Correlation of Thermodynamic Properties of Amine-Water Solutions with Molecular Structure

R. R. DAVISON, D. W. HOOD, and W. D. HARRIS

Texas A & M University, College Station, Texas

The solutions of amines and water are in several respects among the most interesting that have been studied. They give some of the most perfect examples of lower consolute temperatures with fast breaking, almost flat solubility curves near the critical solution point. Their heat and entropy of solution are very high, and with few other solutions do the thermodynamic properties show greater sensitivity to molecular structure.

The activity coefficients for these solutions are inordinately difficult to fit with equations such as the Margules, Redlich-Kister, etc., requiring as many as six constants. It has been found however that some of the properties can be correlated in terms of structural parameters which are measures of the steric and inductive contribution of the substituent groups. A very good correlation of the heat of solution at infinite dilution of amines in water is given. An equation of the Margules type employing orthogonal polynomials is given for which the constants are similarly correlated. Five six-carbon atom amines at 10°C. are included in the latter correlations, and the activity coefficients of all of these are represented in terms of two structural parameters.

While it is the aim of statistical thermodynamics to formulate theories by which macro properties of compounds and solutions can be calculated from molecular properties, in practice less ambitious approaches are usually employed. The properties of solutions are often estimated from those of the components. One of the best known methods of this type for predicting deviations from ideality is that of Hildebrand (*1*) employing solubility parameters calculated from molar volumes and heats of vaporization. A similar approach has been developed by Gilmont, Zudkevitch, and Othmer (*2*).

Pierotti, Deal, and Derr (*3*) have correlated the activity coefficients at infinite dilution for a number of homologous series of solutes in various solvents in terms of parameters characteristic of the series. If the binary solutions are such that they can be represented by a two-constant polynomial satisfying the Gibbs-Duhem equation (Margules, Van Laar, etc.), then the activity coefficients at infinite dilution are sufficient for calculating the thermodynamic excess functions and the vapor-liquid equilibrium provided the vapor pressures of the pure components are known. Most of the series correlated by this method involve straight chain alkyl groups. Secondary alcohols required different correlating constants than primary alcohols, and branching in the immediate vicinity of the functional group prevented correlation. Another approach (*4*), (*5*) assumes that the interaction between molecules is equal to the sum of group interactions which are not influenced by other atoms or groups within the molecule.

CORRELATING PARAMETERS FOR AMINE—WATER SOLUTIONS

None of these methods can correlate the behavior of strongly hydrogen bonding systems such as amines and water. For instance the mutual solubility (*6*) may change considerably with changes in the carbon chain. The group interaction theories could not predict this, nor can any theory depending on a two constant polynomial. In view of the high heats of solution and unusual solubility curves there must exist high energy specific interaction, probably consisting of hydrogen bonds formed by the water hydrogen and the amine nitrogen.

Taft (*7*) has shown that the rates of many chemical reactions can be correlated in terms of inductive and steric effects characteristic of substituent groups on the reactants. These factors were determined from the rates of ester hydrolysis. The inductive contribution is defined by

$$\sigma^* \equiv \frac{1}{2.48}\left[\log\left(\frac{k}{k_o}\right)_B - \log\left(\frac{k}{k_o}\right)_A\right] \tag{1}$$

The rates in acid catalysis are independent of the inductive effect, so the steric constant E_s is defined by

$$E_s = \log\left(\frac{k}{k_o}\right)_A \tag{2}$$

Hyperconjugation effects due to α hydrogens tend to decrease the rate constants for ester hydrolysis. The substitution of an alkyl group for an α hydrogen increases the steric effect which decreases the rate constant while decreasing the hyperconjugation effect and thereby increasing the rate constant. Hancock, Meyers, and Yager (*10*) have separated the steric and hyperconjugation effects and calculated corrected steric constants which are given by

Table 1. Heats of Solution of Amines at Infinite Dilution and Substituent Constants

Amine	$\Sigma\sigma^*$	$\Sigma E_s{}^c$	ΣE_s	$-H^E\left(\frac{\text{cal.}}{\text{mole}}\right)$
Ethylamine	+0.880	0.26	+2.41	6,300
Propylamine	+0.865	−0.03	+2.12	6,150
i-butylamine	+0.855	−0.60	+1.55	6,000
Diethylamine	+0.290	−0.44	+1.10	8,200
di-*n*-propylamine	+0.260	−1.02	+0.52	7,550
di-isobutylamine	+0.240	−2.16	−0.62	7,050
diisopropylamine	+0.110	−1.84	+0.30	7,750
ethyl,S-butylamine	+0.180	−1.80	+0.04	7,750
Trimethylamine	0	0	0	9,000
Triethylamine	−0.300	−1.14	−0.21	9,887
Dimethyl,t-butylamine	−0.300	−2.46	−1.54	8,241

