Chemical Engineering Science 68 (2012) 443–448

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Semi-regular solution: General behavior

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ARTICLE INFO

Article history:
Received 10 June 2011
Received in revised form
19 September 2011
Accepted 2 October 2011
Available online 6 October 2011

Keywords:
Regular solution
Volatility
Azeotrope
Phase equilibria
Adsorption
Shortcut

ABSTRACT

We have described the behavior of a subgroup of regular solutions not very far from ideality (Hildebrand, 1929, 1947, 1951) that is analogous to the behavior of ideal solutions. For this subgroup the composition of each phase in equilibrium may be related logarithmically. We have found that some cases of isothermal, isobaric and ternary liquid–vapor systems in equilibrium follow this scheme. In each case the resulting calculations of phase compositions are in good agreement with the experimental data reported in the literature. This approach is consistent with correlations frequently used in liquid–liquid case (known as the Othmer-Tobias (1942) and Hand (1930) equations), as well as adsorption of liquid on solid (known as Langmuir–Freundlich isotherm (Dąbrowski et al., 1979)). For fluids mixtures presenting this behavior we use the term of semi-regular mixtures. For this kind of fluid mixtures it can be found a simplified procedure to relate the equilibrium compositions that may be used as "shortcut" for chemical engineering designs.

1. Introduction

In processes design preliminary numerical evaluations are currently done in "shortcut" using simplified theoretical models (Gilliland, 1940; Underwood, 1948; Jafarey et al., 1979). These evaluations are also potentially useful for studying the operating conditions of distillation columns as well as its control. In general these calculation methods are empirical correlations of simple use, yet yielding in many cases the same predictions than other methods based on exact analytical solutions for the tray-by-tray calculations (Sundaram and Evans, 1993).

One limitation of these empirical correlations of simple use is the assumption of ideality of the mixtures in the liquid phase. Furthermore, this limitation is emphasized when using the relative volatility α_{ij} for species i and j as a constant in the description of the liquid–vapor equilibrium

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \tag{1}$$

Here y and x are concentrations in the vapor and liquid phases, respectively. This equation defining α_{ij} may be assumed to be exact only when the vapor phase behaves like an ideal gas and the liquid mixture fulfills the Raoult Law. Under these conditions the thermodynamics consistency can be obtained only when $\alpha_{ij} = P_i^0/P_j^0$. Another arbitrary value for this coefficient probably will not describe adequately the shape of the curve y_i vs. x_i. However, the simplicity of the relation (1) allows an analytical connection between the equilibrium compositions along a distillation column in conditions of infinite reflux. This relation is the well known Fenske (1932) equation.

On the other hand, the model of regular solutions was characterized by Hildebrand (1929, 1947 and 1951) as a result of his study on solubility topics. From then on, this approach has been considered as a powerful tool for understanding both the solubility phenomena and the phase equilibrium. When a mixture presents an ideal solution behavior in what concerns the mixing entropy, this is an appropriate way to describe a regular solution. Therefore, the contribution to non-ideality in this type of mixtures only comes from the mixing heat. Yet, the implementation of this model together with mass balance is quite cumbersome, despite of the fact that it is one of the simplest ways to treat real models.

In the present work we have examined the possibility of obtaining an expression as simple as Eq. (1), yet providing an adequate description of the equilibrium compositions of regular solutions having a behavior not too far from ideality.

2. Semi-regular solutions: liquid–vapor equilibrium

Let us start by writing Eq. (1) under the form

$$\ln\left(\frac{y_i}{y_j}\right) = \ln\left(\frac{x_i}{x_j}\right) + \ln\alpha_{ij} \tag{1b}$$

It can be seen in this simple linear relation that the slope is equal to one. In the case of a non ideal solution (but not too far

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0009-2509/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2011.10.002

from ideality) we may expect that an additional term should be considered in Eq. (1b), namely

$$\ln\left(\frac{y_i}{y_j}\right)=\ln\left(\frac{x_i}{x_j}\right)+\ln\left(\frac{\gamma_i}{\gamma_j}\right)+\ln\alpha_{ij} \tag{2}$$

