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THERMODYNAMICS OF TAUTOMERIC SOLUTIONS: VAPOUR–LIQUID EQUILIBRIUM FOR ACETYLACETONE–NON-ASSOCIATING COMPONENT MIXTURES

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ABSTRACT

A method is proposed for calculating isothermal vapour–liquid equilibria for binary mixtures of acetylacetone with non-associating components. It uses the thermodynamic equilibrium constant of the tautomerization of acetylacetone and the NRTL equation for expressing the activity coefficients of the keto and enol tautomers of acetylacetone and non-associating components. Calculated values agree satisfactorily with experimental results, showing the utility of the proposed method.

INTRODUCTION

Acetylacetone (2,4-pentanedione) has two tautomers of enol and keto forms, which cannot be separated experimentally. A binary mixture of acetylacetone and an organic solvent is considered as a pseudo-ternary mixture of two tautomers of acetylacetone and an organic solvent. Inoue et al. [1] measured the vapour–liquid equilibria of pure acetylacetone and various acetylacetone–organic solvent mixtures, namely acetylacetone–cyclohexane, –carbon tetrachloride, –toluene, –benzene and –chloroform at 25 °C over the whole concentration range, and calculated the activity coefficients for keto and enol tautomers of acetylacetone and solvents by means of the Wilson equation using experimental results on the temperature-dependence of the tautomerization and the effect of solvents on the keto–enol equilibrium. Dallos and Ratkovics [2] presented a method for calculating isothermal vapour–liquid equilibria for three binary mixtures out of the five studied by Inoue et al.: acetylacetone–benzene, –cyclohexane and –carbon tetrachloride [1]. Dallos and Ratkovics [2] used the thermodynamic

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equilibrium constant of the tautomerization K_T defined by the activities of the tautomers

$$K_T = (x_K^0 \gamma_K^0)/(x_E^0 \gamma_E^0) = (x_K \gamma_K)/(x_E \gamma_E) \tag{1}$$

where the activity coefficients of the tautomers are calculated from the UNIQUAC model [3] and the mole fractions of the tautomers in the solvent can be estimated in the whole range of solvent composition $(0 < x_S < 1)$ using experimental values of the ratios of the tautomers in pure acetylacetone and in infinitely diluted solution.

$$\ln(x_E/x_K) = (1 - x_S) \ln(x_E^0/x_K^0) + x_S \ln(x_E^\infty/x_K^\infty) \tag{2}$$

We present another approach to correlate isothermal vapour–liquid equilibria for the five mixtures cited above.

SOLUTION MODEL

We also use the thermodynamic equilibrium constant K_T given by eqn. (1) for the keto–enol equilibria in pure acetylacetone and in binary mixtures of acetylacetone with solvent components. The activity coefficient of any chemical species i is expressed by the NRTL model [4]

$$\ln \gamma_i = \frac{\sum_j^N \tau_{ji} G_{ji} x_j}{\sum_k^N G_{ki} x_k} + \sum_j^N \frac{x_j G_{ij}}{\sum_k^N G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l^N x_l \tau_{lj} G_{lj}}{\sum_k^N G_{kj} x_k} \right) \tag{3}$$

with $\tau_{ij} = a_{ij}/T$ and $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, where the non-randomness parameters $\alpha_{ij} (= \alpha_{ji})$ are taken as 0.3 throughout this work.

The vapour pressures over the temperature range 22.02–40.01° C and the equilibrium constants x_K^0/x_E^0 in the range 10–40 ° C for pure acetylacetone, measured by Inoue et al. [1] are represented by eqns. (4) and (5)

$$\log P(\text{Torr}) = 8.09857 - 2119.52/T \tag{4}$$

$$\log(x_K^0/x_E^0) = -477.9/T + 0.9578 \tag{5}$$

Assuming the vapour phase ideality of acetylacetone, we can express the total pressure of acetylacetone as the sum of the partial pressure of the tautomers of acetylacetone

$$P_A = P_K^0 x_K^0 \gamma_K^0 + P_E^0 x_E^0 \gamma_E^0 \tag{6}$$

where the subscripts K and E denote the keto and enol forms, respectively, and the vapour pressures of the tautomers are represented by

$$\log P_I^0 \ (\text{Torr}) = A_I - B_I/T \qquad I = \text{K, E} \tag{7}$$

Two NRTL energy parameters, a_{KE} and a_{EK}, and the coefficients of eqn. (7) can be obtained by minimizing the sum of the squares of the deviations between calculated and experimental total pressures. A simplex method was used for minimization [5]. The values obtained are

