Hydrogen Bond Cooperativity in Suprabinary Complexes. Vapor Pressure Data for the Methanol-*n*-Hexadecane-*N*,*N*-Dimethyltetradecylamine System

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Abstract: Vapor pressure data for methanol dissolved in solutions covering the entire binary solvent composition range between *n*-hexadecane and *N*,*N*-dimethyltetradecylamine are reported. Dilute solution data for methanol-amine complexes are fit within experimental precision by the $1 - \infty$ model with two parameters, K_{11} and K_∞. The results of model-independent treatment of the dilute solution data, via a Gibbs-Duhem type of integration, support both the uniqueness of the $1 - \infty$ model for the present system and the presence of cooperative hydrogen bonding effects. We have been able to demonstrate by use of these experimental data both an increase in the basicity of the oxygen atom in methanol upon formation of the 1:1 complex MeOH··-N-R$_3$ and an increased acidity (relative to monomeric methanol) of the free end proton in small linear methanol chain polymers. Additionally, values of K_{11} for AB complex formation in dilute solution are compared with K_{11} values predicted via a pure base approach. K_{11} values from the pure base approach are substantially larger than the dilute solution K_{11} values thus implying the presence of rather large activity coefficient effects occurring as the solvent is varied over the composition range from pure hexadecane to pure amine.

Introduction

The solute vapor pressure method used in our laboratory allows extremely precise determination of the distribution of a volatile solute between vapor phase and nonvolatile solvent over a range of solute concentration and temperature. In the past we have used the method to study suprabinary (involving more than two monomeric units) hydrogen-bonded complexes of self-associated alcohols[1-4] and alcohol heteroassociation with proton-accepting bases.[4-6] Our recent heteroassociation studies have been restricted to dilute solutions of a nonvolatile base in *n*-hexadecane.[5,6] In the present study distribution data for methanol between vapor and solutions covering the entire binary composition range between *n*-hexadecane (Hx) and *N*,*N*-dimethyltetradecylamine (DMTDA) have been obtained at three temperatures. The presentation and discussion of our experimental results will be divided into three sections: (1) cooperativity effects on the formation of suprabinary hydrogen bonded complexes in dilute solution; (2) comparison of thermodynamic data for 1:1 complexes in dilute solution with the predictions of a pure base technique for estimating K for 1:1 complex formation; and (3) activity coefficient effects on formation of MeOH-DMTDA complexes over the solvent composition range from pure Hx to pure DMTDA.

Most investigations of alcohol-base 1:1 complex formation have utilized solutions quite dilute in alcohol and containing an excess of base. The rationale for choosing these conditions has been to avoid having to make corrections for alcohol self-association and to attempt to convert nearly all complexed alcohol present to the form of the 1:1 complex. The solute vapor pressure (SVP) method obviates the necessity for using only solutions very dilute in alcohol since this technique allows precise correction for the amount of self-complexed alcohol at any concentration level up to several tenths molar alcohol. Recent SVP experiments have shown that there is hardly any range of excess base concentration which can be used to convert all heteroassociated alcohol present to the 1:1 complex except in the limit of vanishingly small alcohol concentration.

For a number of years we have been interested in cooperativity effects on complexes of alcohols with proton acceptors such as amines and amides. Our thermodynamic studies[4-6] have shown that the process of forming the 1:1 complex

$$ROH + B \rightarrow ROH \cdots B$$
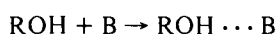
transforms the oxygen atom in the 1:1 complex into a basic site

essentially as effective as the original electron donor atom in B. In fact, for the alcohol-base-inert solvent systems we have studied,[4-6] the following reaction occurs with a negative free energy change:

$$2(ROH \cdots B) \rightarrow B + ROH \cdots ROH \cdots B$$
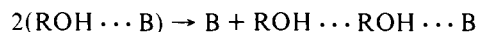
At first glance this may seem surprising, since in cases where B is an aliphatic tertiary amine there is a general tendency to assume that the 1:1 AB complex predominates over all others because of the very strong basicity of the amine. For example, a recent study involving ^{13}C relaxation times was based on the assumption that in equimolar mixtures of pure alcohol and pure pyridine essentially only a 1:1 complex is formed.[7] In marked contrast to this we have found in the present study and in earlier work that even in solutions very dilute in alcohol ($\sim 10^{-3}$ M) and containing excess amine the presence of complexes higher than 1:1 is readily observable. Moreover, in the present work, we find that in the extreme case of pure amine as solvent, complexes of the type A$_m$B are formed readily when the alcohol to amine concentration ratio is less than 1:100.

Clearly, these alcohol-base systems possess some very interesting thermodynamic characteristics which have largely escaped previous quantitative description. An important simplification factor in the study of heterocomplexes of alcohols with tertiary amines is that essentially only chain structures can be formed since there is no free end OH proton capable of leading to a cyclic heterocomplex. This is in strong contrast to the study of alcohol self-association, where a given complex may be either cyclic, linear, or a mixture of both forms. With a sensitive experimental technique, thermodynamic parameters (for sequential addition of alcohol monomer to tertiary amine) can be obtained which are related unambiguously to chain structures involving a single amine molecule. The solute vapor pressure method is not only ideal for the study of alcohol-base systems but, as we shall show, provides detailed and accurate information about complex hydrogen bonding equilibria that could not be obtained by use of any other single experimental technique.

Gas-liquid chromatography techniques have been in use for several years as a means of estimating equilibrium constants for formation of 1:1 complexes.[8] The basic requirement of these GLC techniques is the same as that for our SVP method: accurate determination of the limiting partition coefficient for

a volatile solute between vapor and nonvolatile solvent phase. However, unlike chromatographic methods, the SVP technique can easily provide highly accurate data over a range of volatile solute concentration including the limiting value at infinite dilution. Additionally, the SVP method is not affected by complications—such as interfacial and solid support adsorption of the volatile solute—which call for significant corrections in GLC measurements.[9]

In this article we will compare values of equilibrium constants for formation of 1:1 complexes obtained by the SVP technique for dilute solutions and apparent equilibrium constants—also obtained by the SVP method—calculated via what may be called a pure base approach. The pure base approach assumes that the limiting activity coefficient of monomeric alcohol (as well as that of other solution components) is invariant over the binary solvent composition range from pure hydrocarbon to pure base.

The assumption that activity coefficient effects cancel has often been made in studies of hydrogen bonded and charge transfer complexes. While this assumption may be relatively good for solutions quite dilute in donor and acceptor, one generally finds a breakdown in the constant activity coefficient ratio assumption when either donor or acceptor concentrations are varied over a wide range. In the present work we find that activity coefficients are significantly affected by varying solvent composition over the range from hydrocarbon to pure amine. Our results will be briefly compared to results for similar alcohol–base systems obtained by a GLC technique via a modified pure base approach.[9]

Experimental Section

Vapor pressure measurements for solutions of methanol in *n*-hexadecane (Hx), in N,N-dimethyltetradecylamine (DMTDA), and in Hx–DMTDA mixtures were made as previously described.[5,6] The experimental measurement may be briefly described as a process of sequential volumetric addition of MeOH vapor to an evacuated system containing nonvolatile solvent. A more complete description of the procedure is given in the supplementary material along with the experimental vapor pressure data (Table I). Methanol pressures were measured with a Mensor Corp. fused quartz Bourdon tube pressure gage with a minimum resolution of 0.001 Torr. Methanol and *n*-hexadecane were purified as previously described.[6] N,N-Dimethyltetradecylamine was a technical quality product of K & K Chemical Co. and was extensively purified before use. CHN analysis of the amine (expected values in parentheses) gave the following results: C, 79.40 (79.58); H, 14.77 (14.61); N, 5.51 (5.80). The temperature of the thermostatic bath enclosing the vapor pressure apparatus was controlled to within ±0.003 °C at 25, 35, and 45 °C.

