Structure and Amine-Water Solubility in Desalination by Solvent Extraction

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IN THE SOLVENT extraction process for desalinating water, solvents must show sharp changes in solubility with changes in temperature, and also a high selectivity for salt over water. Because this selectivity decreases rapidly as the water content increases, solubility must be sensitive to temperature in the range where water has a low solubility in the solvent.

Of the compounds studied, amines, particularly secondary and tertiary, have the most desirable properties. They show lower consolute temperatures because nitrogen to hydrogen bonds, which are broken by heating, are formed. Solubility of water in amines bears some relation to the basic dissociation constants for amines—i.e., electron-releasing substituents that increase electron density on the nitrogen and thereby increase the basicity of this element, increase the solubility of water. Other groups which sterically hinder the nitrogen, decrease its basicity and thus decrease solubility of water in the amine.

On the other hand, multiple substitution of alkyl groups on or near the nitrogen, which increases both the negativity of the nitrogen and steric hindrance, has the desirable effect of greatly reducing solubility at higher temperatures and increasing solubility at lower temperatures. In the work described here, straight chain and substituted amines of five to 13 carbon atoms were studied.

EXPERIMENTAL

Cloud Points. Solubility data were obtained by observing the cloud point of weighed mixtures in sealed tubes or by titrating the amine in each phase of an equilibrated mixture.

Because of a slight clouding which occurred below the actual cloud point over a concentration range from about 5 to 40 weight % of water in most tertiary amines, coexistent phases were titrated to determine the actual solubility curve. The bottle containing the heterogeneous mixture was submerged in a constant temperature bath until both phases were clear. Without removing the bottle from the bath, a sample of each phase was withdrawn through a hypodermic needle and titrated in methanol with standard hydrochloric acid to an electrometric end point as determined with a Beckman Model G pH meter.

Solvents. Most of the secondary and tertiary amines were synthesized for this research or distilled from commercial products and were of very high purity. The data for triethylamine were taken from the literature (*9*) and are for a commercial product. *N*-Methyl-1-methylbutylamine, methylethylisopropylamine, and dimethylisopropylamine (Union Carbide Chemicals Co.) and di-*n*-propylamine (Matheson Coleman and Bell) were used without further purification.

All the primary amines were commercial products of varying purity. Solubility curves for *n*-octylamine (*12*), *n*-dodecylamine (*12*), and methyldiethylamine (*3*) have been previously determined and agree favorably with present results.

SOLUBILITY CURVES

The outstanding feature of the solubility curves, Figures 1 to 6, is the increase in the temperature sensitivity of solubility in going from primary to tertiary amines and the smaller, but similar effect of substitution on the α-carbon atom. Figure 2 may appear to be contradictory to the latter statement considering the behavior of the C_7 and C_8 normal amines, but all normal amines above C_6 tend to form gels with water at low temperatures and the solubility curve may deviate sharply in this neighborhood. For the normal amines, C_{10} and above, liquid phases do not exist beyond certain concentration ranges as indicated by the lower end of the solubility curves. The 1-methyl substitution apparently prevents the molecular order necessary for gel formation even for the C_{13} amine.

The curves for tertiary amines, Figure 6, are so sharp that the most easily distinguished difference is in the con-

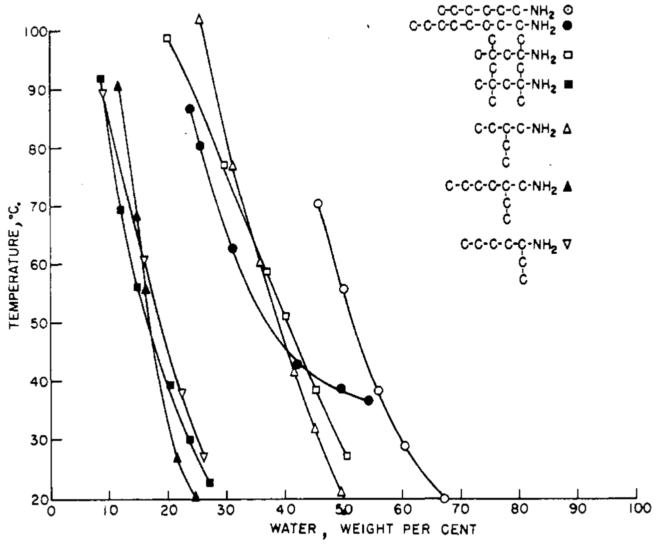

Figure 1. Branching of primary amines reduces solubility and may increase sensitivity to temperature

