FINAL TECHNICAL COMPLETION REPORT
OWRT PROJECT A-046-OKLA

USE OF THE NONPOLAR ANALOG MODEL IN INFERRING THE EXTENT OF ORDERING AROUND SOLUTE MOLECULES IN WATER

A-046-OKLA

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Evidence has been presented to show that water molecules in the vicinity of nonpolar solutes are more highly ordered than molecules in bulk water.[1-3] Thermodynamic information (e.g., solubility, energy of solution, and volume data) seems to indicate that hydrocarbon molecules or groups in aqueous media are surrounded by one or two molecular layers of water having markedly lower entropy than ordinary liquid water. The concept of hydrophobic bonding is based partly on the premise that hydrocarbon-hydrocarbon group interactions are favored by an entropic effect; that is, when two hydrocarbon groups bind to each other, part of the water "shell" surrounding the separated groups is thought to be reconverted into normal liquid water, with an attendant entropy increase. Energetic effects are not negligible, but the driving force for association of nonpolar groups is often thought of as being largely entropic. However, the large energy terms associated with formation of the cavity enclosing a nonpolar solute must play an important role in aqueous solution phenomena.[4,5]

In the present report, we compare the thermodynamic properties of nonpolar solutes in water with the corresponding properties of water in nonpolar media, in an attempt to learn more about the nature and extent of the ordered region surrounding solutes in aqueous systems. Methods which are reliable for predicting thermodynamic properties for transfer reactions in nonpolar mixtures are employed in conjunction with a model of aqueous solute systems to estimate thermodynamic parameters characteristic of the ordered region.

A Model for Dilute Solutions of Nonpolar Nonelectrolytes.

Many lattice and group interaction theories are in current use for correlating and predicting the thermodynamic properties of nonelectrolyte solutions.[6-8] For our purpose, an interfacial energy model related to a method introduced by Langmuir is both convenient and satisfactory.[9] Initially, we will apply this model to the vaporization of a nonpolar solute molecule (B) from its infinitely dilute solution in a nonpolar solvent (A). Throughout, we will use the unit molarity, ideal dilute solution standard state as the activity basis for all solutes.

Consider first the evaporation of a single B molecule from pure liquid B (See Fig. 1). The first step involves creating a cavity the size of a B molecule, and requires expenditure of energy $\varepsilon_{BB}A_B$, where ε_{BB} is the molecular energy of contact between contiguous B molecules per unit of contact area, and A_B is the area of a B molecule. (We assume A_B is calculable from the known shape and molar volume of B, and that this value of area will not change as B is placed in different liquid media.)

In step 2, the cavity collapses, to return the remaining liquid B to the normal liquid condition. The energy change for this second step is $-\frac{1}{2}\varepsilon_{BB}A_B$. The net expenditure of energy for the process illustrated in Fig 1 is thus

$$\Delta\varepsilon = \varepsilon_{BB}A_B - \tfrac{1}{2}\varepsilon_{BB}A_B \qquad (1)$$

The molar energy of vaporization of B is therefore

$$\Delta E_{B,B\rightarrow V} = \tfrac{1}{2}N\varepsilon_{BB}A_B \qquad (2)$$

and the corresponding expression for the vaporization of A is

$$\Delta E_{A,A\to V} = \tfrac{1}{2} N \varepsilon_{AA} A_A \tag{3}$$

where N as Avogadro's number. Similarly, if a molecule of B is evaporated from an infinitely dilute solution in solvent A, creation of a cavity the size of a B molecule requires energy $\varepsilon_{AB}A_B$ (where ε_{AB} is the energy of interaction per unit area of contact of A and B molecules). When the cavity closes up, the energy change is $-\tfrac{1}{2}\varepsilon_{AA}A_B$. Therefore, the total energy change for vaporizing a mole of B from infinitely dilute solution in A is

$$\Delta E_{B,A\to V} = N \{\varepsilon_{AB} - \varepsilon_{AA}/2\} A_B \tag{4}$$

Analogously, to evaporate a mole of solute A from infinitely dilute solution in solvent B requires expenditure of energy

$$\Delta E_{A,B\to V} = N \{\varepsilon_{AB} - \varepsilon_{BB}/2\} A_A \tag{5}$$

Equations 2-5 can be combined to give

$$\Delta E_{B,A\to V} = \Delta E_{B,B\to V} + \frac{A_B}{A_A} (\Delta E_{A,B\to V} - \Delta E_{A,A\to V}) \tag{6}$$

and the symmetrical relation

$$\Delta E_{A,B\to V} = \Delta E_{A,A\to V} + \frac{A_A}{A_B} (\Delta E_{B,A\to V} - \Delta E_{B,B\to V}) \tag{7}$$

For a pair of nonpolar liquids, A and B, these equations can be used to predict the molar energy of vaporization of A dissolved in B from the reciprocal energy of vaporization of B dissolved in A, and vice versa.

Figure 2 indicates the reliability of eqs 6 and 7, using literature data processed by Yeo.[10] Abscissa values, $\Delta E^{calc}_{i,\ j\to V}$, represent energies of vaporization of solutes i from solvents j, calculated from eqs analogous to 6 and 7; the ordinate values are experimental quantities. For the nonpolar systems the agreement of calculated and experimental values is generally quite good, and even for mixtures of nonpolar liquids with polar, non-hydrogen-bonded liquids, relative errors are small. Large discrepancies are observed for mixtures of alcohols with nonpolar liquids.[10]

Gibbs free energy relations similar to eqs 6 and 7 can also be derived. When unit molarity, ideal dilute solution states are used, standard Gibbs free energies of vaporization for solutes i ($\Delta G_{i,j\to V}$) are nearly proportional to the corresponding internal energies of vaporization ($\Delta E_{i,j\to V}$) for a given solvent (j). Although the proportionality constant is somewhat solvent-dependent, for most nonpolar solvents (S) the slope of a plot of $\Delta G_{i,V\to S}$ vs. $\Delta E_{i,V\to S}$ is in the range 0.55 to 0.65.[11] Therefore, the relations

$$\Delta G_{B,A\to V} = \Delta G_{B,B\to V} + \frac{A_B}{A_A} (\Delta G_{A,B\to V} - \Delta G_{A,A\to V}) \qquad (8)$$

and

$$\Delta G_{A,B\to V} = \Delta G_{A,A\to V} + \frac{A_A}{A_B} (\Delta G_{B,A\to V} - \Delta G_{B,B\to V}) \qquad (9)$$

should be expected to apply with somewhat poorer reliability than eqs 6 and 7. (Standard states required in these equations are 1 M, ideal dilute solution states, even for components in their own pure liquid phase.[11,12] When treating thermodynamic data for a pure liquid in this way, the molar energy is equal to that of the liquid compound, but the molar entropy and free energy differ by $-R \ln \overline{V}$ and $RT \ln \overline{V}$, respectively, from the corresponding quantities for the pure liquid, where $\overline{V}$ is the molar volume of the liquid in liters/mole.)

Figure 3 is a plot of $\Delta G^{calc}_{i,j\rightarrow V}$ vs. experimental values of $\Delta G_{i,j\rightarrow V}$ for a number of nonelectrolyte systems. Again agreement is reasonably good for the nonpolar mixtures, and also for mixtures of nonpolar with slightly polar liquids. Calculated results for mixtures of hydrogen-bonded liquids with nonpolar liquids are not at all in agreement with experimental values.

