CALCULATION OF SOLID-LIQUID EQUILIBRIA USING THE MODIFIED BWR EQUATION OF STATE OF LEE AND KESLER

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The solubility of solid hydrocarbons and inorganics (carbon dioxide and hydrogen sulfide) in liquid hydrocarbons was correlated using the modified BWR equation of state of Lee and Kesler and the pseudocritical method to compute the fugacity coefficient of the solute in subcooled liquid. This method requires two binary parameters, k_{12} and s_{12} , for each binary pair to be computed from experimental solid-liquid equilibrium data. These parameters are tabulated for a large number of binary systems. The correlation resulting from this investigation will be valuable in the design of cryogenic processes.

Introduction

In recent years increasing attention has been devoted to the thermodynamics of solid-liquid equilibria, due to the practical importance of cryogenic processes such as liquefaction and transportation for natural gas. Preston and Prausnitz^{22,23}) recently presented a review of solid-solubility data and a thermodynamic framework for estimating the solubility of solids in cryogenic liquid solvents. Preston and Prausnitz, and Cheung and Zander¹⁾ used a modification of the theory of regular solution. Jensen and Kurata⁶⁾, and Hoshino *et al.*³⁾ applied successfully the Wilson equation to solid-liquid equilibria. The Wilson equation has been a good model for solid carbon dioxide solubility in light hydrocarbons, but two additional empirical parameters for each binary system have been required for better agreement with experimental data (Jensen and Kurata⁶⁾). Although for the prediction of vapor-liquid equilibria numerous approaches have been made, based on an equation of state such as the Benedict-Webb-Rubin (BWR) or Redlich-Kwong equations, there are few such approaches for the prediction of solid-liquid equilibria. This is due in part to the lack of a reliable equation of state at low reduced temperatures. In this respect, Lee and Kesler have presented a modified BWR equation of state which is applicable down to 0.3 or below at reduced temperatures. Further, it has been shown in the literature (Reid *et al.*²⁴⁾) that this equation is good for prediction

of thermodynamic properties such as PVT and enthalpy.

The purpose of this paper is to present a way to correlate and predict solid solubility in liquids using the Lee-Kesler equation of state. Our work is somewhat similar to but more general than that of de Mateo and Kurata²⁾, who used a modified Redlich-Kwong equation of state for the correlation of solubility of solid hydrocarbons in liquid methane.

1. Thermodynamics of Solid-Liquid Equilibria

Solid-liquid equilibria considered in this study are those for which the solid phase is assumed to be pure solute and the liquid phase is a saturated solution of the solute in the solvent. For such a system, the equation of equilibrium is given by

$$f_1^{os} = \gamma_1 x_1 f_1^{ol} \quad (1)$$

where f_1^{os} is the fugacity of pure solid, f_1^{ol} is the fugacity of pure, subcooled liquid, x_1 is the mole fraction of the solute in the solution, and γ_1 is the activity coefficient of the solute referred to the fugacity, f_1^{ol} . All of these terms are evaluated at the pressure and temperature of the system. Arranging Eq. (1), solid solubility is expressed as

$$x_1 = \frac{f_1^{os}/f_1^{ol}}{\gamma_1} = \frac{f_1^{os}/f_1^{ol}}{\phi_1^l/\phi_1^{ol}} \quad (2)$$

where ϕ_1^l is the fugacity coefficient of the solute in liquid mixtures, and ϕ_1^{ol} is the fugacity coefficient of the pure liquid solute. The activity of component 1 can be evaluated by the relation

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Fig. 1 Comparison of vapor pressures of propane and *n*-octane

$$\ln \frac{f_1^{os}}{f_1^{ol}} = -\frac{\Delta S_f}{R} \left(1 - \frac{T_t}{T}\right) + \frac{\Delta C_p}{R} \left(\frac{T_t}{T} - 1\right) - \frac{\Delta C_p}{R} \ln \frac{T_t}{T} - \frac{\Delta V}{RT_t} (P - P_t) \quad (3)$$

where T_t is the triple-point temperature, ΔS_f is the molar entropy of fusion of the solute, and ΔC_p and ΔV are the differences between the liquid and solid molar heat capacities and molar volumes respectively. For temperatures not much below the melting temperature of the solute, T_m , and for normal pressures, Eq. (3) becomes

$$\ln \frac{f_1^{os}}{f_1^{ol}} = -\frac{\Delta S_f}{R} \left(1 - \frac{T_m}{T}\right) \quad (4)$$

