

# EFFECT OF ASSOCIATION IN THE VAPOUR PHASE ON THE VALUE OF ACTIVITY COEFFICIENT\*

Ivona MALJEVSKÁ

Department of Physical Chemistry,  
Prague Institute of Chemical Technology, 166 28 Prague 6

Received November 1st, 1977

The relations were obtained between the thermodynamically consistent activity coefficient of associating component and the activity coefficient calculated irrespective of the association in the vapour phase. The analysis is limited to binary systems with one associating component and is given for the two cases: (a) the associating component dimerizes only, (b) the associating component forms, in addition to a dimer, one higher associate, too.

To calculate the thermodynamically consistent values of activity coefficients in associating systems it is necessary to complete the *a priori* information on types of associates occurring in the system by the values of corresponding equilibrium constants of association in the vapour phase. With regard to the absence of these values some works have appeared in which the approximation of ideally associating system (which decidedly complies well in the vicinity of atmospheric pressure) is replaced by the assumption that the original  $n$ -component system behaves as an ideal mixture of ideal gases (*i.e.* by the assumption which generally does not hold for these systems even at very low pressures).

By the term ideally associating system is meant here the "macroscopically"  $n$ -component system in which all the deviations from ideal behaviour are caused just by association and whose "microscopic" mixture, *i.e.* the mixture formed by  $n$  species of monomers and  $r$  species of associates, behaves consequently as an ideal mixture of ideal gases.

Let us have a mixture formed by  $n$  "macroscopic" or  $s > n$  "microscopic" substances. Each "microscopic" substance  $i$  is defined by the vector

$$k_i \equiv (k_{i1}, k_{i2}, \dots, k_{in}), \quad k_{ii} \geq 0, \quad i = 1, 2, \dots, n \quad (1)$$

where  $k_{ii}$  is the number of monomeric units of the  $i$ -th component in the given molecule.

\* Part LXXXI in the series Liquid-Vapour Equilibrium; Part LXXX: This Journal 42, 2233 (1978).

The vectors  $k_i$  will be numbered so that for  $l \in \langle 1, n \rangle$  monomeric molecules will be considered and for  $l \in \langle n+1, s \rangle$ , where  $s = n + r$ , associated molecules will be concerned.

"Macroscopic" substances will be indexed by capital letters A, B, ..., N.

For the activity coefficient of associating substance under the temperature  $T$  and the system pressure  $P$  holds

$$\begin{aligned} \gamma_L(T, P) &= f_L(T, P) / [x_L f_L^0(T, P)] = \\ &= f_L(T, P) / [x_L f_1^*(T, P_{(T)}^0)] \exp \left[ 1/RT \int_P^{P^0} v_L^0 dP \right], \quad l \in \langle 1, n \rangle \end{aligned} \quad (2)$$

where the value of the exponential term is practically equal to unity,  $v_L^0$  is the molar volume of pure liquid component L,  $x_L$  is the mole fraction of substance L in the liquid phase,  $f_L$  its fugacity,  $f_L^0$  its fugacity in a standard state,  $f_1$  denotes the fugacity of monomer of substance L and  $f_1^*$  the fugacity of monomer in the pure component L at temperature  $T$  and saturated vapour pressure  $P^0$ .

In case of an ideally associating system, the monomer of substance L in Eq. (2) can be replaced by partial pressures, so that

$$\gamma_L = P_1 / (x_L P_1^*) . \quad (3)$$

To obtain the value of activity coefficient it is sufficient in this case to calculate the partial pressures of monomer of the given component in mixture and in pure substance L. To this purpose it is necessary to solve a system of  $s$  equations from which  $r$  equations is of the type

$$K_{n+p} = P_{n+p} / \prod_{i=1}^n P_i^{k_{i,n+p}}, \quad p = 1, 2, \dots, r, \quad (4)$$

where  $K_{n+p}$  are the equilibrium constants of association related to the standard state of pure gaseous component in an ideal state at the system temperature and the unit pressure, the exponent  $k_{i,n+p}$  is the value of the  $i$ -th component of the vector  $k_{n+p}$ ;  $(n-1)$  equations for mole fractions of "macroscopic" substances in the vapour phase is of the type

$$y_M = \sum_{i=1}^s k_{mi} P_i / \sum_{i=1}^s \sum_{j=1}^n k_{ji} P_i, \quad M = A, B, \dots, N-1 \quad (5)$$

and the last equation is the equation for total pressure in ideally associating system

$$P = \sum_{i=1}^s P_i . \quad (6)$$

When calculating  $P_1^*$  the system of equations simplifies to the equations of the type (4) for the equilibrium constants of the homoassociate formations and to the equation (6) for the saturated vapour pressure above the pure associating substance.

