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Prediction of Unsymmetric Convention Liquid-Phase Activity Coefficients of Hydrogen and Methane

A corresponding states method has been developed to predict the binary parameter in the unsymmetric-convention one-term Margules relation for binary activity coefficients of H_2 and CH_4 in solvents. In addition to the solvent density, only characteristic volumes used previously for partial molar volumes at infinite dilution and pure solvent compressibility are required. Comparisons with experiment for nonpolar solvents indicate that use of the method is usually significantly more accurate than assuming ideal solution (Henry's law).

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SCOPE

In the prediction of vapor-liquid equilibria in systems which contain supercritical components, such as hydrogen and methane at normal temperatures, there are special thermodynamic problems. Normal methods involve reference states requiring pure liquid phase properties which cannot be experimentally measured for these species and often are not conveniently obtained by extrapolation from data at temperatures below the critical. The usual approach is to use Henry's law where the reference state composition is infinite dilution of the supercritical component. While the assumption of ideal solution is satisfactory at very low concentrations of solute, it is less accurate as the concentration increases and activity coefficients in the unsymmetric convention must be used to account for deviations from ideality.

This work provides a method to predict such activity coefficients for hydrogen and methane in single solvents. It is a consistent extension of a corresponding states theory used previously for liquid compressibility and partial molar volumes of gases in solutions.

CONCLUSIONS AND SIGNIFICANCE

In general, the correlation [Equations (13) to (18)] requiring no additional binary information yields significantly more accurate results for bubble pressures and vapor mole fractions than does use of Henry's law in noncryogenic systems containing hydrogen and methane in nonpolar solvents. It is expected that the same should be true for polar solvents.

It has been well established that the unsymmetric convention is a convenient and accurate method for use in predicting vapor-liquid equilibria in systems containing substances which are significantly above their critical temperatures (Prausnitz, 1968, 1969). In general at moderate pressures, deviations from Henry's law are not great so that the data which are needed for liquid fugacities are Henry's constant at the temperature of the system and a convenient reference pressure, an approximate expression describing activity coefficients in the so-called "un-

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symmetric" convention and the partial molar volume at infinite dilution. The purpose of this paper is to show a simple correlation for obtaining the activity coefficients of hydrogen and methane from a corresponding states method with the same basis used previously for compressibilities and partial molar volumes at infinite dilution (Brelvi and O'Connell, 1972). No additional binary information is required and satisfactory accuracy is obtained.

THERMODYNAMIC FRAMEWORK

The unsymmetric convention is useful for substances which are to be present in liquid solution to only a small degree, that is, solutes such as gases, solids, or nearly immiscible liquids. The liquid fugacity of such a solute is calculated from the equation

$$f_1^L = x_1 \gamma_1^* f_1^R \exp\left[\int_{P^R}^{P} \frac{\bar{v}_1^L}{RT}\, dP\right] \tag{1}$$

where x_1 is the mole fraction, γ_1^* is the activity coefficient referred to infinite dilution at the reference pressure, P^R, (that is, it is a function only of x and T when P^R has been chosen)

$$\lim_{x_1 \to 0} \gamma_1^* = 1 \tag{2}$$

For a single solvent, f_1^R is Henry's Constant at the same reference pressure.

$$\lim_{\substack{x_1 \to 0 \\ P \to P^R}} f_1/x_1 = f_1^R \equiv H_1 \tag{3}$$

Finally, $\bar{v}_1^L$ is the partial molar volume. A convenient reference pressure P^R for binary systems is the saturation pressure of the pure solvent at the system temperature since this is a state accessible by simple extrapolation of experimental data (Prausnitz, 1969). However, other reference pressures can easily be used (Prausnitz et al., 1967; Prausnitz and Chueh, 1969).

For the solvent component the liquid fugacity is

$$f_2^L = x_2 \gamma_2 f_2^R \exp\left[\int_{P^R}^{P} \frac{\bar{v}_2^L}{RT}\, dP\right] \tag{4}$$

where

$$\lim_{x_2 \to 1} \gamma_2 = 1 \tag{5}$$

and f_2^R is the fugacity of pure 2 as a liquid at the reference pressure P^R.

