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Molecular Thermodynamics of Gases in Mixed Solvents

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The general thermodynamic relation between Henry's constant for a solute in a mixed solvent and Henry's constants for the solute in the pure solvents is discussed in terms of limiting activity coefficients. The inadequacy of several common excess free energy expressions is shown, and results are presented for a form of Kirkwood-Buff solution theory based on pair distribution functions. Several unknown integrals in the theory are approximated by an empirical function of solvent composition and of solvent properties which generally predicts experimental data for gases in both simple and complex binary solvents with good accuracy. Prediction of fugacities of gaseous components in ternary and higher solvents and in nonideal solutions is considered.

Many chemical processes involve separations of solutes from multicomponent solvents. Distillation or stripping of gases, crystallization of solids, or extraction of slightly soluble substances all can involve this type of system. In these cases it is often convenient to use Henry's constant in the mixed solvent as the reference fugacity for the dilute component. This is based on experience with pure solvents which indicates that deviation from Henry's law often occurs only when significant amounts of solute are dissolved in the liquid. Although several treatments of solutes, particularly gases, in mixed solvents have appeared in recent years (*1* to *7*), most have dealt with particular equations for the excess free energy in the multicomponent mixture which are of limited application.

In this paper the general thermodynamic relationship for a solute in a mixed solvent is presented and the approximate equations which lead to previous results for gases are indicated. A general solution theory, based on the method of Kirkwood and Buff (*8*) but derived for a multicomponent solvent, is then used to obtain the mixed solvent Henry's constant in terms of pure solvent Henry's constants and integrals of the pair distribution functions of the system. Finally, since it is not possible to evaluate some of these integrals presently, particularly for complex mixtures, an empirical expression is developed for gases in mixed solvents which contains only readily accessible properties of the solvents and the solvent mixture. The results of this expression are compared with data for several systems of a gas in a binary solvent and the accuracy is better than with other methods not involving parameters from the multicomponent data. One multicomponent parameter is often sufficient to provide extremely good agreement for data over the entire range of solvent composition.

REFERENCE FUGACITY FOR A SOLUTE IN MIXED SOLVENTS

The primary aim in this work is to develop a method of predicting the fugacity of a solute in a mixed liquid solvent. This fugacity is equal to that in any other phase (solid, liquid, or gas) and is used to determine the distribution of the solute between the phases involved. The liquid fugacity can be expressed as

$$f_i^L = x_i\gamma_i(P^0)f_i^0(P^0)\exp\int_{P^0}^{P}\frac{\overline{v}_i}{RT}\,dP \tag{1}$$

where the activity coefficient and reference state fugacity are both given at the reference pressure, and the system temperature.

The product $\gamma_i(P^0)f_i^0(P^0)$ can be obtained from two commonly used conventions. One is the symmetric convention for activity coefficients where all components follow

$$\lim_{x_i\to 1}\,(\gamma_i f_i^0) = f_i^{0L}(P^0) \tag{2}$$

The reference fugacity is the pure component fugacity of i as a liquid at the reference pressure. For subcritical components, P^0 is usually the saturation pressure. For components which are not liquids at T, a hypothetical pure component liquid fugacity must be used.

The unsymmetric convention for activity coefficients is where Equation (2) is used for subcritical components j and Equation (3) is used for all solute components i.

$$\lim_{x_i \to 0} (\gamma_i f_i^0) \equiv \lim_{x_i \to 0} (\gamma_{i,j}^* H_i) = H_{i,j}(P^0) \tag{3}$$

Thus the reference state of i is the solute at infinite dilution and the reference fugacity is Henry's constant. The reference pressure is usually the saturation pressure of the solvent. Prausnitz (*1*, *6*, *9*) has shown the value of the unsymmetric convention for activity coefficients of gases in solution. In particular, the unsymmetric convention is more useful for dilute solutions since there is no need to determine the hypothetical reference fugacity by extrapolating experimental data that are often available only far from the pure solute composition. In addition, the activity coefficient is often close to unity up to moderate solute concentrations and can be predicted relatively well from simple functions of composition.

