LIQUID–VAPOUR EQUILIBRIUM IN STRONGLY ASSOCIATING BINARY SYSTEM PROPIONIC ACID–CYCLOHEXANE

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Received March 5th, 1979

Equilibrium data for the propionic acid–cyclohexane system at the pressure of 101·3 kPa are presented. The activity coefficients have been obtained by the simultaneous solution of equations of the phase and the chemical equilibrium and correlated by the Wilson, HMW, NRTL and Orye equations.

If we assume that propionic acid is an equilibrium mixture of monomeric and dimeric molecules, it holds (on the assumption of an ideally associating mixture) for the pure acid

$$P^0_A = P^*_{A1} + P^*_{A2}\,, \tag{1}$$

$$K_A = P^*_{A2}/P^{*2}_{A1} \tag{2}$$

and for the acid in a mixture with non-associating component (cyclohexane)

$$P = P_{A1} + P_{A2} + P_C\,, \tag{3}$$

$$y_A = (P_{A1} + 2P_{A2})/(P + P_{A2})\,, \tag{4}$$

$$K_A = P_{A2}/P^2_{A1}\,, \tag{5}$$

where K_A is the equilibrium constant of dimerization, P^*_{A1} and P^*_{A2} the partial pressure of the monomer and dimer, respectively, of the substance A in the pure substance A at the system temperature T and corresponding saturated vapour pressure P^0_A, P_{A1} and P_{A2} is the partial pressure of monomer and dimer, respectively, of the substance A in the mixture, P_C is the partial pressure of the non-associating substance C, y_A is the "macroscopic" mole fraction of the substance A in the vapour phase and P is the total pressure.

The activity coefficient of the associating substance in an ideally associating system is given by the relation[1]

$$\gamma_A(T, P) = P_{A1}(T, P)/x_A P^*_{A1}(T, P_{(T)})\,. \tag{6}$$

It holds for the non-associating substance

$$\gamma_C(T, P) = P_C(T, P)/x_C P^0_C(T, P_{(T)}) , \tag{7}$$

where x_A and x_C denotes the mole fraction of the substance A and C, respectively, in the liquid phase. The partial pressures of monomer of associating substance, needed for calculating the activity coefficient, can be obtained by solving Eqs (*1*)–(*5*).

In this work we have measured vapour–liquid equilibrium in the propionic acid–cyclohexane system at 101·3 kPa with the aim to find a suitable correlation equation for this strongly associating system.

EXPERIMENTAL

Preparation of pure substances. Propionic acid (pure, Lachema, Brno) has been used after twofold rectification on a twenty-plate glass column on adding several crystals of $KMnO_4$. Predried nitrogen has been bubbled *via* a capillary inserted to the bottom of distillation vessel to ensure smooth boiling. Heat leakage to the environment have partly been compensated by heating the column mantle. Cyclohexane (analytical reagent grade, Lachema, Brno) has been distilled on a packed column one meter long from a mixture with P_2O_5. Constants of the substances used are given in Table I.

Experimental equipment used for measuring vapour–liquid equilibrium had been described previously[2]. The analysis of the samples of the vapour and liquid phases has been carried out densimetrically. For the calibration, 15 points have been measured. The density dependence on composition has been correlated by the polynomial in the form

$$d = d^0_A x_A + d^0_C x_C + x_A x_C [A_1 + A_2(x_C - x_A) + A_3(x_C - x_A)^2] , \tag{8}$$

where d^0_i is the density of the pure component i. By the least-squares method, the following values of constants have been found: $A_1 = -0{\cdot}1185$, $A_2 = 0{\cdot}0260$, $A_3 = -0{\cdot}0099$. The mean square error $\sigma = 1{\cdot}1 \,.\, 10^{-4}$, the maximum error in composition $S_x = 1 \,.\, 10^{-4}$.

TABLE I

Physico-Chemical Constants of Substances Used

Substance	n_D^{20}	d^{20}	t_{nbp}, °C
Propionic acid	1·3865 1·3865–1·3866 (ref.[9])	0·9934 0·99336 (ref.[9])	141·1 140·8–141·3 (ref.[9])
Cyclohexane	1·4262 1·42623–1·42630 (ref.[9])	0·7784 0·7783–0·7785 (ref.[9])	80·7 80·70–80·85 (ref.[9])

RESULTS AND DISCUSSION

The measured and calculated equilibrium data are presented in Table II. For calculating we have used the Antoine constants reported by Wichterle and Linek[3] (for propionic acid) and by Boublík and coworkers[4] (for cyclohexane). To express the effect of association, the equilibrium constant of dimerization of propionic acid from the data by Taylor[5] has been employed.