Data Treatment and Results

1. Dilute Solution. The fundamental assumption employed in analysis of the dilute solution data is that each molecular solute species (monomer or aggregate) obeys Henry's law. The monomer MeOH molarity in solution is expressed by

$$C_A = K_D \frac{P_A}{RT} \quad \text{where} \quad \frac{P_A}{RT} = C_A{}^V \quad (1)$$

where P_A is monomer alcohol pressure (total pressure corrected for a small amount of vapor nonideality), K_D is the infinite dilution distribution (partition) coefficient for partitioning MeOH between vapor and *n*-hexadecane, and $C_A{}^V$ is the vapor phase molarity of monomeric alcohol. The total or formal MeOH concentration in solution in a base–Hx mixture can be generally represented by

$$f_A = C_A + \sum_{i=2}^{n} i K_i C_A{}^i + \sum_{j=1}^{m} j K_{j1} C_A{}^j C_B \quad (2)$$

where the quantity $C_A + \Sigma i K_i C_A{}^i$ represents the monomer concentration of alcohol plus all possible self-associated alcohol species (in future referred to as $f_A{}^{homo}$) and the quantity
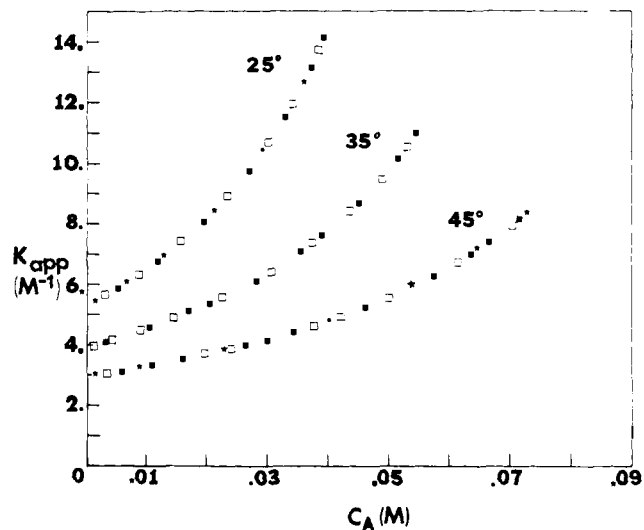

Figure 1. K_{app} (eq 4) vs. methanol monomer concentration, C_A. ★, 0.051 M DMTDA; □, 0.106 M DMTDA; ■, 0.162 M DMTDA. For clarity, only about 20% of the available data points appears.

$\Sigma j K_{j1} C_A{}^j C_B$ represents the total concentration of MeOH complexed with the base DMTDA. The latter quantity will be referred to in future as Δf_A. The total amine concentration (f_B) is given generally by

$$f_B = C_B + K_{11} C_A C_B + K_{21} C_A{}^2 C_B + \cdots$$

$$= C_B + \sum_{j=1}^{m} K_{j1} C_A{}^j C_B \quad (3)$$

where the quantity $\Sigma K_{j1} C_A{}^j C_B$ will be referred to as Δf_B. C_A and C_B are monomer MeOH and amine concentrations, respectively.

We have previously shown that our solute vapor pressure technique allows extremely precise division of f_A data into the terms $f_A{}^{homo}$ and Δf_A.[5,6] For any fixed value of C_A (or P_A) both Δf_A and f_B are proportional to C_B. If our Henry's law assumption is correct and no base self-association occurs, the ratio $\Delta f_A/f_B$ should only be a function of monomer alcohol concentration C_A. Utilizing an apparent equilibrium constant defined by

$$K_{app} = \Delta f_A/f_B C_A \quad (4)$$

a plot of K_{app} vs. C_A (or P_A) should give a unique curve independent of initial amine concentration.[6]

Figure 1 presents a plot of K_{app} vs. C_A for our dilute solution MeOH–DMTDA data. It is obvious that the three data sets (for three different inital amine concentrations in Hx) generate essentially identical curves at a given temperature. The congruence of these curves provides very strong support for our Henry's law assumption and the assumption that species involving more than one base molecule do not form. The fact that the curves do not diverge with increasing C_A indicates that the heteroequilibrium constants apparently do not vary with total concentration in the dilute solution region. The rapid upward curvature of K_{app} in Figure 1 is direct proof of the importance of suprabinary species of the type $A_m B$. We may note that if only a 1:1 complex existed K_{app} would *decrease* with increasing C_A.

We have previously treated similar systems by assuming that a unique K_{11} for 1:1 complex formation exists and that subsequent additions of a monomer MeOH to the AB complex give the same free-energy change:

$$A + B = AB; K_{11}$$

and

$$A_{m-1}B + A = A_m B; \quad K_\infty \text{ for } m \geq 2 \quad (5)$$
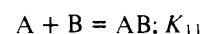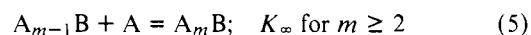
Table II. Least-Squares Values of K_{11} and K_∞ for Methanol-*N*,*N*-Dimethyltetradecylamine Complexes in Dilute Solution[a]

Temp, °C	$f_B = 0.051$ M		$f_B = 0.106$ M		$f_B = 0.162$ M	
	K_{11}	K_∞	K_{11}	K_∞	K_{11}	K_∞
25	5.37 ± 0.01	12.30 ± 0.01	5.36 ± 0.01	12.27 ± 0.01	5.34 ± 0.01	12.29 ± 0.01
					5.30 ± 0.01	12.35 ± 0.02
35			3.89 ± 0.01	9.14 ± 0.01	3.87 ± 0.01	9.20 ± 0.01
			3.89 ± 0.01	9.14 ± 0.01	3.90 ± 0.01	9.14 ± 0.01
45	2.96 ± 0.01	6.96 ± 0.01	2.91 ± 0.01	6.97 ± 0.01	2.91 ± 0.01	6.98 ± 0.01

[a] All K units are M^{-1}. The root mean square deviation in Δf_A for all fits is in the range from 0.000 02 to 0.000 11 M with an average value for the 11 data sets of 0.000 06 M. The average maximum Δf_A value for all 11 dilute solution data sets is 0.063 13 M.

Table III. Least-Squares Enthalpy and Entropy Values for Formation of MeOH–DMTDA Complexes in Dilute Solution[a]

$-\Delta H_{11}° = 5.87 \pm 0.05$ kcal/mol	$-\Delta S_{11}° = 16.36 \pm 0.16$ cal/deg mol
$-\Delta H_\infty° = 5.54 \pm 0.02$	$-\Delta S_\infty° = 13.59 \pm 0.07$

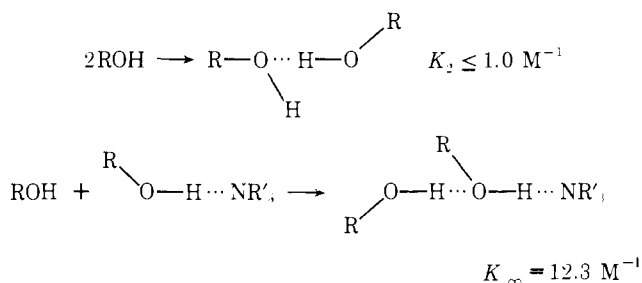[a] These values are based on unit molarity solute standard state and corrected for thermal expansion of solvent.