A Model for Aqueous Solute Systems

The failure of eqs 6-9 to predict properties of hydrogen-bonded systems implies that local order in the vicinity of solute molecules introduces thermodynamic terms not accounted for in the simple interfacial contact model. Although the problem of determining the nature and extent of ordered water regions around aqueous solutes is quite difficult, we suggest that something can be learned about the organized water regions by determining differences between observed evaporation energies and free energies of aqueous solutes and values of these quantities calculated from the interfacial model.

We now consider the evaporation of a nonpolar solute, B, from its infinitely dilute aqueous solution. Figure 4, step 1 is the process of evaporating B from aqueous solution, leaving a hole the size of a B molecule. The ordered water region originally present around solute B is not altered in this step. In step 2, the ordered region is transformed into normal liquid water, but the hole persists. (No consideration is given here to the possibility that there may be a small volume change accompanying reorientation of the water molecules.) Finally, in step 3, the cavity collapses, and only ordinary bulk water remains.

If the 3-step process presented in the preceding paragraph is a reasonable one for describing the evaporation of solute B, it should be possible to infer thermodynamic constants for the rearrangement of ordered water (step 2) from calculated values of thermodynamic constants for steps 1 and 3 and the measurable properties of the overall evaporation of B. We propose that it is reasonable to calculate ΔE and ΔG for the initial evaporation of B and the collapse of the cavity (step 1 plus step 3) by using eqs 6 and 8, where A now represents water, and where it is assumed that the area of a water molecule and the interfacial energy or free energy of interaction (per unit area) of B with water are the same in the aqueous system as in a solution of water in the solvent B. The fact that water is more highly ordered around B in the original aqueous solution than in bulk should not greatly change the inductive and dispersive interactions between these water molecules and B. (Our confidence in this assumption is strengthened by the success of the nonpolar analog model[13,14] as applied to dilute solutions of polar solutes in nonpolar media; in these systems, orientation effects are absent, and the polar solute-nonpolar solvent interactions lead to energy and free energy effects which are apparently no more difficult to model than the dispersive interactions in completely nonpolar systems.) The collapse of the cavity (step 3) involves only the creation of new water-water contacts between molecules already in the normal liquid condition, and the ΔE and ΔG contributions from these interactions should be predicted properly by the interfacial model (and included in eqs 6 and 8).

By difference, then, one may estimate that the energy and free energy terms pertaining to step 2 are

$$-\Delta E_{\text{orientation}} = \Delta E_{B,H_2O\to V} - \Delta E_{B,B\to V} - \frac{A_B}{A_{H_2O}}(\Delta E_{H_2O,B\to V} - \Delta E_{H_2O,H_2O\to V}) \qquad (10)$$

and

$$-\Delta G_{\text{orientation}} = \Delta G_{B,H_2O\to V} - \Delta G_{B,B\to V} - \frac{A_B}{A_{H_2O}}(\Delta G_{H_2O,B\to V} - \Delta G_{H_2O,H_2O\to V}) \qquad (11)$$

(The latter expression--eq 11-- should be somewhat less reliable than eq 10 because of failure of the assumption that transfer free energies are strictly proportional to transfer energies.)

In Figure 5, $-\Delta E_{\text{orientation}}$ and $-\Delta G_{\text{orientation}}$ (calculated from eqs 10 and 11) are plotted vs. molar volume$^{2/3}$ for a number of nonpolar and slightly polar solutes in water. (The molar volume$^{2/3}$ terms are nearly proportional to molecular area, provided the molecules are approximately spherical.) Several features of the plot are of interest. First, the energies and free energies of orientation are quite large--on the order of tens of kilocalories per mole for the systems represented in the plot. Second, there is an approximately linear increase in both the energy and free energy of orientation with increasing molecular area, as might be expected if the number of water molecules which are oriented around a given solute is proportional to the solute area. The ΔG and ΔE values both seem to tend toward zero at values of molar volume$^{2/3}$ approximately equal to 10 (cc/mole)$^{2/3}$; this may indicate that solute molecules which are sufficiently small can be accomodated in the liquid water structure with a mimimum of reorientation of water molecules.[3] Finally, for the 13 systems for which both the energy and free energy of orientation can be calculated, the two quantities are quite nearly directly proportional to each other; the empirical relation $-\Delta G_{\text{orientation}} = 0.50(-\Delta E_{\text{orientation}})$ provides a good correlation of results for these systems.

One can interpret the results in Fig 5 by assuming that the transformation of normal liquid water into more highly structured water (the reverse of step 2 in Fig 4) involves the conversion of liquid water into an ordered structure energetically similar to ice. If this is roughly correct, the approximate number of molecules involved in the reorientation, n, can be calculated from the expression $n = -\Delta E_{\text{orientation}} \div 1440$ cal/mole, where 1440 cal/mole is the energy of fusion of ice. Table I lists values of n and molecular area (in $\mathring{A}^2$) for the 13 systems for which energy of orientation data are available. Included in the table are estimated values of n for systems for which $-\Delta G_{\text{orientation}}$ (but not $-\Delta E_{\text{orientation}}$) has been computed. For these systems the relation $n = 2(-\Delta G_{\text{orientation}})/1440$ cal/mole has been used. Molecular areas have been estimated by assuming that each solute molecule is spherical, with a molecular volume equal to the molar volume of the pure liquid divided

TABLE I

ESTIMATED NUMBER OF ORIENTED WATER MOLECULES AND AREA PER ORIENTED MOLECULE FOR AQUEOUS SOLUTES

solute	$-\Delta E_{orientation}$(kcal/mole)	n[a]	A_{solute}(Å^2)[b]	A_{solute}/n(Å^2/molecule)
CCl_4	22.9	15.9	144	9
C_6H_6	18.0	12.5	136	11
$C_6H_5CH_3$	21.9	15.3	153	10
m-$C_6H_4(CH_3)_2$	24.4	17.0	168	10
C_6H_5Cl	19.0	13.3	148	11
o-$C_6H_4Cl_2$	21.7	15.0	159	11
$C_6H_5C_2H_5$	23.4	16.3	168	10
CCl_3CH_2Cl	18.4	12.8	155	12
$CHCl_2CH_2Cl$	15.8	11.0	140	13
CCl_3CH_3	20.4	14.2	146	10
CH_2ClCH_2Cl	13.5	9.4	135	13
$CHCl_2CH_3$	16.1	11.2	131	12
$CHCl_3$	15.5	10.8	126	12
$C_6H_5C_4H_9$	33.8[c]	23.6	197	8
p-C_6H_5Cl	21.6[c]	15.0	157	10
C_6H_5Br	20.9[c]	14.5	151	10
n-C_7H_{16}	30.4[c]	21.2	190	9

TABLE I (continued)

solute	$-\Delta E_{orientation}$(kcal/mole)	n^{a}	$A_{solute}(\mathring{A}^{2})^{b}$	$A_{solute}/n(\mathring{A}^{2}$/molecule)
n-C_6H_{14}	28.8^{c}	20.0	176	9
n-C_8H_{18}	34.7^{c}	24.1	203	8
2,2,4-$C_5H_9(CH_3)_3$	33.2^{c}	23.1	205	9
c-C_5H_{10}	21.9^{c}	15.2	141	9
c-C_6H_{12}	24.4^{c}	17.0	155	9
c-$C_5H_9(CH_3)$	24.9^{c}	17.3	158	9
c-$C_6H_{11}(CH_3)$	27.3^{c}	19.0	172	9
c-C_6H_{10}	20.7^{c}	14.4	148	10
$CH_2ClCHClCH_3$	27.9^{c}	11.6	144	10

a. $n = -\Delta E_{orientation} \div 1.44$ kcal/mole

b. A_{solute} is the molecular surface area, estimated from molar volume of pure liquid solute.

c. Estimated from $\Delta E_{orientation} = 2\Delta G_{orientation}$.

by Avogadro's number. The ratios of molecular area to n are mostly in the range 9 to 12 $\mathring{A}^2$/molecule. These numbers are reasonably close to the estimated cross-sectional area of a water molecule (12 $\mathring{A}^2$) calculated from the density of liquid water, treating the molecule as sperical.

