

VAPOUR-LIQUID EQUILIBRIUM IN STRONGLY ASSOCIATED SYSTEMS. THE SYSTEMS ACETIC ACID-PROPIONIC ACID AND ACETIC ACID-TRIFLUOROACETIC ACID*

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Vapour-liquid equilibrium was measured in the systems acetic acid-propionic acid and acetic acid-trifluoroacetic acid at normal pressure. Special emphasis has been laid on the correct expression of the P - V - T behaviour in the vapour phase and the analysis of the data obtained.

The vapour-liquid equilibrium data measurement results in obtaining the set of activity coefficients characterizing the liquid system in question. The necessary condition for obtaining consistent data is the correct expression of the vapour phase behaviour. Owing to the small convergence radius of the virial expansion for fatty acids¹, it is not possible to express the deviations from ideal behaviour in the vapour phase of these substances directly from the virial equation of state truncated after the second term as it is common in the vicinity of normal pressure for non-associating or weakly associating systems.

With the strongly associated systems, the idea proved to be very fruitful that the deviations from ideal behaviour in the vapour phase are caused above all by the existence of higher associates in mixture, which results in the presence of lower number of particles than it would correspond to the system composed only of monomeric units.

From the equality of the chemical potentials of associating substance and its monomer²

$$\mu_A = \mu_{A1}, \quad (1)$$

it is possible to derive relation (2)

$$f_A(T, P)/f_A^\circ(T, P_{(T)}^\circ) = f_{A1}(T, P)/f_{A1}^*(T, P_{(T)}^\circ), \quad (2)$$

where

$$f_A^\circ = \lim_{y_A \rightarrow 1} f_A,$$

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and

$$f_{A1}^* = \lim_{y_A \rightarrow 1} f_{A1}.$$

Providing that all the deviations from ideal behaviour in the liquid phase are included into the value of activity coefficient, it is possible to write

$$\begin{aligned} \gamma_A &= f_{A1} / \left(f_{A1}^* x_A \exp \left(\frac{1}{RT} \int_{P_{A^0}}^P V_{m,A}^{ol} dP \right) \right) = \\ &= v_{A1} y_{A1} P / \left(v_{A1}^* y_{A1}^* P_{A^0} x_A \exp \left(\frac{1}{RT} \int_{P_{A^0}}^P V_{m,A}^{ol} dP \right) \right). \end{aligned} \quad (3)$$

To calculate the activity coefficient of strongly associating substance, the knowledge of chemical equilibrium between "microcomponents" of associating substance is therefore indispensable besides the experimental quantities characterizing the phase equilibrium.

Fatty acids are to be modelled very well as a real mixture of monomeric and dimeric molecules³. For a microscopically binary system of two fatty acids, the "macroscopically" five-component system (2 monomers, 2 homodimers and 1 heterodimer) is therefore suitable for an easier expression of behaviour of the vapour phase, and the quality of the activity coefficients obtained depends in this case strongly also on the quality of the used values of homo- and heterodimerization constants.

EXPERIMENTAL

Preparation of Pure Substances

Acetic acid (product of Lachema, Brno) was rectified, on adding acetic anhydride, on a glass forty-plate column.

Propionic acid (product of Soyuzkhimexport) was dried with Na_2SO_4 and then, on adding several crystals of KMnO_4 , rectified on a twenty-plate glass column equipped with an additional heating jacket to compensate heat losses.

Trifluoroacetic acid (A.R., product of Fluka AG) was used without any further purification.

Physico-chemical constants of the substances used are given in Table I.

Apparatus

A recirculation still of the Dvořák-Boublík type was used for measuring the vapour-liquid equilibrium. The difference between the normal and actual barometric pressure was compensated by bubbling nitrogen through corresponding column of glycerol. Temperature was measured by a calibrated 100 Ω Pt thermometer. The boiling points of pure substances given in Table I were measured in the equilibrium still.

