

Short Communications

A Simple Model for the Formation of Mixed Micelles

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Recently, Högfeltd and Soldatov¹ suggested a simple model for the formation of mixed micelles that accounts for ion exchange and water extraction by dinonylnaphthalene sulfonic acid (HD) over a wide range of experimental conditions.^{2–4}

The simplest way to arrive at the model is to regard an HD-micelle as containing HD–HD pairs, a metal ion micelle as containing $\text{Me}_{1/2}\text{D}$ – $\text{Me}_{1/2}\text{D}$ pairs, the mixed micelles also contain $\text{Me}_{1/2}\text{D}$ –HD pairs. A random distribution of these pairs over the micelles leads to the number of HD–HD pairs as proportional to X_{HD}^2 , the number of $\text{Me}_{1/2}\text{D}$ – $\text{Me}_{1/2}\text{D}$ pairs as proportional to $X_{\text{Me}_{1/2}\text{D}}^2$ and the number of mixed pairs as proportional to $2X_{\text{HD}}X_{\text{Me}_{1/2}\text{D}}$, where $X_{\text{Me}_{1/2}\text{D}}$ is the equivalent fraction of metal ions in the micelle. In the following, this quantity will be denoted by \bar{X} . If the property studied is called Y the following expression is obtained from the model:

$$Y = (1 - \bar{X})^2 y_1 + \bar{X}^2 y_2 + 2\bar{X}(1 - \bar{X}) y_3 \quad (1)$$

where y_1 , y_2 and y_3 refer to the property Y for each kind of pair. The factor 2 arises from the fact that for each HD and $\text{Me}_{1/2}\text{D}$ pair two mixed pairs are formed.

It is, of course, possible to determine the three constants y_i by fitting a plot $Y(\bar{X}^2)$ with, e.g., least squares methods. However, in the field of ion exchange the property studied is most often plotted against \bar{X} . It is possible to obtain the desired information from the plot $Y(\bar{X})$ in the following way.

To each homogeneous eqn. (1) there is a corresponding equation

$$Y = (1 - \bar{X}) y_1 + \bar{X} y_2 + \bar{X}(1 - \bar{X}) y_3^1 \quad (2)$$

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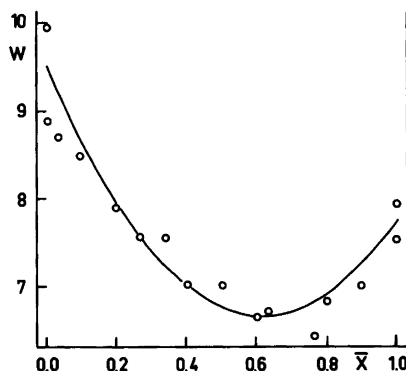


Fig. 1. The number of water molecules extracted per sulfonate group (W) plotted against $\bar{X}(=X_{\text{KD}})$ for the system (K,H)D in heptane at 25 °C. \circ , Exp. points; —, computed from eqn. (4).

From (1) and (2)

$$y_3 = \frac{1}{2}(y_1 + y_2 + y_3^1) \quad (3)$$

From a plot $Y(\bar{X})$ can thus all three constants y_i be determined using eqn. (3). The model can fit curves of a variety of shapes and has been applied to free energy, enthalpy, entropy as well as water extraction.^{2–4}

To illustrate the use of the model, Fig. 1 gives the number of water molecules extracted per sulfonate group (W) plotted against $\bar{X}(=X_{\text{KD}})$ for the system (K,H)D in heptane at 25 °C. The circles are experimental points. The full-drawn curve has been computed from

$$W = 9.5(1 - \bar{X}) + 7.8\bar{X} - 7.5\bar{X}(1 - \bar{X}) \quad (4)$$

The spread in the experimental data suggests an uncertainty of about $\pm 0.5 \text{ cm}^3$ in the constants.

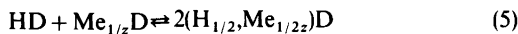
When first applying the concept of mixed micelles to the liquid ion exchange systems studied, plots like that in Fig. 1 were used. In the case of water extraction little physical meaning could be given to negative y_3 -values. The model, however, gives a very simple answer. According to eqn (3) y_3^1 is the number of water molecules expelled from the

organic phase upon formation of the mixed pairs. If we insert the constants from eqn (4) into eqn (3) the following value for $w_3 = y_3$ is obtained.

$$w_3 = 4.9 \pm 0.5$$

using the rough estimate given above for the uncertainty.

In all cases studied so far, in systems where micelles can be expected to exist, water is expelled from the organic phase upon formation of the mixed pairs. The model outlined above is equivalent to the zeroth approximation as denoted by Guggenheim.⁵ In this model it is assumed that two kinds of molecules have a random distribution in spite of nonzero energy of mixing. According to the zeroth approximation the equilibrium constant for the formation of mixed pairs has the statistical value, i.e. $K=4$ for the reaction



In the original treatment it was tacitly assumed that the mixed micelles are formed separately.¹ However, in view of current conception of micellar properties it might be better to assume that something like solid solutions is formed. It is shown elsewhere that the zeroth approximation is not the only possible model compatible with the experimental data.¹ It is the simplest one in agreement with present experimental information, however.

It is interesting to note that the model outlined above is concerned only with distribution of pairs. The size of the micelles does not enter into the expressions. This might be the reason why ion exchange equilibria on HD can be formally treated as if the system contains only monomers.⁶ It also deserves to be mentioned that some ion exchange equilibria on solid resins can also be treated with the formalism outlined above.^{6,7}

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