Summary and Conclusions

The interfacial energy model can be used to estimate the energy, free energy, and entropy of orientation of water molecules around aqueous solutes. The magnitudes of the energies of orientation are in the range 13 to 35 Kcal/mole for hydrocarbon and halogenated hydrocarbon solutes having molar volumes in the range 80 to 170 cc/mole. Gibbs free energies of orientation are nearly half of the energies of orientation; entropies of orientation vary from -22 to -60 e.u./mole.

Assuming that the structured water region around solutes is energetically similar to ice, one can infer that one water molecule is oriented for each 8 to 12 $\mathring{A}^2$ of solute molecular surface. Thus, a reasonable picture of the aqueous solvent region in the vicinity of solutes is that a nearly close-packed molecular layer of water, having ice-like properties, surrounds the dissolved organic molecules. (One could, of course, assume that the ordered region extends through several layers of water molecules, with smaller energetic effects per layer.) The entropy change per mole of ordered water is approximately -2.5 e.u., about half the entropy of fusion of ice at 0°.

The simple energetic model introduced here leads to a description of the structured water region around dissolved organic molecules which is somewhat at variance with current views about hydrophobic interactions. One can use numerical estimates of interaction energies and the energetic effects of ordering to predict the tendency of hydrocarbon groups or molecules to cluster in aqueous solution. For example, if two benzene molecules should form a dimer by planar stacking, the expected loss of water molecules in the ordered region might be on the order of one-third of the total number in the structured region (about 25/3 = 8); therefore, for the reorganization of structured water which accompanies dimerization, $\Delta E \sim 8 \times 1.4$ kcal = 11 kcal and $\Delta S \sim 8 \times 2.5$ e.u. = 20 e.u. The free energy change for this contribution is thus about + 5 kcal, which by itself would strongly oppose clustering. However, during the dimerization process, water-benzene contacts are destroyed and replaced by water-water and benzene-benzene contacts. Letting B and W denote benzene and water molecules, respectively, we can express the energy change for the regrouping of molecular contacts as

$$\Delta E = (2/3)N \{A_B\varepsilon_{BW} - \tfrac{1}{2}A_B\varepsilon_{BB} - \tfrac{1}{2}A_B\varepsilon_{WW}\}$$

or $$\Delta E = (2/3)\frac{A_B}{A_W}(\Delta E_{W,B\to V} - \Delta E_{W,W\to V}) = 2 \times 3.38 - 2 \times 9.91 \text{ kcal} = -13 \text{ kcal}.$$

(In this calculation it is assumed that $A_B/A_W = 3$ and that two-thirds of the molecular area of a benzene molecule--1/3 of the area of each of the two combining molecules--is removed from molecular contact with water as the dimer forms.) The dominant term in this energy expression is the negative internal energy change (-19.8 kcal) which results from the formation of new water-water contacts upon dimerization. Combining the effects of reorganization of structured water and regrouping of molecular contacts, we estimate that the dimerization of benzene should occur exothermically, with a total energy change of about -13 + 11 kcal = -2 kcal. A similar (but probably somewhat less negative) free energy change would be expected, but equations deriving from the present interfacial energy model do not provide reliable estimates of the overall free energy of dimerization.

Analyses such as the preceding lead to the interesting conclusion that the loss of structured water around associating hydrocarbon groups results invariably in positive free energy changes. The entropy change resulting from "melting" of the structured water is positive, but the entropic contribution to the free energy is less in magnitude than the unfavorable endothermic energy change which occurs when the ordered region is diminished in extent. According to the present point of view, the driving force for "hydrophobic bonding" is furnished mainly by formation of new water-water contacts, which produces large negative changes in energy and free energy.[15]

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15. See reference 4 for a discussion of the importance of water-water molecular interactions in aqueous solute systems.

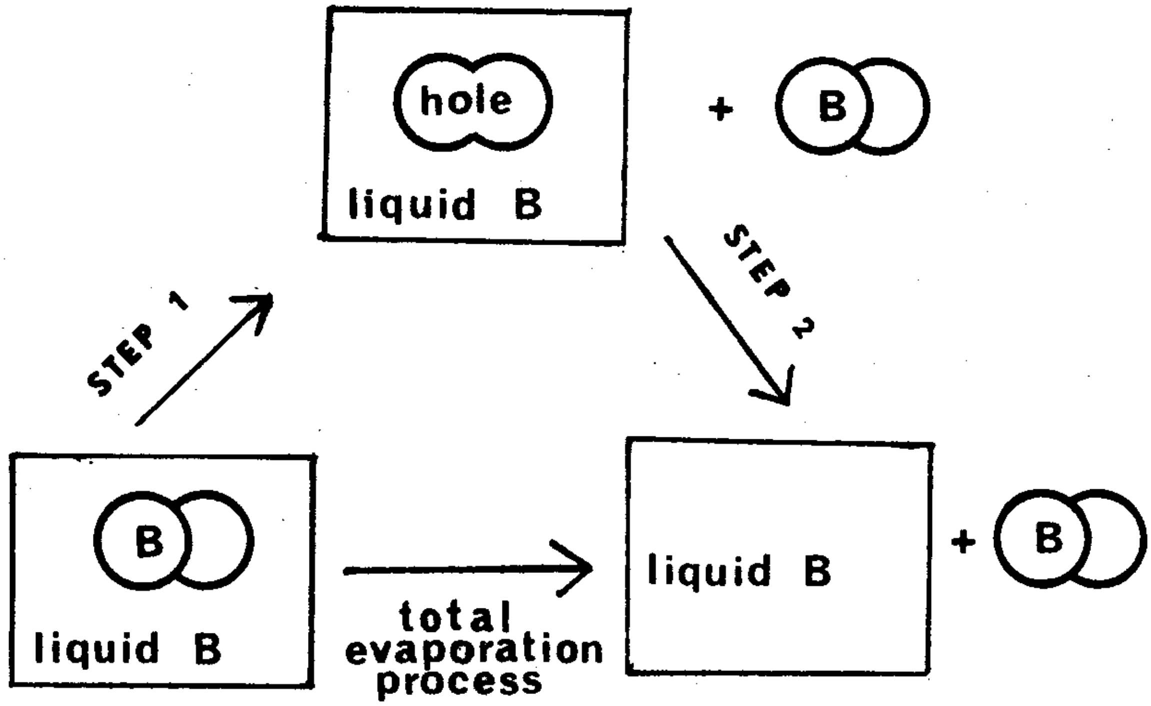

hole
liquid B
+
B
STEP 1
STEP 2
B
liquid B
total evaporation process
liquid B
+
B

Figure 1. Evaporation of a molecule from liquid B.

