A New Stabilizing Index to Correlate Foam Height

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Lowry and Van Winkle (1969) and Hart and Haselden (1969) attempted to correlate their experimental data for foam height with a stabilizing index. This idea was adopted by Moens (1972) to correlate his experimental data for mass transfer efficiency in a packed distillation column. The stabilizing index used by him is based on the overall liquid phase driving force and has the form

$$M = -\frac{d\sigma}{dx}(x - x^*) \tag{1}$$

The index describes the degree of positiveness or negativeness of surface tension positive and negative binary liquid systems. The index has a positive value for a positive system and a negative value for a negative system. From the point of view of using it for correlating purposes, it has the drawback of not being a dimensionless quantity. This can easily be removed by introducing the factor $1/\sigma$ into Equation (1) to obtain

$$M' = -\frac{1}{\sigma}\frac{d\sigma}{dx}(x - x^*) \tag{2}$$

This modification transforms the original index into a dimensionless quantity and also relates it to the absolute value of surface tension at a given concentration.

The correlating properties of the modified stabilizing index M' [Equation (2)] will be illustrated using Moens' (1972) experimental data for the distillation of the *n*-heptane/methylcyclohexane system. First the modified index M' is calculated from the data provided in Table 1 of Moens' paper. Both this index, and the index given by Equation (1), are shown as a function of concentration in Figure 1.

Equation (2) gives, for this system, a slightly less peaked curve than the original index, Equation (1). Generally the differences in the curvatures of the two curves will depend on the type of the σ vs x relationship and on the magnitude of the value of the surface tension of the mixture.

Next, the modified index M' is used to correlate the $N_{OG(r)}$ values taken from Figure 4 of Moens' paper, in which $N_{OG(r)}$ was plotted against the index M, Equation (1). In Figure 2 of this note the values of $N_{OG(r)}$ are shown replotted against the modified index M', Equation (2). It is fairly obvious that the scatter of the data points in Figure (2) is such that the best correlating line, if drawn, would approximate very closely to a straight line. This approximation to a straight line is not so obvious in the corresponding Figure 4 of Moens' paper (1972).

Thus, the modified stabilizing index, as defined by Equation (2), appears to have a more powerful correlating effect and has the definite advantage of being a dimensionless quantity.

NOTATION

M = stabilizing index as defined in Equation (1), dyn/cm
M' = modified stabilizing index as defined in Equation (2), dimensionless
N_{OG} = number of overall gas transfer units
$N_{OG(0)}$ = N_{OG} at zero driving force
$N_{OG(r)}$ = $N_{OG}/N_{OG(0)}$
x = concentration m.v.c. in liquid phase, mole percent

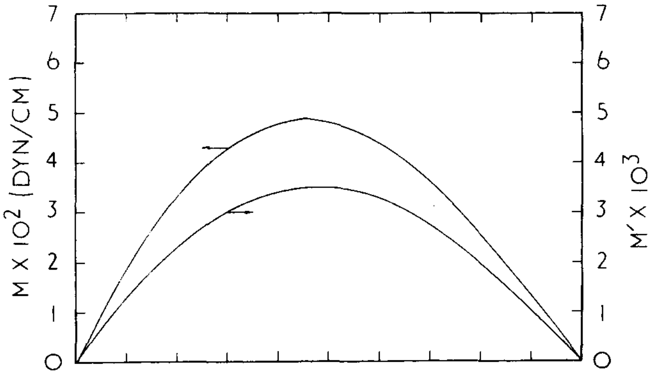

Fig. 1. Stabilizing index M and modified stabilizing index M' as a function of composition for the n-heptane/methylcyclohexane system.

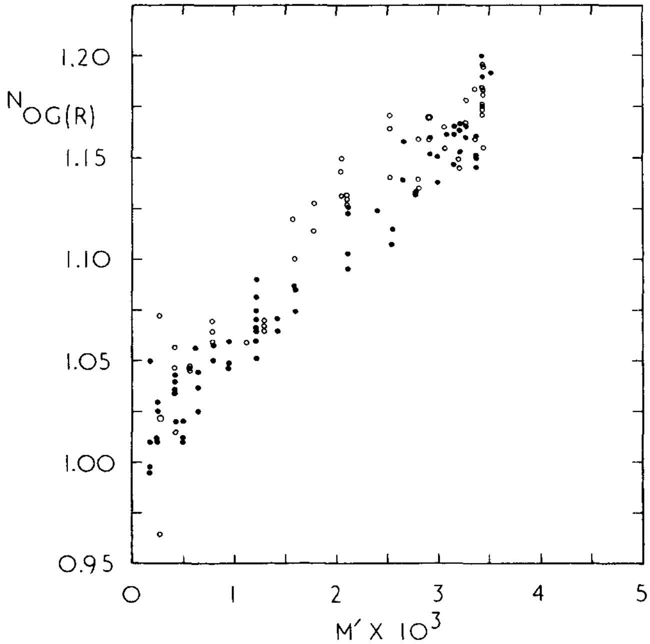

Fig. 2. $N_{OG(R)}$ as a function of the modified stabilizing index, M'
○ measurement for 0% < x < 50%
● measurement for 50% < x < 100%

