

## Acetic acid–water system thermodynamical correlation of vapor–liquid equilibrium data

E. SEBASTIANI and L. LACQUANITI

Istituto di Chimica Applicata e Industriale della Facoltà di Ingegneria, Università di Roma

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**Abstract**—A considerable amount of data for vapor–liquid equilibrium between acetic acid and water are compared with a set of experimental results, obtained by means of a modified Gillespie still at atmospheric pressure.

Using the differential heats of mixing, all the activity coefficients were reported to 25°C; in this manner it was possible to compare also the data related to pressures different from atmospheric.

By means of Redlich and Kister equations, a thermodynamical correlation for the activity coefficients as functions of the temperature and composition was obtained.

### INTRODUCTION

THE ACETIC acid–water system is very important from the theoretical and industrial standpoints; for this reason, it was studied for more than half a century by many authors. In the technical literature, a great amount of experimental data is available, which are generally sufficiently reliable. Nevertheless, a thermodynamical correlation of experimental results has been made only in the last ten or fifteen years. Activity coefficients based on the experimental data, when obtained following the usual procedure, present a great thermodynamical inconsistency, which cannot be due only to accidental errors. Much more consistent data may be obtained, taking into account the acetic acid tendency to form dimers and polymers in the vapor phase; it will be seen that with this assumption, the different data are practically consistent and sufficiently in accordance with each other.

For the system, with which we are concerned, no author considered the temperature influence on the activity coefficients; without this correction, it is impossible to compare the different results.

The objects of this work are the following:

- (i) To present a series of experimentally determined vapor–liquid equilibrium data, obtained by means of a modified vapor–liquid equilibrium still [1], which gave good results with other systems.
- (ii) To calculate the activity coefficients at 25°C and atmospheric pressure, from the results

of the present work and from those of many other authors.

- (iii) To compare the different results in view of determining their eventual agreement.
- (iv) To obtain general analytical expressions, correlating the activity coefficients at atmospheric pressure, as functions of the temperature.

### EXPERIMENTAL RESULTS

In Table 1 the results of twenty-three experimental runs are presented. Distilled water and glacial acetic acid of Carlo Erba (purity 99.9%) with a controlled boiling point of 118.1°C were used. The analysis was performed by titration with NaOH.

In Fig. 1 these experimental results are reported and compared with many others already published and exactly, with those of PERRY [2], which summarize those of BERGSTROM [3], CORNELL and MONTANNA [4] and POVARNIN and MARKOV [5]; with those of GARVIN and HADDAD [6]; with those of OTHMER, SILVIS and SPIEL [7], who report a great amount of data, published before 1951; in addition to the above-mentioned works, Othmer examines the results of BLACHER [8], GARVIN and HUTCHINSON [9], GILMONT and OTHMER [10], PASCAL, DUPUY and GARNIER [11], RAYLEIGH [12], SOREL [13] and YORK and HOLMES [14]; with those of MAREK [15] which are compared with those of CATHALA [16], GARVIN and HUTCHINSON [9], OTHMER *et al.* [7] and VILIM [17]; with those of GARNER. ELLIS and

PEARCE [32], compared with those of CORNELL and MONTANNA [4], BROWN and EWALD [33] and GARVIN and HADDAD [6].

TABLE 1. EXPERIMENTAL RUNS

Temperature (°C)	Mole fraction of water in liquid	Mole fraction of water in vapor
100.8	0.865	0.907
101.7	0.755	0.817
102.4	0.675	0.770
103.5	0.5725	0.678
104.2	0.520	0.635
105.6	0.440	0.556
107.7	0.305	0.420
108.2	0.2825	0.384
108.9	0.250	0.365
110.6	0.175	0.282
108.6	0.257	0.375
110.2	0.190	0.302
112.3	0.127	0.208
113.2	0.1025	0.1725
113.7	0.095	0.150
101.0	0.832	0.887
102.8	0.641	0.750
108.2	0.275	0.417
106.2	0.395	0.515
103.5	0.572	0.680
111.8	0.145	0.227
112.8	0.125	0.1825
109.3	0.230	0.355

On the contrary, ELLIS and BAHARI's data [18] are not reported, because they were obtained at variable pressure from 722 to 755.5 mm Hg and at low concentration ranges.