Analysis of the binary vapour and liquid samples was carried out by measuring density at 20°C in 25 ml pycnometers with accuracy $\delta d = 1 \cdot 10^{-4} \text{ g cm}^{-3}$.

In the system acetic acid(1)–trifluoroacetic acid(2), the dependence of composition on density was expressed in the form

$$x_1 = \frac{169.81138 - 114.021d}{80.377 - 28.785d} + \sum_{i=1}^4 A_i(d - 1.0492)(1.4893 - d) \exp(d^i),$$

where $A_1 = -0.18394$, $A_2 = 0.40218$, $A_3 = -0.18457$, $A_4 = 0.040153$. The maximum deviation $\Delta x_{\max} = 7 \cdot 10^{-4}$. The first term is calculated from the value of molar volume for ideal solution. Thirteen experimental points used for calibration are given in Table II.

In the system acetic acid(1)–propionic acid(2), along with density, the change of refractive index with composition was as well observed for calibration. The measured quantities for 14 experimental points are given in Table III.

The dependence of density on composition was correlated by a polynomial in the form

$$d^{20} = d_1^0 x_1 + d_2^0 x_2 + x_1 x_2 \sum_{i=0}^3 B_i (x_2 - x_1)^i,$$

TABLE I
Physico-chemical constants of substances used

Acid	n_D^{20}	d^{20} , g cm ⁻³	t_{NBP} , °C
Acetic	1.3717	1.0492	117.95
	1.3717–1.3719 (ref. ⁴)	1.0491–1.04926 (ref. ⁵)	117.90 (ref. ⁴)
			118, 1–7 (ref. ⁵)
Propionic	1.3864	0.9933	
	1.3865 (ref. ⁴)	0.9934 (ref. ⁴)	141.35
	1.3866 (ref. ⁵)		140.83 (ref. ⁴) 141.35 (ref. ⁵)
Trifluoroacetic		1.4893	71.95
		1.4890 (ref. ⁴)	71.78–72.2 (ref. ⁵)
		1.48944–1.48957 (ref. ⁶)	

TABLE II
Dependence of density (g cm⁻³) on composition in the system acetic acid(1)–trifluoroacetic acid(2)

x_1	0	0.083	0.125	0.208	0.229	0.376	0.476
d^{20}	1.4893	1.4689	1.4567	1.4295	1.4224	1.3657	1.3230
x_1	0.535	0.683	0.762	0.912	0.966	1.000	
d^{20}	1.2966	1.2262	1.1870	1.1025	1.0705	1.0492	

with the constants $B_0 = -2.12 \cdot 10^{-2}$, $B_1 = -9.3 \cdot 10^{-5}$, $B_2 = 2.33 \cdot 10^{-3}$, $B_3 = 8.43 \cdot 10^{-3}$ and with standard deviation in density $s_d = 1 \cdot 10^{-4}$.

The dependence of refractive index on composition was correlated by the polynomial

$$n_D^{20} = n_{D1}^0 x_1 + n_{D2}^0 x_2 + C x_1 x_2 (x_1 - x_2)^2,$$

with the constant $C = -7.836 \cdot 10^{-4}$ and standard deviation in refractive index $s_n = 9.7 \cdot 10^{-5}$.

RESULTS AND DISCUSSION

To calculate activity coefficients from Eq. (3), it was necessary in both cases to solve a set of equations of mass balance (4) and (5) and of chemical equilibrium (6), (7) and (8):

$$y_{A1} + y_{A2} + y_{C1} + y_{C2} + y_{AC} = 1, \quad (4)$$

$$y_A = \frac{y_{A1} + 2y_{A2} + y_{AC}}{1 + y_{A2} + y_{C2} + y_{AC}}, \quad (5)$$

$$K_{A2} = v_{A2} y_{A2} P_{st} / v_{A1}^2 y_{A1}^2 P, \quad (6)$$

$$K_{C2} = v_{C2} y_{C2} P_{st} / v_{C1}^2 y_{C1}^2 P, \quad (7)$$

$$K_{AC} = v_{AC} y_{AC} P_{st} / v_A v_C y_A y_C P. \quad (8)$$

The constants given in Table IV and the experimental results of vapour-liquid equilibrium given in Tables V and VI were used for calculating.