Δf_A and f_B are then expressed by

$$\Delta f_A = \frac{K_{11}C_AC_B}{(1 - K_\infty C_A)^2} \quad (6)$$

$$f_B = C_B + \frac{K_{11}C_AC_B}{(1 - K_\infty C_A)} \quad (7)$$

Using a value of K_D determined from MeOH–Hx data, least-squares fits of each of the 11 individual dilute solution data sets for MeOH–Hx–DMTDA in Table I may be performed to determine the best values of K_{11} and K_∞.[10] These values and their standard errors are given in Table II. The calculated K values are in quite good agreement and show no obvious trend with amine concentration, in agreement with what might have been expected from Figure 1. Least-squares values of $\Delta H°$ and $\Delta S°$ are presented in Table III.

The results of this analysis are remarkable in that the MeOH oxygen in the 1:1 complex has been transformed to a hydrogen bonding base almost as effective as the tertiary amine nitrogen. We may further emphasize this result by comparing the following reactions:

$$2ROH \longrightarrow R-O\cdots H-O{\overset{\textstyle R}{\underset{\textstyle H}{\Big\backslash}}} \qquad K_2 \le 1.0\ M^{-1}$$

$$ROH + {\overset{\textstyle R}{\underset{\textstyle R}{\Big\backslash}}}O-H\cdots NR'_3 \longrightarrow {\overset{\textstyle R}{\underset{\textstyle R}{\Big\backslash}}}O-H\cdots O-H\cdots NR'_3$$

$$K_\infty = 12.3\ M^{-1}$$

Thermodynamic parameters for MeOH dimerization are not well known. However, it is our firm opinion, based on extensive and precise studies of alcohol association,[1-3] that K_2 for MeOH dimerization in *n*-hexadecane cannot exceed 1.0 M^{-1}. By forming a 1:1 complex with the amine, the MeOH oxygen has been transformed into a hydrogen bonding base at least *ten* times as effective as a monomer MeOH oxygen. Except for previous data from this laboratory[4-6] there are no quantitative experimental thermodynamic data in the literature which are comparable with the present results. By use of the solute vapor pressure (SVP) technique we have a clear and precise method for obtaining thermodynamic data for the initial steps in reaction sequences of the type

$$ROH + NR'_3 \rightarrow ROH\cdots NR'_3$$

$$ROH + ROH\cdots NR'_3 \rightarrow ROH\cdots ROH\cdots NR'_3, \text{ etc.}$$

There are no structure complications here as in alcohol self-association since cyclic alcohol–amine complexes cannot form. There can be little doubt that our thermodynamic parameters characterize the formation of small chains of alcohols bound to a tertiary amine.

The objection might be raised that, although the $1 - \infty$ model provides an extremely good fit of the MeOH–amine SVP data, this model may not be unique and consequently leads to erroneous conclusions based on values of K_∞ which are not physically significant. If this objection can be demonstrated to be groundless we can conclude that the ROH $\cdots$ NR'$_3$ oxygen is a significantly better base than the oxygen in free ROH. In order to substantiate the presence of cooperativity effects it would also be desirable to gain some information about changes in acidity of the free end proton in linear complexes of alcohols like (ROH)$_n$ relative to the monomer ROH acidity. The following procedure answers these questions.

In a recent article[3] we have discussed a method for determining alcohol polymer molecular weight data from SVP data for alcohol–Hx solutions. The formal concentration of alcohol (no base present) is generally given by

$$f_A = C_A + 2K_2C_A^2 + 3K_3C_A^3 + \cdots + nK_nC_A^n \quad (8)$$

The apparent or sum-of-species concentration of alcohol (e_A) is given by

$$e_A = C_A + K_2C_A^2 + K_3C_A^3 + \cdots + K_nC_A^n \quad (9)$$

The following relationship is readily verified:

$$C_A\frac{de_A}{dC_A} = f_A \quad \text{and thus } e_A = \int_{C_A=0}^{C_A}\frac{f_A}{C_A}dC_A \quad (10)$$

The apparent concentration (e_A) can be obtained by numerical integration of vapor pressure data (f_A, C_A) for ROH–Hx systems or, equally well under our assumptions, by numerical integration of f_A^{homo}, C_A data for the ROH–base–Hx system. We can also obtain very useful information from a different type of numerical integration of vapor pressure data for ROH–base–Hx systems in the following manner. Since f_B is a function of C_A and C_B (eq 3):

$$df_B = (\partial f_B/\partial C_A)dC_A + (\partial f_B/\partial C_B)dC_B$$

and

$$df_B = (\Delta f_A/C_A)dC_A + (f_B/C_B)dC_B \quad (11)$$

where $(\partial f_B/\partial C_A)$ and $(\partial f_B/\partial C_B)$ have been evaluated by use of eq 2 and 3. Equation 11 may be rearranged to

$$df_B/f_B - dC_B/C_B = \Delta f_A/f_BC_AdC_A$$

or

$$d\ln(f_B/C_B) = K_{app}dC_A \quad (12)$$

where K_{app} was previously defined in eq 4. The integrated form of eq 12 may be written as
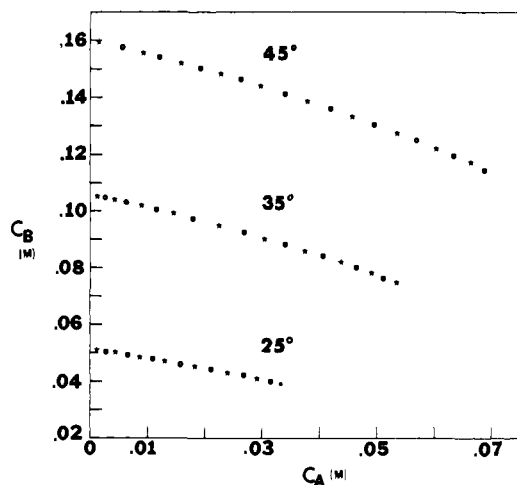
$$\ln(f_B/C_B) = \int_{C_A=0}^{C_A} K_{app}dC_A \quad (13)$$

Figure 2. DMTDA monomer concentration (C_B) vs. methanol monomer concentration (C_A) for three individual data sets. Alternating values of C_B have been determined via eq 13 (★) and determined from the fit of the $1 - \infty$ model (O), respectively.

Figure 3. K_{av} (eq 4) vs. methanol sum-of-species concentration, e_A. □, 0.051 M DMTDA; O, 0.106 M DMTDA; ■, 0.162 M DMTDA.

As previously noted K_{app} is not a function of C_B or f_B and

$$\lim_{C_A \to 0} K_{app} = K_{11}$$

By numerical integration of the K_{app} vs. C_A curves in Figure 1 we obtain the ratio f_B/C_B and hence C_B values since f_B is a known quantity.