Despite its inconvenience, the hypothetical pure component liquid fugacity can be used, without being evaluated, in the derivation of several relationships. Thus Prigogine and Defay (*10*) show that in a binary system

$$\ln (\gamma_{i,j}/\gamma^*_{i,j}) = \lim_{x_i \to 0} \ln \gamma_{i,j} \tag{4}$$

and

$$\ln (\gamma_{i,j}/\gamma^*_{i,j}) = - \lim_{x_i \to 1} \ln \gamma^*_{i,j} \tag{5}$$

We define Henry's constant for i in an M component solvent mixture in the same manner as in Equation (3):

$$\ln(\gamma^*_{i,m} H_{i,m}) \equiv \ln(\gamma_{i,m} f_i^0) \tag{6}$$

Then subtracting a mole fraction average of the binary expressions (3) from the multicomponent expression (6) (other averages such as the volume fraction average may also be used), using Equation (4) and its multicomponent equivalent, and rearranging, we get the general result

$$\ln H_{i,m} - \sum_{j=1}^{M} x_j \ln H_{i,j} = \lim_{x_i \to 0} \ln \gamma_{i,m} - \sum_{j=1}^{M} x_j (\lim_{x_i \to 0} \ln \gamma_{i,m}) \tag{7}^*$$

The use of Equation (5) yields a new general relation

$$\ln H_{i,m} - \sum_{j=1}^{M} x_j \ln H_{i,j} = \sum_{j=1}^{M} x_j (\lim_{x_i \to 1} \ln \gamma^*_{i,j}) - \lim_{x_i \to 1} \ln \gamma^*_{i,m} \tag{8}$$

All the variables must be referred to the same standard state pressure. If the activity coefficient of the solute is unity (ideal mixture) in all the solvents and in the solvent mixture, or for certain expressions for the multicomponent activity coefficients, the right-hand sides of Equations (7) and (8) are zero, yielding a result first derived by Krishchevsky:

$$\ln H_{i,m} - \sum_{j=1}^{M} x_j \ln H_{i,j} = 0 \quad \text{(ideal mixture)} \tag{9}$$

These equations are applicable to any solute. In the present work they will be applied to systems where the solute is a gas since most previous work has considered these situations and data are more readily available.

EXAMPLES USING VARIOUS EXPRESSIONS FOR EXCESS FREE ENERGY

Equations (7) and (8) can be used with expressions for the activity coefficients from models for the excess Gibbs energy. Several examples follow.

1. Porter and Kohler Equations

O'Connell and Prausnitz (*5*) use the one-term Margules (Porter) equation for the excess free energy of the system. This leads to

$$\ln H_{i,m} - \sum_{j=1}^{M} x_j \ln H_{i,j} = - \sum_{\substack{j>k \\ j,k \neq i}}^{M} \sum_{k=1}^{M-1} \alpha_{jk} x_j x_k = \frac{- g^E \text{ (solvents)}}{RT} \tag{10}$$

Thus the deviation of Equation (7) from ideal solution is given by the excess Gibbs function for the mixture of solvents and does not depend upon the gas. Kehiaian (*2*) has shown Equation (10) to be correct also if Kohler's equation (*10*) holds for the mixture. The right-hand side of Equation (10) is usually too large in magnitude when compared with experiment for gases in solution and often is of the wrong sign for complex mixtures (see below).

