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Thermodynamics of tautomeric solutions: vapour–liquid equilibrium for acetylacetone–alcohol mixtures

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Abstract

Isothermal vapour–liquid equilibrium data for systems containing the keto and enol tautomers of acetylacetone and an alcohol are reproduced using a chemical model. The model uses the thermodynamic equilibrium constant for tautomerisation, the four association constants for the alcohol, the solvation constants between the tautomers and the alcohol and the NRTL model to describe the activity coefficients of the pseudo-three components. Calculated vapour–liquid equilibrium values compare well with literature ones for six binary systems.

INTRODUCTION

Acetylacetone (2,4-pentanedione) has simultaneously keto and enol forms due to tautomerism. These two isomers cannot be separated. A stoichiometric binary liquid mixture containing acetylacetone may be regarded as a pseudo-ternary solution composed of keto tautomer, enol tautomer and an organic solvent. The keto fraction of acetylacetone depends not only on temperature but also the concentration of organic solvent. In a previous paper [1], we presented a chemical model to represent binary isothermal vapour–liquid equilibrium data at 25 °C for mixtures of acetylacetone with benzene, cyclohexane, carbon tetrachloride, toluene and chloroform. Kato [2] measured binary isothermal vapour–liquid equilibria for acetylacetone–alcohol mixtures and correlated the experimental activity coefficients using the UNIFAC model. The association model of alcohol solutions based on mole fraction statistics has been published from this laboratory [3].

In this paper we propose an extended model as a combination of the two chemical models in order to obtain good representation of binary isothermal vapour–liquid equilibria for solutions of acetylacetone with methanol, ethanol, propanols, 2-butanol and 2-methyl-2-propanol.

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SOLUTION MODEL

The vapour–liquid equilibrium for the pseudo-ternary systems composed of the enol and keto tautomers of acetylacetone and an alcohol can be correlated from the equation

$$P = P_E^0 x_E \gamma_E + P_K^0 x_K \gamma_K + P_A^0 x_A \gamma_A \tag{1}$$

where vapour-phase ideality is assumed and the activity coefficients of three constituents are given by the NRTL equation [4]

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l^N x_l \tau_{lj} G_{lj}}{\sum_k^N G_{kj} x_k} \right) \tag{2}$$

with

$$\tau_{ij} = a_{ij}/T \tag{3}$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \tag{4}$$

All the nonrandomness parameters $\alpha_{ij} (= \alpha_{ji})$ are set as 0.3.

The keto and enol tautomers satisfy the thermodynamic equilibrium constant K_T as defined by

$$K_T = (x_K^0 \gamma_K^0 / x_E^0 \gamma_E^0) = (x_K \gamma_K)/(x_E \gamma_E) \tag{5}$$

From the vapour pressure (P^0) and the equilibrium constant (x_K^0/x_E^0) data for pure acetylacetone over the temperature range 22.02–40.01°C [5], we [1] estimated the NRTL energy parameters a_{KE} and a_{EK} and coefficients of the vapour pressures of the keto and enol tautomers given by the equation

$$\log P_i^0 = A_i^0 - B_i^0/T \qquad i = \text{K, E} \tag{6}$$

These are $a_{KE} = 94.87$ K, $a_{EK} = -39.02$ K, $A_K^0 = 8.5568$, $B_K^0 = 2391.03$, $A_E^0 = 8.2710$ and $B_E^0 = 2154.90$.

According to the chemical model for the linear or cyclic self-association of alcohol molecules [3], four association constants are defined in terms of the mole fractions of the alcohol species.

$$K_{A_2} = x_{A_2}/x_{A_1}^2 \qquad \text{for } A_1 + A_1 = A_2 \tag{7}$$

$$K_{A_3} = x_{A_3}/x_{A_2} x_{A_1} \qquad \text{for } A_1 + A_2 = A_3 \tag{8}$$

$$K_A = x_{A_{i+1}}/x_{A_1} x_{A_i} \qquad \text{for } A_1 + A_i = A_{i+1},\ i \geqslant 3 \tag{9}$$

$$K_{cy} = \theta/i = x_{A_i}(\text{cyclic})/x_{A_i}(\text{open}) \qquad \text{for } A_i(\text{open}) = A_i(\text{cyclic}),\ i > 4 \tag{10}$$

