A Thermodynamic Correlation of Nonpolar Gas Solubilities in Alcohols

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Two avenues of approach have generally been used to describe the thermodynamic properties of solutions consisting of a nonpolar component and an alcohol which associates through the mechanism of hydrogen bonding.

First, a simplified model of a solution is assumed where the molecules occupy sites on a quasi lattice and the interaction energies of the molecules depend on their mutual orientations. Such a model has been developed by Munster (*23*) and Tompa (*29*). Barker (*1*) assumed a slightly different model where the interaction energies of the neighboring molecules depend on the parts of the molecular surface which are in contact. Once the model has been set up, the statistical method employed follows that used in the theory of strictly regular solutions. Although the agreement between experimental and calculated excess properties of alcohol solutions is good, the validity of the assumed model remains uncertain, since four adjustable parameters are used to fit the data in each model.

The second approach is that of linear association. Alcohols in the liquid state are known to be associated into linear polymers with an equilibrium mixture containing polymers of all degrees of polymerization. This concept of continued association was first introduced by Lassettre (*19*), who studied the effect of linear association in hydrogen bonding systems on the colligative properties of such solutions. Tobolsky and Blatz (*28*) and Flory (*6*) made the initial attempts to treat alcohol solutions with the equations developed for high polymer solutions. Redlich and Kister (*25*) and Kretschmer and Wiebe (*15*) assumed slightly different models for the association phenomena and arrived at similar relations for the partial molal Gibbs free energy of mixing of the nonassociating component. Two parameters must be specified in this approach.

As an extension of the correlations of low-pressure, nonpolar gas solubilities in nonpolar and polar, nonassociated liquids of Yen and McKetta (*30*), a correlation is presented here for estimating such gas solubilities in alcohols. It is based on the theoretical approach of Kretschmer and Wiebe (*15*) which is felt to be the most suitable for correlation purposes. The only correlation for such systems presently available in the literature is that of Gjaldbaek and Niemann (*8*), who empirically correlated the solubilities of nitrogen, argon, and ethane in alcohols by using the equation of Gjaldbaek and Hildebrand (*7*).

THEORETICAL CONSIDERATIONS

For details of the development of Kretschmer and Wiebe, the reader is referred to the original article (*15*). The partial molal Gibbs free energy of the nonassociating component is

$$\Delta\overline{G}_o = RT\left(\ln\phi_o + 1 - \frac{V_o}{V}\right) + bV_o\phi_o^2 \qquad (1)$$

$$\frac{1}{V} = \frac{\phi_o}{V_o} + \sum_{i=1}^{\infty}\frac{\phi_i}{V_i} \qquad (2)$$

The summation is over all i species consisting of i monomeric alcohol molecules. The association equilibrium constant which is assumed independent of i is

$$K' = \frac{c_i}{c_{i-1}c_i} \qquad (3)$$

where $c_i = \phi_i/V_i$. Through various manipulations the following are obtained:

$$\phi_a = \frac{\phi_1}{(1 - K\phi_1)^2} \qquad (4)$$

and

$$\frac{1}{V} = \frac{\phi_o}{V_o} + \frac{\phi_a(1 - K\phi_1)}{V_a} \qquad (5)$$

where $K = K'/V_1$ and ϕ_1 is the volume fraction of alcohol in the monomeric state at equilibrium. ϕ_1 is obtained by solving Equation (4):

$$\phi_1 = \frac{[2K\phi_a + 1 - (4K\phi_a + 1)^{1/2}]}{2K^2\phi_a} \qquad (6)$$

Equation (1) was derived on the assumption that there is no volume change on mixing. However, for processes in which gases are dissolved in liquids, there is a large decrease in volume of the gaseous component. To overcome this difficulty Prausnitz and Shair (*24*) hypothesized a two-step dissolution process. For the partial pressure of the gaseous component equal to 1 atm.

$$a_o = f^{OL} \qquad (7)$$

Since

$$\Delta\overline{G}_o = RT\ ln\ a_o \qquad (8)$$

Equations (1) and (7) combine to give a correlation equation of

$$-\log\phi_o = \log f^{OL} + \frac{1}{2.3}\left(1 - \frac{V_o}{V}\right) + \frac{bV_o\phi_a^2}{2.3RT} \qquad (9)$$