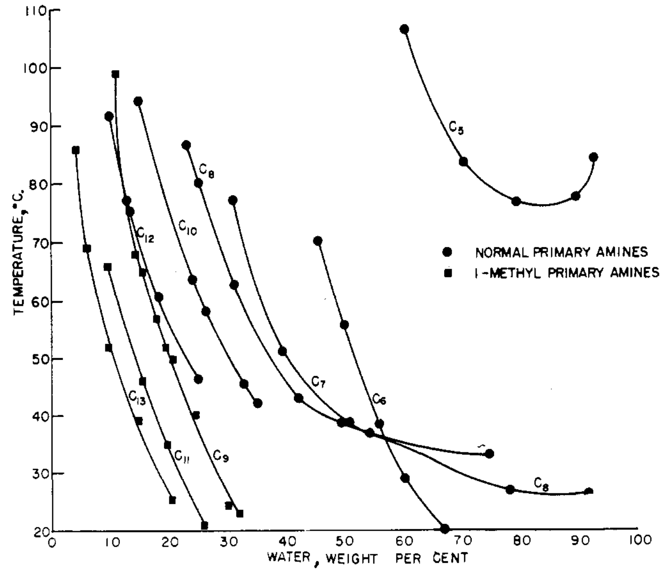

Figure 2. 1-Methyl substitution greatly reduces the solubility of water in primary amines

solute temperature. It is interesting that dimethyl-*tert*-butylamine has the highest consolute temperature among the C_6 *tert*-amines as does ethyl *tert*-butylamine among the C_6 secondaries. Among the C_5 amines, dimethylisopropylamine has the highest consolute temperature for the tertiaries, as does ethylisopropylamine for the secondaries.

THERMODYNAMICS OF BINARY PHASE EQUILIBRIUM

For two binary phases in equilibrium, one may equate the chemical potential for each component in the phase and combine with the Gibbs-Duhem equation to obtain *(6)*.

$$\left(\frac{y-x}{1-x}\right)\frac{\partial\mu_a}{\partial x}\,dx = -\,[y(\overline{S_a'}-\overline{S_a}) + (1-y)(\overline{S_b'}-\overline{S_b})]\,dT$$

$$+\,[y(\overline{V_a'}-\overline{V_a}) + (1-y)(\overline{V_b'}-\overline{V_b})]\,dP \qquad (1)$$

For a system at constant pressure, the last term is zero and for moderate pressure changes it is insignificant. Solving for dx/dT after eliminating the last term, one obtains

$$dx/dT = -\,\frac{y(S_a'-S_a) + (1-y)(S_b'-S_b)}{\left(\frac{y-x}{1-x}\right)\frac{\partial\mu_a}{\partial x}} \qquad (2)$$

but

$$\mu_a = \mu_a^* + RT\ln a$$

where μ_a^* is a function of temperature and pressure only, so

$$\frac{\partial\mu_a}{\partial x} = RT\,\frac{\partial\ln a}{\partial x}$$

At conditions of phase equilibrium,

$$\overline{S_a'} - \overline{S_a} = \frac{\overline{H_{a'}} - \overline{H_a}}{T}$$

and

$$\overline{S_a'} - \overline{S_a} = \frac{\overline{H_a'} - \overline{H_a}}{T}$$

Substituting in Equation 2 yields

$$dx/dT = -\,\frac{[y(\overline{H_a'}-\overline{H_a}) + (1-y)(\overline{H_b'}-\overline{H_b})]}{\left(\frac{y-x}{1-x}\right)RT^2\,\frac{\partial\ln a}{\partial x}} \qquad (3)$$

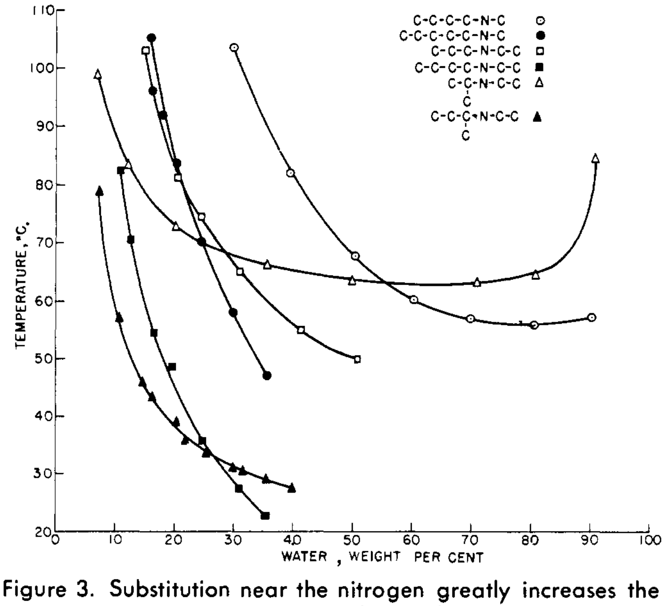

Figure 3. Substitution near the nitrogen greatly increases the temperature sensitivity of secondary amines