Among all these works, OTHMER *et al.* [7] and MAREK's [15] should be the most representative, since they summarize a great amount of experimental data. Nevertheless, it must be pointed out that the first author compared only the vapor composition  $y$  vs. the liquid composition  $x$  and the second author the difference  $y-x$  vs.  $x$ , without taking into account the equilibrium temperature, which, on the contrary, plays a very important role in the thermodynamical correlation. From Fig. 1, it may be easily seen that Othmer's data greatly deviate from the majority of other results just in the temperature determination, especially at high water concentrations, while, for the same  $x$ ,  $y$  and also  $(y-x)$ , are closed with the other values.

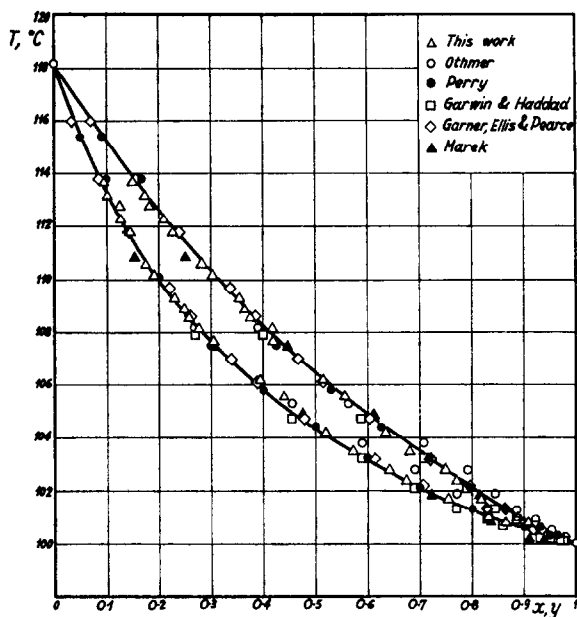


FIG. 1. Temperature-composition curves for acetic acid-water system and experimental data.

The diagrams  $T(x)$  and  $T(y)$  were drawn and are in good agreement with the represented points; as will be shown, a thermodynamically consistent correlation may be obtained from these points.

#### THERMODYNAMICAL TREATMENT OF VAPOR-LIQUID EQUILIBRIUM

Following the theoretical procedure, which was applied by SEBASTIANI [19] in a previous work, activity coefficients at 25°C were obtained by means of the well-known thermodynamical equations:

$$y_i \bar{v}_i P = \gamma_i x_i v_i^0 p_i^0 \exp \int_{p_i^0}^P \frac{v_i^L dP}{RT} \quad (1)$$

and:

$$\ln \gamma_i^0 = \ln \gamma_i + \int_{298}^T \frac{\bar{L}_i}{RT^2} dT - \int_1^P \frac{\bar{v}_i^L - v_i^L}{RT} dP \quad (2)$$

In the case under consideration, the last term in the right-hand side of Eq. (2) is zero, because the experimental data were obtained at atmospheric pressure; on the other hand, if Eq. (2) is applied to pressures other than atmospheric, but not too high, the same term may be put equal to zero, in view of both the small value of  $P$  and the difference  $(\bar{v}_i^L - v_i^L)$ .

The exponential term in Eq. (1) can also be equal to 1, introducing an error of 0.01% on  $\log \gamma_i$ .

Fugacity coefficients are generally related to the deviation from the ideality of the components in the gaseous mixture ( $\bar{v}_i$ ) and in the pure state ( $v_i^0$ ). In the case under consideration, in view of the small value of the pressure, these coefficients should be considered equal to unity; but it is just the thermodynamical inconsistency of activity coefficients, as calculated with Eq. (1), putting  $\bar{v}_i = v_i^0 = 1$ , which has confirmed the existence of some phenomenon in the vapor phase, affecting the fugacity coefficients, much more than the simple deviation from the ideal-gas law.

