

TO THE QUESTION WHETHER HIGHER ASSOCIATES EXIST IN THE VAPOUR PHASE OF ACETIC ACID

Ivona MALIJEVSKÁ

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

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Equilibrium constants for higher associates in an ideal-gas associating mixture are correlated from existing data on the P - V - T behaviour of acetic acid. Further, a model of real-gas dimerizing mixture is tested on the basis of estimated critical properties for monomer and dimer of fatty acids.

A special group of systems requiring specific approach when treating the vapour-liquid equilibrium data is formed by the systems with fatty acids. The reason for it is their strongly non-ideal behaviour and consequently impossibility to express the deviations from ideal behaviour in the vapour phase by the virial equation of state truncated after the second term how it is usually done with simpler systems in the vicinity of normal pressure. When treating these strongly associating substances, it is usually assumed that they occur in the mixture mostly in the form of the monomer and dimer molecules, and to obtain the values of activity coefficients, the equations of phase and chemical equilibrium are solved simultaneously¹. In these calculations, the ideal-gas association model is used, *i.e.* it is assumed that all deviations from ideal behaviour are caused by the associate formation, in this case by the dimer formation.

Nearly all those who have measured the volumetric behaviour^{2,3-4} of fatty acids and evaluated the dimerization equilibrium constants from it, have drawn attention to the fact that this model is not in complete harmony with reality. For instance, the evaluated equilibrium constants of dimerization which should be independent of pressure, exhibit a strong trend with pressure.

The equilibrium interconnection between the monomer and dimer molecules makes an independent measurement of real behaviour of both the species of molecules impossible. Consequently it has been natural that the deviations from measured values have been explained on the basis of "chemical" theory, the presence of one type of higher associates being usually determined *a priori*.

The aim of this work is: 1) To try to obtain the maximum information on the possibility of existence of a higher associate (or higher associates) and its type from the known P - V - T behaviour.

2) To find out whether a sufficiently good description of reality can be reached on the basis of predicted values of the second virial coefficients for a mixture of monomer and dimer molecules.

Correlation of Equilibrium Constants of Higher Associates

If M is the molecular mass calculated from experimental values for a mixture of monomeric and associated molecules, then

$$M = \frac{RTG}{PV} = \sum_{i=1}^n x_i M_i = M_1 \sum_{i=1}^n i x_i, \quad (1)$$

must hold, where R is the gas constant, T the temperature, P the pressure, V the total volume, G the sample mass of acid, M_i the molecular mass of i -mer, x_i the mole fraction of i -mer in mixture of the other associates.

The equilibrium constants were evaluated by the least-squares method using the following objective function

$$\sum_{k=1}^m \left(\frac{RTG}{PVM_1} - 1 - \sum_{i=1}^n i K_{i+1} x_1^{i+1} P^i \right)^2 = \min, \quad (2)$$

where

$$K_i = x_i / x_1^i P^{i-1}, \quad (3)$$

and m is the number of experimental points along one isotherm. The input parameters were the T , P , V , G values from the Bartoň⁵ data on P - V - T behaviour of acetic acid and the value of dimerization constant in the form (related to the standard state of pure substance in a state of ideal gas under the temperature of system and pressure of 1 Pa):

$$\ln K_2 = 7425.84/T - 29.2438. \quad (4)$$

This relation is a low-density limit of values calculated from relation (2) for $i = 2$.

The first approximation of x_1 was obtained on the assumption of dimerization only.

First, the possibility of forming both the trimer and tetramer structures ($i = 1, 2, 3, 4$) was considered. The obtained results were unrealistic; nearly for every temperature, one of the constants was negative.

Then a model was examined in which the higher associate was either trimer ($i = 1, 2, 3$) or tetramer ($i = 1, 2, 4$). The values of association constants are given in Table I for single temperatures.

