
**APPROXIMATE RELATIONS FOR DETERMINING
THE ACTIVITY COEFFICIENT AT VERY LOW CONCENTRATION
BY THE METHOD OF VARIATION OF SOLUTE CONCENTRATION****Bohuslav DOLEŽAL and Robert HOLUB***Department of Physical Chemistry,
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Received August 15th, 1983

The calculation of activity coefficients at very low concentration is described from the experimental data obtained by the method of the variation of solute concentration for a way of saturation with ensured sufficiently long contact time of the liquid and gas phases and intensive stirring of both phases when the amount of the observed component in the vapour phase above the solution is negligible with regard to its content in the liquid phase. Two variants of experimental procedure were considered: stripping by a pure inert gas and by a gas saturated with solvent vapours. The relations derived can be used either directly for computer calculations or on introducing some simplifying assumptions for a rapid manual calculation with a good agreement of the results.

Activity coefficients of components at infinite dilution are one of important thermodynamic quantities employed for the description of phase equilibria. Their experimental determination by the methods usual in studying phase vapour-liquid equilibria, whether in the static or recirculation arrangement, is very uncertain. More hopeful is the use of gas chromatographic methods from which considerably extended is the "Retention Time Method" based on the thermodynamic description of the equilibrium between a solute and a solvent in a chromatographic column. Even though these methods are elaborated to a considerable extent, and the procedures for calculating activity coefficients are proposed, the results are not usually adequate since one is not always successful in evaluating the effect of adsorption on phase boundaries in a reasonable way. That is why the "Inert Gas Stripping Method" proposed by Leroi and coworkers¹ and further developed by Richon, Antoine and Renon^{2,3} appears to be more suitable. In work⁴, another possibility of equilibrium saturation of stripping gas is shown when the manometric measurement of its absolute amount has been used unlike the usually used measurement of the inert gas passage time at its constant flow rate. This method has been checked experimentally, and its theoretical description is also suggested in the cited work⁴ for not too large deviations from the ideal behaviour of the system both in the liquid and the gas phase.

In this work the calculation of γ is suggested in strongly diluted solutions for the case when it is not possible to neglect the nonideal behaviour of individual components of the gas phase as well as of the gas mixture formed from them. As a model we consider an open system composed of a solution of two chemically nonreacting substances through which a gas passes. During the derivation, the procedure used in previous works^{1,5} was kept.

Description of Instantaneous State of System

When deriving the fundamental relations, the material balance of the instantaneous state of system was taken into account. For changes of the amounts of substance of components in an instant of time $dt \rightarrow 0$, the relations

$$dn_i = dn_i^+ - dn_i^-, \quad (1)$$

$$dn^+ = \sum_1^3 dn_i^+, \quad (2)$$

$$dn^- = \sum_1^3 dn_i^- \quad (3)$$

hold.

Outlet stream. The relation between the composition of the liquid phase and the equilibrium gas phase at the outlet is given by

$$\varphi_i y_i P^- = x_i \gamma_i f_i^0; \quad i = 1, 2 \quad (4)$$

$$\varphi_3 y_3 P^- = x_3 H_3. \quad (5)$$

For the amount of substance it must hold

$$dn_i^- = \frac{x_i \gamma_i f_i^0}{\varphi_i P^-} dn^- \quad (6)$$

and

$$dn^- = \frac{\varphi_i P^-}{x_3 H_3} dn_3^-. \quad (7)$$

In work¹, the relation is given between the total amount of substance leaving the system owing to the passage of a given volume of inert gas and the size of this system.

An analogous relation can be reached by replacing the first two addends on the right-hand side of Eq. (3) by the right-hand side of Eq. (6)

$$dn^- = \frac{\varphi_1 \varphi_2 P^- dn_3^-}{\varphi_1 \varphi_2 P^- - x_1 \gamma_1 \varphi_2 f_1^0 - x_2 \gamma_2 \varphi_1 f_2^0} \quad (8)$$

By inserting the change of total amount of substance dn^- at the outlet, expressed in this way, back to Eq. (6) we get the relations

$$dn_1^- = \frac{\gamma_1 n_1 f_1^0}{\varphi_1 n_2 P^-} \left[1 - \frac{\gamma_2 f_2^0}{\varphi_2 P^-} + \left(1 - \frac{\gamma_1 f_1^0}{\varphi_1 P^-} \right) \frac{n_1}{n_2} + \frac{n_3}{n_2} \right]^{-1} dn_3^- \quad (9)$$

and

$$dn_2^- = \frac{\gamma_2 f_2^0}{\varphi_2 P^-} \left[1 - \frac{\gamma_2 f_2^0}{\varphi_2 P^-} + \left(1 - \frac{\gamma_1 f_1^0}{\varphi_1 P^-} \right) \frac{n_1}{n_2} \right]^{-1} dn_3^- \quad (10)$$

which, as a matter of fact, represent the combination of thermodynamic conditions of phase equilibrium with the mass balance in a differential form.