When calculating the statistical estimate of error of the given experimental point, ϱ_i, the following errors in the input parameters have been assumed: $\varrho(T) = 0{\cdot}1$,

TABLE II

Vapour–Liquid Equilibrium at 101·3 kPa

T, K	x_A	y_A	γ_A	γ_C	y_{A1}	y_{A2}	W
354·00	0·049	0·021	5·438	0·984	0·013	0·004	0·060
354·40	0·132	0·042	3·229	1·050	0·021	0·011	0·32
355·65	0·215	0·061	2·450	1·102	0·027	0·018	0·67
356·35	0·320	0·078	1·894	1·229	0·032	0·023	0·94
357·10	0·339	0·083	1·825	1·232	0·034	0·026	0·98
358·20	0·436	0·100	1·551	1·375	0·040	0·032	1
358·20	0·437	0·099	1·543	1·385	0·039	0·032	1
359·70	0·507	0·116	1·413	1·488	0·045	0·038	0·95
359·75	0·535	0·122	1·382	1·568	0·047	0·040	0·89
360·80	0·564	0·135	1·362	1·604	0·051	0·045	0·83
361·55	0·609	0·143	1·284	1·736	0·054	0·048	0·79
363·40	0·655	0·163	1·239	1·830	0·061	0·056	0·77
364·40	0·681	0·168	1·186	1·913	0·064	0·057	0·71
366·10	0·714	0·188	1·168	1·996	0·071	0·065	0·64
366·90	0·733	0·198	1·155	2·071	0·075	0·068	0·61
371·60	0·799	0·246	1·092	2·296	0·096	0·085	0·51
376·95	0·850	0·306	1·049	2·484	0·124	0·107	0·42
377·25	0·854	0·315	1·058	2·508	0·127	0·111	0·40
381·40	0·886	0·375	1·048	2·673	0·156	0·135	0·32
383·10	0·894	0·390	1·028	2·693	0·166	0·139	0·31
392·60	0·944	0·562	1·034	3·037	0·260	0·210	0·16
397·65	0·961	0·654	1·026	3·131	0·320	0·248	0·10
410·10	0·994	0·928	1·028	3·462	0·526	0·375	0·004
411·70	0·997	0·961	1·023	3·654	0·556	0·390	0·001

y_{A1} and y_{A2} is the mole fraction of monomer and dimer, respectively, of propionic acid in the vapour phase.

$\varrho(x) = \varrho(y) = 0{\cdot}001$, $\varrho(P) = 0{\cdot}06$ kPa, $\varrho(P^\circ)/P^\circ = 0{\cdot}001$, $\varrho(K)/K = 0{\cdot}1$. The statistical weights of individual values of $\ln(\gamma_A/\gamma_B)$ have been calculated from the relation

$$w'_i = 1/\varrho_i^2 \tag{9}$$

and transformed to the interval $(0-1\rangle$ so that

$$w_i = w'_i/w'_{max}, \tag{10}$$

where w'_{max} is the maximum value of the statistical weight in the given set of data.

The dependence of the logarithm of activity coefficients on composition is plotted in Fig. 1. To correlate the activity coefficient in dependence on composition we have used the Wilson[6], NRTL[7], HMW[8] and Orye[8] equations (whose forms had been given formerly[2]) and the same equations with their parameters linearly dependent on temperature ($k_{ij} = \alpha_{ij} + \beta_{ij}T$). The constants have been determined by minimizing the squares of deviations of logarithms of the activity coefficient ratios with the weights given in Table II. For the NRTL equation we have chosen $\alpha = 0{\cdot}47$, for the other equations $\alpha = 1{\cdot}0$. The calculated values of constants together with their confidence interval (68 %) and a mean quadratic error given by the relation

$$\sigma = \{\sum_i w_i[Y_i - f(x_i)]^2/\sum_i w_i\}^{1/2} \tag{11}$$

are given in Table III. Better representation of the experimental values when fitted to the four-constant relations has also appeared in back calculation of the vapour phase composition even though the average error $\Delta y \sim 0{\cdot}004$ is not too satisfactory.

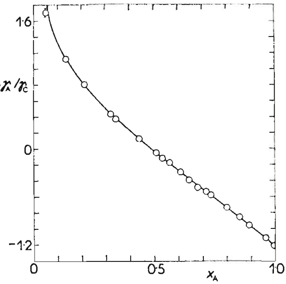

FIG. 1

Dependence of the Logarithm of the Activity Coefficient Ratio on Composition

Points represent experimental values, curve corresponds to the Wilson equation with the values of constants given in Table III.

TABLE III

Constants of Correlation Equations

For each equation, the original values are given in the upper line and the values of the four-constant relations in the lower line.

Equation	$\alpha_{12} \pm \varrho(\alpha_{12})$	$k_{12} \pm \varrho(k_{12})$	$\beta_{12} \pm \varrho(\beta_{12})$	$\alpha_{21} \pm \varrho(\alpha_{21})$	$k_{21} \pm \varrho(k_{21})$	$\beta_{21} \pm \varrho(\beta_{21})$	σ
Wilson		909·8 ± 38·2			305·5 ± 28·5		0·037
	8 391·2 ± 2 235·3		−20·8 ± 6·2	−4 369·9 ± 2 674·7		13·17 ± 7·5	0·024
NRTL		708·4 ± 34·7			484·8 ± 26·8		0·037
	8 543·9 ± 2 167·2		−21·8 ± 6·0	−4 795·0 ± 2 594·9		14·82 ± 7·2	0·024
HMW		543·3 ± 11·1			105·1 ± 10·4		0·032
	3 693·4 ± 487·1		−8·7 ± 1·4	−1 898·4 ± 353·2		5·6 ± 1·0	0·019
Orye		443·9 ± 15·9			−16·4 ± 14·9		0·037
	4 685·9 ± 1 300·0		−11·7 ± 3·6	−3 434·3 ± 0·4		9·510 ± 1 . 10^{-3}	0·020

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Translated by J. Linek.