Activity Coefficients and Henry's Constants by the Pseudocritical Method

Joseph Joffe
Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, New Jersey 07102

A fugacity coefficient expression based on the pseudocritical concept has been applied to the calculation of fugacity and activity coefficients in binary liquid systems at infinite dilution. Thermodynamic properties required for the evaluation of the coefficients were obtained from the Lee–Kesler tables. Binary interaction constants derived from data at one temperature were used to predict infinite dilution activity coefficients and Henry's constants at other temperatures. In two cases, binary interaction constants derived from gaseous volumetric data were used to predict values of Henry's constants. Extension to multicomponent systems is indicated.

In recent years there has been increasing interest in applying the corresponding states principle and the pseudocritical concept to mixtures in the liquid state (*4, 5, 7, 11, 12*). The conventional approach to liquid solutions has been to rely on activity coefficients in describing departure of solution behavior from that of ideal solutions. Various empirical or semiempirical equations, such as the Wilson or the NRTL equations, derived from simplified structural models of the liquid state, have been used to correlate activity coefficient data. In the calculation or correlation of activity coefficients and related properties, such as Henry's constant, the pseudocritical method represents another approach which is based only on very general assumptions regarding the behavior of fluid mixtures.

Fugacity and Activity Coefficients

In a recent paper (*5*) the author used the generalized B–W–R equation of Lee and Kesler (*6*) and the pseudocritical concept to derive an expression for the fugacity coefficient of a component in a mixture, whether gaseous or liquid, and applied this equation to the calculation of vapor–liquid equilibria. It is the purpose of the current paper to explore the application of this equation to the calculation of activity coefficients and Henry's constants in binary liquid systems.

For the binary case of components i and j the equation may be written:

$$\ln \phi_i = \ln \phi_M - \frac{2(U^* - U)}{RTT_c'V_c'}[x_iV_{ci}(T_{ci} - T_c') + x_jV_{cij}(T_{cij} - T_c')] + \frac{2(z-1)}{V_c'}(x_iV_{ci} + x_jV_{cij} - V_c') - \frac{z-1}{z_c'}(z_{ci} - z_c') + (\omega_i - \omega_M)(\ln \phi_M)^{(1)} \quad (1)$$

If the two interaction constants, V_{cij} and T_{cij}, of the binary system are known, then the pseudocritical quantities, T_c' and V_c', can be calculated as explained in the previous paper (*5*) and the fugacity coefficient, ϕ_i, is obtained from eq 1. The activity coefficient, γ_i, follows from:

$$\gamma_i = \phi_i/\phi_i^0 \quad (2)$$

where ϕ_i^0 is the fugacity coefficient of pure i at the temperature and pressure of the binary system. This coefficient may be evaluated from the Lee–Kesler correlation. If the system pressure is below the vapor pressure of the component in question, the liquid-phase fugacity, $\phi_i^0P_r$, has to be extrapolated to the lower pressure. The procedure is straightforward. If, however, the interaction constants, V_{cij} and T_{cij}, are not known and it is desired to establish their values from experimental activity coefficients, then a trial-and-error procedure is required as discussed by White and Chao (*11*).

A considerable simplification in the calculations comes about for the state of infinite dilution. The fugacity coefficient of component i at infinite dilution, ϕ_i^∞, is obtained from eq 1 by setting $x_i = 0$ and $x_j = 1$:

$$\ln \phi_i^\infty = \ln \phi_j - \frac{2(U^* - U)_j}{RTT_{cj}V_{cj}}V_{cij}(T_{cij} - T_{cj}) + \frac{2(z_j - 1)}{V_{cj}}(V_{cij} - V_{cj}) - \frac{z_j - 1}{z_{cj}}(z_{ci} - z_{cj}) + (\omega_i - \omega_j)(\ln \phi_j)^{(1)} \quad (3)$$

The activity coefficient at infinite dilution, γ_i^∞, is given by:

$$\gamma_i^\infty = \phi_i^\infty/\phi_i^0 \quad (4)$$

If component i is the solute and component j is the solvent, Henry's constant, H_{ij}, is given by:

$$H_{ij} = \phi_i^\infty P \quad (5)$$

where P is the system pressure. We consider below the application of eq 3 and 4 to the calculation of activity coefficients at infinite dilution and of eq 3 and 5 to the calculation of Henry's constants.