Two papers concerning acetic acid behavior in the vapor phase have been published; in the first one, by MACDOUGALL [20], the assumption is made, that the acid forms a dimer and a trimer, in the second one, by RITTER and SIMONS [21], a dimer and tetramer. Ritter and Simons exclude the possibility of the trimer formation, because it would necessitate the breaking of an exothermic bond; furthermore the tetramer has resonant structures, not available for the trimer.

The following equations summarize the work of Ritter and Simons:

$$\log K_2 = \frac{3164}{T} - 10.4184 \quad (3)$$

$$\log K_4 = \frac{5884}{T} - 23.4824 \quad (4)$$

where  $K_2$  and  $K_4$  are the equilibrium constants for dimerization and tetramerization, in  $\text{mm}^{-1}$  and  $\text{mm}^{-3}$  respectively.

Assuming that the ideal-gas law holds, if  $p_1$  is the partial pressure of the monomer, the corresponding values for the dimer and the tetramer are:

$$p_2 = K_2 p_1^2 \quad (5)$$

$$p_4 = K_4 p_1^4 \quad (6)$$

The vapor pressure of the pure acetic acid  $p_A^0$  is the sum of three terms, representing the contributions of the three molecular types:

$$p_A^0 = p_1 + p_2 + p_4 \quad (7)$$

This equation allows us to obtain  $p_1$  at every temperature.

In the vapor–liquid equilibrium of the acetic acid–water system, only the monomer is to be considered and then the value of  $p_1$  satisfying Eq. (7) must be used, instead of  $p_A^0$ , usually found in tables or calculated; in the present work the following equation was used [22]:

$$\log p_A^0 = 14.39756 - \frac{9399.86}{T + 424.9} \quad (8)$$

where  $T$  is in °K and  $p_A^0$  in mm Hg; this equation holds from 60°C to 150°C.

It is then possible to define a fictitious fugacity coefficient for the pure vapor, by means of:

$$v_A^0 = \frac{p_1}{p_A^0} \quad (9)$$

For the gaseous acetic acid–water mixture, a similar procedure can be employed, considering the relation between the mole fraction, as usually determined and the number of moles in the gaseous phase:

$$y_A = \frac{n_1 + 2n_2 + 4n_4}{n_1 + 2n_2 + 4n_4 + n_w} \quad (10)$$

where  $n_1$ ,  $n_2$  and  $n_4$  are the number of moles of the monomer, dimer and tetramer and  $n_w$  of water. Substituting for the mole numbers the partial pressures, since the total pressure is:

$$P = p_1 + p_2 + p_4 + p_w \quad (11)$$

Eq. (10) can be written as follows:

$$y_A P = p_1 + (2 - y_A) K_2 p_1^2 + (4 - 3y_A) K_4 p_1^4 \quad (12)$$

In this way, it is possible to calculate  $p_1$  for assigned values of  $y_A$ ,  $P$  and  $T$ .

As with Eq. (9)

$$\bar{v}_A = \frac{p_1}{y_A P} \quad (13)$$

and

$$\bar{v}_w = \frac{p_w}{y_w P} \quad (14)$$

where:  $y_w = 1 - y_A$ . By means of Eqs. (9), (13) and (14), the vapor–liquid equilibrium can be studied on the basis of Eq. (1).

This method was followed by MAREK [15], HANSEN, MILLER and CHRISTIAN [23] and by ARICH and TAGLIAVINI [24, 25]. Furthermore, MAREK and STANDART [26] gave a general theoretical treatment of vapor-liquid equilibria for systems containing an associating component.

