[Research Note]

Sensitivity of Interfacial-tension Predictions to Parachor-method Parameters

Kozo Sato

Geosystem Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN

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The parachor method (PM) is widely used to predict interfacial tension (IFT) but may yield incorrect IFT values, and, thus, adjustment of the PM parameters may be necessary. The sensitivities of IFT predictions to the PM parameters were investigated by examining the Weinaug and Katz method (WKM) and the Lee and Chien method (LCM). Parameter adjustment of only the scaling exponent does not always yield good regression results, and including parachors (or related variables) in a set of regression parameters is recommended. The WKM may result in unrealistic parameter adjustment due to the absence of interrelation between the scaling exponent and the parachor. In contrast, the LCM honors the correct definition of the parachor and tends to yield acceptable IFT predictions within the limits of realistic parameter adjustment.

Keywords

Interfacial tension, Parachor, Regression, Interfacial tension prediction, Parachor method

1. Introduction

Interfacial tension (IFT) is a crucial factor in modeling fluid displacement and distribution behavior[1], so has been an important research target in petroleum engineering. There are three types of prediction methods for IFT: the gradient theory model[2),3)], the parachor method[4)～6)], and the corresponding-state correlation[7)]. The first model is purely theoretical and requires only the properties of the pure components. However, a series of experiments must be conducted to determine parameters for all the components and their binaries. Due to such complications and the failure to provide better results relative to the other two methods, the gradient theory model has not received much attention. The other two methods are closely related. Both are empirical and once the empirical parameters are obtained, they are very easy to use.

However, all three methods may fail to predict IFT values, particularly for multi-component systems[8)]. In this event, one may try to adjust IFT parameters so that the IFT predictions match the experimental IFT data (if available). In connection with equation-of-state (EOS) compositional simulation, IFT predictions based on the parachor method (PM) are widely used. Among such techniques, the Weinaug and Katz[4)] method (WKM) and the Lee and Chien[6)] method (LCM) are reviewed and examined in this study. These two methods were applied for a simple C_1-C_9 system to predict the IFT and undergo a regression process. The sensitivities of IFT predictions to the PM parameters were investigated, and the regression behavior examined.

* To whom correspondence should be addressed.
* E-mail: sato@geosys.t.u-tokyo.ac.jp

2. IFT Prediction

According to Macleod[9)], the IFT (σ) between the liquid and vapor phases of a pure-component system is correlated with the difference in molar densities of liquid and vapor phases.

$$\sigma^{1/4} = [P](\bar{\rho}_L - \bar{\rho}_V) \quad (1)$$

where $[P]$ is the parachor, and $\bar{\rho}_L$ and $\bar{\rho}_V$ are the liquid-phase and vapor-phase molar densities, respectively. The parachor is considered to have a unique value for each compound independent of pressure and temperature. Although Eq. (1) was derived empirically, the physical representation accords with the scaling theory[6)].

Based on the fact that the IFT is negatively correlated with temperature, Brock and Bird[10)] proposed the following corresponding-state identity:

$$\sigma = A_c(1 - T_r)^{\theta} \quad (2)$$

where A_c is a function of critical pressure (p_c), critical temperature (T_c), and boiling point (T_b), T_r is the reduced temperature, and θ is determined empirically[11)] as

$$\theta = 11/9 \quad (3)$$

Equation (2) is applicable to pure-component systems, critical properties of which are known. However, for multi-component systems, it is more useful to express σ as a function of phase properties, such as molar densities.

Lee and Chien[6] showed that, using the scaling theory and the Rayleigh dimensional analysis[12], the relationship between densities and temperature can be written as

$$\rho_{\mathrm{L}} - \rho_{\mathrm{V}} = B\rho_{\mathrm{c}}(1 - T_{\mathrm{r}})^{\beta} \tag{4}$$

where ρ_l is the density of phase l, ρ_{c} is the critical density, B is the proportionality constant, and β is determined through the Ising model[13] as

$$\beta = 5/16 \tag{5}$$

Combining Eqs. (2) and (4) and using $M/V_{\mathrm{c}} = \rho_{\mathrm{c}}$ and $\overline{\rho} = \rho/M$ yields

$$\sigma^{\beta/\theta} = \frac{A_{\mathrm{c}}^{\beta/\theta} V_{\mathrm{c}}}{B}(\overline{\rho}_{\mathrm{L}} - \overline{\rho}_{\mathrm{V}}) \tag{6}$$

where V_{c} is the critical volume and M is the molecular weight.