For the system acetic acid-trifluoroacetic acid, the heteroassociation constant¹² obtained from experimental data, *viz.*

$$\ln K = 8756.92/T - 31.943$$

TABLE III

Dependence of density (g cm^{-3}) and refractive index on composition in the system acetic acid(1)-propionic acid(2)

x_1	0	0.110	0.167	0.248	0.271	0.362	0.411
d^{20}	0.9933	0.9979	0.9999	1.0037	1.0047	1.0088	1.0116
n_D^{20}	1.3864	1.3847	1.3841	1.3829	1.3825	1.3811	1.3805
x_1	0.527	0.566	0.616	0.702	0.785	0.891	1.000
d^{20}	1.0174	1.0198	1.0228	1.0281	1.0336	1.0407	1.0492
n_D^{20}	1.3787	1.3784	1.3774	1.3760	1.3748	1.3733	1.3717

TABLE IV
Constants used

Acid	A, B, C ^a	ref.	M, N ^b	ref.	V _A , V _B ^c	ref.	T _C , K ^d	P _C , MPa ^d	ref.
Acetic	23·36166	11	7425·84	9	31·568	5	585/610	6/4	3
	4457·83 -14·699		29·244		8·34 · 10 ⁻²				
Propionic	23·29189	11	8858·32	7	51·318	5	600/630	5·5/3·3	3
	4442·38 -36·807		33·356		7·92 · 10 ⁻²				
Trifluoroacetic	22·10415	10	7030	8	45·213	10	480/510	3·5/1·5	3
	3243·63 -38·29		29·761		0·106				

^a $\ln P^{\circ} = A - B/(T + C)$, P° in Pa; ^b $\ln K = M/T - N$ (standard state: pure gaseous component at the system temperature and pressure of 1 Pa); ^c $V_m^{\text{ol}} = V_A + V_B T$, V_m^{ol} in cm³ mol⁻¹; ^d in numerator data for monomer, in denominator for dimer.

was employed, and for the system acetic acid-propionic acid, the approximation $K_{AC} = 2(K_A K_C)^{1/2}$ was applied.

The estimates of second virial coefficients from the Martin generalized relation¹⁵

$$B_{ij} = \left\{ 0.188 - \frac{0.468}{T_{r,ij}} [1 + 18.952 \exp(-5T_{r,ij})] \right\} R \frac{T_{c,ij}}{P_{c,ij}} \quad (9)$$

served for calculating the fugacity coefficients of the acid monomers and dimers from the relation

$$\ln v_k = 2 \sum_i x_i B_{ik} / V_m - \ln \left| 1 + \frac{B}{V_m} \right|, \quad (10)$$

where

$$B = \sum_i \sum_j B_{ij} x_i x_j.$$

TABLE V

Equilibrium data for the system acetic acid(1)-trifluoroacetic acid(2), $P = 101.325$ kPa

