THE EFFECT OF VAPOUR SPACE VOLUME ON VAPOUR–LIQUID EQUILIBRIUM MEASURED BY STRIPPING WITH AN INERT GAS STREAM

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The effect of the vapour space size when measuring the vapour–liquid equilibrium by a modified saturation method based on measuring the change in the liquid phase concentration with time is studied in this work. The relation was derived for calculating the correction for the vapour space volume. On using some model solutions of different degree of non-ideality and of different concentration, the magnitude of this correction and its influence on the calculated vapour–liquid equilibrium data is studied. In case of systems of completely miscible liquids, it is not necessary, as a rule, to expect a more significant effect of the vapour space size on vapour–liquid equilibrium.

In preceding work[1] we have presented a modified saturation method of measuring the vapour–liquid equilibrium by inert gas stripping which is based on the measurement of the change of liquid phase composition with time. In the theoretical part of that work, the equation was derived which makes it possible to evaluate statistically the coefficients of G^E equations and the subsequent calculation of activity coefficients and other L–G equilibrium data.

On the assumption that

a) the vapour phase behaves as an ideal gas,

b) the inert gas is saturated with the solution vapours at each moment,

c) the vapour phase is of differential size only, the relation

$$f = \frac{\dfrac{n_L}{x_A}\,\dfrac{dx_A}{d\tau}\,\dfrac{1}{\dot{n}_I}}{1 - (p - \gamma_A p^*_A)/(p - \gamma_A p^*_A x_A - \gamma_B p^*_B x_B)} + 1 = 0 \qquad (1)$$

was derived in the above-mentioned paper from the balance of amount of substance. In terms of m experimental values of function f, the objective function

$$F(\boldsymbol{C}) = \sum_{j=1}^{m} f_j^2 \qquad (2)$$

can be made up. By minimizing the objective function, the vector of coefficients of G^E equation, $\boldsymbol{C}$, can be obtained.

Duhem and Vidal[2] called attention to the fact that the vapour space volume influences the change of solution concentration with time, i.e., the derivative $dx_A/d\tau$ when measuring the limiting activity coefficients by the method of inert gas stripping. Therefore, the authors said included the correction for the vapour space volume above solution into the equation for calculating the limiting activity coefficients. The correction is significant at high values of limiting activity coefficients of components (small mutual miscibility of components). This fact made us extend Eq. (*1*) in this work by the correction for the vapour space volume and study the effect of the solution concentration and the degree of its non-ideality on this correction over the entire concentration range.

THEORETICAL

The schematic diagram of stripping the binary solution with an inert gas in the presence of the vapour space of finite size is illustrated in Fig. 1.

Let us introduce the following assumptions:

a) The temperature and pressure in the system are constant,

b) the vapour phase behaves as an ideal gas,

c) the vapour phase volume is constant, i.e.,

$$V_G = n_G R T/p = \text{const.}, \qquad (3)$$

d) the whole vapour space is perfectly stirred and is in equilibrium with the liquid phase, i.e.,

$$p_A = y_A p = \gamma_A p_A^* x_A , \qquad (4)$$

$$p_B = y_B p = \gamma_B p_B^* x_B , \qquad (5)$$

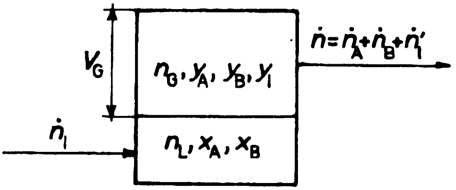

FIG. 1

Balance diagram of inert gas stripping of binary solution *e*) the inert gas solubility in the liquid is neglected. In terms of the material balance of leaving gas, we have

$$\mathrm{d}n/\mathrm{d}\tau = \dot{n} = \dot{n}_{\mathrm{I}}' + \dot{n}_{\mathrm{A}} + \dot{n}_{\mathrm{B}} \,. \tag{6}$$