By using the least-squares method with the same weights for all experimental isotherms, the temperature dependence of both the equilibrium constants were obtained in the form

$$\ln K_3 = 8537.2/T - 45.55, \quad \Delta H^{as} = -70.98 \text{ kJ/mol}, \quad (5)$$

$$\ln K_4 = 13\,779.1/T - 69.72, \quad \Delta H^{as} = -114.56 \text{ kJ/mol.} \quad (6)$$

The standard states are identical with those for dimerization constant (4).

The results obtained for the equilibrium constant of trimer formation are depicted in Fig. 1 (for tetramer, the results are similar). The same temperature dependence from the work by Johnson⁴ is given for comparison. Both the lines intersect in the region of temperatures where the measurements of both authors overlap.

The back calculation of volume for the experimental values of temperature and pressure at input gave in both the cases results at the limit of experimental accuracy, some isotherms being represented better by the model with dimer and trimer molecules, others by the model with dimer and tetramer molecules.

Thus, if we use the P - V - T data as a criterion, it is not possible to decide, whether trimer or tetramer is more probably present in the mixture.

Real Behaviour of Monomer and Dimer

Now an attempt followed to replace the model of ideal-gas associating mixture by a model of real-gas dimerizing mixture. In the calculations we started from estimated

TABLE I
The values of equilibrium constants obtained by correlation

T	398.58	383.15	368.55	352.71	337.95	323.11
$K_3 \cdot 10^{10}$	0.36	1.5	0.43	7.6	41	30
$K_4 \cdot 10^{14}$	0.063	0.36	0.23	7.4	54	120

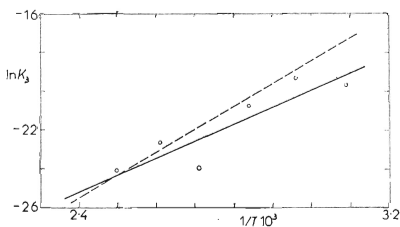


FIG. 1
The dependence of trimerization constant on temperature; ----- Johnson⁴, ——— this work

critical properties of monomer and dimer of fatty acid which are given in Table II for acetic acid, propionic acid and butyric acid. The details concerning to the estimation of these quantities are given in Appendix.

On the basis of critical properties of monomer and dimer of acetic acid, their second virial coefficients were estimated in terms of the relation proposed by Martin¹²

$$B_i = 0.188 - \frac{0.468}{T_{ri}} [1 + 18.952 \exp(-5T_{ri})] R \frac{T_{ci}}{P_{ci}}, \quad (7)$$

where

$$T_{ri} = T/T_{ci}, \quad (8)$$

and T_{ci} , P_{ci} are the critical temperature and pressure.

When calculating the thermodynamic equilibrium constants defined by

$$K^{th} = \frac{v_2 x_2 P_{st}}{v_1^2 x_1^2 P}, \quad (9)$$

where $P_{st} = 1$ Pa and v_i is the fugacity coefficient of i -mer, we started from the composition calculated for the value of dimerization constant at a pressure approaching to zero. Then the second virial coefficient of mixture was calculated, the second cross virial coefficient being estimated in terms of Eq. (7) with

$$T_{c_{12}} = (T_{c_1} T_{c_2})^{1/2} \quad \text{and} \quad P_{c_{12}} = (P_{c_1} P_{c_2})^{1/2}, \quad (10)$$

and the fugacity coefficients from the relation

$$\ln v_k = 2 \sum_i x_i B_{ik}/v - \ln |1 + B/v| \quad i = 1, 2. \quad (11)$$

$$k = 1, 2$$

TABLE II
Critical properties

Value	Acetic		Propionic		Butyric	
	monomer	dimer	monomer	dimer	monomer	dimer
T_c , K	585	610	600	630	610	650
P_c , MPa	6	4	5.5	3.3	5.4	2.8

From the corrected value of equilibrium constant (Eq. (9)), a new composition of mixture was calculated and the cycle was repeated as far as the composition was changed. In Eq. (11), $v = V/n$, where n is the number of moles.