2. Wilson Equation

Prausnitz et al. (*13*) use the Wilson equation for all systems, including those containing gases.[*] For a binary solvent this yields

$$\ln H_{1,m} - \sum_{j=2}^{3} x_j \ln H_{1,j} = - \ln \left[x_2 \left(\frac{\Lambda_{12}}{\Lambda_{13}} \right)^{x_3} + x_3 \left(\frac{\Lambda_{13}}{\Lambda_{12}} \right)^{x_2} \right] - \frac{x_2 x_3 (1 - \Lambda_{23}) \Lambda_{21}}{x_2 (1 - \Lambda_{23}) + \Lambda_{23}} - \frac{x_2 x_3 (1 - \Lambda_{32}) \Lambda_{31}}{x_3 (1 - \Lambda_{32}) + \Lambda_{32}} \tag{11}$$

No progress can be made without knowledge of Λ_{12}, Λ_{13}, Λ_{31}, and Λ_{21} which characterize gas-solvent nonideality. Thus, in order to describe ideal solution behavior ($H_{i,m}$), parameters describing nonideality are necessary! This is true for any complex (and thus realistic) expression for the excess free energy.

Prausnitz et al. (*13*) chose $\Lambda_{31} = \Lambda_{21} = 0$, leading to

$$\ln H_{i,m} - \sum_{j=2}^{3} x_j \ln H_{1,j} = - x_3 \ln (H_{1,3}/H_{1,2}) - \ln \left[1 + x_3 \left(\frac{H_{1,2}}{H_{1,3}} \right) \right] \tag{12}$$

Unfortunately the right-hand side of Equation (12) yields values which are always negative and thus at variance with many data (see below).

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[*] This equation apparently first appeared in an appendix of reference *6* and implicitly in the derivation of some of the equations in reference *1*.

[*] Prausnitz et al. also use Henry's constant for the gas in a single reference solvent as the reference fugacity for gaseous components. That is, for a gaseous component

$$\lim_{\substack{x_i \to 0 \\ x_r \to 1}} (\gamma_i^* f_i^0) = H_{i,r}(P^0)$$

where r is a suitably chosen reference solvent. However, this results in serious errors on occasion, indicating that the mixed solvent Henry's constant may be a better choice.

3. Van Laar Equation

Prausnitz and Chueh (*1, 6*) and Boublik and Hala (*7*) use the equivalent of Equation (7) with volume fractions and the Wohl form of the Van Laar equation to obtain

$$\ln H_{i,m} - \sum_{j=1}^{M} \Phi_j \ln H_{i,j} = \frac{-v_{ci}}{2} \sum_{\substack{j=1 \\ j,k\neq i}}^{M} \sum_{k=1}^{M} \alpha_{jk}\Phi_j\Phi_k - \Delta \tag{13}$$

where Φ_j is the volume fraction, α_{jk} is the two-body interaction parameter, and Δ contains three-body and higher-order terms. Ignoring Δ leads to a result similar to Equation (10). On the other hand, the result obtained from the dilated Van Laar model (*1*) using Equation (8) for a binary solvent is

$$\ln H_{1,m} - \sum_{j=2}^{3} \Phi_j \ln H_{i,j} = v_{c1} \left\{ \alpha_{11}(ms)\,[1+\eta_1(ms)] - \sum_{j=1}^{M} \Phi_j \alpha_{11}(j)\,[1+\eta_1(j)] \right\} \tag{14}$$

Since the mixing rules for α and η are complex, there is a slight inconsistency mainly because the dilated Van Laar model, which is more accurate for gases in solution, does not follow from the usual Van Laar expression and Equation (4). However, the consequences of this for calculations are probably very small.

It is not surprising that some of the above free energy expressions, developed primarily for subcritical components, are at variance with the experimental data. Equation (5) implies that for $\ln \gamma_i^*$, both the slope and curvature with mole fraction are the same as those of $\ln \gamma_i$. However experiment (*1, 9*) shows that activity coefficients for gases have a negative second derivative, whereas subcritical components have a positive one. The dilated Van Laar model yields the only expression listed above which, with normal parameter values, has a negative curvature at finite concentrations. However, even for this equation, near the limit $x_i \to 0$, the curvature abruptly changes. In view of these discrepancies, more fundamental ways of obtaining the Henry's constant in the mixed solvent were explored.