### Effect of Dimerization

Let us consider now the simplest associating system, the "macroscopic" binary system (A-B) in which the component A dimerizes, *i.e.* the system in which, from "microscopic" point of view, three types of substances occur defined by the vectors

$$k_1 \equiv (1, 0), \quad k_2 \equiv (0, 1), \quad k_3 \equiv (2, 0). \quad (7)$$

By solving the system of Eqs (4)–(6) it is possible to obtain for this system the following relation for partial pressures of monomers

$$P_{1,\text{dim}} = \{\sqrt{[1 + 4K_3 P y_A(2 - y_A)]} - 1\} / [2K_3(2 - y_A)], \quad (8)$$

$$P_{1,\text{dim}}^* = (\sqrt{(1 + 4K_3 P_A^0)} - 1) / (2K_3), \quad (9)$$

$$P_{2,\text{dim}} = P - P_{1,\text{dim}} - K_3 P_{1,\text{dim}}^2, \quad (10)$$

$$P_{2,\text{dim}}^* = P_B^0, \quad (11)$$

where the subscript dim denotes the values calculated on the assumption of the existence of dimer of substance A only in associating mixture.

Let us compare now the value of activity coefficient of associating component calculated from the relation (3) with the value which we would obtain on the assumption of ideal behaviour of the vapour phase, *i.e.* without making allowance for the possibility of dimerization of the substance A in the vapour phase:

$$\gamma_{A,\text{id}} = P y_A / (x_A P_A^0). \quad (12)$$

For high values of dimerization constant holds

$$\lim_{K_3 \rightarrow \infty} \gamma_{A,\text{dim}} = \gamma_{A,\text{id}} \sqrt{\{P_A^0 / [P y_A(2 - y_A)]\}}. \quad (13)$$

From the relations (8) and (9) we obtain after development into the Taylor series

$$\begin{aligned} P_{1,\text{dim}} &= (P_{1,\text{dim}})_{K_3=0} + (\partial P_{1,\text{dim}} / \partial K_3)_{K_3=0} K_3 + o(K_3^2) = \\ &= P y_A - P^2 y_A^2 (2 - y_A) K_3 + o(K_3^2), \end{aligned} \quad (14)$$

$$P_{1,\text{dim}}^* = P_A^0 - P_A^{02}K_3 + o(K_3^2). \quad (15)$$

On neglecting the second- and higher-order terms (if  $K_3 \ll 1$ ) it holds

$$\gamma_{A,\text{dim}} = \gamma_{A,\text{id}}[1 - Py_A(2 - y_A)K_3]/(1 - P_A^0K_3). \quad (16)$$

For both limiting values of  $K_3$  (relations (13) and (16)) consequently holds

$$\text{if } Py_A(2 - y_A) > P_A^0 \text{ then } \gamma_{A,\text{dim}} < \gamma_{A,\text{id}}, \quad (17)$$

$$\text{if } Py_A(2 - y_A) < P_A^0 \text{ then } \gamma_{A,\text{dim}} > \gamma_{A,\text{id}}. \quad (18)$$

Only in the case that

$$Py_A(2 - y_A) = P_A^0 \text{ it holds } \gamma_{A,\text{dim}} = \gamma_{A,\text{id}}. \quad (19)$$

To extend these conclusions to arbitrary value of the equilibrium constant  $K_3$  it is necessary to prove that the activity coefficient is a monotonous function of  $K_3$ . The proof is carried out in Appendix.

For a concrete magnitude of the equilibrium constant the activity coefficient of associating component acquires a value which lies within the range given by the relations (13) and (16).