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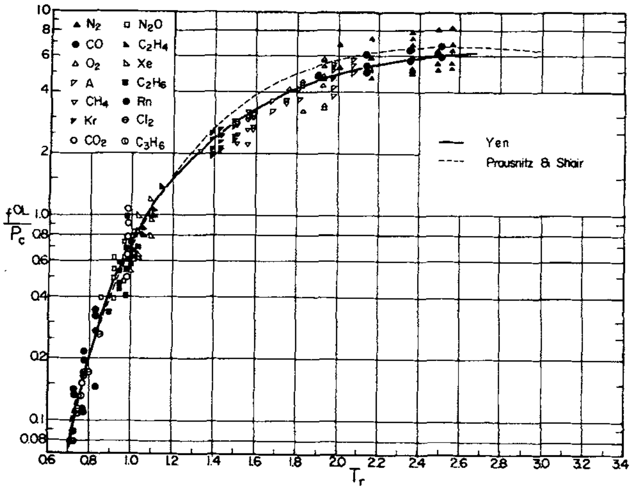

Fig. 1. Fugacity of hypothetical liquid at pressure of 1 atm.

DEVELOPMENT OF THE CORRELATION

This correlation is designed to be as compatible as possible with the correlations of Yen and McKetta (*30*) of which this work is an extension. Therefore, the parameters f^{OL} and V_o are the same in all three correlations. The fugacity of the hypothetically condensed gas should be independent of the nature of the liquid involved but temperature-dependent. It can be correlated by the principle of corresponding states into a reduced fugacity plot of f^{OL}/P_c vs. T_r given in Figure 1.

For convenience, helium, hydrogen, and neon are correlated separately in Figure 2. The hypothetical fugacity and molal volume for helium, neon, and cyclopropane were calculated from solubility data in nonpolar liquids (*3, 4, 11, 17, 27*) by the methods outlined by Yen and McKetta (*30*). Low-pressure solubility data for *n*-butane, *i*-butane, and propane in nonpolar liquids are not available. However, hypothetical liquid fugacities for these gases can be determined from the general correlation of Figure 1.

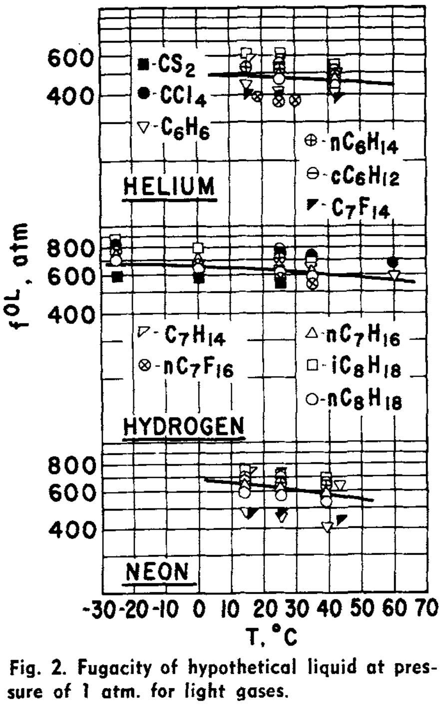

Fig. 2. Fugacity of hypothetical liquid at pressure of 1 atm. for light gases.

TABLE 1. MOLAL VOLUMES OF HYPOTHETICAL LIQUID AND GAS SOLUBILITY DATA IN ALCOHOLS

Gas	Molal volume cc./g.-mole	Molal volume Reference	Solubility data Temperature range, °C.	Solubility data Reference
Argon	55.0	*30*	15 to 37	*2, 17*
n-Butane	101.4	*26*	25 to 50	*13, 14*
i-Butane	105.5	*26*	10 to 50	*13, 14*
Carbon dioxide	62.0	*30*	15 to 25	*10*
Carbon monoxide	40.2	*30*	25 to 50	*20*
c-Propane	68.0	*21*	0 to 40	*21*
Ethane	70.0	*30*	25 to 35	*2, 8*
Ethylene	50.0	*30*	25	*2*
Helium	33.0	*21*	15 to 37	*17*
Hydrogen	37.3	*30*	0 to 50	*10, 22*
Methane	50.7	*30*	18 to 37	*2, 18*
Neon	49.8	*21*	15 to 37	*17*
Nitrogen	40.0	*30*	−25 to 50	*2, 8, 12*
Nitrous oxide	51.0	*30*	18 to 36	*16*
Oxygen	49.6	*30*	−25 to 50	*12*
Propane	89.5	*26*	0 to 50	*13, 14*

Some data (*9*) indicate that the partial molal volumes of gases in alcohols are not significantly different from those in nonpolar liquids. Although not strictly so, the molal volumes are preseumed to be independent of temperature for the purposes of the correlations. The molal volumes of the alcohols and the gases were taken as constant at their 25°C. value. The molal volumes of the gases are given in Table 1, and the molal volumes and solubility parameters for the alcohols are given in Table 2.