Many expressions for activity coefficients as functions of composition and temperature can be found (Prausnitz, 1969), but the simplest is the one-term Margules equation for excess free energy. For a binary, this yields

$$\begin{aligned} \ln \gamma_1^* &= A_{12}(x_2^2 - 1) = -A_{12}(2x_1 - x_1^2) \\ \ln \gamma_2 &= A_{12} x_1^2 \end{aligned} \tag{6}$$

This can be obtained either by conversion of the empirical Porter equation in the symmetric convention to the unsymmetric convention (Prausnitz, 1969) or from a statistical mechanical solution theory (O'Connell, 1971). We propose to use the quantities in the latter, along with corresponding states methods developed previously for other solution properties at infinite dilution, to establish a purely predictive method for obtaining A_{12} for hydrogen and methane when data are unavailable.

SOLUTION THEORY

O'Connell (1971) has shown how the use of statistical mechanics of solutions leads to the following equations for thermodynamic properties in binary solutions

$$\frac{1}{\rho \kappa RT} = x_1^2(1 - C_{11}) + 2x_1x_2(1 - C_{12}) + x_2^2(1 - C_{22}) \tag{7}$$

$$\frac{\bar{v}_1^L}{\kappa RT} = x_1(1 - C_{11}) + x_2(1 - C_{12}) \tag{8}$$

$$\left(\frac{\partial \ln \gamma_1^*}{\partial x_1}\right)_{T,P} = x_2[(1 - C_{11})(1 - C_{22}) - (1 - C_{12})^2]\rho \kappa RT \tag{9}$$

where the C_{ij} are integrals of the molecular direct correlation function, and in general depend on temperature, density, and composition. At the limit of infinite dilution of component 1 in solvent 2, these become

$$\frac{1}{\rho_2 \kappa_2 RT} = 1 - C_{22}^0 \tag{10}$$

$$\frac{\bar{v}_1^0}{\kappa_2 RT} = 1 - C_{12}^0 \tag{11}$$

$$\lim_{x_2 \to 0} \left(\frac{\partial \ln \gamma_1^*}{\partial x_1}\right)_{T,P} = (1 - C_{11}^0) - \frac{(1 - C_{12}^0)^2}{1 - C_{22}^0} \tag{12}$$

$$= -2A_{12} \tag{13}$$

Brelvi and O'Connell (1972) have shown how simple functions of C_{22}^0 and C_{12}^0 can be expressed as universal functions of only the solvent density reduced by a suitable characteristic parameter. In equation form these are

$$\ln(2 - C_{22}^0) = -0.42704(\tilde{\rho}_2 - 1) + 2.089(\tilde{\rho}_2 - 1)^2 - 0.42367(\tilde{\rho}_2 - 1)^3 \tag{14}$$

$$\begin{aligned} \ln\left[-C_{12}^0 \left(\frac{v_2^*}{v_1^*}\right)^{0.62}\right] &= -2.4467 + 2.12074\tilde{\rho}_2 \qquad 2.0 \leq \tilde{\rho}_2 \leq 2.785 \\ &= 3.02214 - 1.87085\tilde{\rho}_2 + 0.71915\tilde{\rho}_2^2 \qquad 2.785 \leq \tilde{\rho}_2 \leq 3.2 \end{aligned} \tag{15}$$

where

$$\tilde{\rho}_2 = \rho_2 v_2^* \tag{16}$$

and v_i^* values are tabulated (Brelvi and O'Connell, 1972).

We here publish a correlation of C_{11}^0 for hydrogen-solvent and methane-solvent systems. The hydrogen-solvent correlation is based on experimental data for hydrogen in *n*-butane (Aroyan and Katz, 1951), *n*-hexane (Nichols et al., 1957), and benzene (Connolly, 1962); the temperature and reduced density ranges being 277°K $< T <$ 513°K, and $\rho_2 > 2.1$. Similarly, the methane correlation is derived from data in *n*-butane (Sage, 1940), *n*-hexane (Shim and Kohn, 1962), and *n*-decane (Sage and Lacey, 1950) in the temperature and reduced density ranges, 298°K $< T <$ 444°K, and $\rho_2 > 2.1$. Other data examined included methane in *n*-pentane (Sage and Lacey, 1950), and *n*-heptane (Reamer et al.) and hydrogen in argon (Volk and Halsey, 1960). For all but the hydrogen-benzene system, where A_{12} values are tabulated (Connolly, 1962), the method of obtaining the H_{12} and A_{12} values from experimental data was to find values which minimized sum-squared deviations of liquid mole fractions assuming the values of pressure and temperature were as given. The Redlich-Kwong equation of state of Prausnitz and Chueh was used (1969) for vapor-phase fugacities. The reference pressure was the saturation pressure of the solvent at the temperature of the system. The partial