The mole fraction of the *i*-th component in gas

$$y_i = \dot{n}_i/\dot{n} \,. \tag{7}$$

The gas pressure is the sum of partial pressures of components

$$p = p_{\mathrm{A}} + p_{\mathrm{B}} + p_{\mathrm{I}} \,. \tag{8}$$

By combining Eqs (*4*) – (*8*), we get

$$\dot{n} = \dot{n}_{\mathrm{I}}' \frac{p}{p - p_{\mathrm{A}}^{*}\gamma_{\mathrm{A}}x_{\mathrm{A}} - p_{\mathrm{B}}^{*}\gamma_{\mathrm{B}}x_{\mathrm{B}}} \,, \tag{9}$$

where $\dot{n}_{\mathrm{I}}'$ is the flow of amount of substance of inert gas at the apparatus outlet and differs from the flow of the inert gas amount of substance at the inlet, $\dot{n}_{\mathrm{I}}$. This difference is caused by the saturated vapour pressure drop of solution during distillation, and therefore the inert gas accumulates in the vapour space. For a time interval dτ, the inert gas balance is

$$\mathrm{d}n_{\mathrm{I}} = \mathrm{d}n_{\mathrm{I}}' + \mathrm{d}(n_{\mathrm{G}}y_{\mathrm{I}}) \,. \tag{10}$$

Since n_{G} = const., after dividing by dτ we get

$$\dot{n}_{\mathrm{I}} = \dot{n}_{\mathrm{I}}' + n_{\mathrm{G}} \frac{\mathrm{d}y_{\mathrm{I}}}{\mathrm{d}\tau} \,. \tag{11}$$

From the equilibrium relations follows

$$y_{\mathrm{I}} = 1 - \frac{\gamma_{\mathrm{A}}x_{\mathrm{A}}p_{\mathrm{A}}^{*}}{p} - \frac{\gamma_{\mathrm{B}}x_{\mathrm{B}}p_{\mathrm{B}}^{*}}{p} \,. \tag{12}$$

From this on differentiating with respect to time

$$\frac{\mathrm{d}y_{\mathrm{I}}}{\mathrm{d}\tau} = -\left(\gamma_{\mathrm{A}} + x_{\mathrm{A}}\frac{\partial\gamma_{\mathrm{A}}}{\partial x_{\mathrm{A}}}\right)\frac{\mathrm{d}x_{\mathrm{A}}}{\mathrm{d}\tau}\frac{p_{\mathrm{A}}^{*}}{p} - \left(\gamma_{\mathrm{B}} + x_{\mathrm{B}}\frac{\partial\gamma_{\mathrm{B}}}{\partial x_{\mathrm{B}}}\right)\frac{\mathrm{d}x_{\mathrm{B}}}{\mathrm{d}\tau}\frac{p_{\mathrm{B}}^{*}}{p} \,. \tag{13}$$

Since $dx_A = -dx_B$, after inserting into Eq. (*11*), combining with Eq. (*3*) and after rearranging

$$\dot{n}_I' = \dot{n}_I + \frac{V_G}{RT}\frac{dx_A}{d\tau}\left[p_A^*\left(\gamma_A + x_A\frac{\partial\gamma_A}{\partial x_A}\right) - p_B^*\left(\gamma_B - x_B\frac{\partial\gamma_B}{\partial x_A}\right)\right]. \tag{14}$$

If we designate

$$k_1 = \frac{V_G}{RT}\left[p_A^*\left(\gamma_A + x_A\frac{\partial\gamma_A}{\partial x_A}\right) - p_B^*\left(\gamma_B - x_B\frac{\partial\gamma_B}{\partial x_A}\right)\right]. \tag{15}$$

Equation (*14*) can be written after rearranging in the form

$$\dot{n}_I' = \dot{n}_I + k_I x_A\frac{d\ln x_A}{d\tau}. \tag{16}$$

Further balance which is to be made up, is the balance of component A. At the time moment $d\tau$

$$-d(x_A n_L) = n_G dy_A + y_A dn. \tag{17}$$

On differentiating the product on the left-hand side of the balance, we get

$$-n_L dx_A - x_A dn_L = n_G dy_A + y_A dn. \tag{18}$$

With regard to assumption *c*), the accumulation of the overall amount of substance in the vapour space is zero, i.e.,

$$dn = dn_I - dn_L. \tag{19}$$

In Eq. (*18*) we replace dn_L and dy_A from Eqs (*19*) and (*4*), and the equation is divided by $d\tau$

$$-n_L\frac{dx_A}{d\tau} + x_A\dot{n} - x_A\dot{n}_I = \frac{n_G p_A^*}{p}\frac{d(\gamma_A x_A)}{d\tau} + \frac{\gamma_A p_A^* x_A}{p}\dot{n}. \tag{20}$$

