DESCRIPTION OF THE EQUILIBRIUM SINGLE-STAGE EXTRACTION FROM A FLOWING RAFFINATE INTO A BATCH OF EXTRACTION SOLVENT

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Relations are derived for calculating the trace concentration of investigated component contained in a real fluid extracted in a flow set-up with one stirred batch of extraction solvent dosaged. The presented method of derivation stems from the assumptions of sufficient stirring and the rapid establishment of thermodynamic equilibrium in the defined system of constant volume, containing one batch of extraction solvent through which flows continuously the raffinate containing the constant trace concentration of extracted component. The relations derived describe both the mutual limited miscibility of the liquids involved and the excess mixing effects.

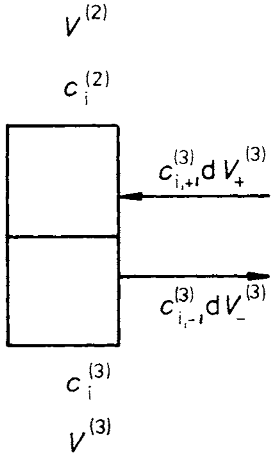
The single-stage extraction of components of trace concentrations from a flowing liquid phase into a batch of extraction solvent of limited miscibility is, from the point of view of accomplished concentrations of investigated components in extract, one of the most suitable ones[1-4].

Among the first who used this mode in the organic trace analysis of water were Ahnoff and Josefsson[1,2] who developed an apparatus for continuous extraction with a stationary extraction solvent lighter than water. They derived in their work the mathematical relations describing the extraction curves of components investigated. This simplified model is, however, applicable only in the case of negligible mutual solubility of the phases involved. The wider exploitation of the equilibrium single-stage extraction from flowing raffinate into the batch of extraction solvent in analytical practice, however, requires the relation to be derived which would stemmed from its real description.

The above-mentioned extraction system is to be schematically illustrated in Scheme 1, where, such as in the following text, the indexed symbols are used for the given quantities. The quantity concerning the extraction solvent has superscript (2). The quantity concerning the extracted solution has superscript (3). Subscripts 0, 2, 3, i, $+$, and $-$ assign a quantity to the beginning, majority component of extracting phase, majority component of extracted solution, investigated component i, inlet and outlet of the system, respectively. The internal balance of the system of equilibrium single-

-stage extraction from the flowing raffinate into a batch of extraction solvent which stems from the amount of substance of investigated component i in both phases inside the system considered, can be written in the form

$$n_i = n_i^{(2)} + n_i^{(3)} . \tag{1}$$



SCHEME 1

If the amount of substance is expressed by means of the product of concentration of substance and volume, Eq. (*1*) can be rewritten into the form

$$n_i = c_i^{(2)} V^{(2)} + c_i^{(3)} V^{(3)} . \tag{2}$$

The total differential of this expression has the form

$$dn_i = dc_i^{(2)} V^{(2)} + dV^{(2)} c_i^{(2)} + dc_i^{(3)} V^{(3)} + dV^{(3)} c_i^{(3)} . \tag{3}$$

Any change of amount of substance inside the system can be brought about only by changes of the entering and leaving amounts of substance, which is expressed in a differential form by the relation

$$dn_i = dn_{i,+} - dn_{i,-} . \tag{4}$$

Assuming the constant concentration of component i in the phase entering the extraction system and the outlet concentration to be equilibrium one, then Eq. (*4*) can be rewritten into the form

$$\mathrm{d}n_i = c_{i,+}^{(3)}\,\mathrm{d}V_+^{(3)} - c_i^{(3)}\,\mathrm{d}V_-^{(3)}\,. \tag{5}$$

In the interval of small numbers, it is possible to express the total equilibrium concentration of component i in extract as a function of total equilibrium concentration of component i in the phase of extracted solution by the equation

$$c_i^{(2)} = D_i c_i^{(3)}\,, \tag{6}$$

where the concentration distribution ratio D_i characterizes component i, and is constant in the above-mentioned interval considered.