TABLE 1. COMPARISON OF PREDICTIONS WITH EXPERIMENTAL DATA FOR REPRESENTATIVE SYSTEMS

System		Temp.,		A_{12}			Bubble pressure, atm.			y_2		
(1)	(2)	°K	H_1, atm.	predicted	x_1 exp	x_1 fit[a]	exp	ideal[b]	nonideal[c]	fit[a]	ideal[b]	nonideal[c]
CH_4	nC_4H_{10}	344.2	214.06	1.058	0.0242	0.0246	13.61	13.82	13.52	0.6444	0.6369	0.6479
					0.0885	0.0883	27.23	31.27	26.88	0.3746	0.3448	0.3778
					0.1514	0.1526	40.84	52.89	38.53	0.2854	0.2621	0.2945
					0.2119	0.2110	54.46	84.00	48.31	0.2441	0.2608	0.2544
CH_4	nC_7H_{16}	310.9[e]	204.95	0.119	0.1	0.1	21.65	22.50	21.96	0.0103	0.0074	0.0075
					0.2	0.2	45.59	49.74	47.26	0.0089	0.0056	0.0056
					0.3	0.3	72.70	85.04	78.00	0.0092	0.0053	0.0059
CH_4	nC_6H_{14}	373.2[e]	244.11	0.377	0.03	0.03	10.00	10.10	9.93	0.2724	0.2666	0.2707
					0.1065	0.1067	30.00	31.90	29.50	0.1178	0.1071	0.1123
					0.216	0.2163	60.00	70.64	59.06	0.0869	0.0736	0.0758
H_2	nC_6H_{14}	277.6	1,195.03	0.319	0.028	0.0276	34.04	34.92	34.29	0.0029	0.0029	0.0027
					0.12	0.1227	170.2	174.8	160.1	0.0015	0.0011	0.0011
					0.199	0.1948	306.3	357.0	294.8	0.0017	0.0010	0.0010
H_2	C_6H_6	473.2	1,130.61	1.202	0.0162	0.0161	33.51	34.33	33.54	0.5103	0.5054	0.5150
					0.0504	0.0509	75.30	84.16	74.91	0.2711	0.2442	0.2661
					0.0948	0.0944	134.0	183.1	133.9	0.1836	0.1469	0.1726
H_2	nC_4H_{10}	298.2	1,118.35	1.058	0.019	0.0174	22.12	24.03	23.92	0.1253	0.1111	0.1149
					0.062	0.0639	76.92	85.61	73.88	0.0473	0.0413	0.0454
					0.080	0.0850	103.1	117.0	95.55	0.0399	0.0340	0.0301
					0.216	0.2078	306.3	—[d]	306.3	0.0310	—[d]	0.0241

[a] Values of x_2, y_2 obtained when experimental binary data fitted to minimize sum squared deviation in x_1 with T and P specified. Differences with experimental x_1 indicate possible errors in measurements which strongly affect calculated bubble pressures.

[b] $\ln\gamma_1^* = 0$.

[c] Equations (6) used.

[d] No convergence in solving equations of equilibrium. Generally means predicted pressure too large.

[e] Data not used in development of equations (17) and (18).

TABLE 2. PHASE EQUILIBRIA IN HYDROGEN (1) ARGON (2) SYSTEM AT 87°K

x_1		Pressure, bar			y_2		
Exp	Fit[a]	Exp	Ideal[a]	Nonideal[a]	Fit[a]	Ideal[a]	Nonideal[a]
0.0253	0.0253	24.54	18.91	26.57	0.0617	0.0739	0.0612
0.0349	0.0350	34.44	23.55	38.63	0.0524	0.0648	0.0532
0.0451	0.0449	44.91	27.29	53.54	0.0481	0.0600	0.0511
0.0671	0.0671	71.46	31.89	97.86	0.0467	0.0559	0.0626
0.0758	0.0756	82.70	32.66	123.72	0.0479	0.0553	0.0762
0.0829	0.0832	93.49	32.94	152.19	0.0496	0.0551	0.0969