The product $\gamma_A x_A$ on the right-hand side of the equation is differentiated. After dividing the equation by x_A and rearranging, we get

$$\dot{n}\left(1 - \frac{\gamma_A p_A^*}{p}\right) = \dot{n}_I + n_L\frac{d\ln x_A}{d\tau} + \frac{n_G p_A^*}{p}\frac{d\ln x_A}{d\tau}\left(\gamma_A + x_A\frac{\partial\gamma_A}{\partial x_A}\right). \tag{21}$$

On substituting for n_G/p from Eq. (*3*) and for $\dot{n}$ from Eq. (*9*)

$$\dot{n}_I' \, \frac{p - \gamma_A p_A^*}{p - \gamma_A p_A^* x_A - \gamma_B p_B^* x_B} = \dot{n}_I + \frac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\left[n_L + \frac{V_G p_A^*}{RT}\left(\gamma_A + x_A \frac{\partial \gamma_A}{\partial x_A}\right)\right]. \tag{22}$$

Let us denote

$$A_p = \frac{p - \gamma_A p_A^*}{p - \gamma_A p_A^* x_A - \gamma_B p_B^* x_B}, \tag{23}$$

$$k_2 = \frac{V_G p_A^*}{RT}\left(\gamma_A + x_A \frac{\partial \gamma_A}{\partial x_A}\right). \tag{24}$$

After substituting from Eqs (*23*) and (*24*), Eq. (*22*) takes the form

$$\dot{n}_I' A_p = \dot{n}_I + \frac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\,(n_L + k_2)\,. \tag{25}$$

As it follows from the arrangement of experiment presented in our preceding paper[1], the measurement of $\dot{n}_I$ is substantially simpler than the measurement of $\dot{n}_I'$. ($\dot{n}_I$ is measured directly on the basis of pressure drop of inert gas on the throttle capillary before entering the liquid, whereas before measuring $\dot{n}_I'$, it is necessary first to remove vapours of solution from the gas, e.g., by adsorption or freezing out.) Therefore we exclude $\dot{n}_I'$ from Eq. (*25*) in terms of Eq. (*16*):

$$\left(\dot{n}_I + k_1 x_A \frac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\right) A_p = \dot{n}_I + \frac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\,(n_L + k_2) \tag{26}$$

or

$$\dot{n}_I\,(1 - A_p) = \frac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\,(k_1 A_p x_A - n_L - k_2)\,. \tag{27}$$

By rearranging Eq. (*27*), we get the corrected form of function (*1*), valid for the systems which have the vapour space of volume V_G:

$$f_v = \frac{\dfrac{\mathrm{d}\ln x_A}{\mathrm{d}\tau}\,\dfrac{n_L}{\dot{n}_I}\,(1 + C_G)}{1 - A_p} + 1 = 0\,. \tag{28}$$

C_G is the correction for the vapour space volume

$$C_G = n_L^{-1}(k_2 - k_1 A_p x_A) . \tag{29}$$

Coefficients k_1 and k_2 are defined by Eqs (*15*) and (*24*). Both the coefficients are functions of the solution temperature and composition and are directly proportional to the vapour space volume. It means that the correction C_G is to be expressed by the relation

$$C_G = \frac{V_G}{n_L} f(T, p, x_A) . \tag{30}$$

The computation of coefficients in the G^E equations in terms of f_v is carried out in the same way as on using function (*1*) in ref.[1], viz. by minimizing the objective function

$$F(\boldsymbol{C}) = \sum_{j=1}^{m} (f_v)_j^2 . \tag{31}$$

DISCUSSION

Effect of Non-Ideality and Concentration of Solution on Correction C_G

It follows from Eq. (*28*) that the concentration change of the given component with time, i.e., the absolute value of derivative $\mathrm{d}\ln x_A/\mathrm{d}\tau$ decreases with increasing correction for the vapour space volume, C_G. The correction given by Eqs (*29*) and (*30*) is directly proportional to the vapour space volume and indirectly proportional to the liquid amount of substance. The presence of quantities γ_i and x_i in Eq. (*29*) indicates also the effect of the solution non-ideality and concentration on C_G. Further this effect will be investigated in more detail.