Some substances undergo solid-phase transitions from one crystal structure to another. For these solutions, if the temperature of interest is less than the transition temperature, T_{trans} , the expression for the fugacity ratio becomes

$$\ln \frac{f_1^{os}}{f_1^{ol}} = -\frac{\Delta S_f}{R} \left(1 - \frac{T_m}{T}\right) + \frac{\Delta S_{trans}}{R} \left(1 - \frac{T_{trans}}{T}\right) \quad (5)$$

where ΔS_{trans} is the molar entropy of transition. For the temperatures and entropies of fusion and other solid-phase transitions, the extensive tables of Preston *et al.*^{22,23} are available. The fugacity coefficients of the pure solute and those of the solute in mixtures were calculated from the equation of state together with the pseudocritical method, as described in the following section.

2. Generalized BWR Equation of Lee-Kesler, and Its Application to Mixtures by the Pseudocritical Method

In solid-liquid equilibria the solution temperature

is necessarily below the triple-point temperature of the solute. Therefore, the equation of state used to calculate fugacity coefficients must be able to represent the thermodynamic properties of such subcooled liquid. We chose two equations of state which appeared to be promising at lower temperatures: the Lee and Kesler¹² three-parameter corresponding-states correlation, and a modification of the BWR equation of Nishiumi and Saito¹⁹. The Starling modification of the BWR equation (Starling and Han²⁰) was not considered since it was found to be inaccurate at lower reduced temperatures (Nishiumi and Saito¹⁹).

Figure 1 shows a comparison of experimental and calculated vapor-pressure curves for propane and octane. The solid line represents the vapor pressure of the subcooled liquid, obtained by extrapolating the liquid-vapor pressure curve from the triple-point temperature to the solution temperature. In this diagram the calculated vapor-pressure curves of the two equations of state are also plotted. It is shown that both equations have their own limitations in application: for the Nishiumi and Saito equation down to 0.3 at reduced temperature and for the Lee and Kesler equation down to 0.24. At lower temperatures than these, the thermodynamic properties of the subcooled liquid cannot be calculated satisfactorily. The need for calculations at such lower temperatures often arises in the case of solid solubility for heavier hydrocarbons in liquid methane or ethane. Consequently, the Lee and Kesler equation was adopted in this study.

The Lee and Kesler¹² equation is an extended and improved version of the Pitzer-Curl tables based on a modified BWR equation of state. The compressibility factor of a real fluid is related to properties of a simple fluid ($\omega=0$) and those of *n*-octane as a reference fluid.

$$Z = Z^{(0)} + (\omega/\omega^R)(Z^{(R)} - Z^{(0)}) \quad (6)$$

where $\omega^R=0.3978$. Other thermodynamic functions (fugacity coefficient and enthalpy departure) have been derived from Eq. (6).

In applying the Lee-Kesler equation to mixtures, we used the pseudocritical method. Its use for the calculation of component fugacities and application to phase equilibria has been proposed by a number of investigators, among them Pitzer and Hultgren²¹, Leland *et al.*¹³, Leach *et al.*¹¹, Yorizane *et al.*^{27,28}, Leyendecker and Gunn¹⁴, and Joffe⁷. However, very little work has been reported concerning the application of the pseudocritical method to solid-liquid equilibria. According to a three-parameter corresponding-states theory (Joffe⁷), the fugacity coefficient of component *i* in the mixture can be written as follows

$$\ln \frac{f_i}{P x_i} = \ln \frac{f_m}{P} + \frac{n}{T'_c} \left(\frac{\partial T'_c}{\partial n_i} \right)_{T, P, n_j} \frac{H_m - H_m^*}{RT} - \frac{n}{P'_c} \left(\frac{\partial P'_c}{\partial n_i} \right)_{T, P, n_j} (Z_m - 1) + n \left(\frac{\partial \omega_m}{\partial n_i} \right)_{T, P, n_j} \left(\frac{\partial \ln(f_m/P)}{\partial \omega_m} \right)_{T, P, P'} \quad (7)$$