Inlet stream. There are two limiting possibilities for the description of inlet stream from the point of view of composition of the gas phase: Either a pure inert gas is used or this gas is saturated with the solvent vapours so that loss of solvent from the system may be minimized in a defined way.

In the first case the mass balance is simplified as $dn_1^+ = 0$, $dn_2^+ = 0$ and $dn_3^+ = dn^+$. The mass balance is then expressed by the relations

$$dn_i = -dn_i^-, \quad i = 1, 2 \quad (11)$$

$$dn_3 = dn_3^+ - dn_3^- \quad (12)$$

In the second case an inert saturated with vapours of solvent under defined conditions T^+ , P^+ is inserted into the system so that

$$dn_1^+ = 0 \quad (13)$$

and

$$dn_{2i}^+ = dn_{2i}^- \quad (14)$$

Description of System Behaviour in Finite Time Interval

For the aim pursued, the expression of γ_1 at very low concentration of the given component on the basis of thermodynamic and balance data, the composition

of solution must be made up so that $x_1 \rightarrow 0$ applies, and with regard to the justified assumption of low solubility of inert in solution $x_3 \rightarrow 0$, too. Considering that then as well holds $x_2 \rightarrow 1$, and at a constant temperature of solution and pressure above it, it is possible to consider also $\gamma_2 \rightarrow 1$. Solubility of the inert in solution is thus comparable to its solubility in pure solvent under the same conditions,

$$H_{3,\text{mix}1+2} \approx H_{3,2}, \quad (15)$$

and the mole fraction x_3 can then be expressed as

$$x_3 = \frac{n_3}{n_2} = \frac{\varphi_3 P_3^-}{H_{3,2}}. \quad (16)$$

By combining Eqs (1) and (16) for component 3 we get

$$dn_3^- = dn_3^+ - \frac{\varphi_3 P_3^-}{H_{3,2}} dn_2. \quad (17)$$

For a linear dependence of the detector response on the amount of substance of a component in injection, it is possible to express the relation between the composition of the system measured and the areas enclosed by chromatographic elution peaks, in case of the analysis of the liquid phase by the relation

$$\frac{x_1(n_3^+)}{x_2(n_3^+)} = \frac{n_1(n_3^+)}{n_2(n_3^+)} = \frac{S_1(n_3^+)}{S_2(n_3^+)}, \quad (18)$$

and when analysis in the gas phase, by the equality

$$\frac{x_1(n_3^+)}{x_2(n_3^+)} = \frac{n_1(n_3^+)}{n_2(n_3^+)} = \frac{S_1(n_3^+)}{S_2(n_3^+)} \frac{\gamma_1(0)}{\gamma_1(n_3^+)} \frac{\varphi_1(n_3^+)}{\varphi_1(0)} \frac{\varphi_2(0)}{\varphi_2(n_3^+)}. \quad (19)$$

On the assumption that establishing equilibrium between the liquid and vapour phases takes place, which is conditioned by a sufficient contact time of the carrier gas with the solution⁵, it is possible to carry out the derivations for single arrangements as follows:

Stripping by a pure inert gas

From Eqs (9)–(10) follows

$$d \ln n_1(n_3^+) = \gamma_1(n_3^+) \frac{\varphi_2(n_3^+) f_1^0}{\varphi_1(n_3^+) f_2^0} d \ln n_2(n_3^+), \quad (20)$$

and on combining with Eqs (18) and (19), it is possible to write for the case of analysis of the liquid phase

$$d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} = \left[\gamma_1(n_3^+) \frac{\varphi_2(n_3^+) f_1^0}{\varphi_1(n_3^+) f_2^0} - 1 \right] d \ln n_2(n_3^+), \quad (21)$$

and for the analysis of the gas phase

$$d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} - d \ln \gamma_1(n_3^+) \frac{\varphi_2(n_3^+)}{\varphi_1(n_3^+)} = \left[\gamma_1(n_3^+) \frac{\varphi_2(n_3^+) f_1^0}{\varphi_1(n_3^+) f_2^0} - 1 \right] d \ln n_2(n_3^+). \quad (22)$$

The instantaneous amount of substance of the solvent can be expressed by the dependence

$$n_2(n_3^+) = n_2(0) + \int_0^{n_3^+} dn_2, \quad (23)$$

where dn_2 follows from Eqs (10) and (11) on the assumption of the validity of Eqs (15) and (16) in the form

$$dn_2 = - \frac{f_2^0}{\varphi_2(n_3^+) P^-} \left[A(n_3^+) - \frac{f_2^0}{\varphi_2(n_3^+) P^-} \frac{\varphi_3(n_3^+) P_3^-(n_3^+)}{H_{3,2}} \right]^{-1} dn_3^+, \quad (24)$$

where

$$A(n_3^+) = 1 - \frac{f_2^0}{\varphi_2(n_3^+) P^-} + \left(1 - \frac{\gamma_1(n_3^+) f_1^0}{\varphi_1(n_3^+) P^-} \right) \frac{n_1(n_3^+)}{n_2(n_3^+)} + \frac{\varphi_3(n_3^+) P_3^-(n_3^+)}{H_{3,2}}. \quad (25)$$