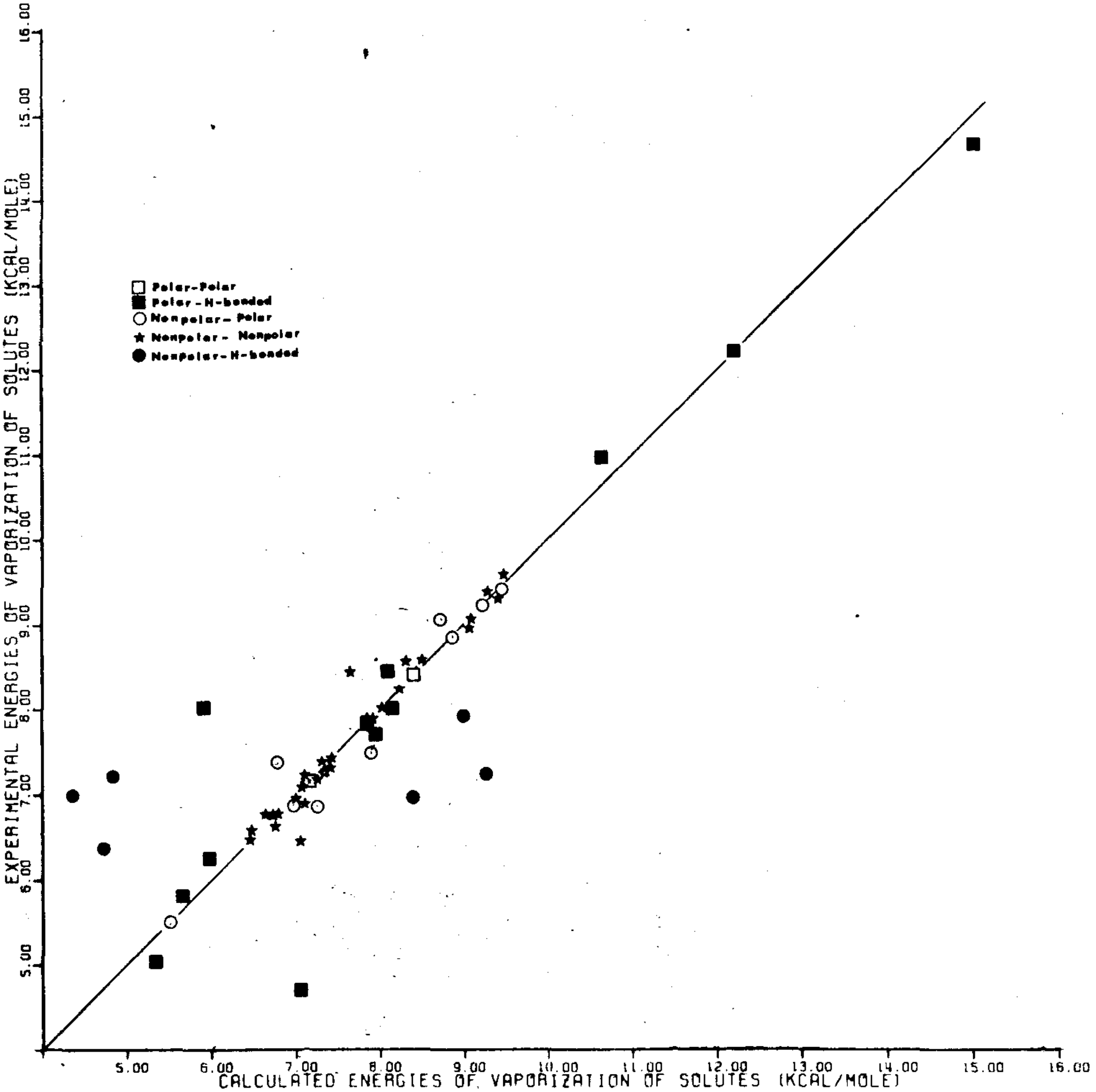


Figure 2. Experimental and calculated energies of vaporization of solutes from infinitely dilute solution in various solvents. Points are coded to represent various classes of mixtures. Data tabulated in reference 10.

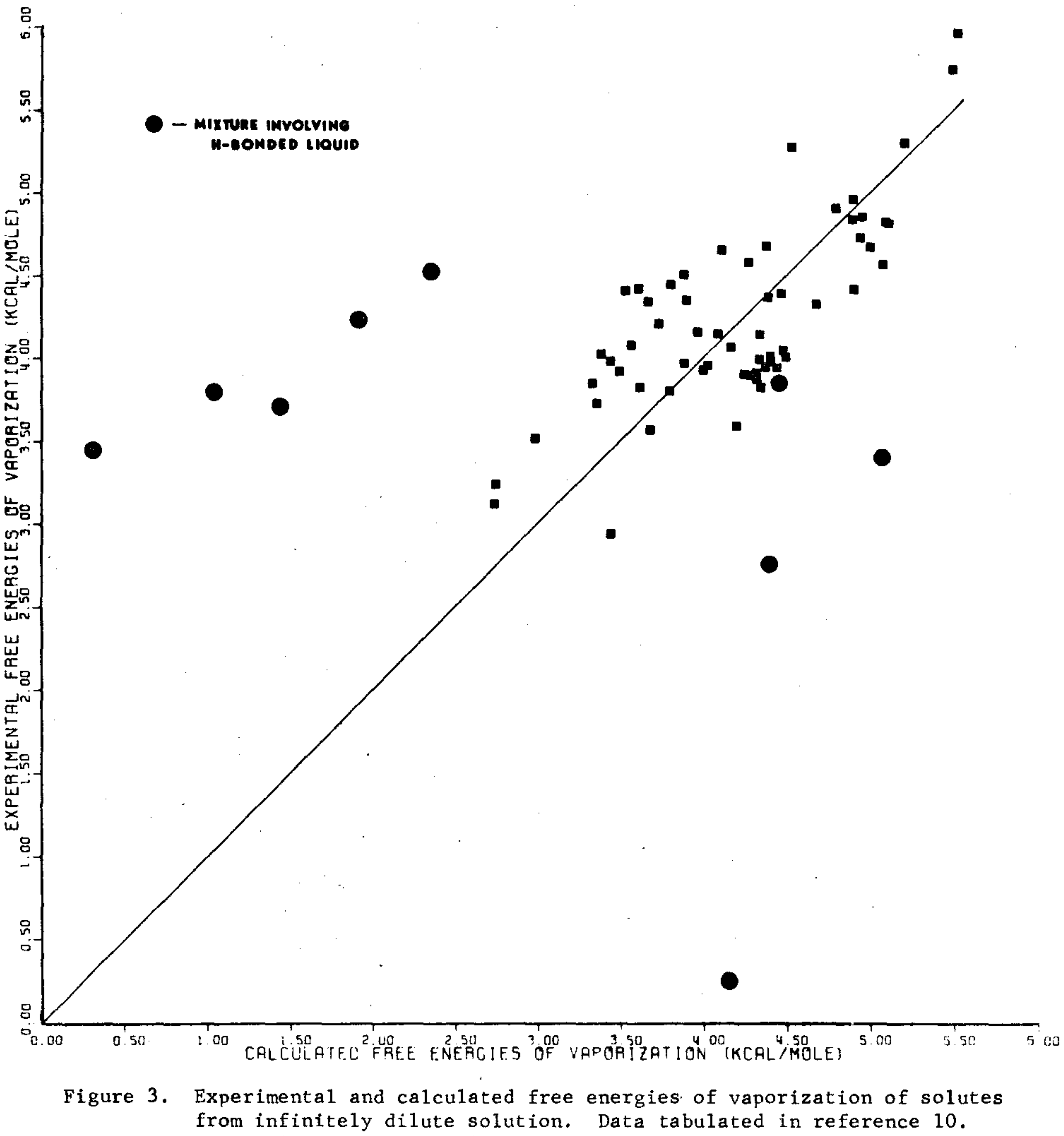


Figure 3. Experimental and calculated free energies of vaporization of solutes from infinitely dilute solution. Data tabulated in reference 10. Unit molarity, ideal dilute solution standard states are employed for solutes.