The results for acetic acid (for the lack of experimental data, similar calculations were not carried out for the other acids mentioned) are given in Figs 2 and 3 for two temperatures. The vertical line segments mark the variance due to inaccuracies in input values of critical quantities. The dashed line represents the model of the ideal-gas dimerizing mixture with K_2 defined in terms of Eq. (3) for mole fractions calculated on the basis of experimental data from Eq. (1) for $i = 2$.

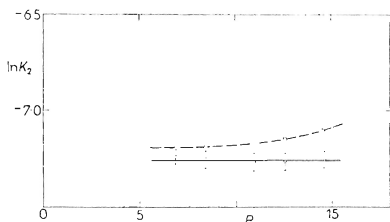


FIG. 2

The dependence of dimerization equilibrium constant on pressure (kPa) at $T = 337.95$ K; ----- the results obtained for ideal-gas dimerizing system, — the results obtained on considering real behaviour in the vapour phase

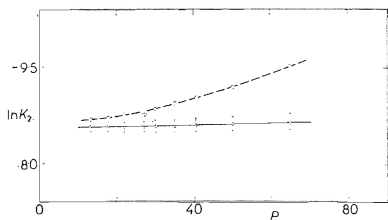


FIG. 3

The dependence of dimerization equilibrium constant on pressure (kPa) at $T = 383.5$ K; ----- the results obtained for ideal-gas dimerizing system, — the results obtained on considering real behaviour in the vapour phase

It is evident from the figures that on considering the real behaviour of monomer and dimer of the acid, we were fully successful in suppressing the undesirable dependence of the dimerization equilibrium constant on pressure.

Similarly, also the values of total volume of mixture calculated for experimental values of temperature and pressure at input, and on the assumption that the P - V - T behaviour of monomer and dimer can be expressed in terms of the virial equation of state with the first two terms, agreed within the range of experimental error with the experimental values. Thus, it is possible to state that on taking the real behaviour of monomer and dimer molecules of acetic acid in the vapour phase into account, it is possible to describe its P - V - T behaviour within experimental accuracy.

CONCLUSION

From the presented work it is evident that the dependence of dimerization constant on pressure need not always be an evidence of existence of small amounts of higher associates.

In case of acetic acid we succeeded in full suppressing the trend mentioned by inserting the real behaviour of monomer and dimer molecules in the vapour phase, the fugacity coefficients being predicted on the basis of data estimated independently of the data on the P - V - T behaviour of this acid.

As a by-product, the work yields also reliable estimate of critical properties of monomer and dimer of acetic, propionic and butyric acids.

APPENDIX

The fundamental problem when estimating the critical properties of monomer and dimer of the fatty acids was a very limited amount of usable information. All the data which could be employed when solving this task are given in Tables III and IV; besides these data, only the structural formula of monomer and its cyclic dimer is known.

The latter are sufficient to estimate critical properties of real substances by the Forman-Thodos method. Ambiguity in defined contributions (*e.g.*, $-\text{COOH}$ group could not be identified with carboxylic group because the monomer and dimer molecules present in mixture can

TABLE III

The molecular masses and critical properties of fatty acids

Acid	M_1	M_2	T_c , K (ref. ⁶)	P_c , MPa (ref. ⁶)
Acetic	60.05	120.1	594.8	5.79
Propionic	74.08	148.16	612.7	5.36
Butyric	88.10	176.20	628.2	5.3

TABLE IV
The temperature dependence of saturated vapour pressures and equilibrium constants

Value	Acetic Acid			Propionic acid			Butyric acid		
	A	B	C	A	B	C	A	B	C
K^{fs}	7 425.84	29.2437 (ref. ⁵)	—	7 635.37	29.838 (ref. ⁸)	—	6 999.93	28.1492 (ref. ⁹)	—
K_1^{NS}	3 120.28	6.5239 (ref. ¹)	—	4 695.5	8.679 (ref. ¹⁰)	—	5 294	9.7057 (ref. ¹¹)	—
P_A^0 , Pa	23.3616	4 457.83	-14.699 (ref. ⁷)	23.2918	4 442.38	-36.807 (ref. ⁷)	24.3894	5 231.27	-30.1 (ref. ⁷)

$$s \ln K = A/T - B; \ln P = A - B/(T + C).$$

never more exhibit specific interactions) leads to a considerable dependence of resulting critical properties on the choice of contributions. In this situation it was desirable to try to estimate the critical properties still by another method, and to confront the results.