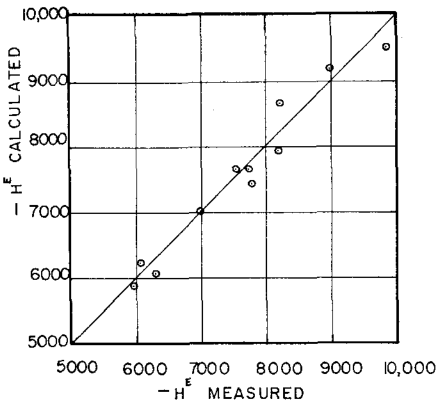

Fig. 1. Heats of solution at infinite dilution of amines in water compared with calculated values.

$$E_s^c = E_s + 0.306\ (N - 3) \qquad (3)$$

in which N is the number of α hydrogens. They have shown that for ester hydrolysis E_s better correlates the rate constants, but for reactions not involving α hydrogens E_s^c was shown to be superior. Properties other than rates of reaction such as heats of reaction (*8*) and dipole moments (*9*) have been correlated in terms of σ^* or E_s.

The heats of solution of amines in water at infinite dilution in Table 1 were correlated in terms of the sum of the inductive constants and the sum of the steric constants for all the substituents on the amine nitrogen. The result of a multiple regression was found to be

$$-H^E\ (\text{cal./mole}) = 9{,}235 - 3{,}415\ \Sigma\sigma^* + 639.6\ \Sigma E_s^c \quad (4)$$

with a correlation coefficient of 0.980 and a standard deviation of 266 cal. The result with E_s rather than E_s^c was

$$-H^E\ (\text{cal./mole}) = 8{,}497 - 4{,}690\ \Sigma\sigma^* + 856.9\ \Sigma E_s \quad (5)$$

with a correlation coefficient of 0.976 and a standard deviation of 314 cal. The measured values of H^E are plotted vs. those calculated from Equation (4) in Figure 1. Some of these data were taken from "The Critical Tables," while others were calculated from the rate of change of the activity coefficient at infinite dilution. The temperatures at which the H^E values were measured varied from about 15° to 25°C. In view of the diversity of the sources of data the degree of correlation is remarkable.

POLYNOMIAL FITTING OF THE AMINE—WATER DATA

If the activity coefficients of the amine—water solutions could be represented by a one- or two-constant polynomial, an obvious extension of the above results would be to correlate these constants in the same manner, which is equivalent to correlating the activity coefficients at infinite dilution. It has been found (*11*) however that four or more constants are required to adequately represent the data.

Usually G^E/RTx_1x_2, $Ln\gamma_1/x_2^2$, $Ln\gamma_2/x_1^2$, or $Ln(\gamma_1/\gamma_2)$ are expressed as polynomials of x_1, x_2, or $(x_1 - x_2)$ in a manner consistent with the Gibbs-Duhem equation. The choice is arbitrary, especially when many constants are used. The constants may be determined by a least-square fit or by other methods, but as they are not independent of one another they cannot be correlated independently, if at all.

Orthogonal polynomials may be used to fit data, and they have several properties that are useful. The constants are independent of each other, so that adding or subtracting terms has no effect on the remaining terms. Since the constants are calculated by integration or summation over the curve being fitted, they bear a definite relation to the shape of the curve and are more likely to be capable of correlation. Jost and Rock (*12*) used discontinuous orthogonal polynomials, involving a summation rather than an integration, to determine the constants for alcohol toluene solutions. An important set of polynomials of this type are those of Tchebycheff. If $T_J(Z)$ is the Tchebycheff polynomial

$$f(Z) = \sum_J A_J T_J(Z) \qquad (6)$$

and the constants A_J are given by

$$A_J = \sum_Z f(Z) \cdot T_J(Z) / \sum_Z T_J^2(Z) \qquad (7)$$

The first six polynomials from Birge (*13*) were used. The abscissa scale Z is defined in terms of the mole fraction of amine by

$$Z = \frac{x}{\Delta x} - \frac{x_E - x_o}{2\Delta x} \qquad (8)$$

The evenly spaced values of x used as data points are divisible by Δx, so that only integral values of Z result. The activity coefficients were determined as a function of concentration at 10°C. for five six-carbon atom amines by integrating the Gibbs-Duhem equation with the total pressure curves for those amines. The total pressure curves are shown in Figure 2 and were determined by a static

