VAPOUR-LIQUID EQUILIBRIUM IN THE TERNARY SYSTEM CYCLOHEXANE-ACETIC ACID-PROPIONIC ACID

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Dedicated to late Academician Eduard Hála.

Isobaric equilibrium data ($P = 101{\cdot}3$ kPa) for the system cyclohexane-acetic acid-propionic acid have been measured by two different analytical techniques. Activity coefficients calculated by simultaneous solving of equations for the chemical and phase equilibria were subjected to a consistency test based on inaccuracies determined from the error propagation law, and were correlated by Wilson's equation. The activity coefficients measured were compared with those calculated from binary vapour-liquid equilibrium data and with values predicted by the UNIFAC method.

A large number of experimental binary vapour-liquid equilibrium data have been used in proposing methods for estimating activity coefficients and for determining the parameters for the various groups necessary for predicting the activity coefficients by the group contribution method. These methods have been developed primarily for estimating the activity coefficients of multicomponent mixtures ($n > 2$). Their verification is, however, frequently limited by the scarcity of experimental data for multicomponent systems.

The aim of the present work was to contribute to the data base and to study strongly associating systems.

EXPERIMENTAL

Preparation of Pure Substances

All the chemicals used were supplied by Lachema Brno, and were purified before use as described below. Cyclohexane was freed from thiophene by shaking with concentrated sulphuric acid, pre-dried with P_2O_5, and distilled twice on a packed column. Acetic acid was purified by double distillation on a 40-plate bubble-cap column. Propionic acid with added $KMnO_4$ was distilled on a 20-plate bubble-cap column furnished with a heated jacket.

The physicochemical properties of the compounds used in the measurements of the first nine experimental points listed in Table II are given in Table I. In these measurements densities and refractive indices were used to determine the compositions of the liquid and vapour phases.

For the compounds used in the subsequent measurements, the purities as determined by gas chromatografic analysis using a flame ionization detector, which does not respond to water, were as follows: cyclohexane and propionic acid, 99·90%; acetic acid, 99·92%.

Procedure

The circulation apparatus used to measure the vapour–liquid equilibrium is described elsewhere[2].

The majority of experimental points for the compositions of the liquid and equilibrium vapour phases were obtained using a CHROM 61 gas chromatograph equipped with a flame ionization detector and a CI-100 integrator (Laboratorní přístroje, Prague). A glass column 990 mm in length and 2 mm in diameter was packed with SE-10 (Laboratorní přístroje, Prague) and operated isothermally at 150°C. Both the injector and detector temperatures were 160°C. Very good separation was achieved with nitrogen as the gas carrier. Calibration analyses were carried out to convert the peak area ratio to composition of the sample.

RESULTS AND DISCUSSION

In order to obtain thermodynamically consistent activity coefficients, it is necessary to describe correctly the non-ideal behaviour of the components in the vapour phase. A model of a chemically reacting mixture was used, and the presence of the following six components in the vapour phase was assumed: cyclohexane monomer, monomers of both acids, dimers of both acids, and a mixed dimer (further referred to as true components).

In this case, the activity coefficient may be expressed as

$$\gamma_i(T, P) = \frac{f_{i1}(T, P)}{x_i f^*_{i1}(T, P^{\circ}_{(T)})} \exp\left[1/RT \int_P^{P_i^{\circ}} \mathscr{V}_i^{\circ 1}\, \mathrm{d}P\right], \qquad (1)$$

where T is the temperature, P is the pressure, x_i is the nominal mole fraction of i-th component in the liquid phase, R is the gas constant, f is the fugacity, and $\mathscr{V}_i$ is

TABLE I

Physicochemical properties of the compounds studied

Compound	n_D^{20} measured	n_D^{20} ref.[1]	d^{20} measured	d^{20} ref.[1]
Cyclohexane	1·4262	1·42623	0·7784	0·77855
Acetic acid	1·3717	1·3719	1·0492	1·04926
Propionic acid	1·3864	1·3865	0·9933	0·9934

TABLE II

Vapour–liquid equilibrium data for the system cyclohexane(1)–acetic acid(2)–propionic acid(3)