Activity Coefficients at Infinite Dilution

If the activity coefficients at infinite dilution are known for a binary system at a given temperature, the binary interaction constants, V_{cij} and T_{cij}, of eq 3 can be calculated and eq 3 and 4 can be used to find activity coefficients at infinite dilution at another temperature. The procedure is illustrated here with the help of the correlation by Funk and Prausnitz (*3*) of the activity coefficients in a number of aromatic-saturated hydrocarbon systems at essentially atmospheric pressure, at temperatures of 25 to 75 °C. The Redlich–Kister parameters, *A*, *B*, and *C*, established by Funk and Prausnitz, yield values of activity coefficients at infinite dilution in accordance with:

$$\ln \gamma_1^\infty = A - B + C \quad (6)$$

and

$$\ln \gamma_2^\infty = A + B + C \quad (7)$$

With the help of the Redlich–Kister parameters at 25 °C and eq 6, 7, and 4, the fugacity coefficients ϕ_1^∞ and ϕ_2^∞ are established for each binary. Substitution into eq 3 yields two equations for each binary, containing two unknowns, V_{cij} and T_{cij}. Simultaneous solution of the two equations is readily carried out but is not recommended, since the results are not always consistently reliable. Application to infinitely dilute solutions is a severe test of the pseudocritical concept. It is probably too much to expect that binary interaction constants determined from data at one end of the concentration range of a binary mixture will hold accurately in all cases at the other end of the range.

Accordingly, the following procedure has been adopted: the constant V_{cij} is calculated from the Lee–Kesler mixture rule,

$$V_{cij} = (1/8)(V_{ci}^{1/3} + V_{cj}^{1/3})^3 \quad (8)$$

Table I. Activity Coefficients at Infinite Dilution in Aromatic-Saturated Hydrocarbon Systems

Components		Funk and Prausnitz (*3*)				This work			
		25 °C		75 °C		75 °C		% deviation	
1	2	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
n-Pentane	Benzene	2.09	1.97	1.78	1.85	1.82	1.72	2.2	−7.0
n-Hexane	Benzene	2.15	1.66	1.72	1.47	1.84	1.47	7.0	0.0
n-Heptane	Benzene	2.15	1.53	1.69	1.30	1.83	1.34	8.3	3.1
n-Octane	Benzene	2.03	1.73	1.70	1.43	1.66	1.50	−2.4	4.9
Cyclopentane	Benzene	1.55	1.67	1.40	1.61	1.42	1.49	1.4	−7.5
Methylcyclopentane	Benzene	1.72	1.74	1.53	1.62	1.52	1.54	−0.7	−4.9
Methylcyclohexane	Benzene	1.80	1.76	1.56	1.47	1.55	1.56	−0.6	6.1
n-Hexane	Toluene	1.76	1.67	1.55	1.52	1.56	1.52	0.6	0.0
n-Heptane	Toluene	1.57	1.25	1.33	1.30	1.43	1.19	7.5	−8.5
Methylcyclopentane	Toluene	1.53	1.59	1.35	1.44	1.37	1.47	1.5	2.1
Cyclohexane	Toluene	1.63	1.73	1.40	1.55	1.43	1.57	2.1	1.3
Methylcyclohexane	Toluene	1.42	1.57	1.25	1.38	1.28	1.46	2.4	5.8
Cyclohexane	Benzene	1.93	1.67	1.37	1.71	1.64	1.50		
						Av abs % dev:		3.1	4.3