KIRKWOOD-BUFF SOLUTION THEORY

All the equations above involve more or less empirical expressions for activity coefficients. Statistical mechanical theories can lead to more accurate approximations, and of the three general solution theories that have been formulated (*8, 14, 15*), the method of Kirkwood and Buff (*8*) was chosen for development. Recent progress in calculating radial distribution functions may lead eventually to direct application for the systems of interest here. However, for the present, an empirical expression must be used for some of the exact integrals which appear in the final expressions.

The basis for the Kirkwood-Buff expressions is in statistical mechanical fluctuation theory which relates integrals of the radial distribution function to the dependence of the molecular concentration on the chemical potential. By matrix manipulation, general expressions for multicomponent systems have been developed (*16*) and the final result for the activity coefficient in a binary is

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P,N_2} = \frac{-x_2(H_{11}+H_{22}-2H_{12})}{1+x_1x_2(H_{11}+H_{22}-2H_{12})} \tag{15}$$

where

$$H_{ij} = H_{ji} \equiv \frac{1}{v} \int (g_{ij}^{(2)} - 1)\, dv \tag{16}$$

and $(g_{ij}^{(2)} - 1)$ is called the total correlation function (*17*). For a ternary, the result is

$$\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P,N_3} = \frac{\dfrac{x_2x_3f_{23}}{(x_2+x_3)} - x_2f_{12} - x_3f_{13} - x_2x_3W}{1 + x_1x_2f_{12} + x_1x_3f_{13} + x_2x_3f_{23} + x_1x_2x_3W} \tag{17}$$

where

$$f_{ij} = H_{ii} + H_{jj} - 2H_{ij} \tag{18}$$

and

$$\begin{aligned} W = (&H_{11}H_{33} + H_{11}H_{22} + H_{22}H_{33} - 2H_{12}H_{33} \\ &- 2H_{13}H_{22} - 2H_{11}H_{23} + 2H_{13}H_{23} + 2H_{12}H_{23} \\ &+ 2H_{12}H_{13} - H_{12}^2 - H_{13}^2 - H_{23}^2) \end{aligned} \tag{19}$$

In general, the composition dependence of H_{ij} is not known, so it is not possible to integrate Equations (15) and (17). However, useful results can be obtained for a gas (i) in solution by solving for $\ln \gamma_i$ in a Taylor's series about $\ln \gamma_i$ when i is at infinite dilution.

$$\ln \gamma_i = (\ln \gamma_i)_{x_i=0} + x_i\left(\frac{\partial \ln \gamma_i}{\partial x_i}\right)_{x_i=0} + \frac{x_i^2}{2}\left(\frac{\partial^2 \ln \gamma_i}{\partial x_i^2}\right)_{x_i=0} + \ldots \tag{20}$$

In addition to describing nonideality, Equation (8) may then be used to obtain mixed solvent Henry's constants if Equation (20) is assumed to describe the composition dependence of $\ln \gamma_i$ to the limit $x_i = 1$. To terms consistent to the second order in the mole fraction of a gas (*1*) in a binary solvent (*2, 3*)

$$\ln \gamma_1^* = \left(x_1 - \frac{x_1^2}{2}\right) \left[\frac{x_2x_3f_{23}^+ - (x_2f_{12}^+ + x_3f_{13}^+)(x_2+x_3)}{(x_2+x_3)^2 + x_2x_3f_{23}^+}\right] + \ldots \tag{21}$$

where the $^+$ denotes that component 1 is in infinite dilution in the mixed solvent and thus the f_{ij}^+ are functions of the solvent composition. For a single solvent ($x_3 = 0$)

$$\ln \gamma_1^* = -\left(x_1 - \frac{x_1^2}{2}\right) f_{12}^0 \tag{22}$$

where the superscript 0 indicates that component 1 is in infinite dilution in the single pure solvent. Equation (22) is the familiar one-term Margules relation in the unsymmetric convention, since f_{12}^0 is independent of composition.