Although various sets of mixing rules for calculating the pseudocritical constants have been proposed, the following set of mixing rules (van der Waals' one-fluid theory) was adopted.

$$\left. \begin{aligned} V'_c &= \sum_i \sum_j x_i x_j V_{cij} \\ T'_c &= \sum_i \sum_j x_i x_j V_{cij} T_{cij} / V'_c \\ Z_{ci} &= P_{ci} V_{ci} / RT_{ci} \\ Z'_c &= \sum_i x_i Z_{ci} \\ P'_c &= Z'_c R T'_c / V'_c \\ \omega_m &= \sum x_i \omega_i \end{aligned} \right\} \quad (8)$$

$$\left. \begin{aligned} V_{cij} &= (1 - s_{ij})(V_{ci}^{1/3} + V_{cj}^{1/3})^3 / 8 \\ T_{cij} &= (1 - k_{ij}) \sqrt{T_{ci} T_{cj}} \end{aligned} \right\} \quad (9)$$

where k_{ij} and s_{ij} are parameters determined from binary solid-liquid equilibrium data.

Derivatives of pseudocriticals required in Eq. (7) are as follows:

$$\left. \begin{aligned} \frac{n}{V'_c} \left(\frac{\partial V'_c}{\partial n_k} \right) &= \frac{2}{V'_c} \left[\sum_i x_i V_{cik} - V'_c \right] \\ \frac{n}{T'_c} \left(\frac{\partial T'_c}{\partial n_k} \right) &= \frac{2}{T'_c V'_c} \sum_i x_i V_{cik} (T_{cik} - T'_c) \\ \frac{n}{P'_c} \left(\frac{\partial P'_c}{\partial n_k} \right) &= \frac{n}{T'_c} \left(\frac{\partial T'_c}{\partial n_k} \right) - \frac{n}{V'_c} \left(\frac{\partial V'_c}{\partial n_k} \right) + \frac{n}{Z'_c} \left(\frac{\partial Z'_c}{\partial n_k} \right) \\ \frac{n}{Z'_c} \left(\frac{\partial Z'_c}{\partial n_k} \right) &= \frac{1}{Z'_c} [Z_{ck} - Z'_c] \\ n \left(\frac{\partial \omega_m}{\partial n_k} \right) &= \omega_k - \omega_m \end{aligned} \right\} \quad (10)$$

The critical properties used throughout this work were taken from Reid *et al.*²⁴⁾ and the acentric factors were taken from Passut and Danner²⁰⁾.

3. Solubility Calculations and Correlation of Solid-Liquid Equilibria

The solubility of component 1 in component 2 was calculated by solving Eqs. (2) to (10) by an iterative procedure. Throughout this work, Eq. (4) or (5) was used instead of Eq. (3) for the expression of the activity of component 1, because calculations with Eq. (3) did not lead to appreciable improvements. The solubility, in general, is calculated at the system temperature by a trial-and-error procedure. This pro-

Fig. 2 Solubility of benzene in ethane

cedure, however, is undesirable for systems in which immiscible liquids form or solid solubility varies greatly with small temperature changes, because in such cases the calculations tend not to converge. The pressure and the liquid mole fractions were selected as the independent, known variables; the program calculates the equilibrium temperature. Successive estimates of the temperature were made using a Newtonian interpolation and extrapolation technique. The pressure used in these calculations was that reported in the experimental data, except for the system where the experimental pressure was not reported, in which the vapor pressure of pure solvent at the system temperature was used. We calculated the solubility in three ways: first, assuming $k_{12}=s_{12}=0$; second, using $s_{12}=0$ and an empirical k_{12} which best reproduces the experimental solubility data; third, using an empirical k_{12} and s_{12} . Some typical results are shown in Figs. 2 to 7.