In the MAREK work [15] the formation of the tetramer is not considered and isobaric data are directly handled: this is equivalent to neglecting the temperature effect on the activity coefficients. This is justified by the facts that the influence of both the tetramer formation and the temperature effect do not introduce serious error, on one hand owing to the small value of  $K_4$  and, on the other hand, to the closeness of the boiling points of pure components, together with the small values of the differential heat of mixing, except for very dilute solutions of water in acid and acid in water.

Neglecting the tetramer formation, it is also possible to obtain an analytical solution for Eqs. (9), (13) and (14); but the tetramer partial pressure cannot be neglected, because it can be as high as 5% of the dimer.

ARICH and TAGLIAVINI [25] handle three sets of isothermal data, at temperatures of 69.7, 79.9 and 89.9°C and take into account the formation of the tetramer; they have also obtained approximated analytical functions to calculate  $v_A^0$ ,  $\bar{v}_A$  and  $\bar{v}_W$  [24].

HANSEN, MILLER and CHRISTIAN [23] used isothermal data at 25°C, assuming the hypothesis of MACDOUGALL [20] of formation of trimer instead of the tetramer; but at such low temperature there is no practical difference and also these authors used analytical equations to calculate fugacity coefficients, putting  $K_4=0$  in Eqs. (7) and (12).

The constant  $K_2$ , according to MACDOUGALL, is 1.63, while Eq. (3) gives  $K_2=1.556$ : the results are therefore comparable.

In order to rationally compare the various results, it is convenient to report all the activity coefficients to 25°C and 1 atm; since all the experiments were carried out at a sufficiently low pressure, it is sufficient to study only the effect of the temperature.

#### INTEGRAL AND DIFFERENTIAL HEATS OF MIXING

The integral heat of mixing was determined by SANDONNINI [27]; these values are also reported in

the LANDOLT-BÖRNSTEIN Tabellen [28]; they are given in Table 2 and plotted in Fig. 2. It is possible to fit these data, following the procedure suggested by REDLICH, KISTER and TURNQUIST [29], by the general equation:

$$L = x_W(1 - x_W)[a + b(2x_W - 1) + c(2x_W - 1)^2 + d(2x_W - 1)^3] \quad (15)$$

which, in this case, must be applied assuming the following values for the constants:

$$a = 294$$

$$b = -198$$

$$c = -3$$

$$d = -436$$

By analytical procedure, the differential heats of mixing were calculated:

$$\begin{aligned} \bar{L}_A &= 3925x_W^2 - 16440x_W^3 + 26124x_W^4 - 13952x_W^5 \\ \bar{L}_W &= 925 - 7850x_W + 28585x_W^3 \\ &\quad + 43564x_W^4 - 13952x_W^5 \end{aligned} \quad (16)$$

The numerical values of  $\bar{L}_A$  and  $\bar{L}_W$  reported in Table 2 and Fig. 3, were obtained by means of the above-mentioned equations.

TABLE 2. INTEGRAL AND DIFFERENTIAL HEATS OF MIXING OF THE SYSTEM ACETIC ACID-WATER (cal/mole)

$x$	$L$	$\bar{L}_W$	$\bar{L}_A$
0	0	+925	0
0.05	+37.4	+598	+ 7.9
0.10	+60.6	+379	+ 25.3
0.20	+80.9	+153	+ 62.8
0.30	+84.1	+77	+ 87.0
0.40	+80.9	+49	+102
0.50	+73.5	+24	+123
0.60	+60.2	- 8	+163
0.70	+39.1	-35	+212
0.80	+12.8	-40	+223
0.90	- 8.1	-20	+ 96
0.95	- 9.7	- 6.5	- 70
1.00	0	0	-343

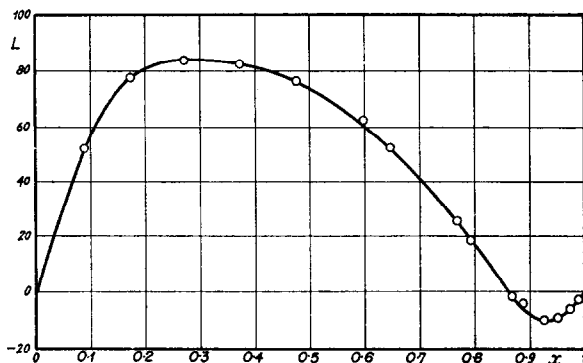


FIG. 2. Integral heat of mixing.

