed here permit mapping of the thermodynamic properties of the relatively simple nonpolar solute–nonpolar solvent systems into those of the inherently more complicated polar solute–nonpolar solvent systems. By knowing the energy of transfer of a polar solute, it is possible to make a reliable estimate of the free energy of transfer. An important application of the NPA model is the prediction of solvent effects on molecular complex formation equilibria; such effects are not well understood, and the techniques presented here should be quite generally applicable in predicting them.

Conductance and Ion Pair Formation of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I) Perchlorate. III. In Acetonitrile–Carbon Tetrachloride and Water–Dioxane Mixtures

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Conductance of bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate was measured at 25° in CH_3CN–CCl_4 ($11 \leq D \leq 36$) and water–dioxane ($10 \leq D \leq 19$) mixtures. The conductance parameters derived from the analysis with the Fuoss–Onsager–Skinner 1965 conductance theory indicated that the chelate salt is more dissociated in the former mixtures than in the latter and that the plot of log K_A vs. $1/D$ shows a concave-downward curvature in water–dioxane mixtures. These association behaviors were discussed in terms of the interaction of the chelate salt with polar solvent components.

Introduction

In a series of our conductance studies on the bulky and symmetrical electrolyte, bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate in nonaqueous and binary mixed solvents, it was found that the chelate salt is more dissociated in these solvents than the tetrabutylammonium perchlorate and bromide,[1] the cation of which was confirmed to be hydrodynamically equivalent to the chelate cation from the comparison of the Walden products in several alcohols.[2] Two factors were assumed that gave rise to smaller association constants for the chelate salt. The first is the stabilization of the chelate cation by dipolar aprotic solvents such as nitrobenzene,[1] acetone, and methyl ethyl ketone.[2] The second is the decrease in charge density on the chelate cation arising from the coordination bond between Cu(I) and the aromatic ligands. In order to further ascertain the above assumptions, conductance of the chelate salt was measured at 25° in CH_3CN–CCl_4 and water–dioxane mixtures. The former mixtures are composed of dipolar aprotic and nonpolar solvents and the latter of dipolar protic and nonpolar solvents. Therefore these mixtures correspond to $PhNO_2$–CCl_4 and $MeOH$–CCl_4 mixtures examined previously,[1] respectively.

Experimental Section

Materials. Bis(2,9-dimethyl-1,10-phenanthroline)Cu(I) perchlorate (Dojin Chemicals Ltd.) was recrystallized from acetone solution and its analytical data were as follows: found(%): H, 4.11; C, 58.05; N, 9.67 (calcd(%): H, 4.17; C, 58.03; N, 9.67). Acetonitrile and dioxane were purified by the Berns and Fuoss[3] and Lind and Fuoss[4] methods, respectively. Specific conductance was 3.3×10^{-8} mho cm^{-1} for the former and was negligible for the latter. Conductivity water was prepared by passing distilled water through mixed-bed ion exchange resin just before use and its specific conductance was usually less than $8 \times$

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(2) K. Miyoshi, *J. Phys. Chem.*, **76**, 3029 (1972).
(3) D. S. Berns and R. M. Fuoss, *J. Amer. Chem. Soc.*, **82**, 5585 (1960).
(4) J. E. Lind and R. M. Fuoss, *J. Phys. Chem.*, **65**, 999 (1961).