Even though a great deal of relations is known for expressing the dependence of activity coefficients on composition (see, e.g., the monograph by Hála and coworkers[3]), to be able to express the approximate character of dependence of correction C_G on the degree of non-ideality and on the concentration of solution, it is sufficient to use the simple symmetric second order equation

$$\gamma_A = \exp[A(1 - x_A)^2] , \tag{32}$$

$$\gamma_B = \exp(A x_A^2) , \tag{33}$$

$$\frac{\partial \gamma_A}{\partial x_A} = \gamma_A 2A(x_A - 1), \tag{34}$$

$$\frac{\partial \gamma_B}{\partial x_A} = \gamma_B 2A\, x_A. \tag{35}$$

In terms of the given relations, the diagram of dependence of correction C_G on mole fraction x_A (Fig. 2) was constructed. Coefficient A in Eqs (*32*) to (*35*) was chosen partly for usual completely miscible liquids, i.e., $A \in \langle -2, 2 \rangle$, partly for partially miscible liquids, i.e., $A > 2$. On choosing A for the latter liquids, it was seen to it that the solubility of component A in component B was 0.1, 0.02, 0.01, 0.002 and 0.001 (in mole fractions). For the remaining quantities in Eq. (*29*), the values were chosen which correspond to the usual experiment ($V_G = 5 \cdot 10^{-5}$ m^3, $p_A^* = 20$ kPa, $p_B^* = 10$ kPa, $p = 100$ kPa, $T = 320$ K, $n_L = 0.2$ mol). In terms of the values given, the ratio $V_G/n_L = 2.5 \cdot 10^{-4}$ m^3 mol^{-1}. For a solution with mole mass 100 g mol^{-1} and with density 1 g cm^{-3}, it corresponds to the ratio of volume of vapour and liquid equal to 2.5. The following conclusions can be drawn from the diagram:

1. For $x_A < 0.1$, the simple rule holds: The greater the value of A the greater also the correction, C_G changing little with concentration.
2. For completely miscible liquids and the volume of vapour space chosen by us, the correction is of little significance ($C_G < 0.02$) over the whole concentration range.
3. For partially miscible liquids, we recommend to consider always the correction for the vapour space.

Effect of the Vapour Space Size on the Calculated L–G Equilibrium Data for Completely Miscible Liquid Pairs

It follows from the calculated corrections C_G that the effect of vapour space volume on the L–G equilibrium data of completely miscible liquids determined by the method of inert gas stripping will not probably be significant. More concrete envisage of this effect was obtained by a simulated experiment.

For 16 values $x_A \in \langle 0.05, 0.95 \rangle$ with a step $\Delta x_A = 0.06$, the values of $\mathrm{d}\ln x_A/\mathrm{d}\tau$ were calculated from Eq. (*28*). The other input data were chosen as follows:

a) Constant data

$$n_L = 0.2 \text{ mol};\ T = 320 \text{ K};\ \dot{n}_I = 6.26 \cdot 10^{-6} \text{ mol s}^{-1};$$

$$p_A^* = 20 \text{ kPa};\ p_B^* = 10 \text{ kPa};\ p = 100 \text{ kPa}.$$

b) Variable data

$$A = -2,\ 0,\ 2;\ V_G = 5\ .\ 10^{-5},\ 5\ .\ 10^{-4}\ \mathrm{m}^3.$$

In this way, altogether 6 sets of data of simulated experiments were obtained, each set consisting of results of 16 "measurements". In terms of Eqs (*4*), (*5*), (*32*) and (*33*), "accurate" values of mole fractions in the vapour phase were simultaneously calculated.

For 6 sets of simulated input data, on using the assumption $C_G = 0$ and the procedure given in our foregoing paper[1], the pairs of coefficients A_{12} and A_{21} of the Margules third order equation were calculated:

$$\ln \gamma_A = x_B^2\,[A_{12} + 2\,x_A\,(A_{21} - A_{12})]\,, \tag{36}$$

$$\ln \gamma_B = x_A^2\,[A_{21} + 2\,x_B\,(A_{12} - A_{21})]\,. \tag{37}$$

For single x_A, the mole fractions of component in vapour, y_A^c, and their deviations from the "accurate" data, $y_A^c - y_A$, were calculated from Eqs (*4*), (*5*), (*36*) and (*37*). The average and maximum deviation was determined for each data set. The results are summarized in Table I.