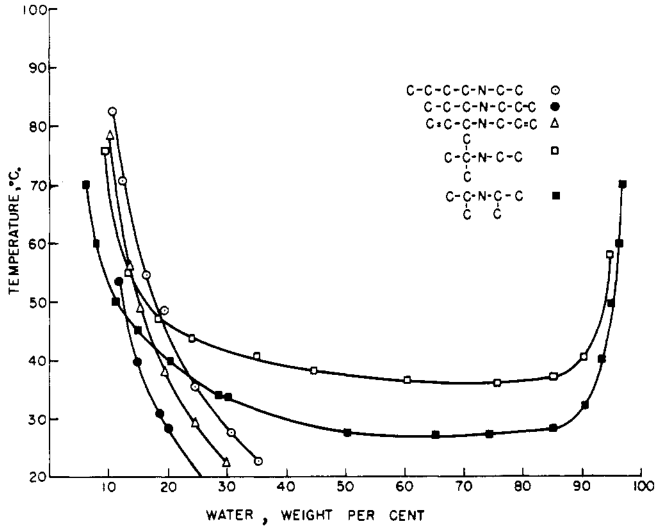

Figure 4. Solubility of water in secondary amines decreases with increasing symmetry

The numerator of Equation 3 is equal to the differential heat of solution. Except near the consolute point, y is very nearly one for the amine-water systems which are discussed here. Setting y equal to one and substituting Δh, the differential heat of solution, Equation 3 becomes

$$dx/dT = \frac{\Delta h}{RT^2\frac{\partial\ln a}{\partial x}} \qquad (4)$$

Very few data are available to verify the dependence of dx/dT upon Δh. Figure 7 shows heats of solution *(1, 7)* of various amines in water at infinite dilution. These values do not correspond to Δh in Equation 3, but it is interesting that the heat of solution increases in going from primary to tertiary amines as does the value, in general, of dx/dT. Of greater significance perhaps is the fair correlation obtained between the heat of solution at infinite dilution and the inductive effect, σ^* *(13)*. The highly branched and substituted compounds have a large inductive effect upon the amine nitrogen. It should be observed, however, that the allyl group (Figures 4 and 6) behaves, as far as solubility is concerned, very nearly as a propyl group in spite of its less negative inductive contribution.

The effects of the activity term in the denominator of Equation 4 on solubility may be readily demonstrated. It

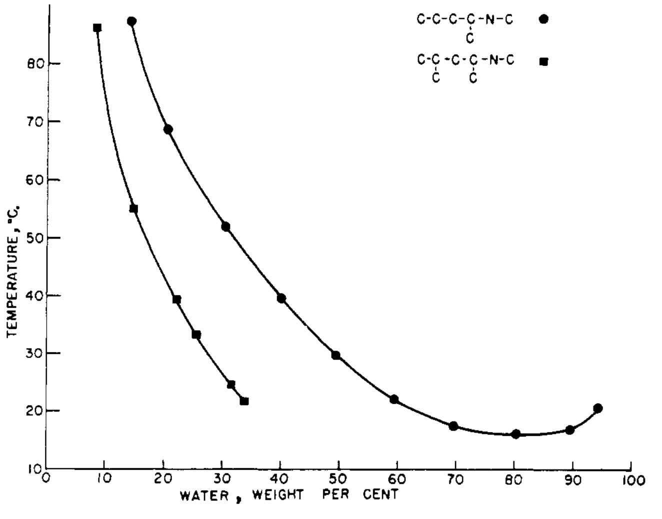

Figure 5. Substitution distant from the nitrogen is less effective

has been observed (5) that the addition of salt to the water-amine system causes a greater depression of the water content of the amine for those compounds which show a sharp change in solubility with temperature. This clearly indicates that a large change in water content is required to offset the lowering of water activity due to the addition of salt. Partial pressure data for triethylamine are available (8) for a temperature within 1° C. of its lower consolute temperature. The partial pressure of water is almost constant from a mole fraction of 0.25 to 1, indicating a very small value for $\partial \ln a/\partial x$. Triethylamine has also a high heat of solution with water, and consequently the extreme sensitivity of its solubility curve to change in temperature could be anticipated.