T, K	x_1	y_1	γ_1	γ_2
391.14	0.974	0.975	1.005 ± 0.003	0.243 ± 0.017
391.18	0.928	0.928	1.001 ± 0.003	0.267 ± 0.012
391.02	0.886	0.880	0.994 ± 0.003	0.290 ± 0.012
390.85	0.839	0.820	0.974 ± 0.003	0.320 ± 0.012
390.45	0.808	0.778	0.961 ± 0.003	0.341 ± 0.012
389.62	0.785	0.746	0.956 ± 0.003	0.359 ± 0.012
387.75	0.694	0.620	0.891 ± 0.006	0.421 ± 0.011
384.90	0.619	0.521	0.830 ± 0.010	0.478 ± 0.010
383.78	0.600	0.495	0.812 ± 0.012	0.497 ± 0.009
383.89	0.594	0.489	0.803 ± 0.012	0.498 ± 0.009
379.25	0.512	0.385	0.705 ± 0.018	0.581 ± 0.007
377.16	0.471	0.338	0.654 ± 0.021	0.617 ± 0.006
375.30	0.441	0.303	0.610 ± 0.021	0.648 ± 0.005
373.79	0.423	0.276	0.568 ± 0.022	0.680 ± 0.004
370.32	0.368	0.214	0.477 ± 0.021	0.730 ± 0.004
366.72	0.312	0.163	0.416 ± 0.020	0.785 ± 0.003
364.98	0.288	0.139	0.376 ± 0.019	0.812 ± 0.003
359.30	0.209	0.078	0.278 ± 0.015	0.881 ± 0.003
354.30	0.138	0.040	0.216 ± 0.013	0.928 ± 0.003
350.27	0.079	0.018	0.173 ± 0.014	0.961 ± 0.002
347.04	0.029	0.006	0.148 ± 0.027	0.983 ± 0.002

The system acetic acid–trifluoroacetic acid exhibits great negative deviations from ideal behaviour (strong affinity to form heterodimer) whereas the system acetic acid–propionic acid is practically ideal.

The following errors in input quantities were considered when analysing the experimental data: $s_y = s_x = 0.001$, $s_T = 0.05$ K, $s_p = 50$ Pa, $s_{p_0}/P^\circ = 0.003$, $s_{K_A}/K_A = 0.05$, $s_B/B = 0.3$, and $s_{K_C}/K_C = s_{K_{AC}}/K_{AC} = 0.1$ for the system acetic acid–propionic acid, and $s_{K_C}/K_C = s_{K_{AC}}/K_{AC} = 0.05$ for the system acetic acid–trifluoroacetic acid. On their basis, the standard deviations at the individual experimental points

$$s_{\gamma,j} = \sqrt{\sum_i \left(\frac{\partial \gamma}{\partial \xi_i} \right)^2 s_{\xi_i}^2}, \quad j = 1, \dots, NP, \quad (11)$$

TABLE VI

Equilibrium data for the system acetic acid(1)–propionic acid(2), $P = 101.325$ kPa

T. K	x_1	y_1	γ_1	γ_2
391.91	0.968	0.978	1.000 ± 0.002	1.131 ± 0.105
393.65	0.867	0.910	1.005 ± 0.003	1.073 ± 0.069
395.76	0.759	0.834	1.011 ± 0.004	1.044 ± 0.055
397.10	0.692	0.780	1.011 ± 0.005	1.051 ± 0.048
398.01	0.653	0.750	1.012 ± 0.006	1.040 ± 0.033
398.81	0.613	0.712	1.008 ± 0.007	1.056 ± 0.039
399.89	0.569	0.676	1.011 ± 0.008	1.041 ± 0.035
399.94	0.565	0.672	1.011 ± 0.009	1.043 ± 0.034
400.15	0.553	0.660	1.010 ± 0.009	1.048 ± 0.033
401.04	0.515	0.627	1.013 ± 0.011	1.039 ± 0.029
401.71	0.485	0.601	1.018 ± 0.012	1.031 ± 0.026
402.15	0.472	0.586	1.012 ± 0.013	1.034 ± 0.025
402.73	0.448	0.562	1.011 ± 0.013	1.033 ± 0.023
402.81	0.444	0.559	1.013 ± 0.014	1.030 ± 0.023
404.20	0.381	0.497	1.022 ± 0.018	1.024 ± 0.018
404.25	0.332	0.448	1.057 ± 0.023	1.040 ± 0.015
406.00	0.301	0.417	1.049 ± 0.024	1.009 ± 0.013
408.26	0.218	0.319	1.062 ± 0.033	1.001 ± 0.008
408.69	0.201	0.299	1.071 ± 0.035	0.999 ± 0.008
411.25	0.108	0.171	1.086 ± 0.049	0.998 ± 0.006
411.65	0.095	0.154	1.098 ± 0.052	0.996 ± 0.005
412.75	0.049	0.086	1.171 ± 0.067	0.998 ± 0.005
413.02	0.044	0.073	1.102 ± 0.067	1.000 ± 0.005
413.83	0.016	0.030	1.226 ± 0.109	0.998 ± 0.005
413.86	0.009	0.018	1.308 ± 0.178	1.003 ± 0.005