Figure 2 shows the results for the benzene-ethane system¹⁵⁾. The broken line represents ideal solubility. The results with $k_{12}=0.010$ and $s_{12}=0$ intersect the experimental values and cannot reproduce them adequately, whereas the results with two parameters ($k_{12}=0.009$ and $s_{12}=0.022$) can satisfactorily reproduce the experiment. Similar results were obtained for other systems. Then two binary parameters (k_{12} and s_{12}) for each system were determined empirically in the subsequent calculations. Table 1 presents k_{12} and s_{12} values for several binary systems determined from the solid-solubility calculations using data taken from the literature. Most k_{12} and s_{12} values are near zero. However, even a small variation from zero can appreciably affect estimated properties.

Figure 3 shows the results for solubility of three n -

Table 1 Binary interaction parameters k_{12} and s_{12} from solid-liquid equilibrium data

Systems Solute(1)–Solvent(2)	k_{12}	s_{12}	Temperature range [K]		Mole fraction range X_1		RMS ^a dev. [K]	Max. ^b error [K]	Data source
CO ₂ –Methane	0.100	−0.230	194.6	124.9	0.126	0.0008	1.4	3.1	(1)
CO ₂ –Ethane	0.128	−0.202	213.2	105.4	0.9108	0.00013	1.6	3.4	(6)
CO ₂ –Propylene	0.085	−0.030	140.0	120.4	0.024	0.0068	1.8	2.2	(1)
CO ₂ –Propane	0.147	−0.169	212.0	108.2	0.8274	0.00025	1.3	4.5	(6)
CO ₂ – <i>n</i> -Butane	0.161	−0.153	213.2	135.4	0.855	0.00268	0.7	1.7	(6)
CO ₂ – <i>n</i> -Hexane	0.177	−0.139	215.7	177.2	0.9723	0.0382	1.1	1.6	(4)
CO ₂ – <i>n</i> -Heptane	0.182	−0.115	215.6	182.2	0.6801	0.0519	1.0	2.3	(4)
H ₂ S–Methane	0.099	0.011	162.4	119.0	0.017	0.0012	2.4	4.5	(1)
H ₂ S–Ethylene	0.014	0.031	157.5	120.1	0.58	0.099	0.2	0.3	(1)
H ₂ S–Ethane	0.133	−0.855	159.8	120.1	0.096	0.0055	0.7	1.1	(1)
H ₂ S–Propylene	0.040	−0.005	159.5	120.1	0.59	0.134	0.3	0.5	(1)
H ₂ S–Propane	0.109	−0.496	176.5	142.5	0.33	0.03	0.8	1.1	(1)
H ₂ S– <i>n</i> -Butane	0.110	−0.105	183.5	141.5	0.77	0.055	1.8	2.3	(1)
Acetylene–Methane	0.156	−0.182	143.1	93.3	0.0125	0.68E−4	0.7	1.2	(18)
<i>n</i> -Butane–Methane	−0.016	0.013	127.6	90.2	0.7766	0.0208	0.8	1.1	(9) (16)
<i>n</i> -Pentane–Methane	−0.009	0.001	139.8	90.2	0.826	0.186E−2	2.0	6.9	(9) (16)
<i>n</i> -Hexane–Methane	−0.025	0.071	176.6	99.4	0.9437	0.77E−4	1.3	3.3	(10) (25)
Benzene–Methane	−0.017	0.046	199.8	99.4	0.0014	0.39E−6	1.8	3.1	(10)
Toluene–Methane	−0.014	0.057	149.7	92.1	0.866E−3	0.36E−5	1.8	4.3	(10)
<i>n</i> -Heptane–Methane	−0.032	0.082	160.9	94.2	0.0126	0.91E−5	1.5	3.4	(10)
Benzene–Ethane	0.009	0.022	265.0	175.0	0.7648	0.00845	0.9	1.6	(15)
Cyclohexane–Ethane	−0.009	0.064	255.0	145.0	0.9030	0.0665	3.0	4.5	(15)
<i>n</i> -Octane–Ethane	−0.008	0.054	210.0	150.0	0.701	0.00553	1.0	1.5	(8)
<i>trans</i> -Decalin–Ethane	0.026	0.024	240.0	150.0	0.9287	0.00511	0.6	1.3	(15)
<i>n</i> -Decane–Ethane	−0.023	0.077	235.0	165.0	0.5953	0.938E−3	1.4	2.4	(8)
<i>n</i> -Dodecane–Ethane	−0.015	0.088	255.0	195.0	0.5558	0.624E−3	1.1	1.9	(8)
Benzene–Propane	0.009	−0.009	277.35	241.15	0.9855	0.306	0.3	0.6	(17)
<i>p</i> -Xylene–Propane	−0.010	0.012	281.7	255.6	0.888	0.296	0.3	0.7	(5)
Naphthalene–Benzene	−0.001	0.012	346.2	270.1	0.90	0.05	0.7	1.5	(29)
Benzene–Cyclohexane	0.024	−0.008	275.8	231.0	0.95	0.05	1.6	4.0	(29)
Naphthalene– <i>n</i> -Hexane	0.006	0.003	343.1	292.4	0.80	0.10	0.2	0.3	(29)
Naphthalene–Cyclohexane	0.010	0.030	350.0	270.7	0.95	0.05	0.5	0.8	(29)
Benzene– <i>n</i> -Hexane	0.016	0.005	233.7	275.5	0.95	0.30	0.4	0.6	(29)
Acetylene–Ethylene	0.000	0.280	143.1	103.1	0.218	0.034	0.9	2.3	(18)
Cyclohexane–R-22	0.057	−0.228	272.2	235.4	0.9658	0.691	1.5	2.6	(3)
Benzene–R-22	0.025	−0.123	275.6	242.6	0.9597	0.460	0.3	0.5	(3)