The solvation constants between alcohol *i*mers and the tautomers are defined by

$$K_{\mathrm{AK}} = x_{\mathrm{A}_i\mathrm{K}}/x_{\mathrm{A}_i}x_{\mathrm{K}} \qquad \text{for } \mathrm{A}_i + \mathrm{K} = \mathrm{A}_i\mathrm{K} \tag{11}$$

$$K_{\mathrm{AE}} = x_{\mathrm{A}_i\mathrm{E}}/x_{\mathrm{A}_i}x_{\mathrm{E}} \qquad \text{for } \mathrm{A}_i + \mathrm{E} = \mathrm{A}_i\mathrm{E} \tag{12}$$

The stoichiometric mole fractions of the tautomers and the alcohol are expressed in terms of their monomer mole fractions and the equilibrium constants.

$$x_{\mathrm{K}} = \frac{\left\{x_{\mathrm{K}_1} + K_{\mathrm{AK}}x_{\mathrm{K}_1}\left[x_{\mathrm{A}_1} + K_{\mathrm{A}_2}x_{\mathrm{A}_1}^2 + \dfrac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^3}{(1-z)}\right]\right\}}{S} \tag{13}$$

$$x_{\mathrm{E}} = \frac{\left\{x_{\mathrm{E}_1} + K_{\mathrm{AE}}x_{\mathrm{E}_1}\left[x_{\mathrm{A}_1} + K_{\mathrm{A}_2}x_{\mathrm{A}_1}^2 + \dfrac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^3}{(1-z)}\right]\right\}}{S} \tag{14}$$

$$x_{\mathrm{A}} = \left\{\left(1 + K_{\mathrm{AK}}x_{\mathrm{K}_1} + K_{\mathrm{AE}}x_{\mathrm{E}_1}\right)\left[x_{\mathrm{A}_1} + 2K_{\mathrm{A}_2}x_{\mathrm{A}_1}^2 + \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^3(3-2z)}{(1-z)^2}\right]\right.$$
$$\left. + \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}K_{\mathrm{A}}^2\theta x_{\mathrm{A}_1}^5}{(1-z)}\right\}/S \tag{15}$$

where $z = K_{\mathrm{A}}x_{\mathrm{A}_1}$ and the sum S is given by

$$S = x_{\mathrm{K}_1} + x_{\mathrm{E}_1} + \left(K_{\mathrm{AK}}x_{\mathrm{K}_1} + K_{\mathrm{AE}}x_{\mathrm{E}_1}\right)\left[x_{\mathrm{A}_1} + K_{\mathrm{A}_2}x_{\mathrm{A}_1}^2 + \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^3}{(1-z)}\right]$$
$$+ \left(1 + K_{\mathrm{AK}}x_{\mathrm{K}_1} + K_{\mathrm{AE}}x_{\mathrm{E}_1}\right)\left[x_{\mathrm{A}_1} + 2K_{\mathrm{A}_2}x_{\mathrm{A}_1}^2 + \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^3(3-2z)}{(1-z)^2}\right]$$
$$+ \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}K_{\mathrm{A}}^2\theta x_{\mathrm{A}_1}^5}{(1-z)} \tag{16}$$

The monomer mole fraction of the pure alcohol x_{A}^0 is obtained from eqn. (17).

$$x_{\mathrm{A}_1}^0 + K_{\mathrm{A}_2}x_{\mathrm{A}_1}^{02} + \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}x_{\mathrm{A}_1}^{03}}{(1-z^0)} - \frac{K_{\mathrm{A}_2}K_{\mathrm{A}_3}\theta}{K_{\mathrm{A}}^3}$$
$$\times\left[\ln(1-z^0) + z^0 + \frac{z^{02}}{2} + \frac{z^{03}}{3} + \frac{z^{04}}{4}\right] = 1 \tag{17}$$

The chemical potentials of the stoichiometric and true species must be equal [6]. The activity coefficients of the tautomers of acetylacetone and the alcohol can be expressed as the sum of chemical and physical contribution terms.

$$\ln \gamma_i = (\ln \gamma_i)_{\text{chem}} + (\ln \gamma_i)_{\text{phys}} \qquad i = \text{K, E, A} \tag{18}$$