Comparing Eqs. (1) and (6),

$$[P] = \frac{A_{\mathrm{c}}^{\xi} V_{\mathrm{c}}}{B} \tag{7}$$

where $\xi = \beta/\theta$. Thus, the empirical correlation Eq. (1), proposed by Macleod[9], can be interpreted as a combination of the σ-T_{r} and $\Delta\rho$-T_{r} correlations. Combining Eqs. (3) and (5) yields ξ = 45/176 = 1/3.911, which is close to the exponent (1/4) proposed by Macleod.

For multi-component systems, the IFT (σ_m) may be expressed by the extension of Eq. (1).

$$\sigma_m^{\xi} = [P_{\mathrm{L}}]\overline{\rho}_{\mathrm{L}} - [P_{\mathrm{V}}]\overline{\rho}_{\mathrm{V}} \tag{8}$$

where $[P_{\mathrm{L}}]$ and $[P_{\mathrm{V}}]$ are the liquid-phase and vapor-phase parachors, respectively. Two different approaches have been proposed to define ξ, $[P_{\mathrm{L}}]$, and $[P_{\mathrm{V}}]$: the WKM and the LCM.

2. 1. Weinaug and Katz Method (WKM)

Weinaug and Katz[4] regarded Eq. (8) as a direct extension of Eq. (1) and estimated the phase parachor $[P_l]$ as a molar average of the component parachor $[P_i]$.

$$[P_l] = \sum_{i=1}^{n_{\mathrm{c}}} x_{li}[P_i] \quad (l = \mathrm{L}, \mathrm{V}) \tag{9}$$

where n_{c} is the number of components and x_{li} is the mole fraction of component i in phase l. In the WKM, the scaling exponent ξ of 1/4 is adopted according to Macleod[9]. Schechter and Guo[5] conducted a comprehensive survey of reported IFT and density data, and concluded that ξ = 1/3.88 is the optimum single constant for IFT predictions. Nonetheless, the approach is similar to the WKM, and for the purpose of this study, examining one of the two is enough. In this paper, the WKM (ξ = 1/4) is employed because of wide use.

2. 2. Lee and Chien Method (LCM)

According to the corresponding-state theorem of mixtures, Lee and Chien[6] used Eq. (7) and defined the phase parachor $[P_l]$ as

$$[P_l] = \frac{A_{cl}^{\xi} V_{cl}}{B_l} \tag{10}$$

where ξ = 1/3.911. It is noteworthy that the component parachor $[P_i]$ is not used to obtain the phase parachor $[P_l]$. The bulk-phase parameters A_{cl}, V_{cl}, and B_l are obtained by applying a simple molar mixing rule to the corresponding component parameters.

$$X_l = \sum_{i=1}^{n_{\mathrm{c}}} x_{li} X_i \quad (X = A_{\mathrm{c}}, V_{\mathrm{c}}, B) \tag{11}$$

where X_l is the phase parameter and X_i is the component parameter.

3. Regression on IFT Data

In the sense of least squares, regression on IFT data may be stated symbolically as

$$\min_{\vec{\alpha}} E(\vec{\alpha}) = \min_{\vec{\alpha}} \sum_{j=1}^{n_m} \left[\frac{\overline{\sigma}_{mj} - \sigma_{mj}(\vec{\alpha})}{\overline{\sigma}_{mj}} \right]^2 \tag{12}$$

where $\vec{\alpha}$ is the regression-parameter vector, n_m the number of measured data to be matched, $\overline{\sigma}_{mj}$ the measured IFT values, and $\sigma_{mj}(\vec{\alpha})$ the predicted IFT values. The IFT prediction requires two types of parameters: ξ and $[P_l]$, which can be adjusted after EOS calculations are completed. In the WKM, the phase parachor $[P_l]$ is given by Eq. (9), where x_{li} is determined by the EOS calculation and cannot be altered. Thus, ξ and the component parachor $[P_i]$ are the possible components of $\vec{\alpha}$. In the LCM, $[P_l]$ is given by Eq. (10), where A_{cl} and V_{cl} are related to critical properties and cannot be manipulated independently. Thus, ξ and B_i are the possible components of $\vec{\alpha}$.