Unfortunately, higher-order terms in Equation (20) are quite complicated, containing, in particular, triplet distribution functions which cannot be well approximated (*8, 16*). Furthermore, Equation (22) suffers from the same deficiency that was mentioned previously: the second derivative of $\ln \gamma_1^*$ with respect to x_1 at infinite dilution has a positive value. However, the next higher-order term in Equation (20) does contribute a term in x_1^2 and can lead to the experimental negative second derivative (*16*). Finally, since the H_{ij} that appear in f_{ij}^+ are different from those that appear in f_{ij}^0, nonideality in binary gas-solvent systems may be required to accurately describe ideality in multicomponent systems as was suggested in the discussion of Equation (11). It is hoped that in the future, direct integration can be performed for approximate forms of the H_{ij} in Equation (16), or other solution theories based on the direct correlation function (*16*) can be implemented which will be useful in Equations (7) and (8). However, for the purpose of obtaining results which will be immediately useful, Equations (21) and (22) were implemented.

GASES IN MIXED SOLVENTS

Equation (21) and its equivalent for ternary and higher-order solvents can be used in Equation (8) to yield Henry's constant in a mixed solvent. For a binary solvent the expression is

$$\ln H_{1,m} - \sum x_j \ln H_{1,j} = \frac{-1}{2}\left[\frac{x_2x_3f_{23}^{+} - x_2f_{12}^{+} - x_3f_{13}^{+}}{1 + x_2x_3f_{23}^{+}}\right] - \frac{-1}{2}\left[x_2f_{12}^{0} + x_3f_{13}^{0}\right] \qquad (23)$$

$$= \frac{x_3}{2}\left[\frac{\partial \ln \gamma_3}{\partial x_3}\right]^{+}_{T,P,N_2} + \frac{x_2}{2}\left[\frac{f_{12}^{+}}{1 + x_2x_3f_{23}^{+}} - f_{12}^{0}\right] + \frac{x_3}{2}\left[\frac{f_{13}^{+}}{1 + x_2x_3f_{23}^{+}} - f_{13}^{0}\right] \qquad (24)$$

Equation (24) is the general expression desired and it can be shown that the first term on the right-hand side is correct to all orders of Equation (20) and thus its contribution is not empirical. If the excess free energy of the solvent mixture is given by the Porter equation, by ignoring the second and third terms in Equation (24), one can recover Equation (10). For more complex mixtures, such as those characterized by the Wilson equation, the absolute values are such that

$$\left|\frac{x_3}{2}\left[\frac{\partial \ln \gamma_3}{\partial x_3}\right]^{+}\right| \lesssim |g^E/RT| \qquad (25)$$

This is usually more consistent with experiment and indicates that Equation (24) is probably better than Equation (10).

Although the last two terms in Equation (24) might simply be ignored, comparison with experiment indicates that this can lead to error. Unfortunately, they also cannot be evaluated. Distribution functions in hard sphere mixtures (*18*) indicate that the relative size difference of the solvent molecules will be important. Using this and the fact that both the last two terms go to zero in the limit of either pure solvent, a simple empirical form was chosen.