$$a_{KE} = 94.87 \text{ K}; \ a_{EK} = -39.02 \text{ K} \tag{8}$$

$$\log P_K^0 \text{ (Torr)} = 8.5568 - 2391.03/T \text{ (K)} \tag{9}$$

$$\log P_E^0 \text{ (Torr)} = 8.2710 - 2154.90/T \text{ (K)} \tag{10}$$

We assume that acetylacetone tautomers and chloroform form 1 : 1 chemical complexes and hence their solvation constants are defined by

$$K_{KC} = \frac{x_{KC}}{x_{K_1} x_{C_1}} \qquad \text{for } x_{K_1} + x_{C_1} = x_{KC} \tag{11}$$

$$K_{EC} = \frac{x_{EC}}{x_{E_1} x_{C_1}} \qquad \text{for } x_{E_1} + x_{C_1} = x_{EC} \tag{12}$$

The nominal mole fractions of the tautomers of acetylacetone are related to the true mole fractions of chemical species present.

$$x_K = \frac{x_{K_1} + K_{KC} x_{K_1} x_{C_1}}{x_{K_1} + 2x_{KC} + x_{E_1} + 2x_{EC} + x_{C_1}} = \frac{x_{K_1} + K_{KC} x_{K_1} x_{C_1}}{1 + K_{KC} x_{K_1} x_{C_1} + K_{EC} x_{E_1} x_{C_1}} \tag{13}$$

$$x_E = \frac{x_{E_1} + K_{EC} x_{E_1} x_{C_1}}{1 + K_{KC} x_{K_1} x_{C_1} + K_{EC} x_{E_1} x_{C_1}} \tag{14}$$

$$x_C = \frac{x_{C_1} + K_{KC} x_{K_1} x_{C_1} + K_{EC} x_{E_1} x_{C_1}}{1 + K_{KC} x_{K_1} x_{C_1} + K_{EC} x_{E_1} x_{C_1}} \tag{15}$$

The total vapour pressure P of acetylacetone–organic solvent systems is given by

$$P = P_K^0 x_K \gamma_K + P_E^0 x_E \gamma_E + P_S^0 x_S \gamma_S \tag{16}$$

and the vapour phase mole fraction of acetylacetone is calculated by

$$y_A = \frac{y_K + y_E}{y_K + y_E + y_S} = \frac{P_K^0 x_K \gamma_K + P_E^0 x_E \gamma_E}{P_K^0 x_K \gamma_K + P_E^0 x_E \gamma_E + P_S^0 x_S \gamma_S} \tag{17}$$

where P_S^0 is the vapour pressure of the pure organic solvent. In the expressions of the activity coefficients for three components, the keto and enol forms of acetylacetone and the non–polar organic solvent, the nominal mole fractions x_K, x_E and x_S are used, and the activity coefficients for the acetylacetone–chloroform system were calculated from $\ln \gamma_I = \ln (x_{I_1}/x_I) +$ eqn. (3), I = K, E, C. Four energy parameters a_{KS}, a_{SK}, a_{ES} and a_{SE} are obtained in fitting the model to the experimental vapour–liquid equilibrium data. A parameter estimation program is similar to that described by Prausnitz et al. [6] minimizing the objective function

$$F=\sum_{i=1}^{N}\left[\frac{(P_i-\hat{P}_i)^2}{\sigma_P^2}+\frac{(T_i-\hat{T}_i)^2}{\sigma_T^2}+\frac{(x_{1i}-\hat{x}_{1i})^2}{\sigma_x^2}+\frac{(y_{1i}-\hat{y}_{1i})^2}{\sigma_y^2}\right] \tag{18}$$

where the standard deviations are as follows: $\sigma_P = 1$ Torr; $\sigma_T = 0.05$ K; $\sigma_x = 0.001$; $\sigma_y = 0.003$, and a circumflex represents the calculated value.

In order to reduce the number of adjustable energy parameters we assumed that

$$a_{\mathrm{ES}}=\beta a_{\mathrm{KS}}; \qquad a_{\mathrm{SE}}=\beta a_{\mathrm{SK}} \tag{19}$$

For the acetylacetone–chloroform system $K_{\mathrm{KC}} = 1.2$ and $K_{\mathrm{EC}} = 2$ at 25 °C were used and for the other systems $K_{\mathrm{KC}} = K_{\mathrm{EC}} = 0$. Values of P_{S}^{0} were taken from Inoue et al. [1].