In case of the non-associating component it holds

$$\gamma_{B,\text{dim}} = P_{2,\text{dim}}/(x_B P_B^0) \quad (20)$$

and considering that  $P_{2,\text{dim}} > Py_B$  it always holds

$$\gamma_{B,\text{dim}} > \gamma_{B,\text{id}} \quad (y_B \neq 1). \quad (21)$$

If we are interested in the effect of dimerization of one of components in the vapour phase on the value of logarithm of the activity coefficient ratio, it is *a priori* possible to decide only that for the case  $Py_A(2 - y_A) < P_A^0$  it will be

$$\ln(\gamma_{A,\text{dim}}/\gamma_{B,\text{dim}}) < \ln(\gamma_{A,\text{id}}/\gamma_{B,\text{id}}). \quad (22)$$

### *Effect of Higher Associates*

Let us assume now that we have calculated activity coefficients with regard to the dimerization of one of components and ask a question what influence upon these values can exert a contingent presence of small amounts of higher associates.

Let us consider again a binary mixture (A-B) in which now "microscopic" substances occur defined by the vectors

$$k_1 \equiv (1, 0), \quad k_2 \equiv (0, 1), \quad k_3 \equiv (2, 0), \quad k_4 \equiv (n, 0), \quad n > 2. \quad (23)$$

By solving the system of Eqs (4)-(6) it is possible to obtain the equation for this case

$$K_4 P_1^n (n y_A - y_A - n) + K_3 P_1^2 (y_A - 2) - P_1 + P y_A = 0. \quad (24)$$

For partial pressures of monomer of associating component we can write

$$P_1 = P_{1,\text{dim}} + P_{1,\text{dim}}^n (n y_A - y_A - n) K_4 / [1 + 2K_3 P_{1,\text{dim}} (2 - y_A)] + o(K_4^2) \quad (25)$$

and

$$P_1^* = P_{1,\text{dim}}^* - (P_{1,\text{dim}}^*)^n K_4 / (1 + 2K_3 P_{1,\text{dim}}^*) + o(K_4^2). \quad (26)$$

On neglecting the second- and higher-order terms (i.e. for very small quantities of higher associates) it holds

$$\gamma_A = P_1 / (P_1^* x_A) = \gamma_{A,\text{dim}} \chi, \quad (27)$$

where

$$\chi = [1 + (\partial P_1 / \partial K_4)_{K_4=0} K_4 / P_{1,\text{dim}}] / [1 + (\partial P_1^* / \partial K_4)_{K_4=0} K_4 / P_{1,\text{dim}}^*]. \quad (28)$$

For  $\chi \cong 1$  it is  $\gamma_A \cong \gamma_{A,\text{dim}}$ .

The following two statements are proved in Appendix:

$$\text{If } P y_A (2 - y_A) \leq P_A^0 \text{ then } \gamma_A^* > \gamma_{A,\text{dim}} \quad (y_A \neq 1), \quad (29)$$

$$\begin{aligned} \text{if } \{ \sqrt{[1 + 4K_3 P y_A (2 - y_A)]} - 1 \} / (2 - y_A) &> \sqrt{(1 + 4K_3 P_A^0)} - 1 \\ \text{then } \gamma_A &< \gamma_{A,\text{dim}} \quad (y_A \neq 1). \end{aligned} \quad (30)$$

The first inequality in Eq. (30) implicates  $P y_A > P_A^0$ .

For the non-associating component the sequence holds

$$\gamma_B > \gamma_{B,\text{dim}} > \gamma_{B,\text{id}}, \quad (31)$$

for, if we do not take into account all the kinds of formed homoassociates of the substance A, we calculate with larger number of molecules of substance A in the

mixture than it really is, which results in lower calculated values of partial pressure of non-associating substance.

Accordingly we can summarize that in the whole interval  $y_A \in (0, 1)$  holds:

If we do not include the effect of the higher associate formations then the calculated values of activity coefficients are always lower for the non-associating substance. For the associating substance they are lower if  $P_{y_A}(2 - y_A) \leq P_A^0$  holds but higher than the adequately calculated values, if it holds  $P_{y_A} > P_A^0$  or the inequality (35). The behaviour of activity coefficient of associating component was not successfully *a priori* determined for the values of saturated vapour pressure of associating substance A within the range

$$P_{y_A} < P_A^0 < P_{y_A}(2 - y_A).$$

As far as the change of logarithms of activity coefficients is concerned it can be stated in advance that for the case  $P_{y_A} > P_A^0$  we shall calculate higher values if we do not take the effect of higher associates into account.