TABLE 1. COMPARISON OF CALCULATED AND EXPERIMENTAL HENRY'S CONSTANTS OF GASES IN BINARY SOLVENTS

Solvents		Gas	Temperature, °K.	Number of data points	Average absolute deviation[a] Eq. (27)	Eq. (10)	Eq. (9)	Eq. (26)[b]	Data reference Gas solubility	Solvent nonideality
Toluene	Heptane	C_2H_4	213.1, 223.1	6	+2.7	−2.3	+10.3	1.3	4	19
Toluene	Methyl cyclohexane	C_2H_4	213.1, 223.1	6	+3.6	−2.0	+11.4	1.9	4	20
Benzene	CCl_2FCClF_2	H_2	298.1	2	0.4	1.7	13.9	0.4	21	21
		Ar	298.1	2	0.8	1.1	15.2	0.6	21	
		C_2H_6	298.1	3	1.3	2.4	11.9	1.3	21	
		C_2F_6	298.1	2	+32.5	+29.9	+51.2	0.0	21	
Hexane	Acetone	C_2H_4	243.1	3	−8.6	+17.3	+24.0	3.3	4	22
		C_2H_2	248.1	3	+31.8	+19.3	+78.5	8.0	4	
CS_2	Acetone	CO	298.1	4	+8.4	+7.0	+42.5	2.5	23	24
Toluene	Aniline	CO	298.1	5	−8.4	−11.6	+8.0	6.8	23	25
Benzene	Aniline	CO	298.1	5	−28.0	−26.1	−5.5	11.9	23	26
Benzene	Nitrobenzene	CO	298.1	5	−11.4	−13.1	−6.3	2.0	23	27
Benzene	Acetone	CO_2	293.1	5	−2.3	−3.6	+3.2	0.9	3	13
Benzene	Chloroform	CO_2	293.1	4	−1.4	−2.6	−1.3	0.7	3	23
Octane	Ethanol	N_2	273.1 to 323.1	3	+4.0	−15.0	+32.4	0.4	28	29
		O_2	273.1 to 323.1	3	+3.8	−15.2	+31.4	0.6	28	
Toluene	Dimethyl formamide	C_2H_2	298.1	3	+7.9	−5.1	+13.5	7.3	4	4
Benzene	Ethanol	CO	298.1	2	−21.7	−32.7	−3.2	2.4	23	13
Benzene	Methanol	CO_2	293.1	4	−23.4	−35.2	−7.2	13.2	3	30, 31
Toluene	Acetic acid	CO	298.1	3	−4.7	−12.5	+12.7	1.2	23	24
Benzene	Acetic acid	CO	298.1	3	−6.6	−12.9	+14.5	5.5	23	32
Acetone	Ethanol	N_2	273.1, 298.1	2	−4.5	−10.0	+9.2	1.6	28	33
		O_2	273.1, 298.1	2	−12.7	−17.7	+0.2	0.3	28	
Acetone	Methanol	CO	293.1	4	2.6	−11.8	2.2	2.6	3	13
Chloroform	Methanol	CO	298.1	1	−5.4	−20.4	+8.1	—	23	13
		CO_2	293.1	4	−10.4	−23.8	−13.3	4.0	3	
Ethanol	Water	N_2	298.1	2	+33.0	−13.0	2.7	0.4	23	34
Methanol	Water	Ar	278.1 to 298.1	21	+19.5	−14.0	9.4	7.5	25	13
		CO_2	293.1	5	+4.4	−23.0	−12.6	3.9	3	
Acetone	Chloroform	C_2H_2	243.1	3	−13.0	−14.3	−29.8	3.5	4	13
		C_2H_4	243.1	3	+2.6	+1.6	−17.4	1.0	4	
		CO	298.1	2	+13.9	+12.8	−3.0	2.2	23	
		CO_2	293.1	3	−1.3	−1.5	−13.4	0.7	3	

[a] The sign on the deviation indicates the direction most of the calculated values were from the data. No sign means equally + and −.
[b] Use of an arbitrary constant for best fit instead of the constant in Equation (27).

$$\ln H_{1,m} - \sum_{j=2}^{3} x_j \ln H_{1,j} = \frac{x_3}{2}\left[\frac{\partial \ln \gamma_3}{\partial x_3}\right]^{+}_{T,P,N_2} + A_{23}\,\Phi_2\Phi_3 \tag{26}$$

where Φ is the solvent volume fraction in the solute-free mixture, and

$$A_{23} \equiv \frac{1050\,|v_2 - v_3|}{T^{1/2}\,v_2 v_3} \tag{27}$$

Equations (26) and (27) contain only solvent properties and thus are independent of the gas. The particular form of Equation (27) was chosen on the basis of the limited data available.