Table II. Activity Coefficients at Infinite Dilution in *n*-Heptane (1)–Methyl Ethyl Ketone (2) System

t, °C	$\gamma_1^\infty{}_{\text{obsd}}$	$\gamma_1^\infty{}_{\text{calcd}}$	$\gamma_2^\infty{}_{\text{obsd}}$	$\gamma_2^\infty{}_{\text{calcd}}$	% dev, γ_1^∞	% dev, γ_2^∞
25	4.35		4.8			
60	3.46	3.36	3.5	3.61	−2.9	3.1
90	2.87	2.80			−2.4	
100			2.6	2.79		7.3

Table III. Activity Coefficients at Infinite Dilution in the Cyclohexane (1)–Methyl Ethyl Ketone (2) System

t, °C	$\gamma_1^\infty{}_{\text{obsd}}$	$\gamma_1^\infty{}_{\text{calcd}}$	% dev
25	3.4		
50	3.0	2.94	−2.0
70	2.7	2.62	−3.0
90	2.5	2.35	−6.0
130	2.25	2.05	−8.9

and T_{cij} is found from the value of ϕ_i^∞ at 25 °C with eq 3. Another value of T_{cij} is found using the value of ϕ_j^∞ at 25 °C. The two values of T_{cij} in all cases differ slightly and are not interchangeable. The value of T_{cij} derived from ϕ_i^∞ at 25 °C, along with V_{cij} obtained from eq 8, is substituted into eq 3 to obtain ϕ_i^∞ at any other temperature, say 75 °C. Similarly, T_{cij} derived from ϕ_j^∞ at 25 °C is used to evaluate ϕ_j^∞ at 75 °C. The activity coefficients at 75 °C are found with eq 4. These calculations have been carried out for a number of the systems correlated by Funk and Prausnitz and the results are presented in Table I. In most cases the agreement between values calculated in this work and the correlated values of Funk and Prausnitz is satisfactory. The cyclohexane–benzene system is an exception. In this case, however, the activity coefficients at infinite dilution, as derived from the Funk–Prausnitz correlation at 75 °C, are believed to be inaccurate (*2*). Omitting this system, the average absolute percent deviation of the calculated values of γ_1^∞ and γ_2^∞ from those of Funk and Prausnitz is respectively 3.1 and 4.3%, which is of the order of the experimental error in such data (*10*).

Another similar test was carried out on the binary systems, *n*-heptane–methyl ethyl ketone and cyclohexane–methyl ethyl ketone, using the data of Pierotti et al. (*8*). The experimental value of the infinite dilution activity coefficient at 25 °C along with eq 8 was used to establish the value of the interaction constant T_{cij}. The latter was then used to evaluate the infinite dilution activity coefficient at other temperatures. These calculations were carried out for *n*-heptane and for methyl ethyl ketone in the first binary, and for cyclohexane in the second binary, based on available experimental data. The results are presented in Tables II and III. The agreement between observed and calculated values is seen to fall within the range of accuracy of experimental data.

Henry's Constants

The application of eq 3 and 5 to the calculation of Henry's constants has been explored with three binary systems: carbon dioxide–*n*-butane, methane–propane, and ethylene–acetone. Prausnitz et al. have reported Henry's constants for these systems at several temperatures (*9*). In the case of the first two systems the binary constants V_{cij} and T_{cij} had been established from volumetric vapor-phase data, as reported in a previous paper (*5*). In calculating the fugacity coefficient of the solute, ϕ_i^∞, with eq 3 the thermodynamic properties of the solvent, j, are required. They are evaluated from the Lee–Kesler correlation (*6*) and are entered along with the critical constants, acentric