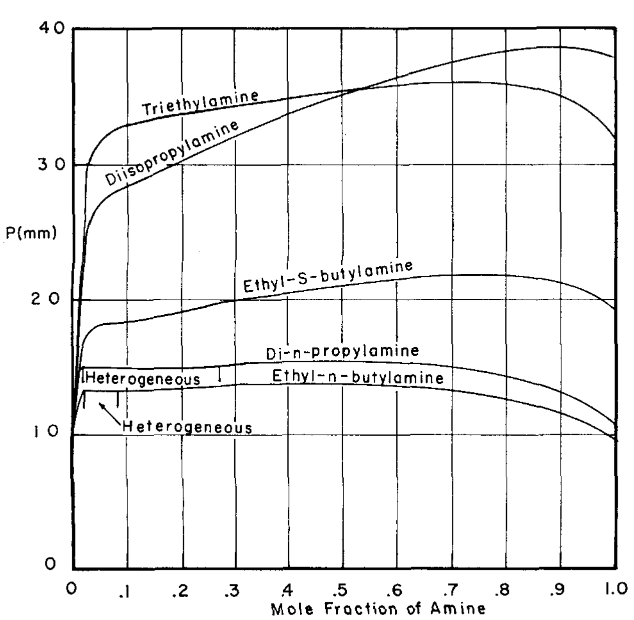

Fig. 2. Vapor pressure curves for amine-water solutions.

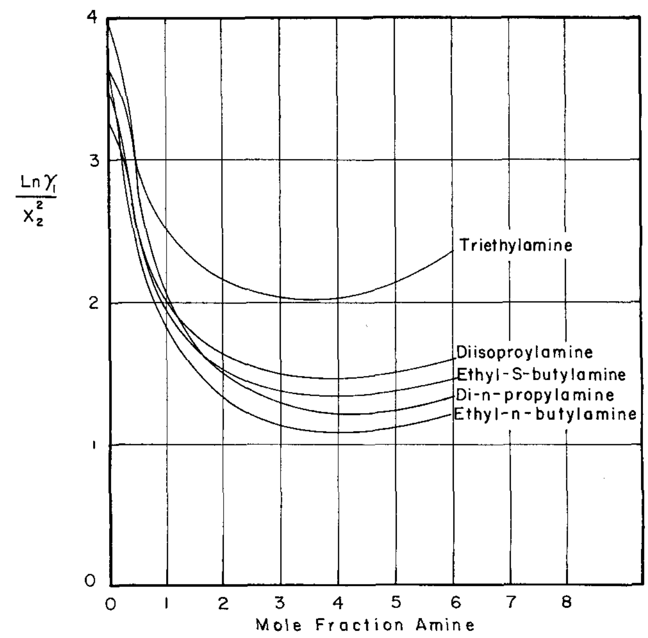

Fig. 3. The functions $Ln\gamma_1/x_2^2$ for the amine-water solutions.

TABLE 2. CONSTANTS FOR THE POLYNOMIAL REPRESENTATION OF $Ln\gamma_1/x_2^2$ FOR AMINE-WATER SOLUTIONS AT 10°C.

$$Ln\gamma_1/x_2^2 = \sum_{J=0}^{n} A_J T_J(Z)$$

$$0 \gtrless x_1 \lesssim 0.6 \Delta x = 0.025$$

TRIETHYLAMINE

J	0	1	2	3	4	5
A_j	0.23347×10	-0.35796×10^{-1}	0.66887×10^{-2}	-0.36256×10^{-3}	0.27663×10^{-4}	-0.98702×10^{-6}

DIISOPROPYLAMINE

J	0	1	2	3	4	5
A_j	0.17759×10	-0.47305×10^{-1}	0.64155×10^{-2}	-0.42213×10^{-3}	0.29617×10^{-4}	-0.85114×10^{-6}

ETHYL-SEC-BUTYLAMINE

J	0	1	2	3	4	5
A_j	0.17016×10	-0.53843×10^{-1}	0.70473×10^{-2}	-0.53166×10^{-3}	0.44218×10^{-4}	-0.20463×10^{-5}

DI-*N*-PROPYLAMINE

J	0	1	2	3	4	5
A_j	0.16817×10	-0.75764×10^{-1}	0.91203×10^{-2}	-0.64760×10^{-3}	0.47825×10^{-4}	-0.20618×10^{-5}

ETHYL-*N*-BUTYLAMINE

J	0	1	2	3	4	5
A_j	0.14904×10	-0.66152×10^{-1}	0.81152×10^{-2}	-0.59923×10^{-3}	0.47025×10^{-4}	-0.37865×10^{-5}

vapor pressure device (*14*). Plots of $Ln\gamma_1/x^2$ are shown in Figure 3.