The physical terms of the three constituents are described by eqn. (2) and the chemical terms are given by

$$(\ln \gamma_{\text{K}})_{\text{chem}} = \ln(x_{\text{K}_1}/x_{\text{K}}) \tag{19}$$

$$(\ln \gamma_{\text{E}})_{\text{chem}} = \ln(x_{\text{E}_1}/x_{\text{E}}) \tag{20}$$

$$(\ln \gamma_{\text{A}})_{\text{chem}} = \ln\left(x_{\text{A}_1}/x^0_{\text{A}_1}x_{\text{A}}\right) \tag{21}$$

CALCULATED RESULTS

Values of the vapour pressures of pure alcohols at 25°C were obtained from Kato [2]. We reduced the number of adjustable parameters, assuming that

$$a_{\text{EA}} = \beta a_{\text{KA}} \qquad a_{\text{AE}} = \beta a_{\text{AK}} \qquad K_{\text{AK}} = K_{\text{AE}} \tag{22}$$

In the correlation of vapour–liquid equilibrium data, the program of Prausnitz et al. [7] was modified to provide an optimum set of the parameters minimizing the objective function

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \tag{23}$$

where a circumflex indicates the calculated value and the standard deviations in the measured values were used as $\sigma_P = 1$ Torr, $\sigma_T = 0.05$ K, $\sigma_x = 0.001$ and $\sigma_y = 0.003$. We did not use experimental values of the equilibrium constant $(x_{\text{K}}/x_{\text{E}})$ to obtain x_{K} in the mixtures. An iterative method was used to calculate x_{K}. First, x_{K} is set as x^0_{K}, then γ_{K} and γ_{E} are calculated from eqn. (2). K_{T} is a product of $(x^0_{\text{K}}/x^0_{\text{E}})$ and $(\gamma^0_{\text{K}}/\gamma^0_{\text{E}})$. A new value of x_{K} is calculated using $x_{\text{K}}(\text{new}) = K_{\text{T}}(\gamma_{\text{E}}/\gamma_{\text{K}})(1 - x_{\text{A}})/\{1 + K_{\text{T}}(\gamma_{\text{E}}/\gamma_{\text{K}})\}$ rearranged from eqn. (5). The next iteration starts until $x_{\text{K}}(\text{new})$ satisfies the criterion $|x_{\text{K}}(\text{new}) - x_{\text{K}}(\text{old})| < 10^{-6}$. These calculations are carried out for each set of the parameters.

Tables 1 and 2 show the association constants for pure alcohols at 25°C [3] and the solvation constants $(K_{\text{AK}} = K_{\text{AE}})$ for acetylacetone–alcohol mixtures at 25°C. Table 3 gives values of a_{KA}, a_{AK} and β and the root-mean square deviations between the experimental and calculated variables and Tables 4–9 detailed calculated results for each system. Figures 1–3 compare the calculated results and the experimental values, showing that the agreement is good.

TABLE 1

Association constants for alcohols at 25 ° C

Component	K_{A_2}	K_{A_3}	K_A	θ
Methanol	70	120	100	90
Ethanol	40	110	45	85
1-Propanol	35	90	40	75
2-Propanol	35	85	30	70
2-Butanol	25	60	30	65
2-Methyl-2-propanol	20	40	30	55

TABLE 2

Solvation constants for acetylacetone–alcohol at 25 ° C

Mixture	K_{AE} ($= K_{AK}$)
Acetylacetone–methanol	110
Acetylacetone–ethanol	55
Acetylacetone–1-propanol	45
Acetylacetone–2-propanol	35
Acetylacetone–2-butanol	40
Acetylacetone–2-methyl-2-propanol	35

TABLE 3

Calculated results obtained from vapour–liquid equilibrium data reduction for binary mixtures of acetylacetone with alcohols at 25 ° C

	Number of data points	Parameters			Root-mean-square deviations				Variance of fit [a]
		a_{KA} (K)	a_{AK} (K)	β	δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	
Acetylacetone–methanol	10	188.91	154.03	1.20	0.54	0.00	0.1	2.8	1.71
Acetylacetone–ethanol	8	124.54	290.62	1.06	0.98	0.00	0.0	5.1	6.21
Acetylacetone–1-propanol	12	167.36	274.99	0.81	0.51	0.00	0.0	10.3	15.97
Acetylacetone–2-propanol	10	97.02	262.97	1.09	0.97	0.00	0.1	3.9	3.82
Acetylacetone–2-butanol	9 [b]	59.81	388.06	0.94	0.72	0.01	0.5	12.5	27.23
Acetylacetone–2-methyl-2-propanol	12	181.70	114.95	1.28	0.62	0.01	0.6	3.9	3.26

[a] Variance of fit = (sum of squared, weighted residuals)/(number of data points – number of parameters).