Stripping by an Inert Saturated by Solvent Vapours

The temperature of presaturation is chosen so that the decrease in amount of solvent from the system should not occur. It is shown in work⁶ that at very low concentrations of the given substance it is necessary to eliminate the difference in pressures between presaturator and solution by increasing the temperature of presaturation by a constant value in comparison with the system temperature. All the other effects are negligible. For a change of amount of substance 1 holds

$$d \ln n_1(n_3^+) = \frac{\gamma_1(n_3^+)}{n_2(0)} \frac{f_1^0}{\varphi_1(n_3^+) P^-} \frac{dn_3^+}{A(n_3^+)}, \quad (26)$$

and in combination with Eqs (18) or (19), for the analysis of the liquid phase follows

the relation

$$d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} = - \frac{\gamma_1(n_3^+)}{n_2(0)} \frac{f_1^0}{\varphi_1(n_3^+) P^-} \frac{dn_3^+}{A(n_3^+)}, \quad (27)$$

and for the analysis of the gas phase, the equation

$$d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} - d \ln \gamma_1(n_3^+) \frac{\varphi_2(n_3^+)}{\varphi_1(n_3^+)} = \frac{\gamma_1(n_3^+)}{n_2(0)} \frac{f_1^0}{\varphi_1(n_3^+) P^-} \frac{dn_3^+}{A(n_3^+)}, \quad (28)$$

where $A(n_3^+)$ is again given by Eq. (25).

Calculation of Activity Coefficient

It is evident from foregoing relations that it is possible to calculate the activity coefficient of the given substance at very low concentrations on the basis of the knowledge of behaviour of components in the measured system and of the experimentally obtained dependence of chromatographic analyses on the amount of stripped inert. On taking account to the accuracy required, it is possible to carry out the calculation directly in terms of Eqs (21)–(25) and (27) and (28), which makes it possible to enumerate all the effects considered. However, in many cases it is sufficient to use an approximate solution.

If the limiting concentration of solute and the value of its activity coefficient admit the possibility to consider the term

$$\left(1 - \frac{\gamma_1(n_3^+)}{\varphi_1(n_3^+)} \frac{f_1^0}{P^-} \right) \frac{n_1(n_3^+)}{n_2(n_3^+)}$$

as negligible or if the accuracy of analytical method allows to start with sufficiently low change of concentration of the given component, it is possible to consider the thermodynamic quantities in Eqs (20)–(28) as concentration independent. The function $A(n_3^+)$ turns so into the form

$$A = - \frac{f_2^0}{\varphi_2 P^-} + \left(1 - \frac{\gamma_1}{\varphi_1} \frac{f_1^0}{P^-} \right) \frac{n_1}{n_2} + \frac{\varphi_3 P_3^-}{H_{3,2}}. \quad (29)$$

The quantities γ_i , φ_i ($i = 1, 2, 3$), n_1 and n_2 are then constant and correspond to the values at a given system composition.

The activity coefficient of the given component is given, for the case without

presaturation, by the relation

$$\gamma_1 = \frac{\varphi_1 f_2^0}{\varphi_2 f_1^0} \left[1 + d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} / d \ln F(n_3^+) \right], \quad (30)$$

where the derivative represents the numerical value of the slope of experimentally obtained dependence of the logarithm of the area ratios enclosed by the elution peaks of solute and solvent on the logarithm of the variable $F(n_3^+)$ which equals

$$F(n_3^+) = 1 - \frac{n_3^+}{n_2(0)} \frac{f_2^0}{f_2 P^-} \left[A - \frac{f_2^0}{\varphi_2 P^-} \frac{\varphi_3 P_3^-}{H_{3,2}} \right]^{-1}. \quad (31)$$

For the modification with presaturation it is sufficient to choose T^+ constant so that equality (14) holds. From Eqs (27) and (28) then follows

$$\gamma_1 = - n_2(0) A \frac{\varphi_1 P^-}{f_1^0} \left[d \ln \frac{S_1(n_3^+)}{S_2(n_3^+)} / dn_3^+ \right], \quad (32)$$

where the last fraction on the right-hand side expresses the slope of experimentally found dependence of natural logarithm of the area ratio enclosed by the elution peaks of the given component and solvent on the amount of substance of inert entered the system.

LIST OF SYMBOLS

A	functional expression
f	fugacity
H	Henry's constant
n	amount of substance
P	pressure
S	area enclosed by elution peaks
T	temperature
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
γ	activity coefficient
φ	fugacity coefficient

Superscripts

0	pure component
+	inlet stream
-	outlet stream

Subscripts

- i summation index
- 1 substance observed
- 2 solvent
- 3 inert

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Translated by J. Linek.