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Comment on solubility parameters from maxima in solubility/solvent plots

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In a recent article by Cave et al. (1980), co-authored by one of us, the study of solubility parameters necessitated calculation of molar volumes of the solvent and solute. An example mentioned in the text involved an empirical polynomial representation for the average molar volume of the binary solution, V^{mix}, viz.,

$$V^{mix} = \alpha + \beta x_2 + \gamma x_2^2 \tag{1}$$

where x_2 represents mole fraction and α, β, and γ are least-squares fit constants. The corresponding partial molar volumes of the solvent ($\bar{V}_1$) and solute ($\bar{V}_2$) were calculated, in the example, by the formulae:

$$\bar{V}_1 = (\alpha - \gamma x_2^2)/x_1 \tag{2}$$

and

$$\bar{V}_2 = \beta + 2\gamma x_2 \tag{3}$$

The authors noted that Eqns. 2 and 3 gave values of $\bar{V}_1$ = 117.8 ml/mol and $\bar{V}_2$ = 105.7 ml/mol, when the experimental solubility (x_2 = 0.361) for butyl-parahydroxybenzoate in *n*-propanol was used. Both values are considerably different from either the molar volume of *pure* *n*-propanol or an estimate for the molar volume of butyl-parahydroxybenzoate (176 ml/mol, as found by Restaino and Martin, 1964). This observation is problematic since the experimental molar volumes of binary mixtures containing *n*-propanol and butyl-parahydroxybenzoate differ from the ideal molar volume approximation,

$$V^{ideal} = x_1\bar{V}_1^0 + x_2\bar{V}_2^0 \tag{4}$$

by less than 1% as demonstrated in Table 2 of ref. 1.

The partial molar volumes are related to the molar volume of the solution by standard thermodynamic relationships (Wall, 1974; Lewis and Randall, 1961; Guggenheim, 1967).

$$\bar{V}_1 = V^{mix} + x_2\left(\frac{\partial V^{mix}}{\partial x_1}\right) \tag{5}$$

$$\bar{V}_2 = V^{mix} - x_1\left(\frac{\partial V^{mix}}{\partial x_1}\right) \tag{6}$$

After performing the indicated differentiation, Eqns. 5 and 6 can be expressed as:

$$\bar{V}_1 = \alpha - \gamma x_2{}^2 \tag{5a}$$

$$\bar{V}_2 = \alpha + \beta + \gamma x_2(1 + x_1) \tag{6a}$$

Using Eqns. 5a and 6a along with the coefficients ($\alpha = 76.451, \beta = 99.007$ and $\gamma = 9.282$) given in the original article, the value of $\bar{V}_1$ and $\bar{V}_2$ can be calculated to be 75.2 ml/mol and 180.9 ml/mol, respectively, for the partial molar volumes of the solvent and solute at $x_2 = 0.361$. Since the ideal and non-ideal values, therefore, are close, it follows that the values denoted 'Butyl[a]' in Table 1 of the original are quite acceptable.

The general conclusions of the original article by Cave et al. (1980) are not affected by the above comment, since the $\bar{V}_2$ values from Eqns. 5/6 and 7 are still close to one another, but on the other hand are lower than expected.

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