[b] We rejected one experimental point which deviated greatly.

TABLE 4

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–methanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT (K)	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100y_K/y_1$ [b] (%)	$100x_K/x_1$ [c] (%)
1	114.80	−0.10	0.00	0.139	−0.0001	0.035	0.0069	2.1783	2.5133	1.0313	7.26	22.50
2	107.46	0.76	0.00	0.288	0.0000	0.050	0.0020	1.7272	1.9056	1.1342	7.26	21.73
3	101.28	−0.06	0.00	0.388	0.0000	0.059	0.0005	1.5182	1.6266	1.2395	7.26	21.24
4	91.76	0.39	0.00	0.544	0.0000	0.077	0.0021	1.2960	1.3276	1.4736	7.26	20.50
5	91.87	1.25	0.00	0.554	0.0001	0.076	−0.0001	1.2853	1.3129	1.4921	7.26	20.45
6	83.33	0.02	0.00	0.638	−0.0001	0.089	0.0011	1.2084	1.2052	1.6689	7.26	20.07
7	76.96	−0.36	0.00	0.694	−0.0001	0.099	0.0005	1.1698	1.1484	1.8114	7.26	19.81
8	58.03	−0.08	0.00	0.824	−0.0001	0.142	−0.0021	1.1155	1.0555	2.2474	7.26	19.23
9	41.52	0.64	0.00	0.903	0.0002	0.215	−0.0033	1.1053	1.0226	2.6132	7.26	18.89
10	34.09	−0.21	0.00	0.927	−0.0001	0.263	−0.0028	1.1056	1.0158	2.7473	7.26	18.78
AAM [d]		0.39	0.00		0.0001		0.0021					

[a] δ, measured value − calculated one.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

TABLE 5

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–ethanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100 y_K/y_1$ [b]	$100 x_K/x_1$ [c]
1	57.57	1.15	0.00	0.064	0.0000	0.037	0.0011	3.1699	3.3613	0.9946	7.26	21.07
2	54.84	1.50	0.00	0.190	0.0000	0.079	0.0014	2.3203	2.3850	1.0365	7.26	20.55
3	53.67	1.53	0.00	0.251	0.0000	0.093	−0.0018	2.0458	2.0741	1.0784	7.26	20.33
4	50.21	0.98	0.00	0.418	0.0000	0.131	0.0071	1.5572	1.5262	1.2683	7.26	19.79
5	48.30	0.46	0.00	0.491	0.0000	0.138	0.0026	1.4230	1.3763	1.3907	7.26	19.58
6	42.14	−0.66	0.00	0.663	0.0000	0.182	0.0104	1.2223	1.1496	1.8005	7.26	19.14
7	32.99	0.10	0.00	0.823	0.0000	0.256	0.0033	1.1347	1.0434	2.3769	7.26	18.79
8	23.55	0.44	0.00	0.914	0.0000	0.384	−0.0052	1.1161	1.0145	2.8090	7.26	18.62
AAM [d]		0.85	0.00		0.0000		0.0041					

[a] δ, measured value − calculated value.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