The function $Ln\gamma_1/x_2^2$ was chosen as the one to be fitted because it can be represented in a two-phase region. It may be seen in Figure 2 that di-*n*-propylamine and ethyl-butylamine have immiscibility regions at 10°C. with the thermodynamic functions being undefined in the region. It can be shown however that

$$\int_{x_1^o}^{x_1'} \frac{Ln\gamma_1}{x_2^2} dx_1 = \frac{Ln\gamma_1'}{x_2'} - \frac{Ln\gamma_1^o}{x_2^o} + Ln \frac{x_1' x_2^o}{x_1^o x_2'} \qquad (9)$$

if x_1^o and x_1' are the equilibrium concentrations.

The concentration and activity coefficients at the limits of the heterogenous region are known, so $(Ln\gamma_1)/(x_2^2)$ may be drawn in by trial in this region until the area under the curve is equal to the right-hand side of Equation (9). There are of course many ways in which the curve may be drawn to satisfy the requirements of Equation (9), so some error is inevitably introduced. The immiscibility gap widens sharply with increasing temperature, and the correlations at higher temperatures were less accurate.

Since $Ln\gamma_1/x_2^2$ becomes inaccurate at small values of x_2^2, the correlation is stopped at 0.6 mole fraction amine which corresponds to 0.894 weight fraction amine.

CORRELATION OF EQUILIBRIUM DATA FOR AMINE—WATER SOLUTIONS

The constants A_J in Table 2 obtained by the Tchebycheff polynomial fit were correlated with the sum of the inductive and steric effects so that

$$A_J = K_J + \rho_J \Sigma\sigma^* + \delta_J \Sigma E_s^c \qquad (10)$$

The results are given in Table 3. Figure 4 shows the error in total pressure in using this correlation.

The correlation is unable to represent exactly the fast breaking region exhibited by all the amines, but this is largely the result of the original polynomials. Di-*n*-propylamine and ethyl-butylamine are less accurately represented because of the immiscible region and because the low vapor pressures and very flat curves resulted in less accurate data.

Substituting Equation (6) in Equation (10) and replacing Z in $T_J(Z)$ with its equivalent [Equation (8)] one gets

$$f(x) = \Sigma(K_J + \rho_J \Sigma\sigma^* + \delta_J \Sigma E_s^c)\, T_J(x_1) \qquad (11)$$

Factoring out $\Sigma\sigma^*$ and ΣE_s^c one may write Equation (11) as

$$f(x) = P_1(x_1) + P_2(x_1)\, \Sigma\sigma^* + P_3(x_1)\, \Sigma E_s^c \qquad (12)$$

in which P_1, P_2, and P_3 are polynomials.

If the values of K_J, ρ_J, and δ_J in Table 3 are used, $f(x)$ is equal to $Ln\gamma_1/x_2^2$, but other relations for $Ln\gamma_2$ or G^E similar to Equation (12) may easily be derived from this polynomial:

$$Ln\gamma_2 = -x_1 x_2 f(x_1) + \int_0^{x_1} f(x_1)\, dx_1 \qquad (13)$$

and

$$\frac{G^E}{RT\, x_1 x_2} = \frac{1}{x_1} \int_0^{x_1} f(x_1)\, dx_1 \qquad (14)$$

or

$$\frac{G^E}{RT\, x_1 x_2} = P_1^*(x_1) + P_2^*(x_1)\, \Sigma\sigma^* + P_3^*(x_1)\, \Sigma E_s^c \qquad (15)$$

TABLE 3. CORRELATION CONSTANTS
(10°C.)