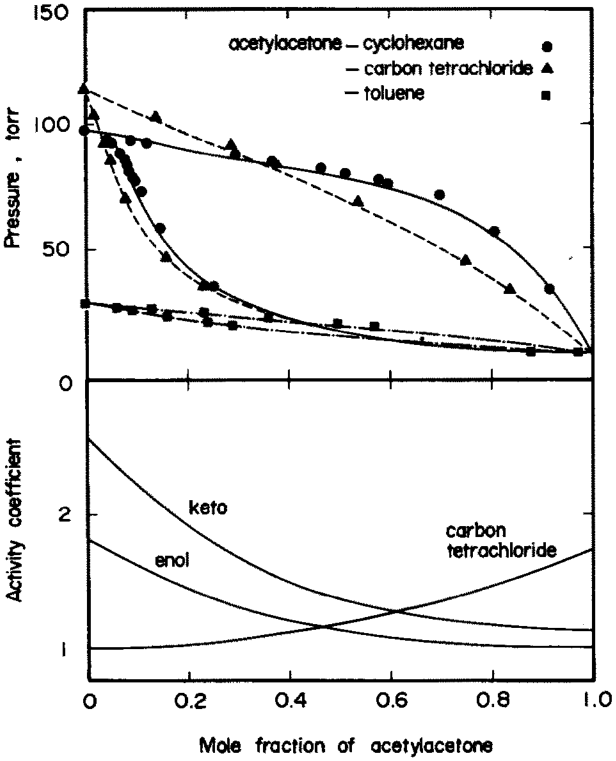

Fig. 1. Vapour–liquid equilibria for pseudo-ternary systems at 25 °C. Experimental (●, ▲, ■). Calculated (———, - - - - - -, ·—·—·).

CALCULATED RESULTS

Table 1 summarizes calculated results for the five binary systems and detailed results are given in Tables 2–6. The vapour phase keto fractions of acetylacetone in the systems studied are calculated and shown in Tables 2–6 as $100y_K/y_A$. A constant value of y_K/y_A means that the solvents have no effect in the vapour phase. The keto fractions of acetylacetone in the liquid phase increase with increase in acetylacetone composition as shown by experimental results [1]. Figures 1 and 2 illustrate the experimental and calculated results for the five binary systems.

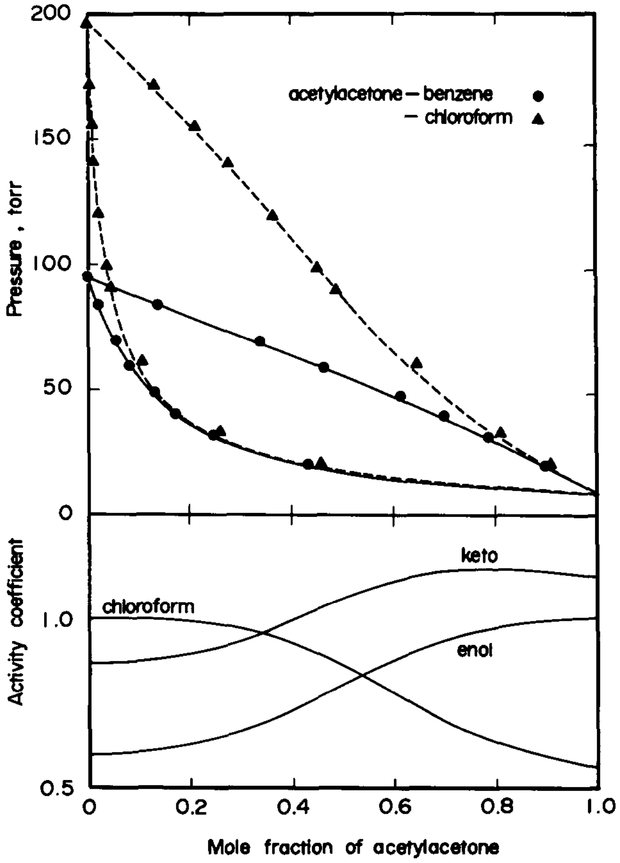

Fig. 2. Vapour–liquid equilibria for pseudo-ternary systems at 25 °C. Experimental (●, ▲). Calculated (———, - - - - - -).