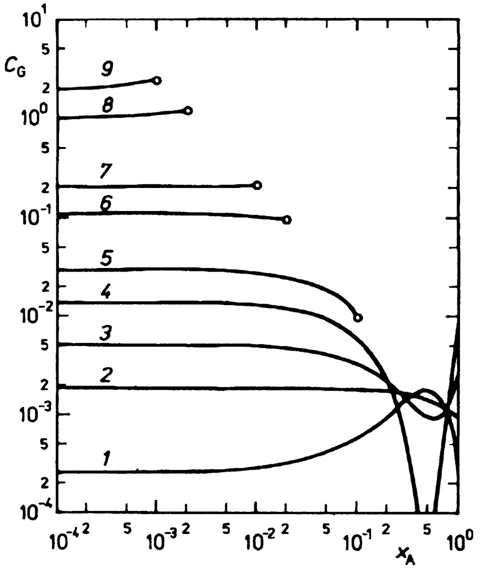

FIG. 2

Dependence of correction C_G on concentration for solutions with different degree of non-ideality. Coefficient *A*: *1* −2, *2* 0, *3* 1, *4* 2, *5* 2.75, *6* 4.05, *7* 4.69, *8* 6.24, *9* 6.92

From the results given in Table I it follows that the deviations of y_A^c from "accurate" y_A reached a more significant value only for a comparatively big vapour space V_G = 5 . 10^{-4} m^3, i.e., for the ratio of vapour and liquid volume about 20 – 30. In this case, the errors in y_A^c due to neglecting the vapour space volume were close to the experimental errors common in measuring vapour–liquid equilibrium.

Note: After the above-mentioned discussion on the effect of vapour space size, it may be reasonable to return to the simplifying assumptions which are used in deriving Eq. (*27*) and are given on page 2073.

A most discussed is condition *c*): the vapour space volume in constant. In fact,

$$dV_G = -dn_L v_L$$

(v_L is the liquid molar volume). However, it is necessary to realize that the judgement of influence of vapour space and the evaluation of parameters of G^E equation is carried out on the basis of known values of derivatives $d\ln x_A/d\tau$ and the given $\dot{n}_I$, n_L and V_G. The change of vapour space volume by dV_G has a backward effect on derivative $d\ln x_A/d\tau$ only through the second-order differential $dV_G dy_A$, which is negligible. In fact, if need be, when integrating Eqs (*27*) or (*28*), it is necessary to take into account that both n_L and V_G are variable, functions of time.

For the second debatable assumption – ideal gas in the vapour phase – it is possible to state that with respect to the little effect of vapour phase volume for completely miscible liquids, the consideration of real gas would just complicate the used relations but does not influence the conclusions of this work.

TABLE I
Comparison of "accurate" equilibrium data with data calculated on neglecting vapour space volume

A^a	V_G^a, m^3	A_{12}^b	A_{21}^b	Deviation $(y_A^c - y_A)^b$	
				average	maximum
-2	5.10^{-5}	-1.9964	-2.0003	1 . 10^{-4}	-2 . 10^{-4}
0		-0.0005	-0.0014	<1 . 10^{-4}	-2 . 10^{-4}
2		1.9993	1.9981	1 . 10^{-4}	-2 . 10^{-4}
-2	5.10^{-4}	-1.9646	-2.0030	9 . 10^{-4}	-20 . 10^{-4}
0		-0.0048	-0.0148	6 . 10^{-4}	-14 . 10^{-4}
2		1.9938	1.9818	12 . 10^{-4}	20 . 10^{-4}

[a] Variable data for calculating $d\ln x_A/d\tau$. [b] Calculated on assumption of C_G = 0.

SYMBOLS

A	coefficient of symmetric G^E equation
A_{ij}	coefficients of Margules equation
A_p	fraction defined by Eq. (*23*)
$\mathbf{C}$	vector of coefficients of G^E equation
C_G	correction for vapour space volume
F	objective function
f	function defined by Eq. (*1*)
f_V	function defined by Eq. (*28*)
G^E	excess Gibbs energy
k_1	coefficient defined by Eq. (*15*)
k_2	coefficient defined by Eq. (*24*)
m	number of experiments
n	amount of substance
$\dot{n}$	flow of amount of substance
$\dot{n}_I$	flow of amount of substance of inert gas at inlet
$\dot{n}_I'$	flow of amount of substance of inert gas at outlet
p	pressure in vapour space
p_i	partial pressure of substance
p_i^*	saturated vapour pressure pressure of pure component
R	gas constant
T	thermodynamic temperature
V_G	vapour space volume
x_i	mole fraction of component in liquid
y_i	mole fraction of component in vapour phase (gas)
γ_i	activity coefficient of component
τ	time

Subscripts

A, B	component
G	vapour space
L	liquid
I	inert gas

Superscripts

*	pure component
c	calculated value

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