Henry's Constant = 861.3 bar.
A_{12} from correlations = 6.281.
[a] Quantities as in Table 1.

molar volume of the solute was the infinite dilution value calculated by Equations (10), (11), (14), and (15), while the experimental pure component molar volume was used for the solvent. Both volumes were assumed independent of pressure. The final equations are

$$\text{Hydrogen} \quad \ln\left[-C_{11}^0 \frac{v_2^*}{v_1^*}\right] = -3.049 + 1.926\,\rho_2 \tag{17}$$

$$\text{Methane} \quad \ln\left[-C_{11}^0 \frac{v_2^*}{v_1^*}\right] = 0.369 + 0.946\,\rho_2 \tag{18}$$

Tables 1 and 2 compare experimental vapor compositions of the solvent components and bubble pressures with calculated values using Equations (1), (4), (6), (13), (14), (15), and (17) or (18). Seven representatives of the nineteen systems considered are shown.

The conclusions we draw from these tables, and other data not shown, are the following:

1. Comparisons of experimental values of liquid mole fraction of the gaseous component and vapor mole fraction of the solvent component with those obtained in fitting (given in Table 1 as x_{fit} and y_{fit}) show that deviations can be as high as 0.005. The calculated bubble pressures are quite sensitive to this $[\partial p/\partial x)_T \simeq H]$ so that some of the large deviations can be attributed to experiments.

2. In only four of the nineteen systems was the ideal solution assumption ($\gamma_1^* = 1$) better than using the general correlation. (In two of these, as well as in three of the rest, both methods yielded comparable errors and these were generally small). In only one of the nineteen cases at the highest measured concentration of the gaseous component did the present method yield bubble pressures in error by 20%; the ideal solution assumption gave such errors in this system plus six others. Similar results for the two methods are obtained for the vapor mole fraction of the solvent component.

3. The present equations are probably not applicable to cryogenic systems where the gases are only slightly above their critical temperature. This can be illustrated by data for the H_2-Ar system at 87°K shown in Table 2 which are not predicted well either by the ideal solution assumption or by the correlation proposed here.

4. We believe the method should be applicable to solvents which are polar just as the previous correlations were, but we have not been able to test this assertion. A troublesome problem is that vapor-phase nonideality is not well described by any equation of state for systems with H_2 or CH_4 with polar substances. Until this difficulty is removed, correlation of vapor-liquid equilibria in such systems will be tenuous regardless of the liquid-phase

activity coefficient correlation used.

We believe the method should be applicable to an N-component system if a careful analysis is used. The general thermodynamic expressions have been developed following Abrams et al. (1974) and comparisons with data are being made. Results will be reported in a future publication.

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NOTATION

A_{12} = coefficient of Margules expression for activity coefficients
C_{ij} = volume integral of molecular direct correlation function between species i and j
f_i = fugacity of component i, bar
H_1 = Henry's constant of solute 1, bar
P = pressure, bar
R = gas constant
T = absolute temperature, °K
v = partial molar volume, cc/g-mole
x = mole fraction
κ = isothermal compressibility, bar^{-1}
ρ = molar density, g-mole/cc
γ = liquid phase activity coefficient

Superscripts

0 = infinitely dilute solution of solute (1)
$\sim$ = reduced property
L = liquid phase
pure = pure component
R = reference state
$*$ = characteristic property; activity coefficient in unsymmetric convention

Subscripts

1 = solute
2 = solvent

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Membranes with Common Ion Pumping

Liquid membranes containing a macrocyclic polyether can move or pump a specific cation against its concentration gradient. The cation flux is not proportional to the difference of the cation concentration but to the difference of the product of cation and anion concentrations across the membrane. The results are inconsistent with existing theories of ion transport, but can be explained in terms of ion pairs.

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SCOPE

This paper describes liquid membranes capable of simultaneously separating and concentrating specific salts. In other words, one salt can penetrate the liquid membranes much more rapidly than others, and under appropriate conditions, can be pumped against its concentration gradient from a solution of low concentration to a solution