TABLE 1

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

	Number of data points	Parameters			Root-mean-square deviations				Variance of fit [a]
		a_{KS} (K)	a_{SK} (K)	β	δP (Torr)	δT (K)	δx ($\times 10^3$)	δy ($\times 10^3$)	
Acetylacetone –cyclohexane	11	300.71	873.15	0.41	1.28	0.01	0.5	6.5	9.13
Acetylacetone –carbon tetrachloride	6	−24.32	326.93	0.64	1.64	0.00	0.0	2.6	6.89
Acetylacetone –toluene	6	−179.51	453.09	0.43	0.49	0.01	0.9	8.6	18.96
Acetylacetone –benzene	7	167.05	−18.15	0.42	1.61	0.01	0.2	4.7	8.93
Acetylacetone –chloroform	9	−86.72	299.96	0.89	2.25	0.01	0.3	3.4	9.66

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

TABLE 2

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(A)–cyclohexane(S) system at 25 ° C

No.	P_m (Torr)	δP [a] (Torr)	δT (K)	x_A	δx	y_A	δy	γ_K	γ_E	γ_S	$100 y_K / y_A$ [b] (%)	$100 x_K / x_A$ [c] (%)
1	93.70	−0.15	0.00	0.092	−0.0002	0.044	0.0062	17.5861	3.3846	1.0183	7.26	4.62
2	92.82	0.20	0.00	0.124	−0.0002	0.052	−0.0061	13.8952	3.0289	1.0329	7.26	5.20
3	88.57	1.30	−0.01	0.299	0.0000	0.074	0.0043	5.1279	1.8613	1.1857	7.26	8.37
4	86.65	1.23	−0.01	0.373	0.0000	0.080	0.0048	3.7683	1.5977	1.2899	7.26	9.64
5	84.06	1.26	−0.01	0.469	0.0000	0.087	0.0053	2.7192	1.3628	1.4660	7.26	11.20
6	81.76	0.56	−0.01	0.517	0.0000	0.091	0.0056	2.3703	1.2772	1.5742	7.26	11.94
7	79.31	0.86	−0.01	0.582	0.0000	0.098	0.0066	2.0146	1.1862	1.7458	7.26	12.91
8	77.89	0.37	−0.01	0.600	−0.0001	0.101	0.0076	1.9341	1.1653	1.7992	7.26	13.17
9	73.67	3.21	−0.02	0.702	0.0001	0.117	0.0079	1.5841	1.0749	2.1561	7.26	14.59
10	59.08	1.20	−0.02	0.809	−0.0002	0.152	0.0090	1.3479	1.0209	2.6616	7.26	16.01
11	35.80	−0.58	−0.02	0.915	−0.0016	0.255	0.0066	1.1958	1.0004	3.3558	7.26	17.40
AAM [d]		0.99	0.01		0.0002		0.0064					

[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 3

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(A)–carbon tetrachloride(S) system at 25 °C

No.	P_m (Torr)	δP [a] (Torr)	δT	x_A	δx	y_A	δy	γ_K	γ_E	γ_S	$100 y_K / y_A$ [b] (%)	$100 x_K / x_A$ [c] (%)
1	103.29	1.72	0.00	0.143	0.0000	0.020	−0.0019	2.0910	1.5486	1.0168	7.26	15.71
2	92.42	2.45	0.00	0.291	0.0000	0.041	−0.0014	1.6843	1.3156	1.0659	7.26	16.43
3	85.49	2.24	0.00	0.377	0.0000	0.054	−0.0009	1.5258	1.2232	1.1079	7.26	16.79
4	70.57	1.43	0.00	0.544	0.0000	0.084	−0.0015	1.3196	1.1034	1.2164	7.26	17.39
5	47.08	0.13	0.00	0.754	0.0000	0.163	0.0018	1.1802	1.0272	1.4043	7.26	17.97
6	35.80	−0.11	0.00	0.838	0.0000	0.236	0.0055	1.1490	1.0129	1.4963	7.26	18.16
AAM [d]		1.35	0.00		0.0000		0.0022					

[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 4

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(A)–toluene(S) system at 25 °C

No.	P_m (Torr)	δP [a] (Torr)	δT (K)	x_A	δx	y_A	δy	γ_K	γ_E	γ_S	$100y_K/y_A$ [b] (%)	$100x_K/x_A$ [c] (%)
1	26.86	0.17	−0.01	0.131	−0.0002	0.063	−0.0003	1.7523	1.2783	1.0097	7.26	15.51
2	25.77	0.56	0.02	0.235	0.0001	0.094	−0.0162	1.5253	1.1883	1.0286	7.26	16.39
3	23.87	0.58	0.01	0.361	0.0001	0.163	−0.0072	1.3482	1.1140	1.0613	7.26	17.21
4	21.59	0.57	−0.01	0.497	−0.0001	0.242	−0.0043	1.2322	1.0631	1.1051	7.26	17.84
5	20.31	0.63	−0.02	0.570	−0.0003	0.291	−0.0049	1.1913	1.0445	1.1313	7.26	18.08
6	10.72	0.09	0.01	0.970	0.0022	0.879	−0.0096	1.1161	1.0053	1.2886	7.26	18.48
AAM [d]		0.43	0.01		0.0005		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 5