To solve Eq. (12) for the optimum $\vec{\alpha}$, the Gauss–Newton method[14] is employed. During the regression process, partial derivatives of $\sigma_{mj}(\vec{\alpha})$ with respect to regression parameters are required. Since the definitions of $[P_l]$ are different, the partial derivatives of σ_m take different forms for the WKM and the LCM. For the WKM,

$$\frac{\partial \sigma_m}{\partial \xi} = -\frac{\sigma_m}{\xi} \ln \sigma_m \tag{13}$$

$$\frac{\partial \sigma_m}{\partial [P_i]} = \frac{\sigma_m^{1-\xi}}{\xi}(\overline{\rho}_{\mathrm{L}} x_{\mathrm{L}i} - \overline{\rho}_{\mathrm{V}} x_{\mathrm{V}i}) \tag{14}$$

and for the LCM,

$$\frac{\partial \sigma_m}{\partial \xi} = -\frac{\sigma_m}{\xi} \ln \sigma_m + \frac{\sigma_m^{1-\xi}}{\xi}(\overline{\rho}_{\mathrm{L}}[P_{\mathrm{L}}] \ln A_{\mathrm{cL}} - \overline{\rho}_{\mathrm{V}}[P_{\mathrm{V}}] \ln A_{\mathrm{cV}}) \tag{15}$$

$$\frac{\partial \sigma_m}{\partial B_i} = \frac{\sigma_m^{1-\xi}}{\xi}\left(-\overline{\rho}_{\mathrm{L}}[P_{\mathrm{L}}] \frac{x_{\mathrm{L}i}}{B_{\mathrm{L}}} + \overline{\rho}_{\mathrm{V}}[P_{\mathrm{V}}] \frac{x_{\mathrm{V}i}}{B_{\mathrm{V}}} \right) \tag{16}$$

4. Results and Discussion

To illustrate the difference between the WKM and the LCM, a fairly simple system C_1-C_9 is examined. IFT for the C_1-C_9 system were measured by Deam and Maddox, as cited by Lee and Chien[6]. The flash calculation used the Peng–Robinson EOS[15] and no parameter adjustment was attempted. **Figure 1** compares the IFT predictions with the experimental data.

The WKM and the LCM both yield IFT values lower than the measured values. Although the LCM gives more consistent results than the WKM in a high-pressure range, the overall prediction quality is not satisfactory. The error $E(\vec{\alpha})$ is 0.2728 for the WKM and 0.1298 for the LCM, and adjustment of the PM parameters is required to obtain better results (to reduce $E(\vec{\alpha})$).

The multivariate regression technique mentioned above was used to match the IFT predictions to the measured data. The following three sets of regression parameters were considered:

(a) scaling exponent ξ only
(b) component parachors $[P_i]$ (or B_i) only
(c) scaling exponent ξ and component parachors $[P_i]$ (or B_i)

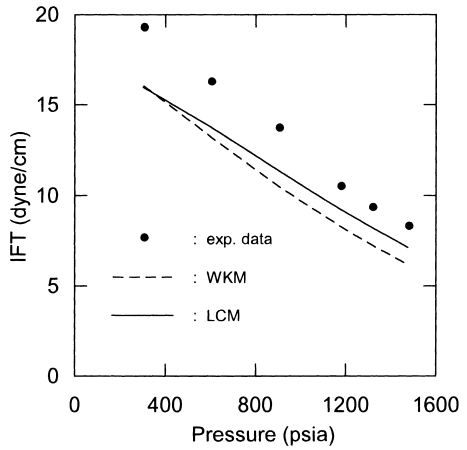

Fig. 1 Comparison of IFT Predictions by the WKM and the LCM with Measured Data for the C_1-C_9 System

Figure 2 shows the regression results with the WKM and the LCM. For both IFT prediction methods, the three different regression schemes yield improved results in the order of (c), (b), and (a). With the best scheme (c), $E(\vec{\alpha})$ were reduced to 0.0017 for the WKM and to 0.0016 for the LCM.

