

Comment on a Generalized Corresponding-States Method for the Prediction of Surface Tension of Pure Liquids and Liquid Mixtures

A simplified expression for the prediction of surface tensions of ternary systems is derived from the generalized corresponding-states method. For n-hexane + n-decane + n-hexadecane mixtures, the newly derived expressions predict the experimental surface tensions to within an average absolute deviation of 2.1%.

In a recent article appearing in this journal, Rice and Tega (1) demonstrated that the surface tension, σ , of a binary mixture could be predicted from a corresponding-states method

$$(\sigma\phi)_{12} = (\sigma\phi)_1 + \frac{\omega_{12} - \omega_1}{\omega_2 - \omega_1} [(\sigma\phi)_1 - (\sigma\phi)_2] \quad [1]$$

$$\phi = T_C^{-1} V_C^{2/3}, \quad [2]$$

where $(\sigma\phi)_1$ and $(\sigma\phi)_2$ refer to the reduced surface tensions of the two pure substances at the same reduced temperature and pressure as the binary mixture, and ω is an acentric factor. The pseudocritical properties of the mixture were defined

$$T_{Cm} V_{Cm} = \sum_i \sum_j X_i X_j T_{Cij} T_{Cij} \quad [3]$$

$$V_{Cm} = \sum_i \sum_j X_i X_j V_{Cij} \quad [4]$$

$$\omega_m = \sum_i X_i \omega_i \quad [5]$$

in terms of the pure component critical temperatures (T_{Cii} and T_{Cjj}) and critical volumes (V_{Cii} and V_{Cjj}). The cross terms T_{Cij} and V_{Cij} ($i \neq j$) were calculated via:

$$T_{Cij} V_{Cij} = \psi_{ij} (T_{Cii} V_{Cii} T_{Cjj} V_{Cjj})^{1/2} \quad [6]$$

$$V_{Cij} = \frac{(V_{Cii}^{1/3} + V_{Cjj}^{1/3})^3}{8} \quad [7]$$

ψ_{ij} representing a binary interaction parameter. Setting $\psi_{ij} = 1$, the authors noted that Eq. [1] predicted the surface tensions of six binary systems to within an average absolute deviation (AAD) of 0.187% and a maximum deviation of 6.49%.

Extension of the corresponding-states method to multicomponent systems involves a series of two reference fluid interpolations (2). If a third component is present, then a second two-fluid expansion must be performed using the third pure component and the properties of the pseudocritical component "12"

$$(\sigma\phi)_{123} = (\sigma\phi)_3 + \frac{\omega_{123} - \omega_3}{\omega_{12} - \omega_3} [(\sigma\phi)_{12} - (\sigma\phi)_3]. \quad [8]$$

Although Eq. [8] appears rather complex, the predictive method can be greatly simplified. Combining Eqs. [1],

TABLE I

Comparison between Experimental Surface Tensions and the Predictions of Eq. [9] for Ternary n-Hexane + n-Decane + n-Hexadecane Mixtures at 303.16°K

$X_{C_6H_{14}}$	$X_{C_{10}H_{22}}$	σ^{exp}	$\sigma^{Eq.[9]}$	Deviations ^a (%)
0.0000	0.9491	23.16	23.17	0.0
0.0000	0.8256	23.82	23.69	0.5
0.0000	0.7346	24.18	24.06	0.5
0.0000	0.5988	24.79	24.60	0.8
0.1420	0.8580	22.28	21.95	1.5
0.1420	0.7532	22.44	22.42	0.0
0.1420	0.6457	22.74	22.88	0.6
0.1420	0.5975	23.06	23.09	0.1
0.1420	0.4467	23.24	23.71	2.0
0.2671	0.7329	21.68	21.04	3.0
0.2671	0.6353	21.84	21.49	1.6
0.2671	0.4795	21.99	22.18	0.9
0.2671	0.3902	22.16	22.58	1.9
0.2671	0.3253	22.24	22.86	2.8
0.5031	0.4969	20.44	19.24	5.9
0.5031	0.3784	20.38	19.84	2.6
0.5031	0.3058	20.33	20.19	0.7
0.5031	0.1547	20.25	20.90	3.2
0.5031	0.0980	20.27	21.16	4.4
0.6002	0.3998	19.98	18.47	7.6
0.6002	0.2761	19.80	19.12	3.5
0.6002	0.1895	19.66	19.55	0.6
0.6002	0.1190	19.52	19.91	2.0
0.6002	0.0698	19.35	20.13	4.0

$$^a \text{Deviations (\%)} = \left| \frac{\sigma^{Eq.[9]} - \sigma^{exp}}{\sigma^{exp}} \right|.$$

[5], and [8], we find that the reduced surface tension of the ternary system is

$$(\sigma\phi)_{123} = (\sigma\phi)_3 + \frac{\omega_{123} - \omega_3}{\omega_{12} - \omega_3} \times \left\{ (\sigma\phi)_1 + \frac{\omega_{12} - \omega_1}{\omega_2 - \omega_1} [(\sigma\phi)_1 - (\sigma\phi)_2] \right. \\ \left. - (\sigma\phi)_3 \right\} = X_1(\sigma\phi)_1 + X_2(\sigma\phi)_2 + X_3(\sigma\phi)_3 \quad [9]$$

a mole fraction average of the pure component properties. It should be noted that Eq. [9] applies only if the pure components are used as reference fluids and a linear mixing rule, Eq. [5], is assumed for the acentric factor. An analogous expression, expressed in terms of compressibility, has recently been reported by Novak and Ruzicka (3).

Table I compares the predictions of Eq. [9] (with ψ_{ii} 's = 1) to the experimental surface tensions of n-hexane + n-decane + n-hexadecane mixtures (4). Inspection of Table I reveals that deviations between predicted and experimental values are less than 3% for many of the

ternary compositions. These calculations further demonstrate the ability of the generalized corresponding-states method for the prediction of multicomponent surface tensions.

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