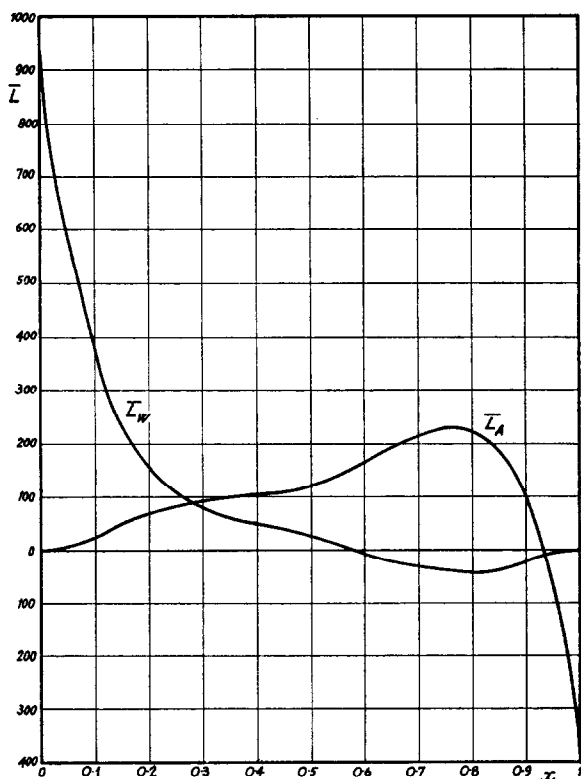


FIG. 3. Differential heats of mixing.

Since the Sandonni data refers to a temperature of 16–18°C, thermal capacities of liquid solutions were controlled, using the values of both SANDONNINI [27] and PERRY [2]; it was verified that  $C_p$  is a linear function of mole fraction, therefore the differences  $(\bar{C}_{pW} - C_{pW})$  and  $(\bar{C}_{pA} - C_{pA})$  are equal to zero, at least in a temperature range near to 25°C.

The good results obtained demonstrate that the constants, used in Eq. (15), may be considered reliable also at higher temperature.

Equation (2) therefore can be written:

$$\log \gamma_i = \log \gamma_i^0 - \frac{\bar{L}_i}{4.576} \left[ \frac{1}{298} - \frac{1}{T} \right] \quad (17)$$

remembering that  $\bar{L}_i$  is a function of the composition, but not of the temperature.

#### ACTIVITY COEFFICIENTS AT 25°C FROM THE EXPERIMENTAL RESULTS

By means of the fugacity coefficients and of Eq. (17), it is possible to calculate the activity coefficients for the acetic acid–water system at 25°C, on the basis of the equilibrium diagram reported in Fig. 1. This diagram takes into account both the data that have already appeared in the literature and those of the present work.

The fugacity coefficients were calculated by trial and error from Eqs. (9), (13) and (14); vapor pressure of the acetic acid was calculated from Eq. (8), while that of water was read in the HODGMAN Table [34], by interpolation.

In Tables 3 and 4 the results of such a calculation are summarized; in Table 3 are reported the equilibrium concentrations, deduced from the equilibrium diagram of Fig. 1 and the fugacity coefficients; in Table 4 the activity coefficients for the isovoric system, and the activity coefficients at 25°C and atmospheric pressure are also reported. These last values are plotted graphically in Fig. 4. It was found that they can be correlated with sufficient accuracy by means of the three-constant REDLICH and KISTER equations [30]:

$$\begin{aligned} \log \gamma_W^0 &= x_A^2 [A^0 + B^0(4x_W - 1) \\ &\quad + C^0(x_W - x_A)(4x_W - 1)^2] \\ \log \gamma_A^0 &= x_W^2 [A^0 + B^0(4x_W - 3) \\ &\quad + C^0(x_W - x_A)(4x_W - 3)^2] \end{aligned} \quad (18)$$

The results obviously satisfy the consistency condition [30]:

$$\int_0^1 \log \frac{\gamma_W^0}{\gamma_A^0} dx_W = 0 \quad (20)$$

and the Gibbs–Duhem equation, since they are correlated with Eq. (18).