4. 1. Parameter Adjustment

Achieving good matching does not always amount to accurate modeling. Unrealistic parameter adjustment may lead to poor predictions for the conditions outside the matching range. Thus, it is important to check whether the parameter adjustment is within a reasonable range.

Table 1 and **Table 2** summarize the adjustment values of individual parameters for the WKM and the LCM, respectively. This summary shows that (1) the regression scheme (a) does not give a satisfactory result for both prediction methods, and (2) with the WKM, the regression scheme (c) results in unrealistically large adjustment of all regression parameters. To increase

Table 1 Parameter Adjustment for the WKM

	Before regression	After regression		
		ξ only	$[P_i]$ only	both
ξ	0.2500	0.2294 (−8%)[a]	—	0.3505 (+40%)
$[P_{C1}]$	72.61	—	59.44 (−18%)	160.90 (+122%)
$[P_{C9}]$	389.32	—	407.39 (+5%)	552.09 (+42%)
$E(\vec{\alpha})$	0.2728	0.0298	0.0020	0.0017

a) ( ) indicates the adjustment percentage.

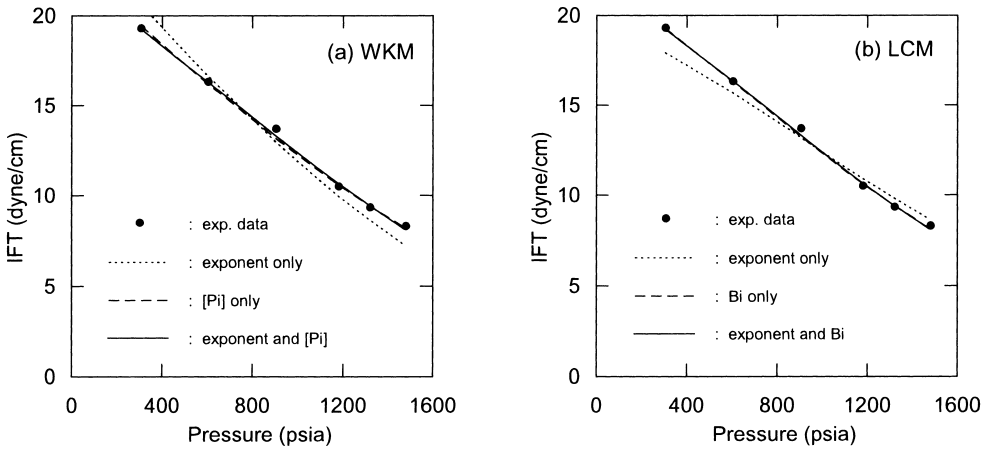

Fig. 2 Regression Results Using (a) the WKM and (b) the LCM

our understanding of these observations, the sensitivities of IFT predictions to the PM parameters were investigated. **Figure 3** through **Fig. 5** respectively show the effects of ξ, [P_{C1}] (or B_{C1}), and [P_{C9}] (or B_{C9}) on the IFT predictions at 600 psia.

Observation (1) is readily understood by knowing that $\partial\sigma_m/\partial\xi$ is not a direct function of x_{li}, as seen in Eqs. (13) and (15). Adjusting ξ can shift IFT values globally (**Fig. 2**) but cannot match the IFT predictions to the actual IFT values at different pressures, where x_{li} are different. **Figure 3** indicates that the IFT prediction with the WKM is negatively correlated with ξ, which is obvious from Eq. (13). In contrast, the prediction with the LCM is positively correlated with ξ. In the LCM, [P_l] is also related to ξ, as indicated by Eq. (10), and its derivative with respect to ξ is

$$\frac{\partial[P_l]}{\partial\xi} = [P_l]\ln A_{cl} \tag{17}$$

This value is usually larger for a liquid phase than for a vapor phase, which implies that as ξ increases [P_L] and [P_V] differ more, and consequently, σ_m becomes larger. Including ξ in the definition of [P_l] through the corresponding-state theorem totally changes the prediction sensitivity to ξ.