Detailed calculated results for the vapour–liquid equilibria of the acetylacetone(A)–benzene(S) system at 25 °C

No.	P_m (Torr)	δP [a] (Torr)	δT (K)	x_A	δx	y_A	δy	γ_K	γ_E	γ_S	$100y_K/y_A$ [b] (%)	$100x_K/x_A$ [c] (%)
1	84.59	0.51	0.00	0.137	0.0000	0.021	0.0023	1.4258	1.1593	1.0037	7.26	16.99
2	70.01	1.91	0.00	0.339	0.0000	0.056	0.0024	1.3197	1.0925	1.0235	7.26	17.24
3	59.96	1.73	0.00	0.464	0.0000	0.082	−0.0012	1.2648	1.0605	1.0457	7.26	17.42
4	48.70	2.62	0.00	0.614	0.0000	0.131	−0.0039	1.2094	1.0313	1.0842	7.26	17.67
5	40.63	1.83	0.00	0.700	0.0000	0.173	−0.0071	1.1826	1.0192	1.1130	7.26	17.83
6	32.05	0.98	−0.01	0.787	0.0000	0.246	−0.0043	1.1591	1.0105	1.1480	7.26	18.00
7	20.78	0.05	−0.02	0.895	−0.0005	0.431	0.0077	1.1349	1.0048	1.2009	7.26	18.22
AAM [d]		1.38	0.01		0.0001		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(A)–chloroform(S) system at 25 ° C

No.	P_m (Torr)	δP [a] (Torr)	δT (K)	x_A	δx	y_A	δy	γ_K	γ_E	γ_S	$100y_K/y_A$ [b] (%)	$100x_K/x_A$ [c] (%)
1	171.84	1.21	0.00	0.134	0.0002	0.003	−0.0018	0.8813	0.6085	0.9999	7.26	14.80
2	155.75	1.03	0.00	0.213	0.0001	0.008	−0.0007	0.8966	0.6269	0.9938	7.26	14.96
3	140.97	0.29	0.00	0.278	0.0000	0.013	−0.0001	0.9226	0.6536	0.9809	7.26	15.13
4	120.54	−0.53	0.00	0.363	−0.0002	0.022	0.0008	0.9705	0.7024	0.9492	7.26	15.41
5	100.11	0.54	0.00	0.453	−0.0001	0.038	0.0030	1.0299	0.7665	0.8961	7.26	15.78
6	91.29	0.74	0.00	0.491	−0.0001	0.049	0.0058	1.0547	0.7956	0.8684	7.26	15.96
7	61.91	4.85	−0.01	0.648	0.0004	0.107	0.0050	1.1304	0.9057	0.7416	7.26	16.78
8	33.92	3.34	−0.02	0.813	−0.0007	0.261	0.0055	1.1474	0.9773	0.6233	7.26	17.66
9	21.85	2.64	−0.01	0.907	−0.0004	0.459	−0.0007	1.1360	0.9965	0.5718	7.26	18.09
AAM [d]		1.69	0.01		0.0003		0.0026					

[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.

CONCLUSIONS

The proposed method is able to reproduce successfully isothermal vapour–liquid equilibria for the five binary systems of acetylacetone with non-associated components studied. The method does not use experimental results of the effect of solvents on the keto–enol equilibrium for acetylacetone in organic solvents and it will be applied for predicting ternary phase equilibria on mixtures of acetylacetone with non-associated components without any additional ternary information. The present approach is extended to correlate isothermal vapour–liquid equilibria for mixtures of acetylacetone with associating components. This work is in progress.

LIST OF SYMBOLS

a_{ij}	binary interaction parameter for *i–j* pair
A, B	constants of eqn. 7
F	objective function as defined by eqn. 8
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
K_{EC}, K_{KC}	solvation constants between the enol and keto forms of acetylacetone and chloroform
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*

Greek letters

α_{ij}	non-randomness 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, C, E, K	acetylacetone, chloroform and enol and keto forms of acetylacetone
C_1, E_1, K_1	monomers of chloroform and enol and keto forms of acetylacetone
EC, KC	chemical complexes of enol and keto forms of acetylacetone with chloroform
i, *j*, *k*, *l*	chemical species
S	organic solvent

Superscripts

0	pure liquid state
∞	infinite dilution

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