COMPARISON WITH EXPERIMENTAL DATA FOR BINARY SOLVENTS

Table 1 shows comparisons with experiment for 20 binary solvent systems, several with data on more than one gas. Figure 1 shows some representative systems where good agreement was found. In essentially all cases $(\partial \ln \gamma_3/\partial x_3)^{+}$ was obtained from the Wilson equation as in Prausnitz et al. (*13*), with the parameters assumed independent of temperature where the solubility data were given at a different temperature from the mixed solvent properties. The results of Table 1 are satisfactory since experimental variations in solubility can be quite high and errors of up to 10% are common. (Many of data are over 50 years old, and the data in reference *4* are given only in graphical form.) In particular, for complex solvents, Equation (26) is usually better than assuming either the ideal solution law Equation (9) or Equation (10), including most of the cases it does poorly. Where Equation (10) is better, the error in the present correlation is usually only slightly different.

The cases where Equations (26) and (27) do extremely poorly (errors greater than 10%), the deviation from the ideal solution equation is often more positive than predicted. This discrepancy points out the dangers of using an empirical function of pure solvent properties such as Equation (27) for complex systems. From the data it is clear the nature of gas needs to be taken into account on occasion, but apparently not as much as might be expected. In any case, it is likely that the present method will provide the best estimate when no mixture solubility data are available. In addition, Equations (26) and (27) seem better in general than using a single reference with corrections for the (usually) unknown nonideality as in Prausnitz et al. (*13*) or the other simplified methods for obtaining Henry's constant in mixed solvents, Equations (9) and (10). To indicate how one mixture data point may be effectively used, Table 1 shows results obtained when the constant in Equation (27) is considered to be a property of each system.

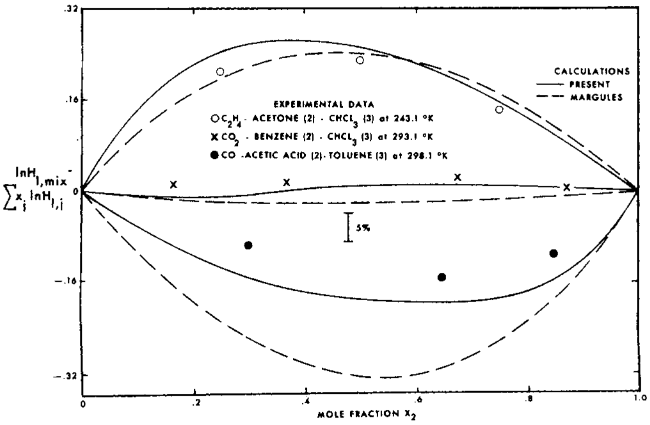

Fig. 1. Deviations of Henry's constant from an ideal solution.

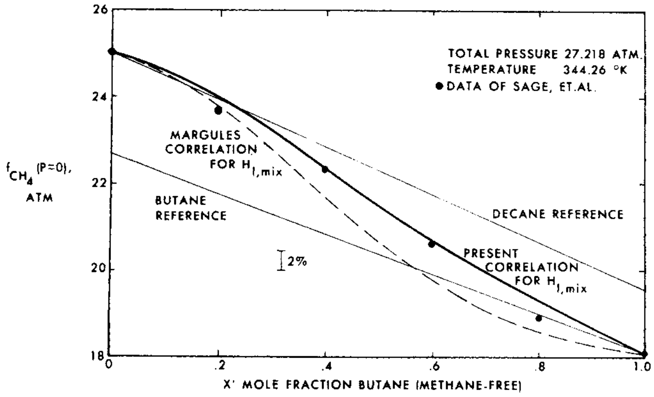

Fig. 2. Zero pressure fugacities of methane in butane-decane mixtures.

MULTICOMPONENT SOLVENTS

The extension of Equations (15) and (17) to higher-order solvents leads to complicated results. However, by ignoring terms involving products of four or more mole fractions, one finds the multicomponent solvent expression to be

$$\ln H_{1,m} - \sum_{j=2}^{M} x_j \ln H_{1,j} = \sum_{j=2}^{M} \frac{x_j(1-x_j)}{2}\left(\frac{\partial \ln \gamma_j}{\partial x_j}\right)^{+}_{T,P,N_k\,k\neq j} + \frac{1}{2}\sum_{j=2}^{M}\sum_{k=2}^{M} A_{jk}\,\Phi_j\Phi_k \tag{28}$$

where A_{jk} is obtained from Equation (27).