The numerical values of the constants are:

$$A^0 = 0.3338$$

$$B^0 = 0.0283$$

$$C^0 = 0.1081$$

The curves plotted in Fig. 4 were calculated from Eq. (18).

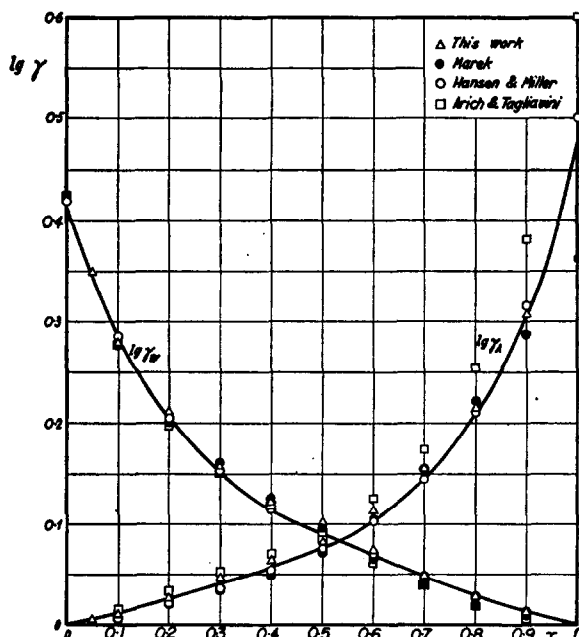


FIG. 4. Activity coefficients at 25°C and 1 atm.

TABLE 3. SMOOTHED EQUILIBRIUM DATA (FROM FIG. 1) AND FUGACITY COEFFICIENTS

Temperature (°C)	x	y	$\bar{v}_A$	$\gamma_A^0$	$\bar{v}_W$
115.4	0.05	0.095	0.379	0.391	1.573
113.2	0.10	0.175	0.367	0.388	1.479
109.9	0.20	0.320	0.3576	0.382	1.349
107.7	0.30	0.430	0.357	0.379	1.265
105.9	0.40	0.535	0.363	0.376	1.198
104.3	0.50	0.640	0.381	0.373	1.138
103.1	0.60	0.728	0.407	0.371	1.094
102.1	0.70	0.805	0.444	0.369	1.060
101.2	0.80	0.871	0.498	0.366	1.035
100.5	0.90	0.935	0.617	0.366	1.012

TABLE 4. ISOBARIC AND ISOTHERMIC ACTIVITY COEFFICIENTS

$x_W$	Activity coefficients at 1 atm pressure		Activity coefficients at 25°C, 1 atm	
	$\log \gamma_W$	$\log \gamma_A$	$\log \gamma_W^0$	$\log \gamma_A^0$
0.05	0.2477	0.0035	0.3495	0.0047
0.10	0.2164	0.0060	0.2799	0.0103
0.20	0.1855	0.0170	0.2103	0.0269
0.30	0.1433	0.0330	0.1553	0.0465
0.40	0.1146	0.0469	0.1219	0.0626
0.50	0.0969	0.0633	0.1007	0.0824
0.60	0.0744	0.0878	0.0733	0.1126
0.70	0.0534	0.1225	0.0480	0.1544
0.80	0.0334	0.1813	0.0273	0.2143
0.90	0.0145	0.2929	0.0112	0.3071

COMPARISON WITH PREVIOUS WORKS

The HANSEN, MILLER and CHRISTIAN data [23], being obtained at a constant temperature of 25°C, are directly comparable. The good agreement, as shown in Fig. 4 and Table 5, is a proof of the small effect of the tetramer formation, which was neglected by these authors. They correlated the experimental data by means of the equations of HANSEN and MILLER [31], more complicated than that of Redlich and Kister, used in this work.