The change of volume of extraction solvent and the same change concerning the extracted solution are related to the volume of extracted solution entering the system. The mathematical expression of these relations is

$$V_0^{(2)} - V^{(2)} = K^{(2)}V_+^{(3)} \tag{7}$$

and

$$V_-^{(3)} = K_-^{(3)}V_+^{(3)}\,. \tag{8}$$

In differential form these relations take the form

$$\mathrm{d}V^{(2)} = -K^{(2)}\,\mathrm{d}V_+^{(3)} \tag{9}$$

and

$$\mathrm{d}V_-^{(3)} = K_-^{(3)}\,\mathrm{d}V_+^{(3)}\,. \tag{10}$$

The total volume occupied by the phases taking part in the extraction is given by their sum

$$V = V^{(2)} + V^{(3)}\,, \tag{11}$$

and we shall assume that it is not changed in the course of the operation so that

$$\mathrm{d}V^{(2)} = -\mathrm{d}V^{(3)}\,. \tag{12}$$

By comparing Eqs (*3*) and (*5*) and on using Eqs (*6*)–(*12*) we get the relation

$$c_{i,+}^{(3)}\,\mathrm{d}V_+^{(3)} - (c_i^{(2)}/D_i)\,K_-^{(3)}\,\mathrm{d}V_+^{(3)} =$$
$$= -c_i^{(2)}K^{(2)}\,\mathrm{d}V_+^{(3)} + V^{(2)}\,\mathrm{d}c_i^{(2)} + (c_i^{(2)}/D_i)\,K^{(2)}\,\mathrm{d}V_+^{(3)} + [(V - V^{(2)})/D_i]\,\mathrm{d}c_i^{(2)}\,. \tag{13}$$

By using further mathematical rearrangements, this first-order total differential equation is transferred to the usual form of recording

$$\frac{\mathrm{d}c_{\mathrm{i}}^{(2)}}{\mathrm{d}V_{+}^{(3)}} + \frac{K_{-}^{(3)} - K^{(2)}(D_{\mathrm{i}} - 1)}{\left(V_{0}^{(2)} - K^{(2)}V_{+}^{(3)}\right)(D_{\mathrm{i}} - 1) + V}\, c_{\mathrm{i}}^{(2)} = \frac{D_{\mathrm{i}}c_{\mathrm{i},+}^{(3)}}{\left(V_{0}^{(2)} - K^{(2)}V_{+}^{(3)}\right)(D_{\mathrm{i}} - 1) + V}\,. \tag{14}$$

Its particular integral complying with the initial condition $c_{\mathrm{i}}^{(2)} = c_{\mathrm{i},0}^{(2)}$ for $V_{+}^{(3)} = 0$ has the form

$$c_{\mathrm{i}}^{(2)} - \frac{D_{\mathrm{i}}c_{\mathrm{i},+}^{(3)}}{K_{-}^{(3)} - K^{(2)}(D_{\mathrm{i}} - 1)}\,\cdot$$

$$\cdot\left[1 - \left(\frac{V_{0}^{(2)}(D_{\mathrm{i}} - 1) + V}{\left(V_{0}^{(2)} - K^{(2)}V_{+}^{(3)}\right)(D_{\mathrm{i}} - 1) + V}\right)^{[1 - K_{-}{}^{(3)}/K^{(2)}(D_{\mathrm{i}} - 1)]}\right] -$$

$$- c_{\mathrm{i},0}^{(2)}\left(\frac{V_{0}^{(3)}(D_{\mathrm{i}} - 1) + V}{\left(V_{0}^{(2)} - K^{(2)}V_{+}^{(3)}\right)(D_{\mathrm{i}} - 1) + V}\right)^{[1 - K_{-}{}^{(3)}/K^{(2)}(D_{\mathrm{i}} - 1)]} = 0\,, \tag{15}$$

if $D_{\mathrm{i}} \neq 1$ and $K^{(2)} \neq 0$.

For $D_{\mathrm{i}} \neq 1$, $K^{(2)} = 0$, and from it following $K_{-}^{(3)} = 1$, the particular integral complying with the above-mentioned initial condition is

$$c_{\mathrm{i}}^{(2)} - D_{\mathrm{i}}c_{\mathrm{i},+}^{(3)}\left[1 - \exp\left(\frac{-V_{+}^{(3)}}{V_{0}^{(2)}(D_{\mathrm{i}} - 1) + V}\right)\right] -$$

$$- c_{\mathrm{i},0}^{(2)} \exp\left(\frac{-V_{+}^{(3)}}{V_{0}^{(2)}(D_{\mathrm{i}} - 1) + V}\right) = 0\,. \tag{16}$$

On the assumption that $D_{\mathrm{i}} = 1$ and $K^{(2)} \neq 0$, we arrive at the equation

$$c_{\mathrm{i}}^{(2)} - \frac{c_{\mathrm{i},+}^{(3)}}{K_{-}^{(3)}}\left[1 - \exp\left(\frac{-K_{-}^{(3)}V_{+}^{(3)}}{V}\right)\right] - c_{\mathrm{i},0}^{(2)} \exp\left(\frac{-K_{-}^{(3)}V_{+}^{(3)}}{V}\right) = 0 \tag{17}$$

and for the case of $D_{\mathrm{i}} = 1$ and $K^{(2)} = 0$ ($\Rightarrow K_{-}^{(3)} = 1$), both Eqs (*16*) and (*17*) hold then simultaneously.