TABLE 6

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–1-propanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100 y_K / y_1$ [b] (%)	$100 x_K / x_1$ [c] (%)
1	21.39	0.25	0.00	0.083	0.0000	0.119	0.0187	3.2508	2.5704	1.0032	7.26	16.60
2	21.42	0.07	0.00	0.191	0.0000	0.188	0.0064	2.5446	2.0484	1.0450	7.26	16.85
3	21.54	0.20	0.00	0.264	0.0000	0.218	−0.0015	2.2036	1.7942	1.0951	7.26	17.01
4	21.45	0.13	0.00	0.291	0.0000	0.229	−0.0024	2.0980	1.7152	1.1182	7.26	17.06
5	21.32	0.01	0.00	0.302	0.0000	0.213	−0.0230	2.0578	1.6851	1.1284	7.26	17.09
6	20.48	−0.56	0.00	0.430	0.0000	0.276	−0.0069	1.6844	1.4050	1.2805	7.26	17.35
7	21.22	0.45	0.00	0.501	0.0000	0.306	−0.0009	1.5361	1.2939	1.3954	7.26	17.49
8	20.07	−0.46	0.00	0.546	0.0000	0.339	0.0161	1.4585	1.2360	1.4813	7.26	17.58
9	19.23	−0.54	0.00	0.643	0.0000	0.359	−0.0039	1.3260	1.1383	1.7067	7.26	17.77
10	16.90	−0.97	0.00	0.773	0.0000	0.446	0.0005	1.2069	1.0539	2.1115	7.26	18.02
11	14.18	−0.84	0.00	0.881	0.0000	0.577	−0.0041	1.1476	1.0164	2.5573	7.26	18.23
12	11.28	−0.61	0.00	0.959	0.0000	0.788	−0.0008	1.1235	1.0053	2.9638	7.26	18.38
AAM [d]		0.42	0.00		0.0000		0.0071					

[a] δ, measured value − calculated value.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

TABLE 7

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–2-propanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100 y_K / y_1$ [b] (%)	$100 x_K / x_1$ [c] (%)
1	42.35	0.42	0.00	0.052	−0.0001	0.043	0.0072	2.8290	3.0717	0.9947	7.26	21.46
2	42.60	1.71	0.00	0.114	−0.0001	0.072	0.0036	2.4464	2.6105	1.0027	7.26	21.17
3	40.16	1.20	0.00	0.250	0.0000	0.120	0.0026	1.8763	1.9333	1.0691	7.26	20.59
4	39.92	1.53	0.00	0.296	0.0000	0.126	−0.0038	1.7414	1.7748	1.1066	7.26	20.41
5	37.74	1.02	0.00	0.437	0.0000	0.160	−0.0021	1.4442	1.4270	1.2747	7.26	19.92
6	34.80	−0.08	0.00	0.565	0.0000	0.194	0.0024	1.2791	1.2326	1.5117	7.26	19.52
7	31.94	−0.19	0.00	0.684	0.0000	0.230	0.0008	0.1848	1.1178	1.8281	7.26	19.19
8	25.92	−0.79	−0.01	0.813	−0.0001	0.307	−0.0002	1.1293	1.0436	2.3089	7.26	18.87
9	23.01	−0.77	0.00	0.859	−0.0001	0.358	−0.0014	1.1193	1.0272	2.5216	7.26	18.76
10	17.32	−0.51	0.00	0.930	0.0001	0.504	−0.0075	1.1128	1.0108	2.8987	7.26	18.61
AAM [d]		0.82	0.00		0.0001		0.0032					

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[a] δ, measured value – calculated value.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

TABLE 8

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–2-butanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT (K)	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100 y_K/y_1$ [b] (%)	$100 x_K/x_1$ [c] (%)
1	18.48	0.10	−0.01	0.046	−0.0009	0.100	0.0155	3.7384	3.4223	0.9973	7.26	18.72
2	18.99	−0.09	−0.01	0.161	−0.0001	0.203	0.0055	2.6425	2.4122	1.0313	7.26	18.68
3	17.97	−0.99	0.01	0.390	0.0000	0.297	−0.0020	1.6512	1.4991	1.2312	7.26	18.60
4	17.51	−1.07	0.00	0.491	0.0000	0.342	0.0068	1.4421	1.3065	1.3710	7.26	18.57
5	17.37	−1.06	−0.02	0.518	−0.0002	0.366	0.0200	1.3990	1.2669	1.4136	7.26	18.56
6	16.24	−1.01	0.00	0.661	0.0000	0.420	0.0043	1.2369	1.1173	1.6803	7.26	18.52
7	15.04	−0.58	−0.01	0.776	−0.0001	0.508	0.0012	1.1638	1.0495	1.9433	7.26	18.50
8	14.01	0.03	−0.02	0.856	−0.0008	0.623	0.0136	1.1343	1.0219	2.1532	7.26	18.49
9	12.24	0.17	0.01	0.930	0.0008	0.732	−0.0219	1.1203	1.0085	2.3697	7.26	18.47
AAM [d]		0.57	0.01		0.0003		0.0101					

[a] δ, measured value − calculated value.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

TABLE 9

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(1)–2-methyl-2-propanol(2) system at 25 ° C