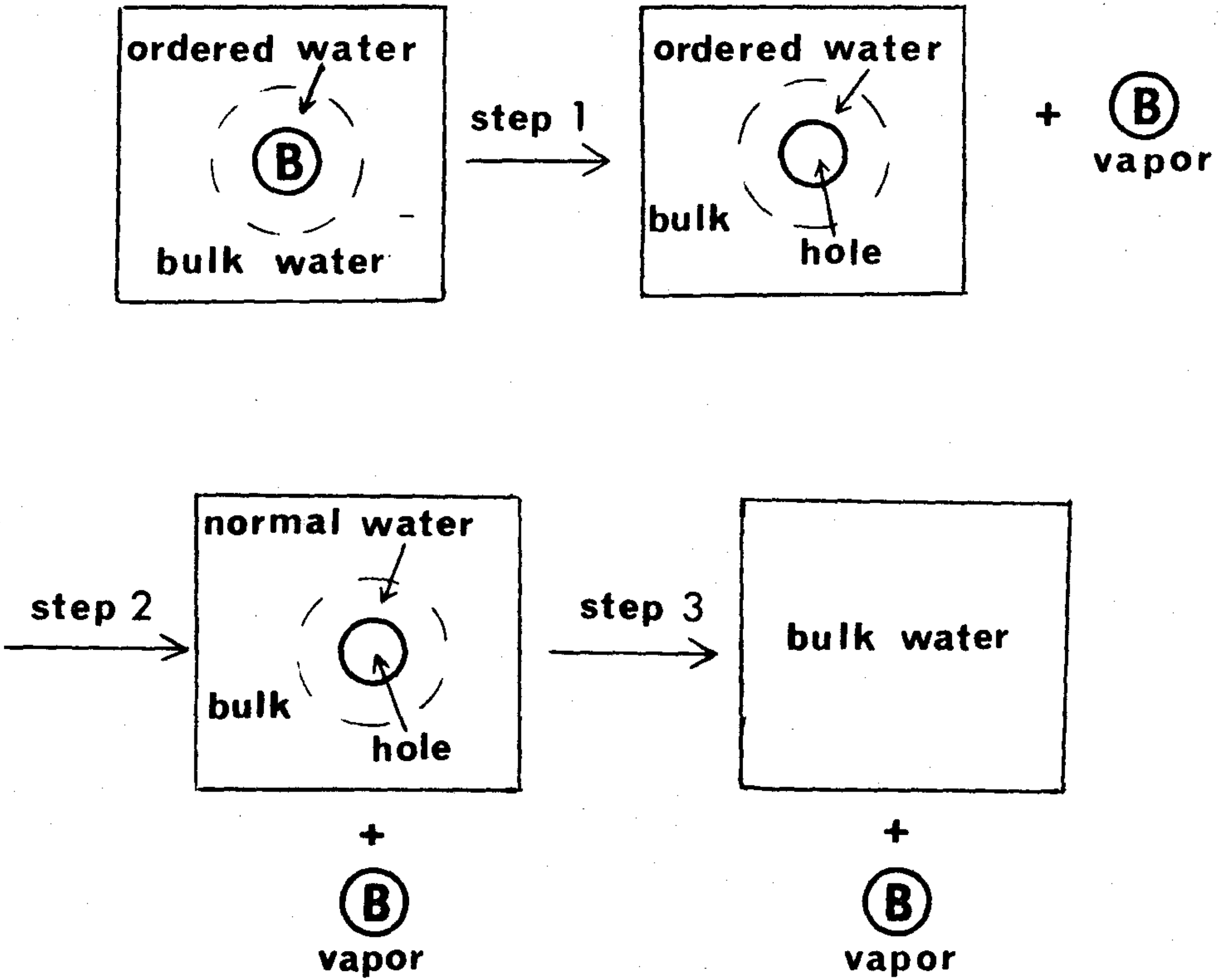
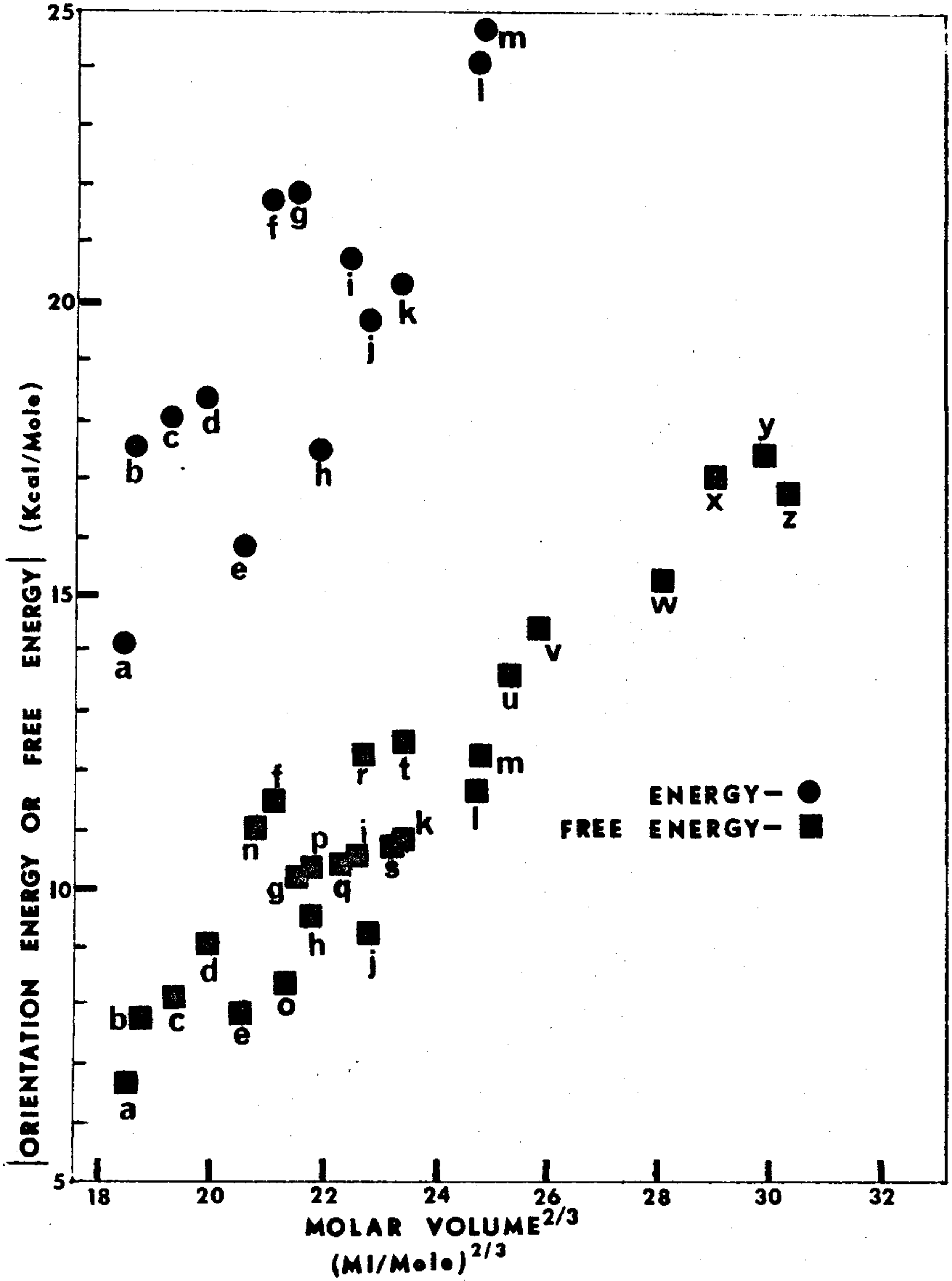