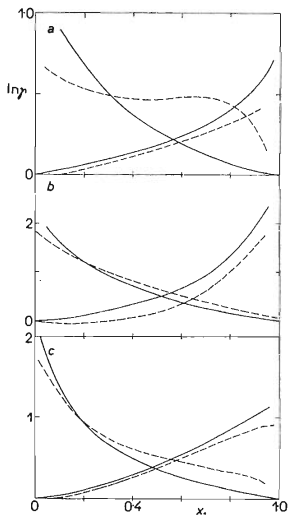


FIG. 1

Dependence of Activity Coefficient on Composition in the System *a* Acetic Acid(1)-Diethyl Ether(2) (ref.<sup>3</sup>), *b* Acetic Acid(1)-*n*-Octane(2) (ref.<sup>4</sup>). *c* Propionic Acid(1)-Cyclohexane(2) (ref.<sup>5</sup>)

Solid line denotes the course of the dependence if the acid dimerization in the vapour is considered, i.e.  $\gamma_{dim}$ , dashed line the course of  $\gamma_{id}$ .

The relations derived can be illustrated on the systems with one fatty acid. It is evident from Fig. 1 that neglecting the fatty acid dimerization in the vapour phase will cause a considerable error when calculating activity coefficients of both components. The corrections for the higher associate formations (in this case the effect of trimerization according to Potter<sup>1</sup> and the effect of quadramers formations according to Ritter<sup>2</sup> was investigated) are several orders lower. Considering that the inaccuracies in values of activity coefficients, which arise from neglecting the higher associate formations, for fatty acids are roughly in accordance with the errors due to inaccuracies when determining the dimerization constants, the effect of higher associates for the systems with aliphatic acids is not usually taken into account.

#### APPENDIX

*Proof of general validity of relations (17), (18) and (19).* If activity coefficient (or its logarithm) is not a monotonous function of equilibrium constant it is possible to find such a value  $K_3$  for which holds

$$\partial \ln \gamma_{A,dim} / \partial K_3 = 0, \quad (32)$$

which implicates

$$\partial \ln P_{1,dim} / \partial K_3 = \partial \ln P_{1,dim}^* / \partial K_3. \quad (33)$$

After inserting for  $P_{1,dim}$  and  $P_{1,dim}^*$  from the relations (8) and (9) it can be, on differentiating and rearranging, obtained the condition

$$Z(1 - \sqrt{[1 + W]}) = W(1 - \sqrt{[1 + Z]}), \quad (34)$$

where

$$Z = 4K_3 P y_A (2 - y_A)$$

and

$$W = 4K_3 P_A^0, \quad y_A > 0, \quad K_3 > 0$$

Eq. (34) is fulfilled there and then if at least one of the following relations holds:

- a)  $4K_3 y_A (2 - y_A) = 0$ ,
- b)  $4K_4 P_A^0 = 0$ ,
- c)  $Z = W$ , which corresponds to the condition (19)  $P_A^0 = P y_A (2 - y_A)$  for which  $\gamma_{A,ld} = \gamma_{A,dim}$  and the activity coefficient is consequently independent of the value of dimerization constant.

In this way we succeeded in proving that the above-mentioned relations (17), (18) and (19) must hold for all  $K_3 > 0$  in the whole range of  $y_A \in (0, 1)$ .

*Proof of statement (29).* To be  $\gamma_A > \gamma_{A,dim}$  it must hold

$$0 < \{P_{1,dim}^{n-1}[n + y_A(1 - n)]\} / [1 + 2K_3 P_{1,dim}(2 - y_A)] < (P_{1,dim}^*)^{n-1} / (1 + 2K_3 P_{1,dim}^*), \quad (35)$$

where  $P_{1,dim}$  and  $P_{1,dim}^*$  can be expressed by the relations (8) and (9).