The volume of one true mole of solution V was calculated by Equations (5)and (6). The association equilibrium constant K may be determined by many different techniques. Unfortunately, in the case of alcohols, there has been no general consensus as to even the approximate values of the equilibrium constant and its temperature dependence. Dannhauser and Bahe (*5*) have determined the temperature dependence of K for a large number of lower alcohols by analyzing dielectric constant data. The difficulty involved in incorporating equilibrium constants from dielectric data into solution theories is that constants obtained from the different sources frequently do not agree. Hence, the procedure was to start with the equilibrium constants for methanol and ethanol by Kretschmer and Wiebe (*15*) from solution data and to estimate the relative values for the other alcohols from the work of Dannhauser and Bahe (*5*). In this manner a consistent set of association equilibrium constants, shown in Figure 3, was obtained.

For systems containing an associating component, the parameter b is too complex to be calculated from pure component properties. Therefore, the correlation Equation (9) is regarded as semiempirical with the parameter b to be determined from experimental data. It is not un-

TABLE 2. MOLAL VOLUMES AND SOLUBILITY PARAMETERS FOR ALCOHOLS

Alcohol	V_a, cc./g.-mole	δ_a, (cal./cc.)$^{1/2}$	Reference
MeOH	40.7	14.35	*26, 8*
EtOH	58.7	12.80	*26, 8*
n-PrOH	75.2	11.95	*26, 8*
i-PrOH	77.0	11.44	*26*
n-BuOH	92.0	11.20	*26, 8*
n-PeOH	108.7	10.90	*26, 8*

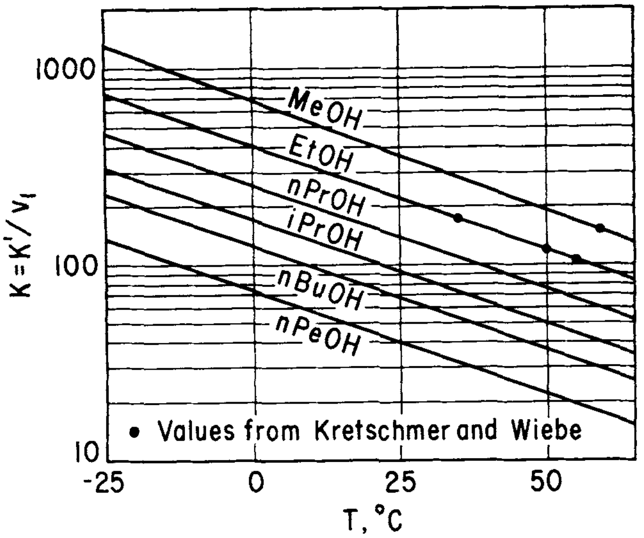

Fig. 3. Temperature dependence of association equilibrium constant for alcohols. *K'* is in units of concentration.

reasonable to expect to find a unique *b* for each gas-alcohol system.

All of the reliable solubility data of nonpolar gases in the lower alcohols (six were considered) were collected from the literature. The sources and temperature range of these data are given in Table 1. The data at 25°C. were used to calculate values of *b* from Equation (9). For each gas *b* was correlated against δ_a by a first-degree equation

$$b = A - B\delta_a \tag{10}$$

by the least squares method. The values of *b* from both Equations (9) and (10) are shown in Figure 4. The parameter *b* was taken to be temperature independent, and the results of the correlation justify this assumption.

For one hundred and sixty-four selected data points over a temperature range of −25° to 50°C., the correlation gives an average deviation of 4.16% between the experimental value of gas mole fraction and the value calculated from Equation (9) by using the value of *b* calculated from Equation (10). The maximum deviation was 22.9% for nitrogen in ethanol at −25°C. With the values of *b* from Figure 4 it is now possible to estimate low-pressure gas solubilities in alcohols when no experimental data are available. Yen and McKetta (*30*) give values of V_o for krypton, xenon, radon, and chlorine for which no experimental solubility data in alcohols have been reported.

The correlation satisfactorily reproduces the temperature dependence of the gas solubilities. Gases with critical temperatures less than 153°K. (between argon and oxygen) have positive temperature coefficients of solubility (solubility increases with increasing temperature). Those gases with critical temperatures greater than 153°K. possess a negative temperature coefficient. The correlation is very successful in accounting for this temperature-solubility reversal.