NONIDEAL SOLUTIONS OF GASES IN MIXED SOLVENTS

Extension of this treatment to systems where the concentration of the gaseous component is not sufficiently dilute to assume γ_1^* is unity can be accomplished in a consistent fashion using Equations (3), (21), and (28). The result is

$$\ln(\gamma^*_{1,m} H_{1,m}) = \sum_{j=2}^{M} \frac{x_j}{(1-x_1)}\left[\ln H_{1,j} - \left(x_1 - \frac{x_1^2}{2}\right) f^0_{1j}\right] + \frac{1}{2}\left\{\sum_{j=2}^{M} x_j(1-x_j-x_1)\left(\frac{\partial \ln \gamma_j}{\partial x_j}\right)^{+}_{T,P,N_k\,k\neq j} + \sum_{j=2}^{M}\sum_{k=2}^{M} A_{jk}\,\Phi_j\Phi_k\right\} \tag{29}$$

and all the $H_{i,j}$ and $\gamma^*_{i,j}$ are at the same P and T. In this formulation, the only additional information required are parameters characterizing nonideality of the gas in the pure solvents in order to predict nonideality of the gas in the mixed solvent.

A system for which data are available to compare Equation (29) with other treatments is shown in Figure 2. In this case the experimental (*36*) and calculated fugacities of methane at zero pressure

$$f_i(P=0) = x_i\,\gamma_i^*\,(P=0)\,H_{i,m}\,(P=0) \qquad (30)$$

are given in the binary solvent butane-decane at 344.26°K. and a total system pressure of 27.218 atm. The mole fraction methane was roughly 0.1. The correction to zero pressure was made with experimental partial molar volumes and the f^0_{ij} were obtained from the experimental binary data. The results for Equation (24) are slightly better than the appropriate extension of Equation (10) to the nonideal case and considerably better than the results obtained from using either solvent as a reference as in Prausnitz et al. (*13*).

CONCLUSION

Expressions have been developed to predict Henry's constants for gases in mixed solvents. A semitheoretical expression containing only solvent properties has been tested for binary solvents and generally satisfactory agreement with experiment has been found. The expression has also been generalized to multicomponent solvents. The consequences of this development also have been discussed for multicomponent solvents where sufficient gas is dissolved to cause deviations from Henry's law.

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NOTATION

A = solvent pair parameter for deviations of Henry's constant from ideal solution [Equations (26) and (27)]
f_{ij} = pair distribution function integrals [Equation (18)]
f_i^L = fugacity of component i in liquid phase
f_i^0 = reference state fugacity of component i
f_i^{0L} = liquid-phase fugacity of pure i
g^E = excess Gibbs energy
g_{ij} = pair (radial) distribution function
$H_{i,j}$ = Henry's constant, atm.
H_{ij} = integral of total correlation function over all space [Equation (26)]
N = number of molecules in system
P = pressure, atm.
P^0 = reference pressure, atm.
R = universal gas constant = 82.06 (cc.) (atm.) (g.-mole) (°K.)
T = absolute temperature, °K.
v = molar volume, cc./g.-mole
$\bar{v}_i$ = partial molar volume, cc./g.-mole
W = collection of correlation function integrals for ternary systems [Equation (19)]
x = mole fraction

Greek Letters

α_{ij} = pair interaction parameter in Wohl expansion coefficients
γ, γ^* = activity coefficients in symmetric and unsymmetric conventions, respectively [Equations (2) and (3)]
Δ = ternary and higher interaction parameters in Wohl expansion for activity coefficients
η = dilation parameter in dilated van Laar model for activity coefficients
Λ = pair interaction parameter in Wilson equation for activity coefficients
Φ = volume fraction

Superscripts

s = saturation
$+$ = infinite dilution of gas in mixed solvent
0 = infinite dilution of gas in pure solvent

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