Figure 3 through **Fig. 5** and Eq. (10) show that, in the LCM, ξ and B_i control [P_l] (and eventually σ_m) interactively. This prevents drastic adjustment of the

Table 2 Parameter Adjustment for the LCM

	Before regression	After regression		
		ξ only	B_i only	both
ξ	0.2557	0.2834 (+11%)[a)]	—	0.2443 (–4%)
[P_{C1}]	72.61	80.20 (+10%)	71.11 (–2%)	72.49 (–0%)
[P_{C9}]	389.32	434.37 (+12%)	410.90 (+6%)	395.57 (+2%)
$E(\vec{\alpha})$	0.1298	0.0148	0.0016	0.0016

a) ( ) indicates the adjustment percentage.

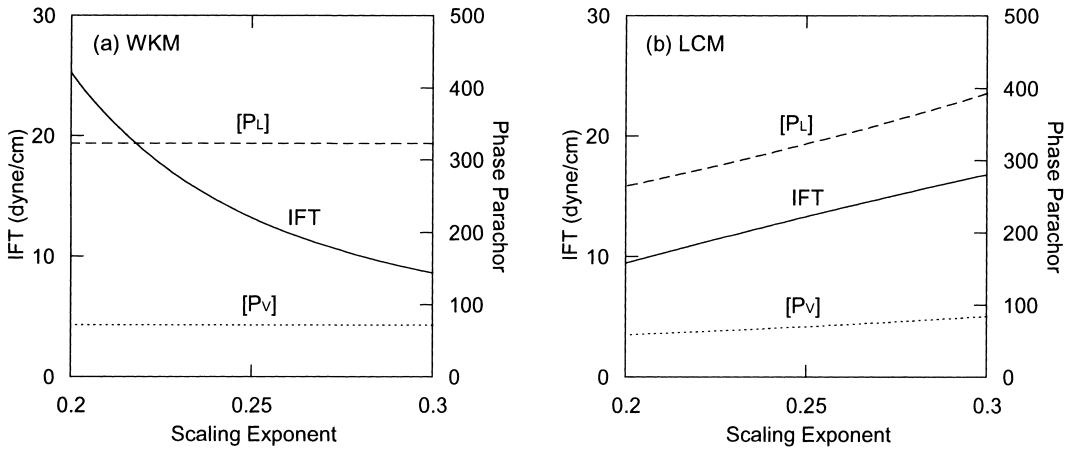

Fig. 3 Sensitivity of IFT Predictions to the Scaling Exponent ξ Using (a) the WKM and (b) the LCM

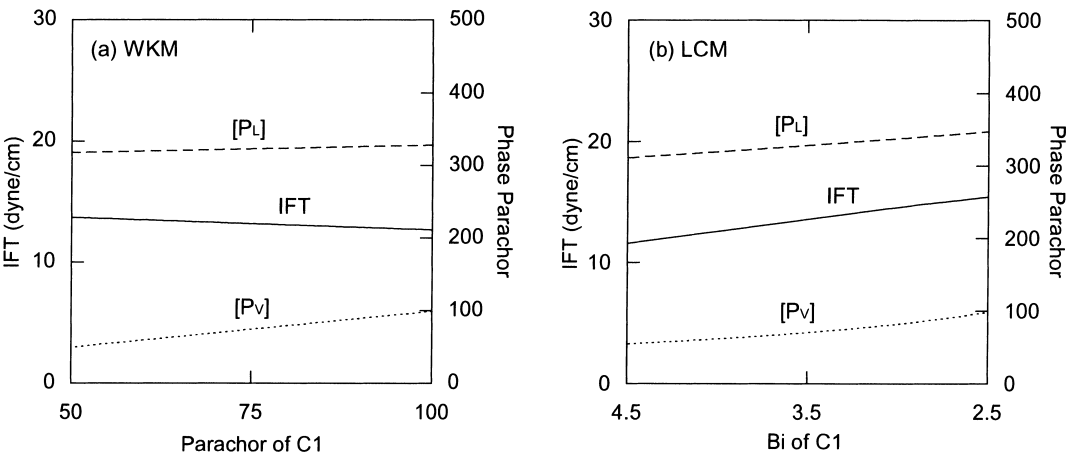

Fig. 4 Sensitivity of IFT Predictions to (a) [P_{C1}] Using the WKM and (b) B_{C1} Using the LCM