In this hetero-vapor pressure experiment the following quantities are directly obtained from the experimental data: C_A, monomer alcohol; f_A, total alcohol concentration, which can be divided into $f_A{}^{homo}$ (self-associated alcohol + monomer) and Δf_A (heterocomplexed alcohol); e_A, apparent or colligative property species alcohol concentration (see eq 9) obtained by numerical integration of $f_A{}^{homo}$ and C_A data; f_B, formal or total base concentration. Note that C_B (monomer base) could not be directly obtained until the development of eq 13. The analysis of the $1 - \infty$ model (eq 6 and 7) results in C_B values dependent on the least-squares values of K_{11} and K_∞.

A stringent check on the physical significance of the $1 - \infty$ model is the direct comparison of the C_B values from the $1 - \infty$ model with the C_B values generated from eq 13, which has been developed independent of any particular association model. Figure 2 displays qualitatively the almost exact correspondence of C_B values from the $1 - \infty$ model with the model independent C_B values from eq 13. These results provide very strong support for the physical significance of the $1 - \infty$ model.

At this point we wish to consider further the question of hydrogen bond cooperativity in suprabinary complexes without using a specific association model. We may recall briefly the total model-free information we now possess from the heteroassociation vapor pressure study:

(1) f_A, f_B, C_A, C_B formal and monomer concentrations of alcohol and base

(2) e_A and $f_A{}^{homo}$ the sum-of-species concentration and formal concentration of alcohol, including only monomeric and self-associated species

(3) Δf_A and Δf_B the formal (total) concentrations of A and B present in heterocomplexes, ($\Delta f_B = f_B - C_B$)

Δf_B is the sum of concentration of the species AB, A_2B, ..., A_mB. We assume that all these species are linear chains (higher A_mB aggregates could be branched, of course) because cyclic alcohol complexes have no free proton to bind with base.
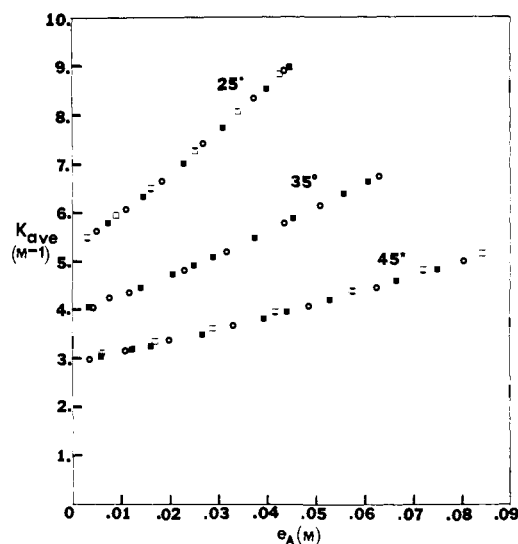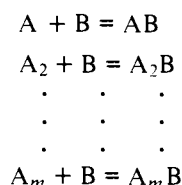
In a different manner we can reconsider the heteroassociation equilibria as the addition of a base monomer to individual self-associated alcohol aggregates:

$$A + B = AB$$
$$A_2 + B = A_2B$$
$$\cdot \quad \cdot \quad \cdot$$
$$\cdot \quad \cdot \quad \cdot$$
$$\cdot \quad \cdot \quad \cdot$$
$$A_m + B = A_m B$$

The average equilibrium constant for all of these reactions (weighted in proportion to the population of hetero- and homoaggregates) is given by

$$K_{av} = \frac{(C_{AB} + C_{A_2B} + \cdots + C_{A_mB} + \cdots)}{(C_A + C_{A_2} + \cdots + C_{A_n} + \cdots)C_B}$$

or   (14)

$$K_{av} = \frac{\Delta f_B}{e_A C_B}$$

The hetero-vapor pressure experiment provides accurate values of all the quantities needed to calculate K_{av}. The results are independent of association model since Δf_B, e_A, and C_B have been obtained without use of any specific model. All heterospecies containing one base molecule contribute to Δf_B and all self-associated alcohol complexes are included in e_A. Figure 3 is a plot of K_{av} vs. e_A for the MeOH–DMTDA data from dilute solution. The limiting value of K_{av} is K_{11} and at a colligative concentration of MeOH of 0.045 M at 25 °C K_{av} has increased by more than 70% over the limiting value. Similar increases in K_{av} are also observed for the 35 and 45 °C data. These increases in K_{av} are rather direct proof of the greatly increased acidity of small self-associated alcohol polymers compared to the acidity of the methanol monomer. For the purpose of emphasizing this acidity increase we may carry the analysis one step further and subtract the contribution of the 1:1 complex from Δf_B and subtract C_A from e_A in eq 14 thus producing a K_{av}' based on complexes A_mB with $m \geq 2$. At e_A values of ca. 0.02 M at 25 °C K_{av}' reaches values of about 50 M^{-1} which demonstrates the remarkably increased acidity of linear alcohol species like A_2, A_3, and A_4. Above e_A values of 0.02 M K_{av}' begins to decrease, possibly indicating the increased presence of cyclic alcohol species which can contribute to the denominator of eq 14 but not to the numerator. Note that if any cyclic self-associated alcohol species are

Table IV. Infinite Dilution Distribution Coefficients for MeOH between Vapor and Solution Mixtures of *n*-Hexadecane and *N,N*-Dimethyltetradecylamine

Temp, °C	ϕ_B[a]						
	1.00	0.832	0.613	0.407	0.199	0.050[b]	0.0
25	185.7 ± 0.3	150.7 ± 0.2	108.0 ± 0.2	72.0 ± 0.2	38.25 ± 0.04	15.45 ± 0.04	8.27 ± 0.04
35	115.0 ± 0.2	94.5 ± 0.2	68.9 ± 0.1	46.05 ± 0.06	25.50 ± 0.04	11.45 ± 0.04	7.03 ± 0.02
45	74.2 ± 0.2	61.0 ± 0.1	44.75 ± 0.05	30.92 ± 0.04	17.74 ± 0.03	8.86 ± 0.02	6.04 ± 0.02

[a] Volume fraction amine. [b] Dilute solution data for 0.16 M amine in *n*-hexadecane.

Table V. Dilute Solution K_{11} values for MeOH–DMTDA Compared with Those Predicted by the Pure Base Technique

Temp, °C	K_{11} (SVP), M^{-1}	K_{11} (eq 16), M^{-1}
25	5.34	6.53
35	3.88	4.72
45	2.92	3.49

present then the observed increase in K_{av} (and K_{av}') is a lower limit to the real increase reflecting enhanced acidity of small alcohol polymers.

The results of our analysis of the dilute solution data justify the use of the 1 − ∞ model. More importantly, we appear to have strong experimental evidence that there is an increase in both oxygen basicity and in proton donor character in small alcohol complexes due to hydrogen bond formation in solution.