or fraction

x^* = x in equilibrium with y

y = concentration m.v.c. in vapor phase, mole percent or fraction

σ = surface tension, dyn/cm

LITERATURE CITED

Hart, D. J., and G. G. Haselden, "The influence of mixture composition on distillation—plate efficiency, Distillation—1969" No. 1 p. 16, Inst. Chem. Engrs., London (1969).

Lowry, R. P., and M. Van Winkle, "Foaming and frothing related to system physical properties in a small perforated plate distillation column,," *AIChE J.*, 15, 665 (1969).

Moens, F. P., "The effect of composition and driving force on the performance of packed distillation columns—I," *Chem. Eng. Sci.*, 27, 275 (1972).

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Ion Pair Formation Model for Sea Salt Solutions

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Data on thermodynamic properties of sea salt solutions along with the correlations to obtain these properties have been published by the authors in a previous paper (Bromley et al., 1974. Those correlations are not entirely satisfactory in the sense that no physical insight is provided. The main constituent of sea salt is NaCl. The properties of sea salt solutions, however, differ considerably from those of NaCl solutions due to the presence of appreciable quantities of bivalent ions, Ca^{++}, Mg^{++}, $SO_4^=$. Previous workers have observed that the $SO_4^=$ ion has a strong tendency to form ion pairs with bivalent cations, particularly with Mg^{++} and Ca^{++} ions. A simple model using the idea of pair formation has been worked out. Predictions based on this model are in very good agreement with the available experimental data.

DESCRIPTION OF THE MODEL

It has been assumed that the ion pair formation takes place primarily between the bivalent cations and anions and that all these pair formations may be represented by a single equivalent reaction

$$M^{++} + X^= \rightleftharpoons MX \tag{1}$$

where M^{++} represents the sum total of all the bivalent cations and $X^=$, the sum total of all the bivalent anions present in sea salt. The ions that are removed to form the uncharged species, contribute little to the charge distribution or potential. An individual ion in the solution does not see any net electrical charge on the pair. Also, the number of particles in the solution is less than in the case where no such pair formation occurs. Thermodynamic properties are usually reported on the basis of total number of ions assuming no pair formation. Hence two sets of thermodynamic quantities can be defined. The first set is defined assuming no pair formation and is referred to as *stoichiometric*. The second view takes pair formation into account and is referred to as *microscopic*. The first set is denoted by the subscript *stoi*. In the following discussion the terms without this subscript pertain to the second set.

The equilibrium constant for pair formation can now be written as

$$K = \frac{m'\gamma'}{(m_{++}\gamma_{++})(m_=\gamma_=)} \tag{2}$$

In order to obtain an expression for the stoichiometric activity coefficient, the following assumptions are made:

1. The activity coefficient of the pair species γ' is unity.
2. The activity coefficients γ_{++} and $\gamma_=$ can be adequately approximated by the Debye-Hückel term, that is,

$$\ln \gamma_{++} = \ln \gamma_= = -2.303\, A\gamma (2)^2 \frac{I^{1/2}}{1 + I^{1/2}} \tag{3}$$

3. The microscopic mean ionic activity coefficient is given by the correlation proposed by Bromley (1973). Thus

$$\ln \gamma_\pm = -2.303\, A\gamma \frac{(\Sigma\, \nu_i Z_i^2) I^{1/2}}{1 + I^{1/2}} + 2.303 \left\{ \frac{(0.06 + 0.6B)}{\left(1 + \frac{1.5I}{\Sigma\, \nu_i Z_i^2}\right)^2} (\Sigma\, \nu_i Z_i^2) I + BI \right\} \tag{4}$$

It can be shown that

$$\ln (\gamma_\pm)_{\text{stoi}} = (1 - 2\nu') \ln \gamma_\pm + \nu' (\ln \gamma_{++} + \ln \gamma_=) - p(\nu') \tag{5}$$

where

$$-p(\nu') = (\nu_{++})_{\text{stoi}} \ln \left(1 - \frac{\nu'}{(\nu_{++})_{\text{stoi}}}\right) + (\nu_=)_{\text{stoi}} \ln \left(1 - \frac{\nu'}{(\nu_=)_{\text{stoi}}}\right) \tag{6}$$