The Lydersen estimation method, however, requires the knowledge of normal boiling point of the substance, in this case, of the monomer and dimer of fatty acids. To estimate this quantity, the saturated vapour pressures of monomer P_1^0 and dimer P_2^0 as a function of temperature were calculated from the equation for saturated vapour pressure of fatty acid (P_A^0):

$$P_A^0 = P_1 + P_2 = \gamma_1 x_1 P_1^0 + \gamma_2 x_2 P_2^0. \quad (D-1)$$

The partial pressures of monomer P_1 and dimer P_2 and the composition of the liquid phase were calculated from the equilibrium constants in the vapour phase

$$K_2^g = P_2/P_1^2 \quad (D-2)$$

and in the liquid phase

$$K_{2N}^1 = x_2/x_1^2 \quad (D-3)$$

(Table V), the activity coefficients from the Flory relation

$$\gamma_i = \exp [\ln (\varphi_i/x_i) + 1 - \varphi_i/x_i], \quad (D-4)$$

where the volume fraction

$$\varphi_i = r_i x_i / \sum_1 r_i x_i \quad (D-5)$$

was calculated for various values of $r_2 : r_1$ up to the maximum ratio 2 : 1.

The equilibrium ratio of concentration of the dimer and monomer molecules in the liquid phase (D-3) for acetic and propionic acids was reported by Freedman¹⁰ in a narrow temperature interval. Bartoň¹¹ correlated the equilibrium ratio for both acids as a function of temperature (a note: the published temperature dependence for propionic acid does not agree with experimental values), and estimated this dependence for butyric acid.

TABLE V
The constants for calculating the saturated vapour pressures of fatty acids

	Acetic acid		Propionic acid		Butyric acid	
	monomer	dimer	monomer	dimer	monomer	dimer
A	22.82	21.31	21.1	21.87	22.35	23.56
B	4.186	3.424	3.189	4.119	4.592	5.467
C	-12.8	-48.6	-37.87	-38.66	38.2	-17.9

This estimate was used for butyric acid, in the temperature dependence of equilibrium ratio for acetic and propionic acids, the first constant $A = \Delta H^{as}/R$ was fixed on the basis of known ΔH^{as}

$$\Delta H_{AA}^{as} = 25.94 \text{ kJ/mol}$$

$$\Delta H_{PA}^{as} = 39.04 \text{ kJ/mol}$$

so that better extrapolation outside the narrow measured temperature interval should be ensured:

$$\ln K_{AA} = 3.120 \cdot 3/T - 6.524,$$

$$\ln K_{PA} = 4.695 \cdot 5/T - 8.679.$$

The values of T_{NBP} were read from saturated vapour pressures of monomers and dimers of fatty acids. They varied within up to 10° for monomer and at most 5° for dimer in dependence on the values of K_2^g and P_A^0 reported by different authors and especially on the choice of the ratio $r_1 : r_2$. The calculated saturated vapour pressures of monomers of acetic and propionic acids are not in reasonable correlation ($T_{NBP}^{AA1} > T_{NBP}^{PA1}$), which gives evidence for internal inconsistency in values of dimerization equilibrium constants.

The intersection of values of critical properties obtained by both estimation methods and confronted with the values of critical properties within the homologous series and with the critical properties of pure acids yields the values presented in Table V. The inaccuracy interval is estimated at 15°C for critical temperatures and less than 1 MPa for critical pressures.

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