The term $\partial \ln a/\partial x$ may be written $\left[\frac{1}{x} + \frac{\partial \ln \gamma}{\partial x}\right]$. Since γ remains finite as x approaches zero, dx/dT must become small as x nears zero.

THE EXCESS FUNCTIONS AND PHASE SEPARATION

In order for a binary liquid mixture to form two phases, it is necessary that the Gibbs free energy, as a function of x, become concave upward. The composition of the two phases will be given by the intercepts of a tangent connecting the two points of equal slopes on the portions of the curve that are concave downward (11). The free energy of mixing is given by

$$g^M = g^I + g^E$$

where g^I is always negative and uniformly concave downward. In order for two phases to form, g^E must be positive and sufficiently large to cause a maximum in g^M. The necessary conditions for this to occur have been discussed elsewhere (2, 4), but there must exist some critical value of g^E above which phase separation will occur.

Now

$$g^E = h^E - Ts^E \tag{5}$$

and for systems exhibiting lower consolute temperatures, h^E must be negative. It is necessary, therefore, that a large negative excess entropy exist for these solutions. The excess enthalpy is not equal to Δh of Equation 4. The value of h^E is given by

$$X_a(\bar{H}_a - h_a) + X_b(\bar{H}_b - h_b)$$

while Δh is given by the numerator of Equation 3. One may expect, however, that h^E and Δh will have the same sign and be of the same order of magnitude. It follows that increasing h^E more than Ts^E will raise the lower consolute temperature and increase the sensitivity of the solubility to changes in temperature. Increasing s^E will lower the consolute temperature.

From the solubility curves and Figure 7 one may readily conclude that an increase in substitution on or near the nitrogen results in an increase in excess enthalpy. An increase in chain length, however, does not greatly change the shape of the curves, but lowers the consolute temperature, indicating that the excess entropy has been increased.

Steric effects are obscured by the corresponding inductive effects, but from Figures 1 and 2 one sees that 1-methyl and 2-ethyl substitution greatly reduces solubility, and it is safe to conclude that the excess entropy was increased.

Equation 4 shows that dx/dT will decrease with the square of the absolute temperature. In addition, the excess heat capacities for these systems are positive, so that increasing the temperature will decrease both s^E and h^E. Because of this, low molecular weight compounds which form two phases at higher temperatures will, in general, show less sharp solubility curves. Diethylamine, which has a very high excess enthalpy of 49.10 (2), does not form two phases until just below 144° C. (10), after which the separation occurs slowly with increasing temperature. If h^E becomes positive as the temperature increases, an upper consolute temperature may exist.

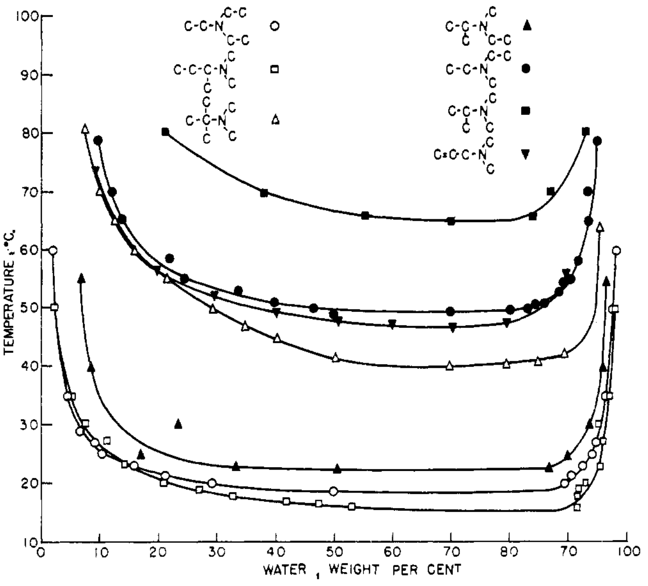

Figure 6. The lower consolute temperature of tertiary amines is increased by branching

CONCLUSION

Many amines are promising as solvents for purifying saline waters. Tertiary amines and highly branched secondary amines containing 5 or 6 carbon atoms in each instance have the best solubility curves.