2. Comparison of Dilute Solution and Pure Base Vapor Pressure Results for AB Complex Formation. Most nonspectral methods for determining complex formation constants can be classified as solubility methods. That is, the increase in solubility of A at constant fugacity in a base–reference solvent mixture, relative to the solubility of A in pure reference solvent, is generally attributed to formation of molecular complexes. This primary assumption is common to several thermodynamic methods, including those involving measurement of static and isopiestic vapor pressures, partition of solutes between nearly immiscible condensed phases, retention volumes by gas–liquid chromatography (GLC), and solubility increases of solids. Techniques for inferring formation constants are essentially the same for all of the solubility methods, as are the problems of determining what part of the enhancement of solubility is due to nonspecific interactions.[11]

In the case of the present vapor pressure technique and considering very dilute solutions where only a 1:1 complex is present eq 15 is applicable,

$$K_D = K_D{}^H(1 + K_{11}C_B) \qquad (15)$$

where K_D is the observed limiting distribution coefficient for the solute A between vapor and a solution phase consisting of base at concentration C_B (large relative to C_A and C_{AB}) in hydrocarbon solvent, $K_D{}^H$ is the limiting distribution coefficient for A between vapor and pure hydrocarbon, and K_{11} is the equilibrium constant for formation of the 1:1 complex. Strictly, K_{11} is equal to $K_{th} + \alpha$ where K_{th} is the true thermodynamic equilibrium constant and α is a measure of nonspecific effects contributing to the solubility of A in the base–hydrocarbon mixture.[17,19] If one assumes that K_{11} is independent of medium then extension to the case of pure B as solvent leads to the equation

$$K_D{}^B = K_D{}^H(1 + K_{11}V_B{}^{-1})$$

and $\qquad (16)$

$$K_{11} = \frac{(K_D{}^B - K_D{}^H)V_B}{K_D{}^H}$$

where $K_D{}^B$ is the distribution coefficient for A between vapor and pure B and V_B is the molar volume of pure B. The pure

Table VI. Infinite Dilution Distribution Coefficients for MeOH between Vapor and Pure *N,N*-Diethyldodecanamide and Comparison of K_{11} (SVP) and K_{11} (eq 16)

Temp, °C	$K_D{}^B$	K_{11} (SVP), M^{-1} [a]	K_{11} (eq 16), M^{-1}
25	675.0	13.1	23.8
35	416.0	9.80	17.3
45	265.0	7.65	12.9

[a] Values taken from Table 11 of ref 6.

base K_{11} can be calculated simply by determining the infinite dilution distribution coefficients for A between vapor and pure hydrocarbon and between vapor and pure base, respectively.

We have determined infinite dilution distribution coefficients, via the SVP method, for MeOH between vapor and solutions covering the entire composition range between pure *n*-hexadecane and pure *N,N*-dimethyltetradecylamine at three temperatures. These values are listed in Table IV. In Table V we compare the K_{11} (SVP) values from our dilute solution study of MeOH–DMTDA (Table 11) with K_{11} values calculated using eq 16. For convenience we refer to the dilute solution equilibrium constant as K_{11} (SVP) and the pure base K_{11} as K_{11} (eq 16). At each temperature K_{11} (eq 16) is substantially (ca. 20%) greater than our dilute solution equilibrium constant for the MeOH–DMTDA 1:1 complex.

Other experimental vapor pressure data from our laboratory can be compared with the pure base prediction of K_{11}. We have previously determined dilute solution K_{11} values for the MeOH–*N,N*-diethyldodecanamide complex at three temperatures.[6] Prediction of K_{11} values from eq 16 requires only the additional step of determining $K_D{}^B$ for partition of MeOH between vapor and pure amide. Table VI gives the infinite dilution distribution constants $K_D{}^B$ for partition of MeOH between vapor and pure amide and compares K_{11} (SVP) values with K_{11} predicted by use of eq 16. There is even greater variance between K_{11} (SVP) and K_{11} (eq 16) for the MeOH–amide system compared with the MeOH–DMTDA system.

Agreement between the K_{11} (SVP) and K_{11} (eq 16) values would require the validity of the equation

$$K_D = K_D{}^H\phi_H + K_D{}^B\phi_B \qquad (17)$$

which requires that K_D (e.g., for a volatile alcohol) be a linear function of ϕ_B (base volume fraction) over the entire composition range between pure hydrocarbon and pure base. ϕ_H is the volume fraction of hydrocarbon solvent. In Figure 4 the K_D values for MeOH from Table IV are plotted as a function of amine volume fraction. Within the small error limits of the data (expected error much smaller than symbol diameter) the K_D results at each temperature conform to the quadratic relation

$$K_D = K_D{}^H\phi_H + K_D{}^B\phi_B + b\phi_H\phi_B \qquad (18)$$

rather than eq 17.

The K_D values for MeOH from Table IV are the first such data, to our knowledge, to have been obtained for a volatile alcohol over the entire concentration range between pure hy-

Table VII. Dependence of Apparent K_{11} and K_∞ Values on DMTDA Volume Fraction in Solutions of High Amine Concentration[a]

Temp, °C		ϕ_B				
		1.00	0.832	0.613	0.407	0.199
25	K_{11}	6.455 ± 0.004	6.242 ± 0.003	5.973 ± 0.003	5.722 ± 0.007	5.492 ± 0.002
	K_∞	15.27 ± 0.03	14.82 ± 0.02	14.23 ± 0.02	13.58 ± 0.02	12.76 ± 0.01
35	K_{11}	4.646 ± 0.004	4.514 ± 0.003	4.343 ± 0.003	4.171 ± 0.002	3.970 ± 0.003
	K_∞	11.07 ± 0.03	10.69 ± 0.02	10.29 ± 0.02	9.91 ± 0.01	9.45 ± 0.01
45	K_{11}	3.432 ± 0.002	3.337 ± 0.002	3.208 ± 0.002	3.109 ± 0.002	2.977 ± 0.002
	K_∞	8.17 ± 0.02	7.99 ± 0.01	7.78 ± 0.01	7.41 ± 0.01	7.14 ± 0.01

[a] All K units are M^{-1}. The root mean square deviation in Δf_A for all fits is in the range from 0.000 04 to 0.000 26 M with an average value for the 15 data sets of 0.000 13. The average maximum Δf_A value for all 15 data sets is 0.2625 M.
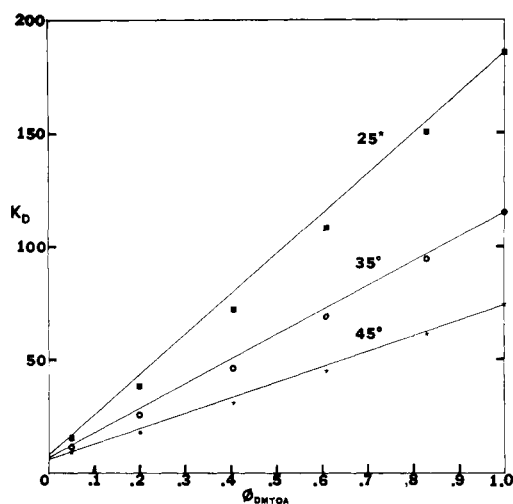

Figure 4. Infinite dilution distribution coefficients for methanol between vapor and solution in *n*-hexadecane-DMTDA mixtures as a function of the volume fraction of amine. Points are experimental; lines are predicted by eq 17.