No.	P (Torr)	δP [a] (Torr)	δT (K)	x_1	δx	y_1	δy	γ_K	γ_E	γ_2	$100 y_K/y_1$ [b] (%)	$100 x_K/x_1$ [c] (%)
1	40.94	0.22	0.00	0.118	0.0000	0.065	0.0007	2.0196	2.4268	1.0305	7.26	23.22
2	39.56	−0.56	0.00	0.177	−0.0001	0.093	0.0043	1.8537	2.1860	1.0600	7.26	22.89
3	39.79	0.02	0.01	0.210	0.0002	0.097	−0.0035	1.7726	2.0687	1.0801	7.26	22.70
4	37.25	−0.56	0.01	0.365	0.0001	0.143	−0.0038	1.4706	1.6338	1.2118	7.26	21.85
5	35.06	−0.70	0.01	0.484	0.0001	0.174	−0.0042	1.3120	1.4034	1.3582	7.26	21.21
6	33.24	−1.53	−0.01	0.530	−0.0002	0.194	0.0025	1.2640	1.3321	1.4272	7.26	20.96
7	32.27	−0.75	0.01	0.600	0.0001	0.208	−0.0052	1.2044	1.2409	1.5487	7.26	20.59
8	27.32	−0.44	−0.01	0.750	−0.0002	0.283	−0.0013	1.1220	1.1003	1.8971	7.26	19.80
9	25.27	0.54	0.02	0.813	0.0005	0.327	−0.0072	1.1051	1.0612	2.0945	7.26	19.46
10	17.06	0.29	0.02	0.931	0.0012	0.539	−0.0046	1.1005	1.0150	2.6006	7.26	18.84
11	14.96	−0.12	0.00	0.949	−0.0001	0.616	−0.0004	1.1034	1.0108	2.7123	7.26	18.74
12	13.61	−0.01	−0.01	0.963	−0.0015	0.695	0.0024	1.1064	1.0081	2.8171	7.26	18.66
AAM [d]		0.48	0.01		0.0004		0.0033					

[a] δ, measured value − calculated value.

[b] Keto form in the vapour phase.

[c] Keto form in the liquid phase.

[d] AAM, absolute arithmetic mean deviation.

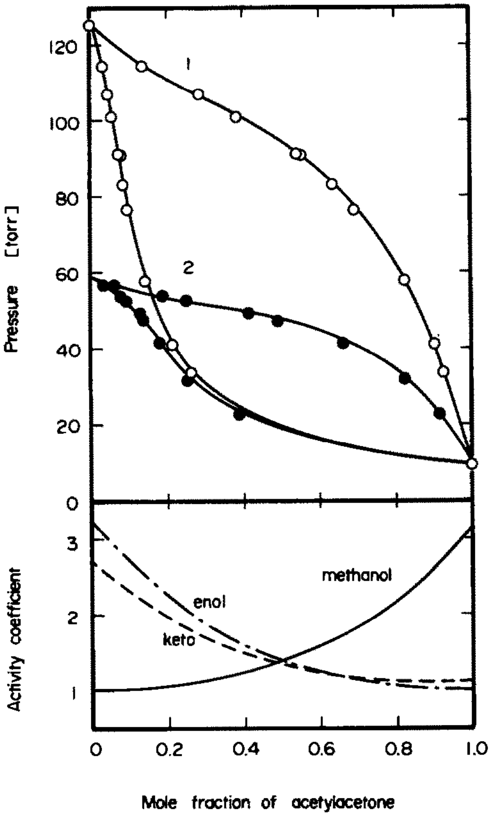


Fig. 1. Vapour–liquid equilibria for pseudo-ternary systems at 25 °C. Experimental data of Kato [2]: 1, acetylacetone–methanol (o); 2, acetylacetone–ethanol (●). Calculated (———, – – – –, —·—·—).

We may conclude that the present model is useful in the correlation of vapour–liquid equilibria for solutions containing the tautomers of acetylacetone and an alcohol.

Fig. 3. Vapour–liquid equilibria for pseudo-ternary systems at 25 °C. Experimental data of Kato [2]: 1, acetylacetone–2-methyl-2-propanol (o); 2, acetylacetone–2-butanol (●). Calculated (———, – – – –, —·—·—).