To be able to calculate the concentration of the component investigated in flowing solution $c_{\mathrm{i},+}^{(3)}$ explicitly involved in Eqs (*15*)–(*17*), it is necessary to know, in addition to the known volumetric data, the values of distribution ratio, analytically determined concentrations of the investigated component in extraction solvent at the beginning $c_{\mathrm{i},0}^{(2)}$ and after finishing the experiment $c_{\mathrm{i}}^{(2)}$ and to evaluate numerically constants $K^{(2)}$ and $K_{-}^{(3)}$.

The changes of volume of the extraction solvent and the phase of extracted solution due to the inlet of extracted solution are expressed in terms of constants $K^{(2)}$ and $K_{-}^{(3)}$ whose definition is given below. The first one is equal to the magnitude of change of the extraction solvent volume brought about by the unit change of the extracted solution volume entering the system. The second one corresponds to the change of the extracted solution volume leaving the system due to the same cause. Both the changes are dependent on the magnitude of values of solubility of the extraction solvent in the extracted solution, of the opposite solubility, that means of extracted solution in the extraction solvent, and of the excess volumes of conjugate solutions occurring in the system.

On adding an infinitesimal volume of extracted solution $\mathrm{d}V_{+}^{(3)}$ to the system which consists of the conjugate solutions of extraction solvent and extracted solution, then the change of volume of extraction solvent is to be divided into the changes concerning the majority component of extracting phase, the component denoted as extracted solution, and the excess volume. The total change is given by the sum of single contributions, which can be expressed by the equation

$$\mathrm{d}V^{(2)} = \mathrm{d}V_2^{(2)} + \mathrm{d}V_3^{(2)} + \mathrm{d}\Delta V^{\mathrm{E}(2)} . \qquad (18)$$

The single changes can be expressed as functions of solubilities, excess volumes and volume added $\mathrm{d}V_{+}^{(3)}$. Equation (*18*) turns then to the form

$$\mathrm{d}V^{(2)} = \frac{s_{23}}{1 - s_{23}s_{32}}\,\mathrm{d}V_{+}^{(3)} + \frac{s_{23}s_{32}}{1 - s_{23}s_{32}}\,\mathrm{d}V_{+}^{(3)} + \\ + \frac{s_{23}}{1 - s_{23}s_{32}}\left(\frac{\mathscr{V}_{\mathrm{m}2}^{\mathrm{E}(2)}}{\mathscr{V}_{\mathrm{m}2}^{0}} + s_{32}\,\frac{\mathscr{V}_{\mathrm{m}3}^{\mathrm{E}(2)}}{\mathscr{V}_{\mathrm{m}3}^{0}}\right)\mathrm{d}V_{+}^{(3)} , \qquad (19)$$

where s_{23} denotes the solubility of extraction solvent in extracted solution, s_{32} the opposite solubility, $\mathscr{V}_{\mathrm{m}2}^{\mathrm{E}(2)}$ and $\mathscr{V}_{\mathrm{m}3}^{\mathrm{E}(2)}$ the excess molar volume of extraction solvent and extracted solution, respectively, both concerning the extracting phase, and $\mathscr{V}_{\mathrm{m}2}^{0}$ and $\mathscr{V}_{\mathrm{m}3}^{0}$ the molar volumes of the respective pure components. By rearranging, Eq. (*19*) changes to the form

$$\mathrm{d}V^{(2)} = \frac{s_{23}}{1 - s_{23}s_{32}}\left(\frac{\bar{\mathscr{V}}_{\mathrm{m}2}^{(2)}}{\mathscr{V}_{\mathrm{m}2}^{0}} + s_{32}\,\frac{\bar{\mathscr{V}}_{\mathrm{m}3}^{(2)}}{\mathscr{V}_{\mathrm{m}3}^{0}}\right)\mathrm{d}V_{+}^{(3)} \qquad (20)$$

on replacing the excess volumes by the difference of the respective molar and partial molar volumes.