Let us denote

$$\alpha = \sqrt{[1 + 4K_3 P y_A(2 - y_A)]},$$

$$\beta = \sqrt{(1 + 4K_3 P_A^0)},$$

$$y = y_A.$$

Then the inequality (35) can be rewritten into the form

$$0 < [n + y(1 - n)] / \alpha \{(\alpha - 1) / [2K_3(2 - y)]\}^{n-1} < [(\beta - 1) / (2K_3)]^{n-1} / \beta, \quad \alpha > 1, \beta > 1 \quad (36)$$

It is possible to prove easily that the function  $(x - 1)^{n-1}/x$  is an increasing in  $x$  and consequently if

$$\alpha \leq \beta,$$

then

$$(\alpha - 1)^{n-1} / \alpha \leq (\beta - 1)^{n-1} / \beta, \quad (37)$$

where the equality holds just for the case  $\alpha = \beta$ . In order that the inequality (36) may hold the inequality must be fulfilled for  $y \neq 1$

$$[n + y(1 - n)] < (2 - y)^{n-1}. \quad (38)$$

If we rewrite the right-hand side of the inequality into the form

$$[1 + (1 - y)]^{n-1} = 1 + (1 - y)(n - 1) + (n - 1)(n - 2)(1 - y)^2/2 + \dots = n - ny + y + (n - 1)(n - 2)(1 - y)^2/2 + \dots \quad (39)$$

the validity of Eq. (38) is obvious. Thus, it has been proved that if

$$\alpha \leq \beta,$$

which implicates

$$P y_A(2 - y_A) \leq P_A^0,$$



then

$$\gamma_A > \gamma_{A,\text{dim}} \quad \text{for} \quad y_A \neq 1.$$

*Proof of statement (30).* If  $\gamma_A < \gamma_{A,\text{dim}}$  it must hold

$$0 < (P_{1,\text{dim}}^*)^{n-1} / [1 + 2K_3 P_{1,\text{dim}}^*] < \\ < (P_{1,\text{dim}})^{n-1} (n + y_A - n y_A) / [1 + 2K_3 P_{1,\text{dim}}(2 - y_A)]. \quad (40)$$

Let us assume that

$$P_{1,\text{dim}} > P_{1,\text{dim}}^*. \quad (41)$$

It holds

$$n + y_A - n y_A > 2 - y_A \quad (42)$$

since

$$(n - 2) - (n - 2) y_A > 0 \quad y_A < 1, \quad n > 2. \quad (43)$$

Consequently

$$(n + y_A - n y_A) / [1 + 2K_3 P_{1,\text{dim}}(2 - y_A)] > \\ > (2 - y_A) / [1 + 2K_3 P_{1,\text{dim}}(2 - y_A)] \quad (44)$$

and simultaneously

$$(2 - y_A) / [1 + 2K_3 P_{1,\text{dim}}(2 - y_A)] = 1 / [1 / (2 - y_A) + 2K_3 P_{1,\text{dim}}] > \\ > 1 / [1 + 2K_3 P_{1,\text{dim}}]. \quad (45)$$

Then also

$$[P_{1,\text{dim}}^{n-1} (n + y_A - n y_A)] / [1 + 2K_3 P_{1,\text{dim}}(2 - y_A)] > \\ > P_{1,\text{dim}}^{n-1} / [1 + 2K_3 P_{1,\text{dim}}]. \quad (46)$$

Considering that the function  $x^{n-1} / (1 + 2K_3 x)$  is an increasing one in  $x$  then on the assumption (41) holds

$$(P_{1,\text{dim}}^*)^{n-1} / [1 + 2K_3 P_{1,\text{dim}}^*] < P_{1,\text{dim}}^{n-1} / [1 + 2K_3 P_{1,\text{dim}}] \quad (47)$$

and therefore the inequality (40) is under this assumption fulfilled.

## REFERENCES

1. Potter E. A., Bender P., Ritter H. L.: *J. Phys. Chem.* 59, 250 (1955).
2. Ritter H. L., Simons J. H.: *J. Amer. Chem. Soc.* 67, 757 (1945).
3. Meehan G. F., Murphy N. F.: *Chem. Eng. Sci.* 20, 757 (1965).
4. Zieborak K., Brzostowski W.: *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* 6, 169 (1958).
5. Malijevská I.: Unpublished results.

Translated by J. Linek.