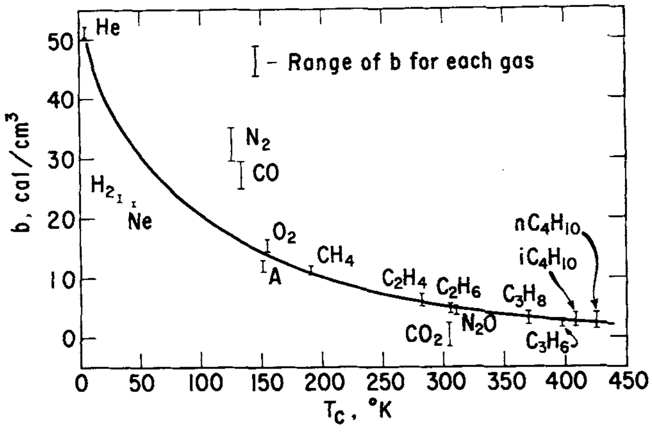

Fig. 4. *b* vs. T_c for nonpolar gases.

CONCLUSIONS

The association model of Kretschmer and Wiebe may be used to correlate semiempirically the low-pressure solubilities of nonpolar gases in the lower alcohols in accordance with Equation (9). The parameter *b* appears to be unique for each gas-alcohol system and may be correlated with the solubility parameter of the alcohol for each gas.

ACKNOWLEDGMENT

This work was carried out under a National Science Foundation Grant.

NOTATION

a = activity
A = parameter in Equation (10)
b = semiempirical parameter in Equation (9)
B = parameter in Equation (10)
c_i = concentration of species $i = \phi_i/V_i$
f^{OL} = fugacity of hypothetical liquid at pressure of 1 atm.
ΔG = Gibbs free energy change
K = association equilibrium constant
K' = KV_1
P = pressure
R = gas constant
T = temperature
V = volume of one true mole of solution
V_a = molal volume of alcohol
V_o = molal volume of hypothetical liquid
δ = solubility parameter
ϕ = volume fraction

Subscripts

a = alcohol
c = critical
i = degree of alcohol polymerization
o = gas
r = reduced
1 = alcohol monomer

Superscripts

M = mixing
$-$ = partial molal quantity

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On the Nonuniqueness of the Entry Length

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The problem of entry length in laminar channel and pipe flows has a very large literature (*1*) which appears to be exclusively preoccupied with flow development starting from an initially flat or uniform velocity profile. The entry length is usually defined as the length at which the centerline velocity reaches 98% of the final value. Boundary-layer equations are generally employed, but there are exceptions (*2*). Considerable precision in this standard calculation is evident; values for channels of (0.034 ± 0.001) WN_{Re} are now accepted. Here W is the channel width and the Reynolds number is based on W and the mean velocity.

During some numerical experiments (*3*) we tried some nonuniform initial profiles for a channel. The program utilized simple finite-difference methods (*4*) to solve the full two-dimensional steady state form of the Navier-Stokes equations. The initial profiles tried were: (1) uniform profile; (2) symmetrical triangular profile; (3) parabolic velocity over central half of channel, zero velocity on outer parts (symmetrical profile); and (4) parabolic velocity over top half of channel, zero velocity on bottom half (asymmetrical profile).

Reynolds numbers up to 100 were tried but no calculations for $N_{Re} \overset{\sim}{>} 50$ were successful. For profile 1, entry lengths of $0.4W$, $0.6W$, and $1.7W$ were recorded at Reynolds numbers of 0.1, 10, and 50, respectively. For $N_{Re} = 50$, the entry length is close to that given by the $0.034\ WN_{Re}$ formula. As $N_{Re} \rightarrow 0$, the entry profile can be shown to die away exponentially (*5*), giving an entry length of about $0.4W$; this agrees with our value for $N_{Re} = 0.1$. Profiles 1 to 4 were tested at $N_{Re} = 10$ (limited by running time), giving entry lengths of $0.6W$, $0.6W$, $0.9W$, and $1.4W$, respectively. In the latter case, the 2% error criterion is unsuitable and the length taken for the centerline axial velocity to become greater than all others was taken as being the entry length. The ironing out of the asymmetry is clearly very slow. Confirmation of these values is available from the work of Kawaguti (*6*), who has solved numerically the problem of a suddenly expanding asymmetrical channel; thus his entry profiles are natural entry profiles and are quite similar to our case (4). Kawaguti (*6*) obtained entry lengths $> 1.2W$, $> 3.2W$ for Reynolds numbers of 16 and 64, respectively. His work also ceases at an upper limit of $N_{Re} = 64$.

The conclusions are:

1. Boundary-layer theory gives reasonable results for entry length at $N_{Re} > 50$ for flat profiles.
2. The inlet length is not a unique quantity but depends upon the inlet profile.
3. Asymmetrical profiles take a very much longer time to settle down than symmetrical profiles.
4. Further research, if any, on inlet lengths should include nonuniform entry profiles. Although some of these points are perhaps obvious, we have not seen them explicitly mentioned before; flow in pipes can be expected to show similar phenomena.

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