TABLE 5. COMPARISON OF ACTIVITY COEFFICIENTS

x	$\log \gamma_W^0$				
	calculated from [18]	derived from Table 4	Hansen and Miller	Arich and Tagliavini	Marek
0	0.4136	—	0.420	0.4257	0.4230
0.05	0.3423	0.3495	—	—	—
0.10	0.2846	0.2799	0.285	0.2798	0.2774
0.20	0.2017	0.2103	0.205	0.1976	0.2038
0.30	0.1494	0.1553	0.155	0.1509	0.1602
0.40	0.1154	0.1219	0.115	0.1152	0.1246
0.50	0.0905	0.1007	0.088	0.0866	0.0937
0.60	0.0687	0.0733	0.070	0.0609	0.0648
0.70	0.0471	0.0480	0.048	0.0386	0.0388
0.80	0.0257	0.0273	0.028	0.0186	0.0200
0.90	0.0079	0.0112	0.011	0.0063	0.0081
0.95	0.0022	—	—	—	—
1	0	0	0	0	0

$\log \gamma_A^0$					
x	0	0	0	0	0
0.05	0.0018	0.0047	—	—	—
0.10	0.0064	0.0103	0.0100	0.0149	0.0087
0.20	0.0207	0.0269	0.020	0.0337	0.0212
0.30	0.0379	0.0465	0.035	0.0505	0.0343
0.40	0.0561	0.0626	0.053	0.0700	0.0489
0.50	0.0764	0.0824	0.075	0.0917	0.0709
0.60	0.1031	0.1126	0.102	0.1255	0.1048
0.70	0.1438	0.1544	0.144	0.1734	0.1539
0.80	0.2089	0.2143	0.210	0.2536	0.2202
0.90	0.3121	0.3071	0.315	0.3813	0.2862
0.95	0.3831	—	—	—	—
1	0.4702	—	0.500	0.600	0.3612

The results of MAREK [15] were reported at 25°C by means of the Eq. (17); the corrected values were plotted in Fig. 4 together with the others; they are in good agreement at every concentration, except for  $\log \gamma_A^0$  at high values of  $x_w$ .

Following the same procedure, the results of ARICH and TAGLIAVINI [25] were reported at 25°C; in Fig. 4 are reported the one obtained from the experimental runs at 79.9°C.  $\log \gamma_w^0$  agree very well, while  $\log \gamma_A^0$  is sensibly different from the other plotted values. Arich and Tagliavini suppose that it may be due to some interaction in the vapor phase between the water and acid molecules, of the same kind as that existing between the acid molecules; nevertheless, this “hydration” was never demonstrated. On the other hand, since all the values of  $\log \gamma_w^0$  are practically coincident, it may be concluded for the accuracy of this coefficient: but in this case, to be thermodynamically consistent with  $\log \gamma_w^0$ ,  $\log \gamma_A^0$  cannot differ from the plotted values.

MAREK [15] assumes that in the liquid phase an aggregation phenomenon takes place, in analogy with the gaseous phase. He also takes into account this last factor and derives a fictitious equilibrium constant, which allows for calculation of the activity coefficients. However, there are not elements to prove this hypothesis and on the other hand, it is not probable that all the deviation in the liquid phase is due to the association, as he postulates.

#### GENERAL EQUATIONS FOR ACETIC ACID–WATER SYSTEM AS FUNCTIONS OF THE TEMPERATURE

Introducing into the Eq. (17)  $\log \gamma_i^0$  and  $\bar{L}_i$  as given by Eqs. (16) and (19), it is possible to obtain  $\log \gamma_w$  and  $\log \gamma_A$  as functions of the temperature; to this end, it is sufficient to use the following values for the constants:

$$A = 0.1182 + \frac{64.24}{T}$$

$$B = 0.1735 - \frac{43.27}{T}$$

$$C = 0.1081$$

$$D = 0.3197 - \frac{95.27}{T}$$

In this way, vapor–liquid equilibrium for the acetic acid–water system can be predicted, at every temperature and pressure, as long as the ideal-gas law holds.