Now, let Ω_{ij} be the energy parameter defined by $(\varepsilon_{ii}+\varepsilon_{jj}-2\varepsilon_{ij})/RT$. When the mixture behaves as a regular solution, we have $\ln(\gamma_i/\gamma_j)=\Omega_{ij}(x_j-x_i)$ and consequently

$$\ln\left(\frac{y_i}{y_j}\right)=\ln\left(\frac{x_i}{x_j}\right)+\Omega_{ij}(x_j-x_i)+\ln\alpha_{ij} \tag{3}$$

Let us now define z as the ratio x_i/x_j. For a binary system $\ln(\gamma_i/\gamma_j)$ may be written as

$$\ln(\gamma_i/\gamma_j)=\Omega_{ij}\left(\frac{1-z}{1+z}\right) \tag{4}$$

The relation expressed in Eq. (4) implies that $\ln(\gamma_i/\gamma_j)=0$ when $z=1$. By developing in a series around $z=1$ the right-hand side of Eq. (4), it can be seen that we have asymptotically

$$\text{series}\left[-\Omega_{ij}\left(\frac{z-1}{z+1}\right)\right]\cong\text{series}\left[-\frac{\Omega_{ij}}{2}\ln(z)\right] \tag{5}$$

given that

$$\begin{aligned}&-\Omega_{ij}(\tfrac{1}{2}(z-1)-\tfrac{1}{4}(z-1)^2+\tfrac{1}{8}(z-1)^2+\ldots)\\&\quad\cong-\tfrac{\Omega_{ij}}{2}((z-1)-\tfrac{1}{2}(z-1)^2+\tfrac{1}{3}(z-1)^2+\ldots)\end{aligned} \tag{6}$$

Taking into account this approximation, one obtains from Eq. (3) a linear expression of the same form as the one corresponding to the ideal solution case, yet having a slope (q_{ij}) that may be different from unity given by $q_{ij}=1-(1/2)\Omega_{ij}$. We thus obtain the following simplified expression

$$\ln\left(\frac{y_i}{y_j}\right)=q_{ij}\ln\left(\frac{x_i}{x_j}\right)+\ln\alpha_{ij} \tag{7}$$

We call semi-regulars solutions to the subgroup of regular solutions fulfilling the above equation. For an ideal mixture ($\Omega_{ij}=0$) the exponent q_{ij} is equal to 1. Furthermore, for positive and negative deviations of the Raoult Law we have $q_{ij}<1$ and $q_{ij}>1$, respectively. In other words, q_{ij} contains information about the mean effect of the neighborhood in the studied phase.

To illustrate the effects of q_{ij} on the form of the curve in the case of Liquid–Vapor Equilibrium (LVE), we have illustrated in Fig. 1a the results of the calculations using Eq. (7) for a hypothetical binary mixture of two fluids having a relative volatility α_{ij} equal to 1.5. Note that when q_{ij} is near to 1 ($q_{ij}=0.9$) the behavior of the mixture is similar to that of an ideal case, while for values near to $q_{ij}=0.5$ it occurs a well defined azeotropic maximum, and for values near to 1.5 it appears an azeotropic minimum which is not shown in Fig. 1. On the other hand, in Fig. 1a also it can be seen in illustrative form, a system where the mean interaction energy is strongly modified by one of the components of the solution (i.e. $\Omega_{ij}=mx_j+\Omega_0$) in such a way that it changes its sign, then q_{ij} will depend on the composition (i.e. $q_{ij}=-\frac{1}{2}mx_j+(1-\frac{1}{2}\Omega_0)$) going from values less than one to values larger than one or vice versa. Due to these changes the system will present a double azeotropy. Additionally, in a real system the double azeotropy appears at close concentrations. In Fig. 1b and c we can observe that this behavior is followed by our model in the case where q_{ij} varies linearly with the concentration of compound j.