Figure 5. Least-squares values of K_∞ and K_{11} for concentrated amine solutions at three temperatures (in descending order 25, 35, and 45 °C) as functions of DMTDA volume fraction, ϕ_B.

drocarbon and pure base. An important result of this study is that the dilute solution K_{11} values for the MeOH–DMTDA complex are not equivalent to the pure base K_{11} values from eq 16. We note that our experimental results do not agree with conclusions drawn from several recent GLC studies. For example, Purnell et al. have claimed that eq 17 is a valid representation of partition data—from GLC measurements—for numerous ternary nonelectrolyte systems involving one volatile component and two nonvolatile solvent components. These systems have included those where complexing by hydrogen bonding and charge transfer occurs as well as systems for which no complex formation is expected to occur.[12-15] More specifically, Martire[8] has suggested that the solution model of Purnell et al. (that is, the linear eq 17) should fit data obtained by Liao and Martire for hydrogen bonded complexes of volatile aliphatic alcohols with di-*n*-octyl ether and di-*n*-octylmethylamine.[9] If, as Martire suggests, eq 17 applies to the GLC data of Liao and Martire, this would require that K_{11} (dilute solution) for these alcohol–base complexes be essentially identical with K_{11} (eq 16).[16] However, Liao and Martire actually have not determined a value of K_{11} (dilute solution) since they only have information concerning the partitioning of volatile alcohols into pure solvent hydrocarbon or pure base.

Our accurate results for alcohol–base systems clearly show that K_{11} (dilute solution) differs markedly from K_{11} (eq 16). Further experimental work on such systems will be needed to determine whether such large differences between K_{11} (dilute solution) and K_{11} (pure base) will normally occur.

In section 3 we consider the effects of concentration-dependent activity coefficient changes on the apparent equilibrium constants calculated for MeOH–DMTDA complexes
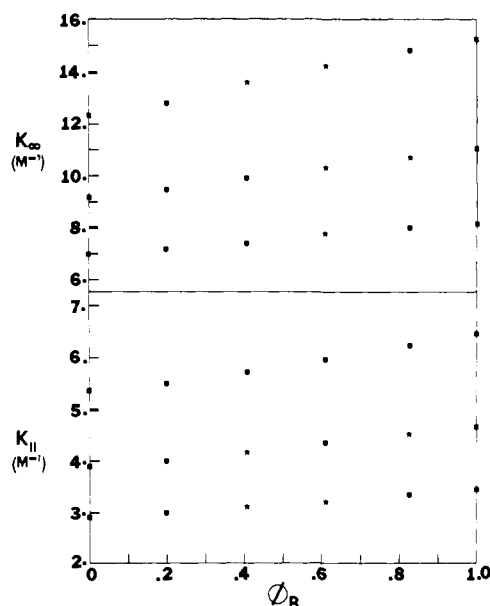
over the entire solvent composition range between Hx and DMTDA.

3. Activity Coefficient Effects on Apparent Equilibrium Constants for Methanol–Amine Complexes. In addition to determining limiting values of the distribution coefficient of methanol between vapor and binary mixtures of the solvents Hx and DMTDA, we have also obtained vapor pressure data for MeOH in each solvent mixture at three temperatures, at MeOH concentrations up to 0.3 M. In order to analyze these data to obtain values of K_{11} and K_∞ (for solvents varying in composition from pure Hx to pure DMTDA) we must assume something about the concentration dependence of activity coefficients of the species involved in the complex formation reactions. It is often assumed in studies of 1:1 complexes that the activity coefficient quotient ($K_{\gamma_1} = \gamma_{AB}/\gamma_A\gamma_B$) for the reaction

$$A + B = AB \tag{1}$$

does not vary as a function of solvent composition.[11] An analogous assumption that $K_{\gamma_{11}} = \gamma_{A_nB}/\gamma_A\gamma_{A_{n-1}B}$ is constant for the reaction

$$A + A_{n-1}B = A_nB \tag{II}$$
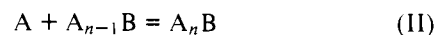
might also be made to infer values of the thermodynamic equilibrium constant K_∞.

If we do assume that activity coefficient effects can be neglected, we obtain the apparent values of K_{11} and K_∞ shown in Table VII and plotted in Figure 5. Clearly, the assumption

Table VIII. Ratios of K_∞ to K_{11} for Concentrated Amine Solutions

Temp, °C	25	35	45
ϕ_b		K_∞/K_{11}	
1.00	2.36	2.38	2.38
0.832	2.37	2.37	2.39
0.613	2.38	2.37	2.43
0.407	2.37	2.37	2.38
0.199	2.33	2.37	2.40

that K_{γ_1} and $K_{\gamma_{11}}$ do not depend on solvent composition cannot be correct, since the calculated values of both K_{11} and K_∞ vary by about 20% over the range of solvent compositions.

A very interesting result of calculating values of K_{11} and K_∞ as described above is that the ratio K_∞/K_{11} is quite nearly constant (2.37 ± 0.07) at all solvent compositions and at all three temperatures. Table VIII lists values of K_∞/K_{11} for the various solutions; these ratios should be compared with values of K_∞/K_{11} from the dilute solution studies (2.43 at 25 °C, 2.36 at 35 °C, and 2.39 at 45 °C). It can be shown that no matter what value is assumed for the activity coefficient of methanol (γ_A) in each solvent mixture, the *ratio* K_∞/K_{11} calculated from the partition data will be almost exactly the same. Thus, decreasing γ_A by several percent leads to the same percentage change in both K_{11} and K_∞, leaving the ratio unchanged. The fact that K_∞/K_{11} is independent of composition implies therefore that activity coefficient effects for the reaction

$$AB + A_{n-1}B = B + A_nB \qquad (III)$$

actually do cancel; i.e., that

$$K_{\gamma_{111}} = \frac{\gamma_B\gamma_{A_nB}}{\gamma_{AB}\gamma_{A_{n-1}B}}$$

is equal to unity. (We assume that for all species, unit molarity, ideal dilute solution states in the solvent Hx are employed.)

The constancy of K_∞/K_{11} indicates that the quotient of two activity coefficient ratios (γ_B/γ_{AB} and $\gamma_{A_{n-1}B}/\gamma_{A_nB}$) is independent of solution composition. It is tempting to suggest that these ratios are individually nearly constant, since in each of the pairs of species (B, AB and $A_{n-1}B$, A_nB) the second molecule forms from the first by addition of a single unit of methanol. If we assume that the two activity coefficient ratios are individually equal to unity, we can show that the apparent linear variation of K_∞ and K_{11} with ϕ_B (see Table VII and Figure 5) owes to the dependence of γ_A^{-1} on ϕ_B. Thus, we deduce that $\gamma_A^{-1} = 1 + \alpha'\phi_B$, where α' is a constant equal to approximately 0.2 at each temperature. Using this expression for ϕ_A^{-1} along with the dilute solution values of K_∞ and K_{11} at each temperature, we can quite closely predict the dependence of the methanol vapor pressure on ϕ_B and the total concentration of methanol. Thus, a least-squares method involving only three adjustable parameters can be used to correlate all the observed vapor pressure results. Although the assumption that $\gamma_B/\gamma_{AB} = \gamma_{A_{n-1}B}/\gamma_{A_nB} = 1$ leads to an excellent fit of data, further examination of activity coefficient effects convinces us that changes in the activity coefficient of methanol are not primarily responsible for the apparent variation of K_{11} and K_∞ with solvent composition (vide infra).

