

Notes

A general model from theoretical cosolvency models

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Abstract

It has been shown that the two theoretical cosolvency models, i.e. the excess free energy, EFE, and the combined nearly ideal binary solvent/Redlich-Kister, CNIBS/R-K, despite different appearances could be converted to a general single model, GSM, using some appropriate substitutions and rearrangements. The general model was a power series equation with respect to the concentration of one of the solvents in a binary solvent system. From the obtained GSM a theoretical justification was provided to the cosolvency equations employing the extended Hildebrand approach, EHA, as well as those methods using an empirical power series equations for expressing the solubility. The accuracy of GSM was compared with that of the original EFE and CNIBS/R-K models and the results suggested differences in the accuracy between the original models and the corresponding GSM, which was attributed to differences in the arrangements of the independent variables in the models. © 1997 Elsevier Science B.V.

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There are at least two theoretical and several semiempirical and empirical equations for expressing the cosolvency, i.e. the solubility of a solute in a binary solvent mixture.

It is the intention of this report to derive a general single model, GSM, from the two theoretical models excess free energy, EFE, (Williams and Amidon, 1984) and the combined nearly ideal

binary solvent/Redlich-Kister, CNIBS/R-K, (Acree, 1992) as well as to provide from GSM a theoretical justification for the semiempirical cosolvency equations based on the Hildebrand approach denoted as the extended Hildebrand approach, EHA, (Adjei et al., 1980; Martin et al., 1982a; Wu and Martin, 1983) and some empirical equations (Martin et al., 1982a; Subrahmanyam et al., 1992; Bustamante et al., 1993; Escalera et al., 1994; O'Reilly and Corrigan, 1995; Reillo et

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al., 1995a), also to compare the accuracy of GSM with EFE and CNIBS/R-K methods.

The theoretical EFE methods are two, three and four suffix equations expressed by Eqs. (1)–(3), respectively:

$$\log X_m = f_a \log X_a + f_b \log X_b + A_{1-3} \left(\frac{q_2}{q_1} \right) f_a f_b \quad (1)$$

$$\begin{aligned} \log X_m = & f_a \log X_a + f_b \log X_b \\ & - A_{1-3} f_a f_b (2f_a - 1) \left(\frac{q_2}{q_1} \right) \\ & + 2A_{3-1} f_a^2 f_b \left(\frac{q_2}{q_3} \right) + C_2 f_a f_b \end{aligned} \quad (2)$$

$$\begin{aligned} \log X_m = & f_a \log X_a + f_b \log X_b \\ & - A_{1-3} f_a f_b (2f_a - 1) \left(\frac{q_2}{q_1} \right) \\ & + 2A_{3-1} f_a^2 f_b \left(\frac{q_2}{q_3} \right) + 3D_{13} f_a^2 f_b^2 \left(\frac{q_2}{q_3} \right) \\ & + C_3 f_a f_b^2 \left(\frac{q_2}{q_3} \right) + C_1 f_a^2 f_b \left(\frac{q_2}{q_1} \right) \end{aligned} \quad (3)$$

where X_m is the solute solubility in the solvent mixture, f_a and f_b are the volume fractions of the solvents a and b in the mixture, X_a and X_b denote the solubility in the solvents a and b and the other terms have been defined in the original paper (Williams and Amidon, 1984).

The second theoretical model, i.e. CNIBS/R-K, in its general form is:

$$\log X_m = f_a \log X_a + f_b \log X_b + f_a f_b \sum_{i=0}^n S_i (f_a - f_b)^i \quad (4)$$

in which S_i is the model constant and n can be equal to 0–3 (Acree, 1992; Acree and Zvaigzne, 1991; Acree et al., 1991). Depending on the values of n four equations can be obtained from Eq. (4).

Despite the different appearances of the two theoretical models EFE and CNIBS/R-K, they can be readily converted to GSM by simple substitutions and hence both can be mathematically considered as a single model.

Substitution of $(1 - f_a)$ for f_b in Eqs. (3) and (4) with $n = 2$ and subsequent rearrangements result in Eqs. (5) and (6), respectively:

$$\begin{aligned} \log X_m = & \log X_b + \left[\log X_a - \log X_b \right. \\ & + A_{1-3} \left(\frac{q_2}{q_1} \right) + C_3 \left(\frac{q_2}{q_3} \right) \left. \right] f_a \\ & + \left[2A_{3-1} \left(\frac{q_2}{q_3} \right) - 3A_{1-3} \left(\frac{q_2}{q_1} \right) \right. \\ & + 3D_{13} \left(\frac{q_2}{q_3} \right) - 2C_3 \left(\frac{q_2}{q_3} \right) + C_1 \left(\frac{q_2}{q_1} \right) \left. \right] f_a^2 \\ & + \left[2A_{1-3} \left(\frac{q_2}{q_1} \right) - 2A_{3-1} \left(\frac{q_2}{q_3} \right) \right. \\ & - 6D_{13} \left(\frac{q_2}{q_3} \right) + C_3 \left(\frac{q_2}{q_3} \right) - C_1 \left(\frac{q_2}{q_1} \right) \left. \right] f_a^3 \\ & + \left[3D_{13} \left(\frac{q_2}{q_3} \right) \right] f_a^4 \end{aligned} \quad (5)$$