^a RMS Dev. [K] = $\sqrt{\frac{\sum_i (T_{cal} - T_{exp})_i^2}{\text{No. of data}}}$

^b Max. error [K] = $\max |T_{cal} - T_{exp}|$

alkanes in ethane⁸⁾. These systems exhibit nearly ideal behavior, and as nonsimilarities among constituents become large, deviations from ideal behavior also become increasingly large.

Figure 4 shows the results for the benzene–cyclohexane system²⁹⁾ which forms a eutectic mixture. As shown in this diagram, we can represent the solubility diagram of the entire binary system with one set of binary parameters. Figure 5 presents the results for the carbon dioxide–*n*-heptane system⁴⁾. In this system immiscible liquids form at high carbon dioxide concentrations, and a small change of temperature results in a large change of solubility. This diagram also shows correlation of the Wilson equation (3-parameter form), and Scatchard-Hamer equation (2-parameter form). Among the three equations tested, both the Wilson equation in 3-parameter form and this work in 2-parameter form gave better results.

The result for the *n*-hexane–methane system^{10,25)} is shown in Fig. 6. This system has already been cor-

related using the Redlich-Kwong equation of state by de Mateo and Kurata²⁾. But at higher temperatures their prediction was in great error, perhaps because of divergence of iterative calculations. Their divergence may be attributed to the calculation procedure performed at constant temperature. In the present work, however, this was improved where calculations were performed at constant compositions as described previously. The result for the benzene–methane system¹⁰⁾ is shown in Fig. 7. This diagram indicates that the effect of pressure on solubility is manifested near the solvent critical temperature. Figures 8 and 9 present k_{12} and s_{12} as a function of the ratio V_{ci}/V_{cj} . These diagrams show the results for mixtures of carbon dioxide with hydrocarbons and those for mixtures of hydrocarbons with hydrocarbons. These correlations serve to estimate parameters (k_{12} and s_{12}) for binaries where insufficient experimental information is at hand. No results for the CO₂–propylene system or for systems containing H₂S were

Fig. 3 Solubility of *n*-alkanes in ethane

Fig. 4 Solid-liquid equilibria for benzene-cyclohexane system

Fig. 5 Solubility of carbon dioxide in *n*-heptane

Fig. 6 Solubility of *n*-hexane in methane

included in these diagrams, because smoothed correlations were not obtained for these systems. One of the reasons for this defect seems to be that for these systems experimental information is of limited quantity.

Conclusions

The equation of state of Lee-Kesler together with the pseudocritical method can correlate the solubility of solids in liquids with sufficient accuracy for most technical purposes. The correlation resulting from this investigation will be valuable in the design of cryogenic processes.