ordered water
B
bulk water
step 1
ordered water
bulk
hole
+
B
vapor
step 2
normal water
bulk
hole
+
B
vapor
step 3
bulk water
+
B
vapor

Figure 4. Evaporation of an aqueous solute species.

Figure 5. Dependence of orientaiton energy and free energy of aqueous solutes on molar surface area (molar volume$^{2/3}$). Solutes: a) CH_2ClCH_2Cl; b) $CHCl_3$; c) $CHCl_2CH_3$; d) C_6H_6; e) $CHCl_2CH_2Cl$; f) CCl_4; g) CCl_3CH_3; h) C_6H_5Cl; i) $C_6H_5CH_3$; j) CCl_3CH_2Cl; k) o-$C_6H_4Cl_2$; l) $C_6H_5C_2H_5$; m) m-$C_6H_4(CH_3)_2$; n) c-C_5H_{10}; o) $CH_2ClCHClCH_3$; p) c-hexene; q) C_6H_5Br; r) c-hexane; s) p-$C_6H_4Cl_2$; t) c-$C_5H_9CH_3$; u) c-$C_6H_{11}CH_3$; v) n-C_6H_{14}; w) n-C_7H_{16}; x) $C_6H_5C_4H_9$; y) n-C_8H_{18}; z) 2,2,4-$C_5H_9(CH_3)_3$.

Results taken from reference 10.

Figure 5. Dependence of orientation energy and free energy of aqueous solutes on molar surface area.



APPENDIX

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A Thermodynamic Method for Predicting Solubilities of Solutes in Nonpolar Solvents

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A general thermodynamic method permits prediction of the temperature dependence of solubilities of solutes distributed between nonpolar solvents and vapor. Only properties of the pure solvents and the solubility of each solute at one temperature are required.

Introduction

Frequent use has been made of empirical linear relations among the thermodynamic variables pertaining to the transfer of solutes from one phase to another. For example, it has been shown that the entropy of vaporization of gases from dilute solution in nonpolar and moderately polar solvents varies linearly with the enthalpy of vaporization (Barclay and Butler, 1938; Bell, 1937). More recently, it has been demonstrated that the entropy of vaporization of gases dissolved in nonpolar solvents is linearly related to the logarithm of gas solubilities or free energies of solution (Hildebrand, *et al.*, 1970). Research from this laboratory has indicated the utility of linear relations between the free energy and energy of transfer of solutes from one phase to another in predicting the effects of solvents on molecular complex formation equilibria (Christian and Grundnes, 1968; Christian and Lane, 1974; Christian, *et al.*, 1973). The present article describes a convenient method for using linear relations of these types in predicting the solubilities of gases and vapors over a wide range of temperatures.

Method of Calculation

Consider the distribution of a solute (i) between the vapor phase (v) and a nonpolar solvent (s). In the dilute solution region, where i obeys the ideal gas equation in the vapor phase and Henry's law in the condensed phase, the partition coefficient for i is constant (at constant temperature) and defined by

$$K_{\mathrm{D,i}} = c_{\mathrm{i,s}}/c_{\mathrm{i,v}} \tag{1}$$

where $c_{\mathrm{i,s}}$ and $c_{\mathrm{i,v}}$ are the equilibrium molar concentrations of i in s and v, respectively. (We assume that the vapor pressure of the solvent is not great enough to cause the fugacity of the gas to differ significantly from its partial pressure, calculated from Dalton's law and the ideal gas equation.) Using the unit molarity ideal dilute solution standard states for i (in both phases), expressions may be derived to relate the internal energy and Gibbs free energy of transfer of solutes from v to s. Thus

$$\Delta G^\circ_{\mathrm{i,v\to s}} = -RT \ln K_{\mathrm{D,i}} \tag{2}$$

and

$$\Delta E^\circ_{\mathrm{i,v\to s}} = RT^2(\mathrm{d} \ln K_{\mathrm{D,i}}/\mathrm{d}T) + \alpha_{\mathrm{S}} RT^2 \tag{3}$$

where α_{S} is the coefficient of thermal expansion of the pure solvent. Note that $K_{\mathrm{D,i}}$ may be calculated from the partial pressure of the solute (p_{i}) and its mole fraction in the condensed phase (x_{i}) by the relation

$$K_{\mathrm{D,i}} = x_{\mathrm{i}}RT/p_{\mathrm{i}}\bar{V}_{\mathrm{S}} \tag{4}$$

where $\bar{V}_{\mathrm{S}}$ is the molar volume of the solvent. Equations 1–4 apply also to the pure solvent itself, where $x_{\mathrm{i}} = 1$, $c_{\mathrm{S,s}} = 1/\bar{V}_{\mathrm{S}}$ and $c_{\mathrm{S,v}} = p_{\mathrm{S}}^\circ/RT$. The vapor pressure of pure solvent (p_{S}°) is assumed to be small enough so that the vapors of the solvent may be treated as ideal.

One reason for casting the thermodynamic equations in the somewhat unfamiliar forms given here (eq 1–4) is the simplicity of the linear free energy–internal energy relations which can be derived for solutes if the unit molarity states are used. Figure 1 shows a plot of $\Delta G^\circ_{\mathrm{i,v\to s}}$ *vs.* $\Delta E^\circ_{\mathrm{i,v\to s}}$ at 25° for a number of solutes in cyclohexane, including the point (x) which pertains to the transfer of the solvent itself from vapor to condensed phase. The intercept at $\Delta E^\circ_{\mathrm{i,v\to s}} = 0$ is approximately $\Delta G^\circ_{\mathrm{i,v\to s}} = 300$ cal/mol, which corresponds to an entropy of transfer of about −3 entropy units. Thus, the transfer of a solute which dissolves in the solvent with no change in partial molar internal energy occurs with an entropy change of about $-3R/2$. Although it might be interesting to speculate about the origin of this entropy term, it is more useful in relation to the present discussion to note that very nearly the same intercept value ($\Delta G^\circ_{\mathrm{i,v\to s}} = 300$ cal/mol at $\Delta E^\circ_{\mathrm{i,v\to s}} = 0$) obtains for all of the nonpolar solvents for which plots of $\Delta G^\circ_{\mathrm{i,v\to s}}$ *vs.* $\Delta E^\circ_{\mathrm{i,v\to s}}$ have been constructed.