In Table 6 some values of  $\log \gamma_w$  at  $x_w=0$  and of  $\log \gamma_A$  at  $x_w=1$ , for different temperatures, are reported.

TABLE 6. LIMIT VALUES OF ACTIVITY COEFFICIENTS (CALCULATED)

Temperature (°C)	$\log \gamma_w$ for $x_w=0$	$\log \gamma_A$ for $x_w=1$
25	0.4136	0.4702
50	0.3662	0.4838
80	0.3083	0.5081
100	0.2763	0.5205
110	0.2625	0.5256
120	0.2488	0.5306

#### NOTATION

- $a, A^0, A$  constants
- $b, B^0, B$  constants
- $c, C^0, C$  constants
- $d, D$  constants
- $K$  equilibrium constants;  $K_2$  for dimer,  $K_4$  for tetramer
- $L$  integral heat of mixing
- $\bar{L}_i$  differential heat of mixing;  $\bar{L}_w$  for water,  $\bar{L}_A$  for acetic acid
- $n_i$  number of moles;  $n_1$  for monomer acetic acid,  $n_2$  for dimer,  $n_4$  for tetramer,  $n_w$  for water
- $P$  total pressure
- $p_i^0$  vapor pressure;  $p_A^0$  for acetic acid
- $p$  partial pressures;  $p_1$  for monomer acetic acid,  $p_2$  for dimer,  $p_4$  for tetramer,  $p_w$  for water
- $T$  temperature
- $v_i^l$  molal volume of liquid;  $\bar{v}_i^l$  molal partial volume
- $x_i$  mole fraction in liquid;  $x_w$  for water,  $x_A$  for acetic acid
- $y_i$  mole fraction in vapor;  $y_w$  for water,  $y_A$  for acetic acid
- $\gamma_i$  activity coefficient;  $\gamma_w$  for water,  $\gamma_A$  for acetic acid
- $\gamma_i^0$  activity coefficient at 25°C and atmospheric pressure;  $\gamma_w^0$  for water,  $\gamma_A^0$  for acetic acid
- $\bar{v}_i$  fugacity coefficient in solution;  $\bar{v}_w$  for water,  $\bar{v}_A$  for acetic acid
- $v_i^0$  fugacity coefficient of saturated vapor;  $v_A^0$  for acetic acid

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**Résumé**—Une somme considérable de données sur l'équilibre liquide-vapeur entre l'acide acétique et l'eau sont comparées à des résultats expérimentaux obtenus au moyen d'un alambic Gillespie modifié et sous pression atmosphérique.

Utilisant les différentielles thermiques du mélange, tous les coefficients d'activation furent signalés à 25°C. Par ce procédé il a été également possible de comparer les données se relatant aux pression autres qu'atmosphérique.

Une corrélation thermodynamique pour les coefficients d'activation en tant que fonctions de la température et de la composition a été obtenue par les équations de Redlich et Kister.

**Zusammenfassung**—Zahlreiche Daten für das Dampfflüssigkeitsgleichgewicht zwischen Essigsäure und Wasser wurden mit einer Reihe experimenteller Ergebnisse verglichen, die mit Hilfe einer modifizierten Gillespie-Kolonnen bei atmosphärischem Druck erhalten wurde.

Unter Benutzung der differentiellen Mischwärme wurden Aktivitätskoeffizienten für 25°C berechnet; auf diese Weise konnten auch Daten für Drucke verglichen werden, die vom atmosphärischen Zustand abweichen.

Mit Hilfe der Redlich-Kister Gleichungen wurde eine thermodynamische Korrelation der Aktivitätskoeffizienten als Funktion der Temperatur und der Zusammensetzung erhalten.