where ξ_1, \dots, ξ_N denote the input quantities, and the weights

$$w_{\gamma,j} = 1/s_{\gamma,j}^2$$

were calculated.

The effect of errors in single input quantities on the value of the activity coefficient can be compared in Figs 1–4. It is evident in all cases that the inaccuracies in the data determining chemical equilibrium have a predominant effect. The concentration ends are an exception where the errors in composition of equilibrium phases come to the fore.

Both the calculated sets of activity coefficients were subject to tests of consistence. They have met the Herington integral test of consistence¹³, and the differential test by Cuncell and Hicks¹⁴ proved both the data to be very consistent. Notwithstanding we did not succeed to correlate the system acetic acid–trifluoroacetic acid within the experimental accuracy by none of the commonly used correlation equations. Both the systems were correlated by the two-constant Redlich–Kister, Wilson, NRTL, Orye and HMW equations. When calculating the constants of correlation equations by the least-squares method, the objective function in the form

$$F = \sum_{i=1}^{NP} w_i [(\ln \gamma_1/\gamma_2)_{\text{exp}} - (\ln \gamma_1/\gamma_2)_{\text{calc}}]^2$$

was used. The calculated values of constants for the first three equations are given along with their standard deviations and covariances and the standard deviation of correlation

$$s = (F/(n - 2))^{1/2}$$

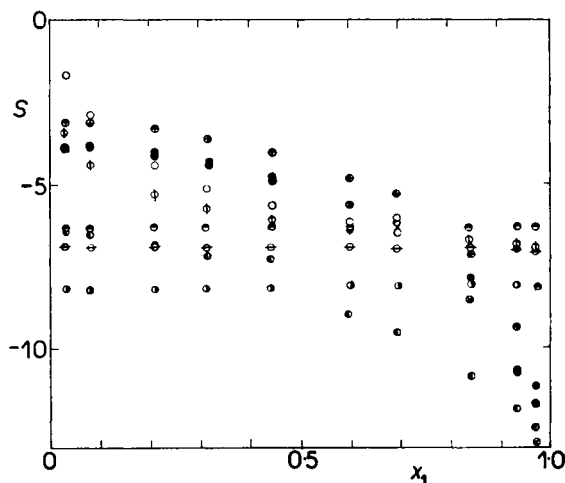


FIG. 1

Effect of errors in input data for the system acetic acid(1)–trifluoroacetic acid(2) on the value of activity coefficient of acetic acid for various compositions. ○ $s_y = 0.001$, ⊙ $s_x = 0.001$, ⊗ $s_T = 0.05$ K, ● $s_P = 50$ Pa, ⊙ $s_{P^0}/P^0 = 0.003$, ● $s_{K_A}/K_A = 0.05$, ⊙ $s_{K_C}/K_C = 0.05$, ⊗ $s_{K_{AC}}/K_{AC} = 0.05$, ● $s_B/B = 0.3$; $S = \frac{1}{2} \ln \left[\sum_i \left(\frac{\partial \ln \gamma}{\partial \xi_i} \right)^2 s_{\xi_i}^2 \right]$

in Table VII. For the system acetic acid–propionic acid, all the results have been roughly equivalent, for the second system, the HMW equation was not able to be used, and the results of correlation by the Orye equation are comparable to those obtained for the Wilson equation.