	K	ρ	δ	r	s
A_0	1.9329	−1.3342	0	0.977	0.785×10^{-1}
A_1	-0.6723×10^{-1}	-0.5661×10^{-1}	-0.1314×10^{-1}	0.953	0.671×10^{-2}
A_2	0.9165×10^{-2}	0.2768×10^{-2}	0.1501×10^{-2}	0.886	0.735×10^{-3}
A_3	-0.5953×10^{-3}	-0.4317×10^{-3}	-0.9657×10^{-4}	0.949	0.532×10^{-4}
A_4	0.4630×10^{-4}	0.3315×10^{-4}	0.8237×10^{-5}	0.923	0.522×10^{-5}
A_5	-0.3524×10^{-5}	-0.3042×10^{-5}	-0.1439×10^{-5}	0.866	0.832×10^{-6}

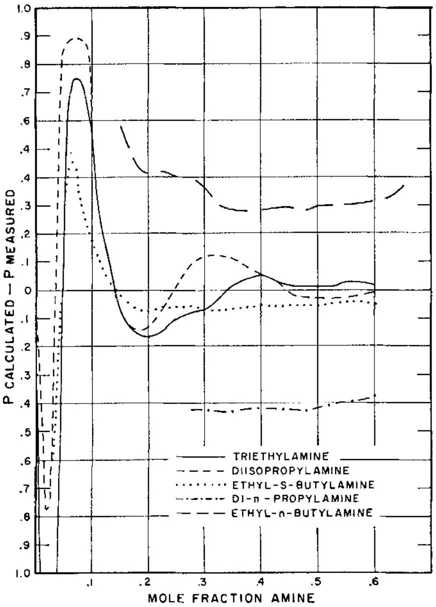

Fig. 4. The error in calculating the total pressure from the structural correlation.

Carrying out the operations specified by Equations (11) to (15) one obtains the following values for $P^*(x_1)$:

$$P_1^*(x_1) = 4.1843 - 15.700x_1 + 55.228x_1^2 - 116.59x_1^3 + 131.95x_1^4 - 60.14x_1^5$$

$$P_2^*(x_1) = 0.04421 - 9.992x_1 + 40.695x_1^2 - 94.092x_1^3 + 110.41x_1^4 - 51.913x_1^5$$

$$P_3^*(x_1) = 0.41354 - 3.2628x_1 + 14.383x_1^2 - 37.067x_1^3 + 48.414x_1^4 - 24.554x_1^5$$

The equilibrium properties of five amine-water solutions at 10°C. are thus represented by an expression containing two characteristic parameters which are functions only of the amine structure.

Five systems are insufficient to establish the values of the three constants in Equation (10) with confidence. Unfortunately there are no families of isomers larger than this for which vapor-liquid equilibrium data are available at one temperature. Even the inclusion of similar compounds of different molecular weight would add only a little more data and would doubtless increase the complexity of the correlation.

CONCLUSION

The heats of solution at infinite dilution of a wide range of aliphatic amines were correlated with Taft's inductive constants and the corrected steric constants of Hancock, Meyers, and Yager.

Activity coefficients for five six-carbon atom amine-water solutions at 10°C. were fitted with Tchebycheff polynomials, and the polynomial constants were also correlated with the inductive and steric constants. The accuracy of the latter correlation could doubtless be improved by more data, especially for mixtures that are homogenous at all concentrations. The success achieved by these structural parameters in correlating thermodynamic properties of solutions in which isomers exhibit large differences points out the inadequacy of any theory which assumes that the interaction between functional groups depends only on the nature of the group and not on other substituents within the molecule.

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NOTATION

A_j = constant coefficient of Tchebycheff polynomial
E_s = a steric factor defined by Equation (2)
$E_s{}^c$ = a steric factor defined by Equation (3)
G^E = excess free energy
H^E = enthalpy of solution, cal./g. mole
k = rate constant for ester hydrolysis
k_o = rate constant for hydrolysis of reference ester
K_j = constant term in regression analysis
n = an integer, the number of data points or the highest term in a summation
P = total pressure
$P(x_1), P^*(x_2)$ = polynomials in x_1
r = correlation coefficient
s = standard deviation
T = absolute temperature, °R.
T_j, T_K = Tchebycheff polynomials
x = mole fraction
x_E = mole fraction of the highest concentration of amine included in the correlation
x_o = mole fraction of the lowest concentration of amine included in the correlation
Z = function of x defined by Equation (8)

Greek Letters

γ = activity coefficient
Δ = an increment
δ = coefficient of the steric constants E_s or $E_s{}^c$
ρ = coefficient of the inductive constant
σ^* = inductive constant

Subscripts

1 = amine or first
2 = water or second
A = acid catalysis
B = base catalysis
J = integer denoting a sequence
k = integer denoting a sequence

Superscripts

o = lower limit of integration
$'$ = upper limit of integration

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