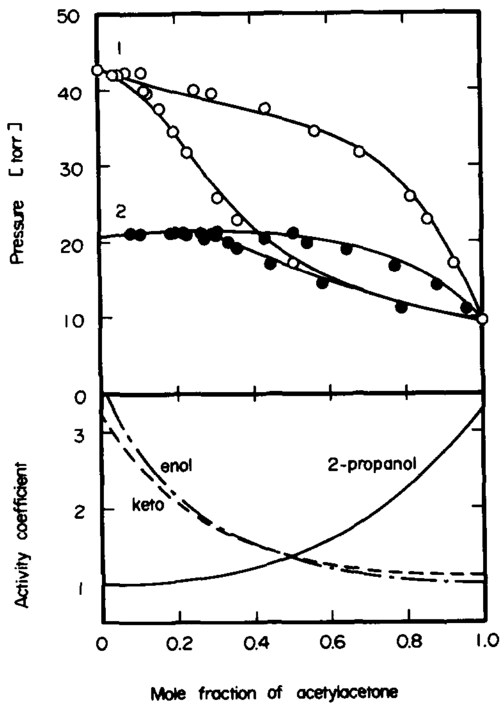
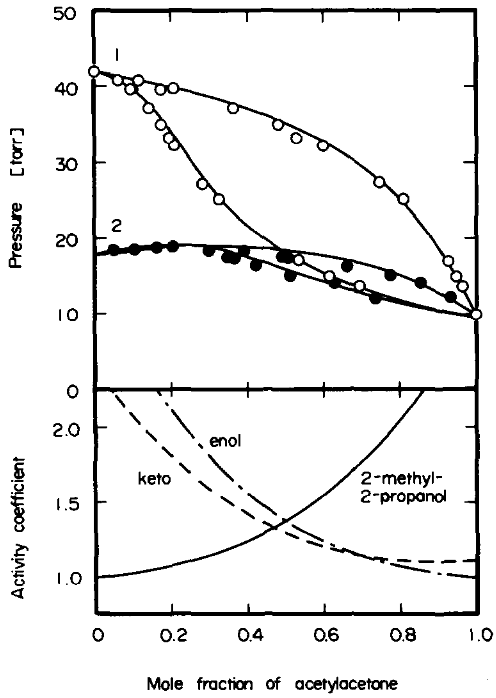


Fig. 2. Vapour–liquid equilibria for pseudo-ternary systems at 25 °C. Experimental data of Kato [2]: 1, acetylacetone–2-propanol (o); 2, acetylacetone–1-propanol (●). Calculated (——, – – – –, —·—·—).



LIST OF SYMBOLS

a_{ij}	NRTL interaction parameter for i–j pair
A^0_E, A^0_K	coefficients of vapour pressure equation defined by eqn. (6)
B^0_E, B^0_K	coefficients of vapour pressure equation defined by eqn. (6)
F	objective function as defined by eqn. (23)
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
K_A	equilibrium constant for open-chain polymer formation of alcohol, $i > 3$
K_{A_2}	equilibrium constant for dimer formation of alcohol
K_{A_3}	equilibrium constant for open-chain trimer of alcohol
K_{AE}, K_{AK}	solvation constants between the enol and keto forms of acetylacetone and open-chain polymers of alcohol
K_{cy}	equilibrium constant for cyclisation of open-chain polymer of alcohol as defined by θ/i, $i > 4$
K_T	thermodynamic equilibrium constant
P	total pressure
P_i^0	vapour pressure of pure chemical species i
R	universal gas constant
T	absolute temperature
x_i	liquid-phase mole fraction of chemical species i
y_i	vapour-phase mole fraction of chemical species i
z	coefficient as defined by $K_A x_{A_1}$

Greek letters

α_{ij}	nonrandomness parameter for i–j pair
β	constant
γ_i	activity coefficient of chemical species i
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid-phase mole fraction and vapour-phase mole fraction
τ_{ij}	coefficient as defined by a_{ij}/T

Subscripts

A, E, K	alcohol, enol and keto forms of acetylacetone
A_1, E_1, K_1	monomers of alcohol and enol and keto forms of acetylacetone
A_iE, A_iK	chemical complexes composed of open-chain polymer of alcohol $i$mer and one of the tautomers of acetylacetone
chem	chemical
i, j, k, l	chemical species
phys	physical

Superscript

^{0}	pure liquid state

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