For the nearly ideal system acetic acid–propionic acid, the back calculation from the correlation equations gives approximately the same average error in the composition of the vapour phase ($\Delta y = 0.002$) as that for the case of ideal solution ($\gamma_1 = \gamma_2 = 1$, $\Delta y = 0.0025$). The activity coefficients estimated by the UNIFAC method result in this case in $\Delta y = 0.0085$.

The high negative deviations from the Raoult law in the system acetic acid–trifluoroacetic acid have been best represented by the two-constant Redlich–Kister

TABLE VII
Constants of correlation equations

Equation	System ^a	$k_1 \pm s(k_1)$	$k_2 \pm s(k_2)$	Covariance (k_1, k_2)	s
Redlich–Kister	1	-1.77 ± 0.02	0.317 ± 0.016	-10^{-4}	1.2
	2	0.104 ± 0.007	-0.049 ± 0.006	-10^{-6}	0.4
Wilson	1	236 ± 22	-800 ± 13	$-14\,352$	2.8
	2	404 ± 22	-283 ± 12	$-19\,044$	0.39
NRTL ($\alpha = 0.47$)	1	-427 ± 7	-136 ± 12	$-5\,041$	1.4
	2	-178 ± 11	286 ± 18	$-14\,400$	0.39

^a 1 system acetic acid(1)–trifluoroacetic acid(2), 2 system acetic acid(1)–propionic acid(2).

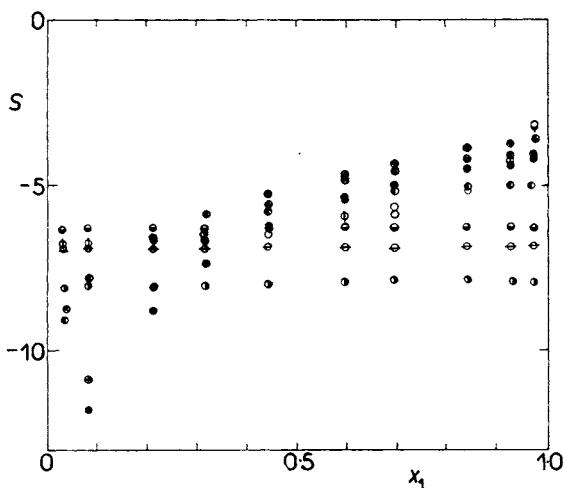


FIG. 2
Effect of errors in input data for the system acetic acid(1)–trifluoroacetic acid(2) on the value of activity coefficient of trifluoroacetic acid for various compositions. Designation is the same as in Fig. 1

equation (in back calculation $\Delta y = 0.008$). A comparison with values obtained by estimating activity coefficients with the UNIFAC method was not possible in this case for, up to now, the interaction parameters of the groups CF—COOH and COOH—CF have not been evaluated. An attempt to evaluate these two group contributions from the measured data on the acetic acid–trifluoroacetic acid was not successful. The best calculated parameters gave at concentration ends as much as 120 per cent deviations in activity coefficients.

FIG. 3

Effect of errors in input data for the system acetic acid(1)–propionic acid(2) on the value of activity coefficient of acetic acid for various compositions. Designation is the same as in Fig. 1 except: $\otimes, \oplus s_{KC}/K_C = s_{KAC}/K_{AC} = 0.1$