On using the same reasoning for the changes of valumes taking place in the phase of extracted solution, we arrive at the equation

$$\mathrm{d}V^{(3)} = \frac{1}{1 - s_{23}s_{32}} \left(\frac{\bar{\mathscr{V}}^{(3)}_{\mathrm{m3}}}{\mathscr{V}^{0}_{\mathrm{m3}}} + s_{23} \frac{\bar{\mathscr{V}}^{(3)}_{\mathrm{m2}}}{\mathscr{V}^{0}_{\mathrm{m2}}} \right) \mathrm{d}V^{(3)}_{+} \,. \qquad (21)$$

In accordance with the above-mentioned interpretation of constant $K^{(2)}$, Eq. (*20*) elucidates its physical meaning.

With respect to the unchangeability of the total volume of involved phases during the operation, the change of volume $\mathrm{d}V^{(3)}_{-}$ is given by the difference of volumetric changes referring to single phases. The result of the difference can be written after an arrangement as

$$\frac{\mathrm{d}V^{(3)}_{-}}{\mathrm{d}V^{(3)}_{+}} = \frac{1}{1 - s_{23}s_{32}} \left[\left(\frac{\bar{\mathscr{V}}^{(3)}_{\mathrm{m3}}}{\mathscr{V}^{0}_{\mathrm{m3}}} + s_{23} \frac{\bar{\mathscr{V}}^{(3)}_{\mathrm{m2}}}{\mathscr{V}^{0}_{\mathrm{m2}}} \right) - s_{23} \left(\frac{\bar{\mathscr{V}}^{(2)}_{\mathrm{m2}}}{\mathscr{V}^{0}_{\mathrm{m2}}} + s_{32} \frac{\bar{\mathscr{V}}^{(2)}_{\mathrm{m3}}}{\mathscr{V}^{0}_{\mathrm{m3}}} \right) \right], \qquad (22)$$

where the right-hand side corresponds to constant $K^{(3)}_{-}$.

Relations (*20*) and (*22*) express constants $K^{(2)}$ and $K^{(3)}_{-}$, respectively, so being defined on the basis of the equilibrium thermodynamic quantities, all the parameters in Eqs (*15*)–(*17*) needed for calculating the unknown concentration $c^{(3)}_{\mathrm{i},+}$ of the investigated component from the experimentally determined volume (V, $V^{(2)}_0$, $V^{(3)}_+$) and concentration ($c^{(2)}_{\mathrm{i},0}$, $c^{(2)}_{\mathrm{i}}$) data.

From the practical point of view it is of advantage to use an extraction solvent which at the beginning of experiment does not contain any amount of component *i* so that $c^{(2)}_{\mathrm{i},0} = 0$. In such a case, the term on the left-hand side in Eqs (*15*)–(*17*) is annuled, and for the sought concentration holds

$$c^{(3)}_{\mathrm{i},+} = \frac{\left[K^{(3)}_{-} - K^{(2)}(D_{\mathrm{i}} - 1)\right] c^{(2)}_{\mathrm{i}}}{D_{\mathrm{i}} \left[1 - \left(\frac{V^{(2)}_0 (D_{\mathrm{i}} - 1) + V}{\left(V^{(2)}_0 - K^{(2)} V^{(3)}_{+}\right)(D_{\mathrm{i}} - 1) + V} \right) \right]^{[1 - K_{-}{}^{(3)}/K^{(2)}(D_{\mathrm{i}} - 1)]}} \qquad (23)$$

or

$$c^{(3)}_{\mathrm{i},+} = c^{(2)}_{\mathrm{i}} / D_{\mathrm{i}} \left(1 - \exp\left\{ -V^{(3)}_{+} / \left[V^{(2)}_0 (D_{\mathrm{i}} - 1) + V\right]\right\}\right), \qquad (24)$$

or

$$c^{(3)}_{\mathrm{i},+} = K^{(3)}_{-} c^{(2)}_{\mathrm{i}} / \left[1 - \exp\left(-K^{(3)}_{-} V^{(3)}_{+} / V\right)\right]. \qquad (25)$$

In practice some convenient circumstances may occur. In case that the excess volumes are zero, the partial molar quantities are equal to the molar quantities of pure substances, and the expression for constant $K^{(2)}$ is reduced to the form

$$K^{(2)} = \frac{s_{23}(1 + s_{32})}{1 - s_{23}s_{32}}\,, \tag{26}$$

and constant $K_{-}^{(3)}$ is equal 1.

A number of practically important systems are noted for comparatively high value of distribution ratio (of the order 10^3 and higher) as well, which can be justifiably used for replacing differences $(D_i - 1)$ in all cases of their occurrence in Eqs (*15*)–(*17*) or (*23*)–(*25*) by the simple value of D_i.

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