We now consider some real systems in order to have an idea of what are the scope and limitations of Eq. (7). In Fig. 2 is illustrated the case of the system n-propanol+n-nonane at 60 °C, corresponding to a relative volatility α_{ij} equal to 5.10 ($\alpha_{ij}=P_i^0/P_j^0$). The value of q_{ij}, in all cases can be determined using linear fit least squares, in Fig. 2a we can see a better degree of approximation around $x_i/x_j=1$. We have illustrated in Fig. 2b the experimental composition of the vapor phase and the calculated one with Eq. (7). Note that using the semi-regular approach we have reproduced the azeotropic behavior, in contrast with the results that one obtains from the ideal solution (see the dashed line in Fig. 2b) despite the fact that in this case an optimum value of relative volatility have been used ($\alpha_{ij}^*\approx 3P_i^0/P_j^0$). Notice that in the calculus of ideal mixtures that is shown in all figures, the optimum values for relative volatility are calculated minimizing: $\sigma_y=\sqrt{\sum(y_{i(cal)}-y_{i(exp)})^2/N}$ and q_{ij}^* is always equal to unit.

In Fig. 3 are shown the vapor compositions for several binary systems at constant temperature. Note that strong hydrogen bonding occurs in all these mixtures. It can be seen in this figure

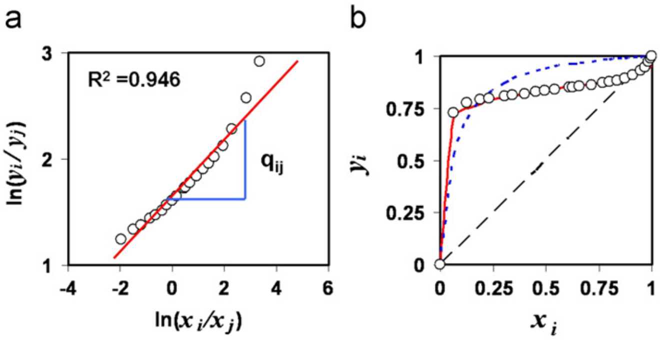

Fig. 2. (a) consistence range of the Eq. (7): ○ experimental data, ▬ linear relation and slope $q_{ij}=0.283$; and (b) composition in phase vapor: ○ experimental data, ▬ calculated with Eq. (7), ⋯ calculated with Eq. (1) ($\alpha_{ij}^*=15.8$), for LVE of the system n-propanol+n-nonane at 60 °C (Berro et al., 1986).

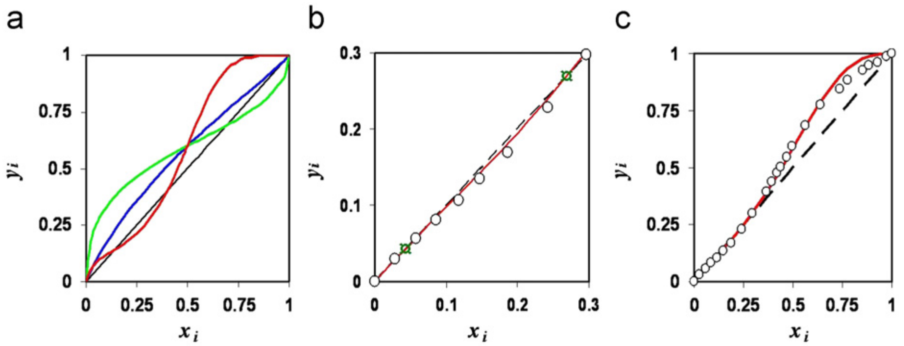

Fig. 1. (a) Effects of q_{ij} on the behavior of one hypothetic binary mixture with a fixed ratio of $\alpha_{ij}=1.5$. In this illustrative case of double azeotropic point, $q_{ij}=ax_j+b$ and its linear parameters are: $a=-3$ and $b=0.8$, (b) and (c) Real binary system with double azeotropes: 1,1,1,4,4,5,5,5,-Decafluoropentane+Oxolane at 26.68 KPa (Loras et al., 2001). Here the linear parameters are: $a=-1.026$ and $b=2.09$.