Thus, the simple equation

$$\Delta G^\circ_{\mathrm{i,v\to s}} = \beta_S \Delta E^\circ_{\mathrm{i,v\to s}} + 300 \text{ cal/mol} \qquad (5)$$

where β_S is a constant characteristic of the solvent alone, summarizes a large amount of information about the transfer of solutes into nonpolar media at 25°. Values of β_S are nearly equal to 0.60 for many common organic solvents, excluding fluorocarbons. For example, β_S = 0.59, 0.64, 0.65, 0.65, and 0.51, respectively, for the solvents heptane, benzene, cyclohexane, carbon tetrachloride, and perfluoroheptane. It should be emphasized that once the intercept value (300 cal/mol) has been accepted as correct for nonpolar solvents in general, no fitting parameters are required in drawing lines such as that which correlates transfer free energies and energies (displayed as in Figure 1) or in calculating values of β_S to use in eq 5. β_S is calculated by using eq 5 with experimental values of the transfer energy and free energy of the pure solvent at 25°.

Hildebrand, *et al.* (1970), have noted that the existence of linear correlations of entropy of solution with log x_i indicates the feasibility of predicting the temperature dependence of the solubility of a gas in a given solvent from the value of its solubility at a single temperature. The simple form of eq 5, and its apparent generality, permits predictions of this type to be made in a straightforward way, using only constants derivable from known experimental properties of the solvent. We start with the observation that log $K_{\mathrm{D,i}}$ commonly varies linearly with T^{-1} over a relatively wide range of temperature, where i represents either the solvent or any solute distributed between vapor and condensed phase. Next, we note that if this linear relation is assumed to hold exactly, eq 3 requires that $\Delta E^\circ_{\mathrm{i,v\to s}} - \alpha_S RT^2$ will be strictly constant. Equation 3 may then be written in the integrated form

$$\ln K_{\mathrm{D,i}} = -\frac{[\Delta E^\circ_{\mathrm{i,v\to s}} - \alpha_S RT^2]_{T=298}}{RT} + \text{constant} \qquad (6)$$

where the bracketed term is to be evaluated at a given temperature, in this case 25°.

Whether $K_{\mathrm{D,i}}$ increases or decreases with increasing temperature depends, therefore, on whether $\Delta E^\circ_{\mathrm{i,v\to s}} - \alpha_S RT^2$ is negative or positive at 25°. There will exist a critical value of $K_{\mathrm{D,i}}$ (say, K_D*) toward which $K_{\mathrm{D,i}}$ will trend as T increases. That is, if $K_{\mathrm{D,i}}$ at 25° is less than $K_{\mathrm{D,i}}$ will equal K_D*. That a unique intersection point whereas if $K_{\mathrm{D,i}} > K_D$*; $K_{\mathrm{D,i}}$ will decrease. Combination of eq 2, 5, and 6 leads to an expression from which K_D* may be calculated explicitly. Thus, if $K_{\mathrm{D,i}} = K_D$*

$$\Delta E^\circ_{\mathrm{i,v\to s}} = \alpha_S RT^2(\text{evaluated at } 298°\mathrm{K}) = (\Delta G^\circ_{\mathrm{i,v\to s}} - 300 \text{ cal/mol})/\beta_S$$

$$-R(298.16°\mathrm{K}) \ln K_D{}^* = 300 \text{ cal/mol} + \alpha_S\beta_S R(298.16°\mathrm{K})^2$$

and

$$K_D{}^* = \exp\left[\frac{-300 \text{ cal/mol}}{(298.16°\mathrm{K})R} - \alpha_S\beta_S(298.16°\mathrm{K})\right] \qquad (7)$$

For cyclohexane, the critical value of the partition coefficient is calculated to be $K_D{}^* = 0.48$, using values of α_S and β_S for that solvent.

In predicting solubilities or partition coefficients of solutes as a function of T, it is useful to invent a hypothetical temperature T*, characteristic of the solvent, at which the log $K_{\mathrm{D,i}}$ *vs.* $1/T$ curves will all intersect and at which $K_{\mathrm{D,i}}$ will equal K_D*. That a unique intersection point will exist can be shown by (a) combining eq 5, 2, and 7 to obtain

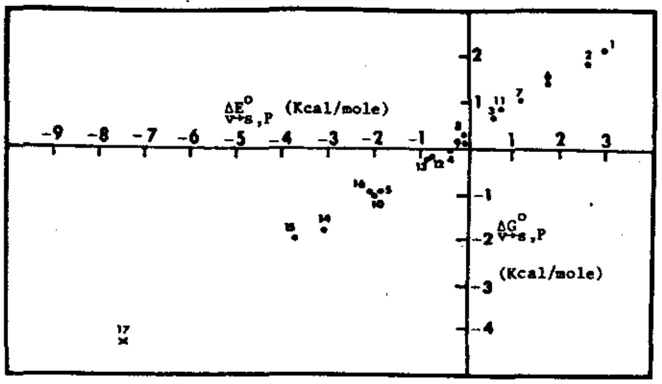

Figure 1. Correlation of energies and free energies of transfer of solutes from gas to cyclohexane at 25°C. Solutes: helium (1); neon (2); argon (3); krypton (4); xenon (5); hydrogen (6); nitrogen (7); oxygen (8); methane (9); ethane (10); carbon tetrafluoride (11); sulfur hexafluoride (12); perfluoropropane (13); propane (14); cyclopropane (15); perfluorocyclobutane (16); cyclohexane (17). See Yeo (1973) for original references.

$$\ln K_{\mathrm{D,i}}(\text{at } 298°\mathrm{K}) = \frac{-\beta_S\Delta E^\circ_{\mathrm{i,v\to s}}}{R(298.16°\mathrm{K})} - \frac{300 \text{ cal/mol}}{R(298.16°\mathrm{K})}$$

$$\ln K_D{}^* = \frac{-300 \text{ cal/mol}}{R(298.16°\mathrm{K})} - \alpha_S\beta_S(298.16°\mathrm{K})$$

and

$$\ln \frac{K_{\mathrm{D,i}}(\text{at } 298°\mathrm{K})}{K_D{}^*} = \frac{-\beta_S}{R(298.16°\mathrm{K})}[\Delta E^\circ_{\mathrm{i,v\to s}} - \alpha_S R(298.16°\mathrm{K})^2] \qquad (8)$$

and (b) by comparing eq 8 with the definite form of eq 6 which is obtained by setting $K_{\mathrm{D,i}} = K_D$* at $T = T$*

$$\ln \frac{K_{\mathrm{D,i}}(\text{at } 298°\mathrm{K})}{K_D{}^*} = -\left(\frac{1}{298.16°\mathrm{K}} - \frac{1}{T^*}\right)\frac{[\Delta E^\circ_{\mathrm{i,v\to s}} - \alpha_S R(298.16°\mathrm{K})^2]}{R} \qquad (9)$$

Equations 8 and 9 can both be valid only if $1/298.16°\mathrm{K} - 1/T^* = \beta_S/298.16°\mathrm{K}$ or

$$T^* = 298.16°\mathrm{K}/(1 - \beta_S) \qquad (10)$$

Thus, no matter which solute is chosen, the temperature at which $K_{\mathrm{D,i}}$ extrapolates to the value K_D* will be the same, *viz.*, that given by eq 10. In other words, if α_S and β_S are known for a given solvent, values of K_D* and T* may be calculated from eq 7 and 10. Then, on a plot of log $K_{\mathrm{D,i}}$ *vs.* $1/T$, the single point (log K_D*) may be located, and a family of straight lines may be drawn radiating from that point. Under the assumptions of the present derivation, these lines will represent possible partition coefficient curves for solutes in the given solvent. K_D data for the pure solvent should also fit on a single straight line drawn from the fixed point (log K_D*, $1/T$*).