$$\begin{aligned} \log X_m = & \log X_b \\ & + [\log X_a - \log X_b + S_0 - S_1 + S_2] f_a \\ & + [-S_0 + 3S_1 - 5S_2] f_a^2 \\ & + [-2S_1 + 8S_2] f_a^3 + [-4S_2] f_a^4 \end{aligned} \quad (6)$$

Comparison of these two equations reveal that both models are in fact identical and have a general form of a power series with respect to f_a which can be written as Eq. (7) or Eq. (8):

$$\log X_m = B_0 + B_1 f_a + B_2 f_a^2 + B_3 f_a^3 + B_4 f_a^4 \quad (7)$$

or

$$\log X_m = \sum_{j=0}^p B_j (f_a)^j \quad (8)$$

where B_0 – B_4 or B_j are related to the corresponding constant terms inside the brackets in Eqs. (5) and (6). Using similar method it can be shown that Eq. (1) and Eq. (4) with $n = 0$ are identical with Eq. (8) when $p = 2$. Also, Eq. (2) and Eq. (4) with $n = 1$ are the same as Eq. (8) when $p = 3$. When the value of n in Eq. (4) equals 3 then the value of p in Eq. (8) assumes 5. If $p = 1$, Eq. (8) will become the log-linear equation of Yalkowsky and Roseman (Yalkowsky and Roseman, 1981).

Employing Eq. (8) a theoretical justification has provided to the semiempirical EHA which was widely used in modelling of cosolvency phe-

nomenon (Adjei et al., 1980; Martin et al., 1980, 1981, 1982a,b, 1985; Martin and Miralles, 1982; Wu and Martin, 1983; Subrahmanyam et al., 1992; Reillo et al., 1993; 1995b). The EHA is:

$$-\log X_m = -\log X_2^i + \frac{V_2 \phi_1^2}{2.303 RT} (\delta_1^2 + \delta_2^2 - 2W) \quad (9)$$

where X_2^i represents the ideal solubility, V_2 is the molar volume of the solute, ϕ_1 denotes the volume fraction of the solvent system in the solution which is usually approximates unity (Chertkoff and Martin, 1960; Yalkowsky et al., 1975; Acree and Bertrand, 1981; Amidon and Williams, 1982; Acree and Rytting, 1983; Regosz et al., 1992; Bustamante et al., 1991, 1993; Escalera et al., 1994), R is the molar gas constant, T is the absolute temperature, δ_1 and δ_2 are the solubility parameters of the solvent and the solute and W is a solute–solvent interaction term and is calculated by the empirical power series Eq. (10):

$$W = C_0 + C_1 \delta_1 + C_2 \delta_1^2 + C_3 \delta_1^3 + C_4 \delta_1^4 + C_5 \delta_1^5 \quad (10)$$

C_0 – C_5 are the curve fitting parameters. Before regressing W versus δ_1 its value is calculated practically from Eq. (11):

$$W = \frac{\log X_m - \log X_2^i + A \delta_1^2 + A \delta_2^2}{2A} \quad (11)$$

in which $A = \frac{V_2}{(2.303RT)}$. Substitution for $\log X_m$ from Eq. (8) with $p = 5$ in Eq. (11) and replacing f_a values in the resulted equation in terms of δ_1 calculated by Eq. (12) (Martin et al., 1993; Bustamante et al., 1993, 1994):

$$\delta_1 = f_a \delta_a + f_b \delta_b = f_a \delta_a + (1 - f_a) \delta_b \quad (12)$$

and subsequent simplification and rearrangements will yield Eq. (10). The values of δ_a and δ_b are the solvents a and b solubility parameters.

A similar method can also be used to provide a theoretical justification for other polynomial power series cosolvency models employing δ_1 or f_a (Yalkowsky and Roseman, 1981; Martin et al., 1982a; Subrahmanyam et al., 1992; Bustamante et al., 1993; Escalera et al., 1994; O'Reilly and Corrigan, 1995; Reillo et al., 1995b).

The corresponding GSM of the three suffix EFE (Eq. (8) up to power 3) and CNIBS/R-K with $n=2$ (Eq. (7) were applied to the 88 data sets whose references were cited in Table 1 of a previous paper (Barzegar-Jalali and Jouyban-Gharamaleki, 1996) and percent overall average errors, %O.A.E., were 3.59 and 3.78, respectively, while the reported %O.A.E. of the original EFE and CNIBS/R-K were 3.95 and 3.07. These differences can be attributed to the different arrangements of the independent variables in the original and the corresponding general models.

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