Nomenclature

f	= fugacity	[atm]
H	= molar enthalpy	[cal·mol ⁻¹]
k_{12}	= binary interaction constant defined in Eq. (9)	[—]
n	= total amount of substance	[mol]
P	= pressure	[atm]
R	= gas constant, 1.9872	[cal·mol ⁻¹ ·K ⁻¹]
	gas constant, 82.054	[cc·atm·mol ⁻¹ ·K ⁻¹]
S	= molar entropy	[cal·mol ⁻¹ ·K ⁻¹]
s_{12}	= binary interaction constant defined in Eq. (9)	[—]
T	= temperature	[K]
V	= molar volume	[cc·mol ⁻¹]

Fig. 7 Solubility of benzene in methane

Fig. 8 Correlation of binary interaction parameters, k_{12}

V_r	= $P_c V / RT_c$	[—]
x	= mole fraction in liquid	[—]
Z	= compressibility factor	[—]
γ	= activity coefficient	[—]
ω	= acentric factor	[—]

⟨Superscripts and subscripts⟩

c	= critical property
f	= fusion
i, j, k	= components in solution
l	= liquid
m	= normal melting point
r	= reduced property
s	= solid
trans	= transition point
(R)	= reference fluid
(0)	= simple fluid
(1)	= deviation function of the Lee-Kesler correlation

Fig. 9 Correlation of binary interaction parameters, s_{12}

- 1 = solute
 2 = solvent
 ' = pseudocritical property of a mixture
 * = ideal gas property

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CORRELATION FOR DYNAMIC HOLDUP IN PACKED BEDS WITH COCURRENT GAS-LIQUID DOWNFLOW

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An equation for dynamic holdup of cocurrent gas-liquid downflow in packed beds was developed on the basis of models in which the interactions among liquid holdup, pressure gradient and liquid flow rate for the gravity-viscosity and the gravity-inertia regimes were taken into account. The dynamic holdup data for beds of glass spheres (0.12–0.43 cm in diameter) with air-water flow were correlated well, in terms of static pressure gradient and total holdup together with the operating variables, by the equation

$$h\phi = 13.5[(Re_L)/(Ga_L^*)]^{1/8} + 1.20(Re_L)(Ga_L^*)^{-1/2}$$

where $Re_L = G_L d_p / \mu_L$ and $Ga_L^* = \rho_L^2 g d_p^3 \{1 - (g_o / \rho_L g h)(dp/dz)\} / \mu_L^2$.

A procedure was also shown for evaluating the dynamic and the total holdups and the static pressure gradient using only such operating variables as particle diameter and superficial velocities of gas and liquid.

Introduction

Liquid holdup may well be considered as one of the basic quantities for design calculation and operation of packed-bed reactors with cocurrent gas-liquid downflow. Holdup has been shown to have a direct influence on mass transfer⁴⁾, heat transfer^{11,14)}, pressure loss⁹⁾ and axial dispersion of liquid⁸⁾. Many investigators have measured holdup and have produced empirical equations, in which various types of parameters were employed, such as the flow parameter χ of Lockhart and Martinelli^{7,13)}, dimensionless numbers such as Reynolds and Galileo numbers^{12,13,15)}, the mass velocity and Reynolds number ratios between gas and liquid^{8,17,18)} and parameters derived from

theoretical considerations on gas and liquid flows in packed beds^{2,5,6)}. Due to the complex gas-liquid interaction, most correlations are applicable only in a few restricted regimes, and some investigators^{13,17)} correlated their experimental data in two separate equations depending on the flow pattern or the gas-liquid interaction regimes. Buchanan¹⁾ correlated the experimental data of the operating holdup in terms of the two dimensionless numbers $(Re_L/Ga_L)^{1/3}$ and $(Re_L/Ga_L)^{1/2}$, which were derived theoretically on the basis of the momentum and the energy balances in the gravity-viscosity model and the gravity-inertia model, respectively. Buchanan's equation seems to be generalized and to be applicable in a wider range of liquid flow rates. The two parameters involved in Buchanan's correlation were examined for correlating the dynamic holdup data⁸⁾ of cocurrent gas-liquid down-

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