Structural characteristics such as size and branching of substituent alkyl groups seem to affect the solubility in a uniform and predictable manner through their effects upon the thermodynamic functions of Equations 4 and 5. Equation 4 in turn shows that certain limitations exist upon the desirable properties of any solvent in that a favorable slope can only be obtained with a high heat of solution and an unfavorable depression of the solubility upon the addition of salt.

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NOMENCLATURE

a = activity
$g, \bar{G}$ = molal and partial molal free energy
g^M, g^I, g^E = molal, ideal molal, excess molal free energy of mixing
$h, \bar{H}$ = molal and partial molal enthalpy
h^E = molal excess enthalpy of mixing
Δh = differential enthalpy of solution, Equations 3 and 4
P = pressure
R = gas constant
$s, \bar{S}$ = molal and partial molal entropy
T = absolute temperature
$\bar{V}$ = partial molal volume
x = mole fraction in amine-rich phase
y = mole fraction in water-rich phase
γ = activity coefficient
μ = chemical potential or partial molal free energy
μ^* = chemical potential of the pure component
σ^* = inductive constant

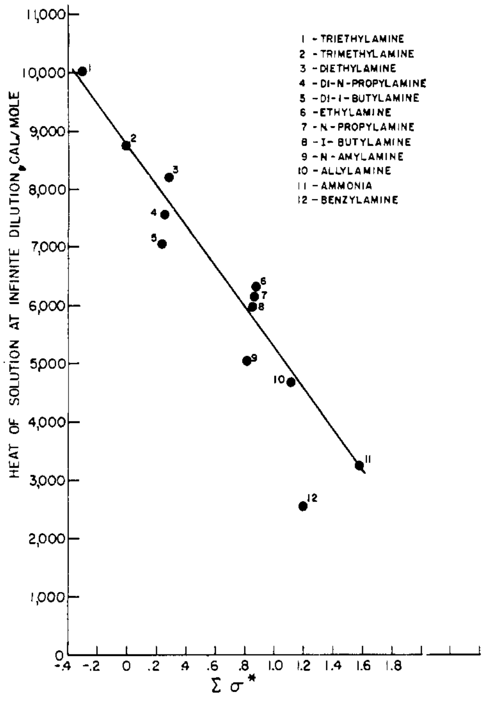

Figure 7. The heat of solutions of amines in water is a function of the total inductive effect

Subscripts

a = water
b = amine

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Selective Solvents for Separation of *n*-Pentane from 1-Pentene by Extractive Distillation

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EXTRACTIVE distillation is widely used on a commercial scale as a method for separating butanes from butylenes. Extractive solvents in commercial use include furfural-water (*3*), acetone-water (*6*), and acetonitrile-water (*4*). These same solvents are also suitable for effecting a separation between butylenes and butadiene, and between methyl butenes and isoprene. The present investigation was undertaken to find solvents which would be superior to those now in commercial use for paraffin-olefin-diolefin separations. Specifically, it was desired to find solvents or solvent mixtures which would produce either an improved selectivity, capacity, or both.

Unfortunately, the theory of nonideal liquid mixtures is not sufficiently well-developed to allow a sound prediction to be made of the performance of any proposed extractive solvent (*2, 10*). An experimental approach is thus necessary to determine the optimum type of structure which extractive solvent molecules should have. Study of a large number of different solvents is required to determine which types of functional groups on the solvent molecule are the most effective, and which of the many possible spacings and arrangements of these groups are the optimum.

Very few literature data exist on the vapor-liquid equilibrium behavior of paraffin-olefin-solvent mixtures. Hess, Naragon, and Coghlan did report such information for a large number of different solvents (*8*), but their data are difficult to use as in most cases their measurements were made at a single pressure (60 p.s.i.g.) and for a single concentration; thus it is not possible to compare different solvents at the same temperature. Other solvent evaluation studies have been reported (*5, 11*), but these are for the separation of aromatics from napthenes and paraffins by extractive distillation. These studies were of no assistance in the present program.

SCOPE OF THIS INVESTIGATION

Emphasis on evaluation of a large number of different solvents made it necessary to limit the number of tests with any given solvent. It was decided to limit the range of experimental composition to an essentially 100% solvent concentration, to vary the temperatures between 0° and 45° C., and to limit to a single pair the hydrocarbons to be separated, *n*-pentane-1-pentene. These C_5 hydrocarbons were chosen in preference to C_4 hydrocarbons to permit the use of low pressure, all-glass apparatus; the difference in the performance of C_4 and C_5 hydrocarbons in the presence of a solvent is not large and may be estimated (*1*). A diolefin was not studied in this work because solvents

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