Table IV. Henry's Constants in Binary Systems

Components		Temp, K	Pressure, atm	Henry's constant, atm		
Solute	Solvent			Calcd	Ref 9	% dev
Carbon dioxide	*n*-Butane	310.93	3.50	71.5	87.7	−18.5
		344.26	8.21	98.7	104.9	−5.9
		377.60	16.41	119.7	114.5	4.5
Methane	Propane	277.60	5.38	141.8	141.7	0.1
		310.93	12.86	160.0	153.8	4.0
		344.26	26.13	165.1	146.0	13.1
		360.93	35.62	156.1		
		366.48	39.13	140.0		
Ethylene	Acetone	273.15	1.09		65	
		293.15	1.24	82	86	−4.7
		313.15	1.55	100	109	−8.3

Table V. Binary Interaction Constants

Component 1	Component 2	V_{c12}, cm^3	T_{c12}, K	
			Comp 1	Comp 2
n-Pentane	Benzene	280.9	503.6	502.9
n-Hexane	Benzene	311.2	522.0	524.2
n-Heptane	Benzene	338.2	536.7	540.5
n-Octane	Benzene	363.1	551.2	548.9
Cyclopentane	Benzene	259.5	528.1	526.0
Methylcyclopentane	Benzene	288.0	537.1	535.0
Methylcyclohexane	Benzene	299.5	554.7	551.9
n-Hexane	Toluene	342.3	542.3	541.2
n-Heptane	Toluene	371.0	559.4	562.6
Methylcyclopentane	Toluene	317.5	555.7	553.8
Cyclohexane	Toluene	312.0	564.0	561.5
Methylcyclohexane	Toluene	329.8	576.3	572.0
Cyclohexane	Benzene	282.8	544.2	545.5
n-Heptane	MEK	342.9	512.7	497.3
Cyclohexane	MEK	287.0	520.1	
Carbon dioxide	*n*-Butane	173.3	313.3	
Methane	Propane	144.3	264.5	
Ethylene	Acetone	165.8	396.4	

factors, and interaction constants of the two components into eq 3. Henry's constants are evaluated from eq 5 at pressures, *P*, specified in the data reference (*9*). Calculated values for the carbon dioxide–butane and methane–propane systems are compared with the data of Prausnitz et al. (*9*) in Table IV. It has been observed in the methane–propane system that Henry's constant passes through a maximum as the system temperature is raised. The calculated values exhibit such a maximum, but at a higher temperature than the tabulated data of Prausnitz et al. (*9*).

Values of interaction constants were not available for the ethylene–acetone system. Accordingly, the datum of Prausnitz et al. for Henry's constant at 273.15 K, along with eq 8, was used to establish V_{cij} and T_{cij} for this system. Henry's constants at two other temperatures were then calculated with eq 3 and 5. The results are compared with the data of Prausnitz et al. in Table IV and show reasonable agreement. The difficulties inherent in predicting, correlating, and extrapolating Henry's constants have been discussed by Cysewski and Prausnitz (*1*).

All binary interaction constants employed in the current work are listed in Table V.

Conclusions

Infinite dilution activity coefficients and Henry's constants in binary systems are readily calculated with a fugacity coefficient expression which is based on the pseudocritical concept. In the case of two systems binary interaction constants derived from volumetric mixture behavior in the gaseous state were used to predict Henry's constants. However, the greatest utility of the proposed method rests on its ability to extrapolate data at one temperature to temperatures at which data are lacking. With the help of expressions derived in an earlier paper (*5*), the procedures discussed in the current paper can be extended to the calculation of activity coefficients and Henry's constants in multicomponent systems. Binary data should suffice to establish the values of interaction constants in such systems.

Glossary

A, B, C	constants in Redlich–Kister equation
H	Henry's constant
P	absolute pressure
R	gas constant
T	absolute temperature
U	internal energy
V	molar volume
x	liquid-phase mole fraction
z	compressibility factor = PV/RT

Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient
ω	acentric factor

Subscripts

c	critical
i,j	component i,j, respectively
ij	pertaining to components i and j
M	mixture property
r	reduced
1,2	component 1,2, respectively

Superscripts

$*$	ideal gaseous state
$'$	pseudoproperty of a mixture
0	pure component
∞	component at infinite dilution
(1)	deviation function of Lee–Kesler correlation

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