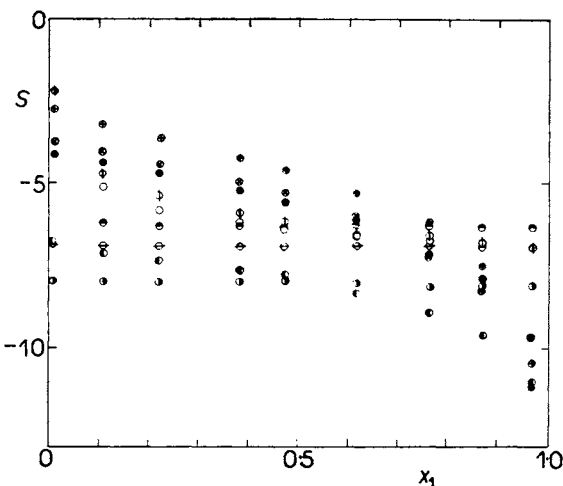
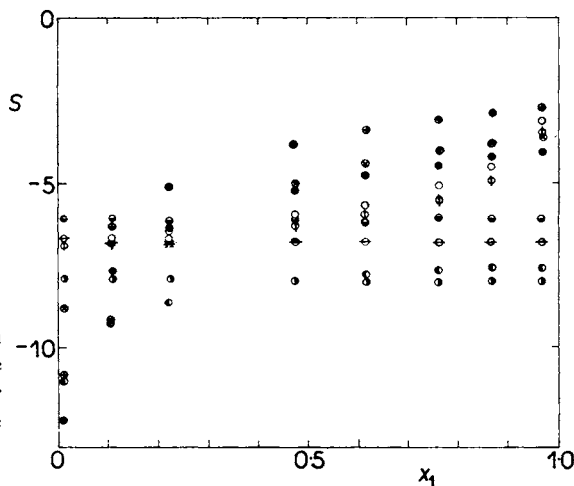


FIG. 4

Effect of errors in input data for the system acetic acid(1)–propionic acid(2) on the value of activity coefficient of propionic acid for various compositions. Designation is the same as in Fig. 3.



The above correlation equations were used in the following form:

Redlich–Kister (two-constant)

$$\ln \gamma_1 = x_2^2 \sum_{i=0}^1 k_{i+1} (x_1 - x_2)^{i-1} (2ix_1 + x_1 - x_2)$$

$$\ln \gamma_2 = x_1^2 \sum_{i=0}^1 k_{i+1} (x_1 - x_2)^{i-1} (-2ix_2 - x_2 + x_1)$$

Wilson

$$\ln \gamma_1 = 1 - \ln (x_1 + x_2 \lambda_{12}) - \frac{x_1}{x_1 + x_2 \lambda_{12}} - \frac{x_2 \lambda_{21}}{x_2 + x_1 \lambda_{21}}$$

$$\ln \gamma_2 = 1 - \ln (x_2 + x_1 \lambda_{21}) - \frac{x_2}{x_2 + x_1 \lambda_{21}} - \frac{x_1 \lambda_{12}}{x_1 + x_2 \lambda_{12}},$$

where

$$\lambda_{12} = \frac{V_{m,2}}{V_{m,1}} \exp\left(-\frac{k_1}{T}\right)$$

$$\lambda_{21} = \frac{V_{m,1}}{V_{m,2}} \exp\left(-\frac{k_2}{T}\right)$$

NRTL

$$\ln \gamma_1 = x_2^2 \left[\frac{k_2}{T} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{k_1}{T} \frac{G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[\frac{k_1}{T} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{k_2}{T} \frac{G_{21}}{(x_1 + x_2 G_{21})^2} \right],$$

where

$$G_{12} = \exp(-\alpha k_1/T)$$

$$G_{21} = \exp(-\alpha k_2/T).$$

LIST OF SYMBOLS

<i>B</i>	second virial coefficient
<i>K</i>	equilibrium constant
<i>T</i>	temperature
<i>P</i>	pressure
<i>NP</i>	number of experimental points
<i>R</i>	gas constant
<i>A, B, C, M, N</i>	constants

V_m	molar volume
f	fugacity
y	composition of the vapour phase
x	composition of the liquid phase
d	density, g cm^{-3}
n_D	refractive index
s	standard deviation
w	statistical weight
μ	chemical potential
γ	activity coefficient
ν	fugacity coefficient

Superscripts

\circ	value for pure substance
*	value of "microscopic" quantity in "macroscopically" pure substance
l	value in liquid

Subscripts

X	refers to "macroscopic" substance X
X1	refers to monomer of substance X
X2	refers to dimer of substance X
XY	refers to heterodimer of substances X, Y
r	reduced quantity
c	critical quantity
st	standard quantity

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