Considering only the dilute solution results, the limiting value of K_D at each value of ϕ_B can be expressed in a form similar to that used previously to describe activity coefficients on the solubility of iodine in mixed solvents.[17] Thus, if only the single complex AB is present, we can express the limiting value of the partition coefficient of methanol as

$$K_D = \lim_{C_A^V \to 0} \frac{C_A + C_{AB}}{C_A^V} = \lim_{C_A^V \to 0} \frac{(a_A/\gamma_A) + (a_{AB}/\gamma_{AB})}{C_A^V}$$

$$(19)$$

where C_A and C_{AB} represent molar concentrations of A and AB in the mixed solvent (Hx + B) and where C_A^V is the molar concentration of monomeric A in the vapor phase. The activities a_A and a_{AB} and the activity coefficients γ_A and γ_{AB} are based on ideal dilute solution standard states in Hx, so that $\gamma_A \to 1$ and $\gamma_{AB} \to 1$ as $\phi_B \to 0$. The thermodynamic equilibrium constant K_{11}^0 is the limiting value of C_{AB}/C_AC_B as $\phi_B \to 0$. (It can be shown that the dilute solution value of K_{11} at each temperature is equal to K_{11}^0 *provided* that one can neglect $\lim_{f_B \to 0}(d\gamma_A/df_B)$ in comparison with K_{11}^0; this assumption would appear to be reasonable in the present system, where K_{11}^0 is approximately 6 L/mol.)[8,18,19]

Equation 19 can be written as

$$K_D = \lim_{C_A^V \to 0} \frac{(a_A/\gamma_A) + K_{11}^0 a_A a_B/\gamma_{AB}}{C_A^V} \qquad (20)$$

which is analogous to eq 10 of ref 17 and similar to equations used in ref 19 and 20. However, in these latter references γ_{AB} seems to have been (implicitly) set equal to unity at all values of ϕ_B.

With the choice of standard states used here, we can replace

$$\lim_{C_A^V \to 0} (a_A/C_A^V)$$

by K_D^H, the value of K_D in pure Hx. Thus, eq 20 becomes

$$K_D = K_D^H[\gamma_A^{-1} + K_{11}^0\gamma_B f_B/\gamma_{AB}] \qquad (21)$$

where it is assumed that $f_B \gg C_A + C_{AB}$ (where f_B is the formal base molarity).

Now, both γ_A^{-1} and γ_B/γ_{AB} can be expressed as polynomials in f_B:

$$\gamma_A^{-1} = 1 + \alpha'f_B + \alpha''f_B^2 + \dots$$

and $\qquad\qquad\qquad\qquad\qquad\qquad (22)$

$$\gamma_B/\gamma_{AB} = 1 + \beta'f_B + \beta''f_B^2 + \dots$$

Including only terms to f_B^2, substitution of eq 22 into eq 21 yields

$$K_D = K_D^H[1 + (\alpha' + K_{11}^0)f_B + (\alpha'' + K_{11}^0\beta')f_B^2]$$

or $\qquad\qquad\qquad\qquad\qquad\qquad (23)$

$$K_D = K_D^H\left[1 + \frac{(\alpha' + K_{11}^0)\phi_B}{V_B} + \frac{(\alpha'' + K_{11}^0\beta')\phi_B^2}{V_B^2}\right]$$

where V_B is the molar volume of B. (Equations 23 are similar to eq 8 of ref 19; however, the constant β' includes the effects of solvent composition on γ_B/γ_{AB}, whereas in ref 19 γ_{AB} is apparently assumed to be unity.)

Empirically, we find that the limiting K_D values for MeOH at all values of f_B are accurately represented by

$$K_D = K_D^H[1 + 5.25f_B + 0.39f_B^2] \text{ at 25 °C}$$

$$K_D = K_D^H[1 + 3.88f_B + 0.26f_B^2] \text{ at 35 °C}$$

$$K_D = K_D^H[1 + 2.88f_B + 0.19f_B^2] \text{ at 45 °C} \qquad (24)$$

The importance of the quadratic terms in eq 24 can be more readily assessed by rewriting them in terms of ϕ_B. Thus,

$$K_D = K_D^H[1 + 17.3\phi_B + 3.5\phi_B^2] \text{ at 25 °C}$$

$$K_D = K_D^H[1 + 12.6\phi_B + 2.8\phi_B^2] \text{ at 35 °C}$$

$$K_D = K_D^H[1 + 9.3\phi_B = 2.0\phi_B^2] \text{ at 45 °C} \qquad (25)$$

At $\phi_B = 1$, the relative contribution of the quadratic term, compared to that of the linear term, is simply the ratio of the quadratic to the linear coefficient in each of eq 25. The fact that the magnitudes of the coefficients of the quadratic terms in eq

25 are so large indicates that α'' is probably not the major component of these terms. (Recall that α'' is the quadratic coefficient in the expression $\gamma_A^{-1} = 1 + \alpha'f_B + \alpha''f_B^2 + \ldots$) Considering the large magnitude of K_{11}^0 in the present systems, it seems plausible to conclude that $K_{11}^0\beta' \gg \alpha''$, so that β' can be estimated from the numerical coefficients of the quadratic terms in eq 24. Comparing these equations with the first of eq 23, we conclude that $\beta \approx 0.073$ at 25 °C, 0.067 at 35 °C, and 0.065 at 45 °C. Neglecting α' in comparison with K_{11}^0, we see that K_{11}^0 at each temperature (calculated from the coefficients of the linear terms in f_B) is virtually equal to the value of K_{11} already inferred from results of the dilute solution study (see Table II).

The preceding discussion leads us to conclude that the major reason for curvature in the plots of K_D vs. ϕ_B is the variation of γ_B/γ_{AB} with amine concentration. Although β' in $\gamma_B/\gamma_{AB} = 1 + \beta'f_B + \beta''f_B^2 + \ldots$ is apparently small (~ 0.07 L mol^{-1}), the product $K_{11}^0\beta'$ in eq 23 is quite important in the present systems, causing the K_D vs. ϕ_B plots to deviate considerably from linearity. One may examine eq 23 in an attempt to understand the conditions under which K_D will vary nearly linearly with ϕ_B or f_B. The term $\alpha'' + K_{11}^0\beta'$ is responsible for the nonlinearity of such plots, and for weakly complexing systems (for which $\alpha' + K_{11}^0 \sim 1$ L mol^{-1} or less) the term $(\alpha'' + K_{11}^0 \cdot \beta')f_B^2$ may be expected to be quite small compared to $(\alpha' + K_{11}^0)f_B$ throughout the range of solvent composition. In our opinion, it is not at all surprising that plots of K_D vs. ϕ_B are often nearly linear when only weak complexes are present.[21]

The argument that curvature in plots of K_D vs. f_B should be relatively more important in the case of systems in which strong complexes are present is supported by results in Table VI for infinitely dilute solutions of methanol in mixtures of n-hexadecane and N,N-diethyldodecanamide. For this system, K_D/K_D^H at $\phi_B = 1$ is 82, whereas the value of this ratio which would be predicted from partition data restricted to the region near $\phi_B = 0$ is 45. If the deviation from linearity in plots of K_D vs. ϕ_B is attributed entirely to the $K_{11}^0\beta'$ term in eq 23, we can conclude that β' is approximately equal to 0.24, 0.23, and 0.20 at 25, 35, and 45 °C, respectively. In other words, both K_{11}^0 and β' are larger for the N,N-diethyldodecanamide system than for the dimethyltetradecylamine system. K_{11}^0 for the former system is 2.5 K_{11}^0 for the latter, and β' for the amide system is about 3.5β' for the amine system. As a result of increases in both these factors, the curvature in plots of K_D vs. f_B is approximately eight times as great for the amide system.