Results

Figure 2 displays partition coefficient data for several solutes in cyclohexane. The solid lines are curves which can be used to predict the variation of $K_{\mathrm{D,i}}$ or the solubility of each solute i with temperature. The calculated curves are seen to provide a reliable prediction of the dependence of $K_{\mathrm{D,i}}$ on T for most of these solutes. Data for the solvent itself indicate that only in the vicinity of the critical point does departure from linearity become pronounced. Similar data and predicted curves are given in Figure 3 for solutes in the solvent carbon tetrachloride. Again, the results show that evaluation of the coordinates

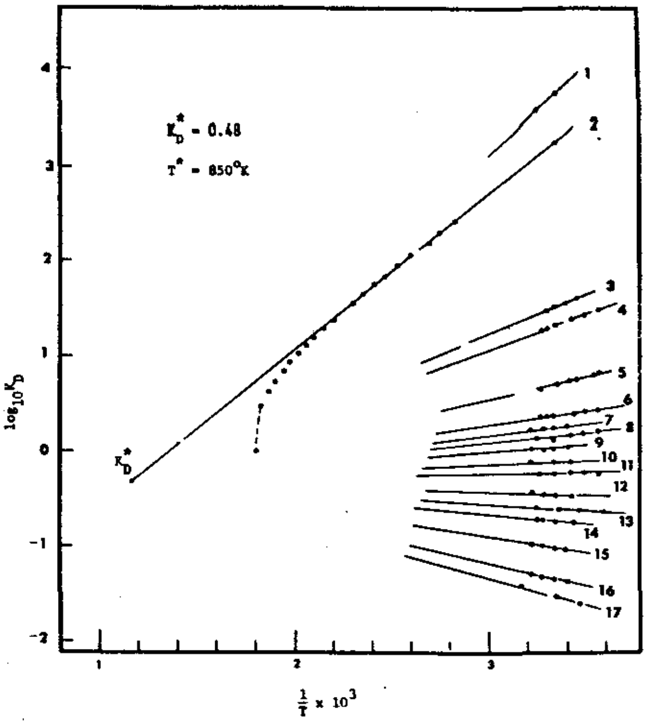

Figure 2. Variation of $K_{D,i}$ with temperature in cyclohexane. Solutes: iodine (1); cyclohexane (2); cyclopropane (3); propane (4); perfluorocyclobutane (5); chlorotrifluoromethane (6); carbon dioxide (7); perfluoropropane (8); krypton (9); methane (10); hexafluoroethane (11); argon (12); carbon tetrafluoride (13); nitrogen (14); hydrogen (15); neon (16); helium (17). See Yeo (1973) for original references.

of the single point, ($\log K_D^*$, $1/T^*$), permits the accurate prediction of partition coefficient curves for a wide variety of solutes. Note that solid solubilities can also be correlated by these curves, provided vapor pressure–temperature data are available for the pure solid.

Discussion

The equations and graphical method presented here are simple and apparently quite general for predicting the thermodynamic behavior of solutes in nonpolar solvents. Partial justification for the fact that polar, as well as nonpolar, solutes can be treated by the method is provided in recent reports from this laboratory on the nonpolar analog (NPA) method (Christian, *et al.*, 1973). In predicting thermodynamic properties of dilute solutions in which orientation (dipole–dipole) forces and retardation effects can be neglected, a polar solute (P) can be replaced by a hypothetical nonpolar analog molecule having the same size and shape and the same total energy of interaction with the solvent as does P. In this way, the inherently complicated polar solute–nonpolar solvent system is mapped into a simpler analog system in which only nonpolar species are involved. So long as only the dilute solution region is considered, the application of theories of solution to such systems is thereby considerably simplified.

Finally, we should like to emphasize the convenience of using unit-molarity, ideal-dilute-solution standard states for solutes in both phases in considering thermodynamic constants for the transfer reactions

solute (gas phase) = solute (dilute solution in solvent S)

When the more common mole fraction states for condensed phases and pressure states for gases are employed, the transfer equilibrium constant is not dimensionless and the standard free energy and entropy changes are not small even for solutes which transfer with nearly zero internal energy change, but if the unit molarity states are used, the solutes for which $\Delta E°_{i,V\rightarrow S} \sim 0$ have free energies of transfer of only a few tenths kcal/mol and partition coefficient (K_D) values on the order of 0.5. The critical K_D^* value (which demarcates the class of systems for which K_D increases with increasing temperature from those for which K_D decreases with increasing T) can be derived simply from properties of the pure solvent. Thus, extensive predictions of thermodynamic constants pertaining to the transfer of solutes from gas to solution can be made solely from experimental information about the solvent.

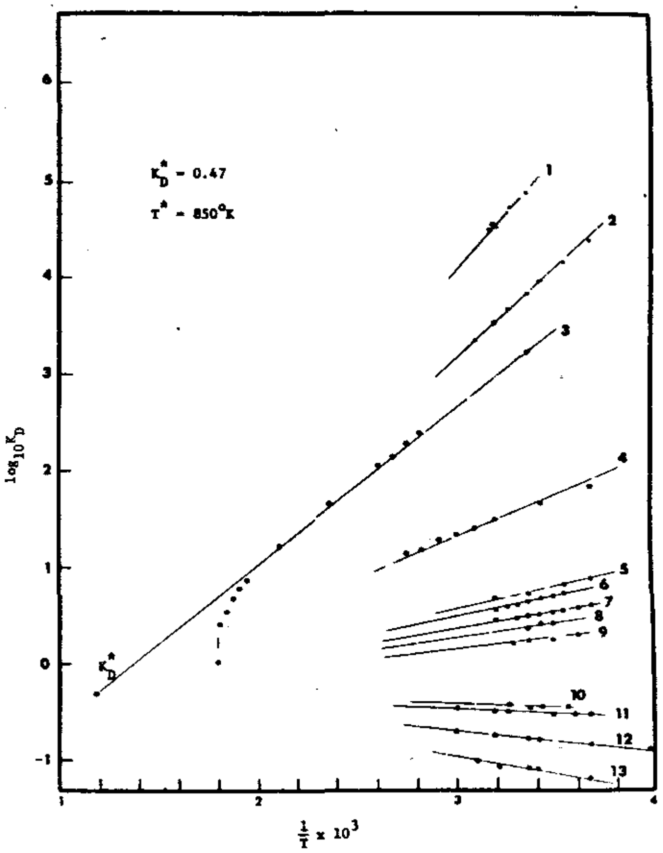

Figure 3. Variation of $K_{D,i}$ with temperature in carbon tetrachloride. Solutes: phosphorus (1); iodine (2); carbon tetrachloride (3); chlorine (4); ethane (5); nitrous oxide (6); acetylene (7); carbon dioxide (8); sulfur hexafluoride (9); nitric oxide (10); argon (11); carbon tetrafluoride (12); hydrogen (13). See Yeo (1973) for original references.

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