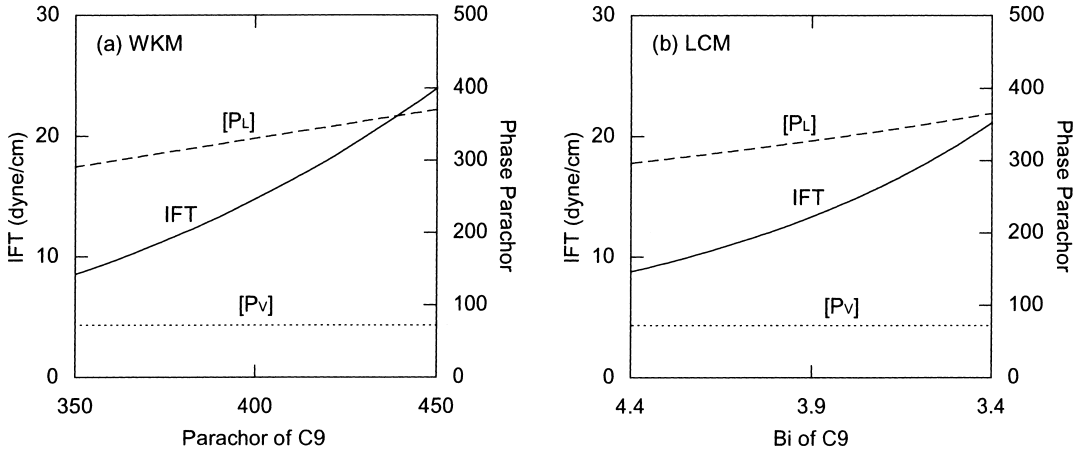

Fig. 5 Sensitivity of IFT Predictions to (a) [P_{C9}] Using the WKM and (b) B_{C9} Using the LCM

regression parameters. In contrast, ξ and [P_i] in the WKM independently affect σ_m. For the C_1-C_9 system, for instance, the predicted IFT values were smaller than the actual values, and [P_{C1}] and [P_{C9}] were positively and largely (122% and 42%, respectively) adjusted. These unrealistic changes were compensated by the positive adjustment of ξ by 40%. Thus, it is deduced that the observation (2) is the consequence of the independence of regression parameters.

In summary, the LCM preserves the physical representation of B_i adjustment, because the phase parachor is defined based on the scaling theory and [P_i] is a function of ξ and B_i. In contrast, the WKM provides no constraint on [P_i] adjustment, because of the absence of interrelation between [P_i] and ξ.

5. Conclusions

The WKM and the LCM coupled with EOS flash calculations do not always yield IFT predictions that are consistent with measured data. Therefore, parameter adjustment may be required for acceptable IFT predictions. The following list summarizes the findings relevant to the regression behavior.

(1) The parameter adjustment of only ξ does not always yield good results. [P_i] (or B_i) should be included in a set of regression parameters.

(2) The WKM can result in unrealistic parameter adjustment because the component parachor [P_i] is not interrelated to ξ, contrary to the correct definition of the parachor.

(3) The LCM honors the correct definition of the parachor and tends to yield acceptable IFT predictions within the limits of realistic parameter adjustment.

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要　　旨

パラコール法パラメーターに対する界面張力予測の敏感度

佐藤　光三

東京大学大学院工学系研究科地球システム工学専攻，113-8658 東京都文京区本郷 7-3-1

界面張力予測のためにパラコール法が広く用いられているが，予測精度が高くない場合にはパラコール法パラメーターの調整が必要となる。この種のパラメーターに対する界面張力予測の敏感度を理解するために，Weinaug and Katz 法（WKM）ならびに Lee and Chien 法（LCM）を取り上げて検討した。その結果，回帰においてスケーリング指数のみを調整しても良好な結果につながるとは限らず，パラコール（あるいはそれに関連した変数）を回帰パラメーターに含めるべきことが判明した。また，WKM はスケーリング指数とパラコールとの相互関係を無視しているため，非現実的なパラメーター調整を引き起こしうることが確認された。これと対照的に，LCM はパラコールの定義に準じた手法であり，界面張力予測を現実的なパラメーター調整の範囲内で可能とする傾向が見受けられる。