Summary and Conclusions

In several investigations, including the present work, we have provided experimental evidence that the formation of a 1:1 hydrogen bonded complex of MeOH with bases transforms the MeOH oxygen into a basic site essentially as effective as the original base.[4-6] Our thermodynamic data for the process A + AB = A$_2$B in dilute solution show that this reaction occurs with a more negative free energy change than the process A + B = AB where B is a strong electron donor such as an amine or an amide. In cases where B is a long-chain tertiary amine there appears to be a steric effect retarding the formation of the 1:1 complex. For example, K_{11}(25 °C) and ΔH_{11}^0 (corrected for thermal expansion of solvent) are 2.08 M^{-1} and -5.76 kcal/mol for formation of the methanol-tri-n-octylamine 1:1 complex[5] while K_{11}(25 °C) and ΔH_{11}^0 for formation of the methanol-DMTDA 1:1 complex are 5.34 M^{-1} and -5.87 kcal/mol. The ΔH_{11}^0 are equal within experimental error while K_{11} is significantly larger for the (presumably) less hindered amine DMTDA. A similar entropic effect is apparent from thermodynamic parameters for formation of iodine complexes with tertiary amines.[22] In alcohol complexes with

tertiary amines values of K_∞ significantly larger than K_{11} may not be primarily due to cooperativity effects. The significant factor in the amine and amide systems which we have studied is that the enthalpy for adding a methanol monomer to the AB complex is close to the enthalpy for forming the 1:1 complex, thus indicating that the oxygen atom of methanol in the 1:1 complex has become a basic site comparable to the original strong N or O donor base. As a consequence of this K_∞ and ΔH_∞ are substantially enhanced relative to whatever reasonable values might be estimated for K_2 and ΔH_2^0 for formation of a methanol dimer in n-hexadecane.

In the present work we have used two different approaches to examine cooperativity effects in the formation of suprabinary hydrogen bonded complexes. The analysis provided by the $1 - \infty$ model for the MeOH–DMTDA system shows that the basic character of the MeOH oxygen increases upon hydrogen bond formation. By use of a Gibbs–Duhem type integration of vapor pressure data we have not only demonstrated that the $1 - \infty$ model is nearly exact for the present system but also we have shown (by the model-independent analysis leading to eq 14) that there is a significant increase in the acidity of the end free proton in small linear MeOH polymers. We have provided quantitative thermodynamic data which show proof for both aspects of hydrogen bond cooperativity occurring in cases where there can be no uncertainty about the linear structure of the complexes involved.

A comparison of the dilute solution K_{11} values and K_{11} from the pure base technique (eq 16) shows that activity coefficient effects are quite important in the present MeOH–amine and MeOH–amide systems. These results suggest that pure base methods, however modified by corrections for changes in activity coefficients of the uncomplexed volatile proton donor, cannot be expected to provide reliable values for K_{11} in the reference solvent. The pronounced curvature in K_D vs. ϕ_B plots is attributable to activity coefficient effects for donor, acceptor, and complex. Even if it were possible to estimate a value of γ_A in the pure base, either theoretically or by use of analogue compounds, application of eq 16 with a correction only for γ_A would not account for activity coefficient effects on the other components. There is, in our opinion, no way to avoid careful studies of the dilute solution region if thermodynamic quantities are to be obtained for donor–acceptor complexes in the reference solvent.

In the case of complexes significantly less stable than the alcohol-base adducts, the linear relation (eq 17) may be adequate to describe the dependence of K_D on ϕ_B. However, this should not be taken as evidence that the microscopic partition model proposed by Purnell et al.[12-15] is valid.

Two recent studies have provided data which indicate that eq 17 does not apply even for systems in which complexes are presumably absent.[23,24]

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Poly(crown ether) Catalyzed Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate

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Abstract: Poly(vinylbenzo-18-crown-6) (P18C6) dissolved in water acts as a neutral polysoap and effectively catalyzes the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate through transfer of the substrate into the aromatic inner core of the tightly coiled polymer. The bound carboxylate decomposes 2300 times faster than in water. The intrinsic binding constant of the anionic solute is vastly increased by adding crown complexable cations. This converts the neutral polysoap into a polycation. The effectiveness of cations in enhancing the binding is $Cs^+ > K^+ \gg Na^+ \gg Li^+$. The most effective system is P18C6–CsCl where bound carboxylate at 25 °C decomposes 14 000 times faster and at 5 °C 86 000 times faster than in water, a significant improvement over other polysoaps. The aromatic hydrocarbon environment and the high charge density of polysoap are believed to be the main factors contributing to the high catalytic activity of this system. Hydrophobic anions such as BPh_4^- and picrate are effective inhibitors by competing with the carboxylate for binding sites.

Poly(vinylbenzo-18-crown-6), abbreviated in this paper as P18C6, strongly interacts with a variety of organic solutes when dissolved in water.[1–3] The polymer, its structure depicted below, exhibits inverse temperature solubility in water, the cloud point being 37 °C. The low intrinsic viscosity (for M_n = 106 000, $[\eta]_0$ at 25 °C in water is only 0.107 as compared to 0.37 in $CHCl_3$) suggests that the macromolecule is in a

P18C6
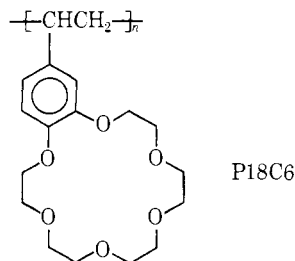
tightly coiled conformation resembling a nonionic micelle or neutral polysoap and stabilized at the polymer–water interphase by water molecules hydrogen bonded to the crown ether oxygen atoms. Hydrophobic interactions cause the organic solutes to solubilize into the apolar polystyrene core of the polysoap. Moreover, binding of anionic solutes can be greatly augmented by means of crown ether complexable cations[4] since the neutral poly(crown ether) now converts into a cationic polysoap.

The solute binding property of poly(vinylbenzo-18-crown-6)

induced us to evaluate its effectiveness to catalyze solvent-sensitive reactions. Such a reaction is the decarboxylation of benzisoxazole-3-carboxylate or that of its derivatives, studied in great detail by Kemp et al.[5–7] Its decomposition into the salicylonitrile salt (the 6-nitro derivative of the carboxylate was used in our study) was shown to be a concerted intermediateless E_2 elimination,[6] slow in water and other protonic solvents, but
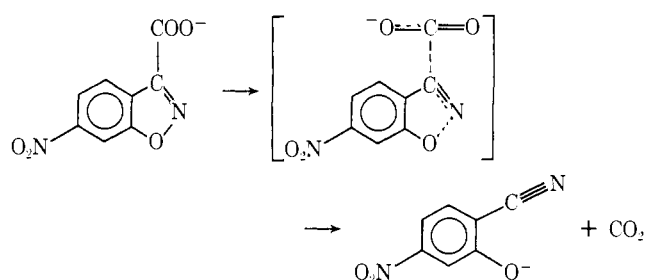
accelerated in media such as benzene and tetrahydrofuran, and extremely fast in dimethyl sulfoxide or hexamethylphosphoramide, the rate constant in the latter solvent being larger than that in water by a factor of 10^8. The solvent effects were rationalized in terms of stabilization or destabilization of the anionic reactant or its charge delocalized transition state. Catalysis can also be accomplished by means of cationic or neutral micelles, e.g., cetyltrimethylammonium bromide.[8–11] The latter study, in particular, led us to investigate in more