No.	T, K	x_1	x_2	y_1	y_2	$\gamma_1 \pm s(\gamma_1)$		$\gamma_2 \pm s(\gamma_2)$		$\gamma_3 \pm s(\gamma_3)$	
1	360·52	0·327	0·159	0·789	0·085	2·144	0·03	1·427	0·19	1·215	0·11
2	361·36	0·255	0·247	0·738	0·123	2·569	0·05	1·211	0·11	1·255	0·10
3	364·78	0·183	0·424	0·672	0·226	3·043	0·09	1·122	0·06	0·994	0·12
4	358·19	0·320	0·351	0·741	0·168	2·256	0·04	1·245	0·08	1·350	0·17
5	354·81	0·609	0·204	0·811	0·134	1·391	0·01	2·052	0·19	1·754	0·37
6	353·79	0·772	0·113	0·863	0·106	1·177	0·01	3·378	0·44	1·862	0·69
7	361·28	0·289	0·245	0·754	0·130	2·304	0·04	1·321	0·12	1·146	0·11
8	355·32	0·656	0·133	0·857	0·100	1·317	0·01	2·579	0·33	1·330	0·35
9	363·57	0·344	0·062	0·828	0·046	1·923	0·03	2·000	0·55	1·046	0·09
10	384·27	0·051	0·398	0·378	0·348	4·143	0·41	1·060	0·04	1·017	0·05
11	386·24	0·035	0·503	0·293	0·455	4·606	0·66	1·032	0·03	1·042	0·06
12	387·55	0·023	0·681	0·205	0·616	5·014	1·10	0·987	0·02	1·103	0·09
13	387·21	0·018	0·762	0·180	0·685	5·752	1·62	0·985	0·02	1·119	0·12
14	383·60	0·021	0·851	0·216	0·715	6·504	1·60	0·988	0·02	1·087	0·21
15	371·97	0·058	0·822	0·417	0·539	5·564	0·49	1·016	0·02	1·000	0·28
16	379·67	0·047	0·640	0·365	0·485	4·981	0·54	0·996	0·03	1·084	0·10
17	370·68	0·088	0·610	0·503	0·389	4·336	0·25	1·054	0·03	1·057	0·13
18	362·17	0·173	0·544	0·627	0·295	3·311	0·10	1·150	0·05	1·083	0·17
19	357·83	0·284	0·476	0·684	0·250	2·441	0·05	1·283	0·06	1·260	0·23
20	367·45	0·164	0·339	0·648	0·201	3·057	0·10	1·156	0·07	1·071	0·09
21	375·10	0·112	0·259	0·586	0·184	3·359	0·15	1·141	0·08	1·021	0·05
22	377·49	0·046	0·754	0·380	0·538	5·610	0·62	0·982	0·02	0·972	0·15
23	366·17	0·104	0·711	0·533	0·411	4·965	0·24	1·061	0·03	0·997	0·22
24	374·93	0·080	0·533	0·497	0·359	4·204	0·27	1·024	0·04	0·989	0·09
25	355·42	0·480	0·227	0·791	0·134	1·707	0·02	1·748	0·15	1·460	0·22

TABLE II
(*Continued*)

No.	T, K	x_1	x_2	y_1	y_2	$\gamma_1 \pm s(\gamma_1)$		$\gamma_2 \pm s(\gamma_2)$		$\gamma_3 \pm s(\gamma_3)$	
26	360·86	0·311	0·176	0·777	0·094	2·210	0·04	1·391	0·17	1·213	0·11
27	365·05	0·136	0·499	0·598	0·296	3·760	0·14	1·163	0·05	1·032	0·12
28	375·62	0·096	0·395	0·541	0·266	3·667	0·19	1·039	0·05	1·012	0·07
29	377·69	0·065	0·544	0·443	0·393	4·369	0·34	1·015	0·03	1·025	0·08
30	361·27	0·220	0·450	0·665	0·248	2·783	0·07	1·236	0·06	1·087	0·15
31	371·58	0·099	0·493	0·556	0·312	4·061	0·21	1·064	0·04	0·961	0·09
32	375·01	0·068	0·612	0·463	0·413	4·657	0·34	1·008	0·03	1·011	0·11
33	367·83	0·117	0·565	0·570	0·328	3·898	0·17	1·058	0·04	1·045	0·13
34	376·03	0·083	0·449	0·490	0·338	3·882	0·24	1·116	0·04	0·952	0·07
35	378·02	0·061	0·558	0·437	0·405	4·580	0·38	1·012	0·03	1·000	0·09
36	374·05	0·095	0·417	0·543	0·283	3·860	0·20	1·079	0·05	0·990	0·07
37	357·61	0·432	0·247	0·773	0·141	1·747	0·02	1·573	0·13	1·396	0·19
38	361·92	0·297	0·199	0·755	0·113	2·198	0·04	1·401	0·15	1·189	0·10
39	361·87	0·325	0·193	0·756	0·109	2·020	0·03	1·402	0·15	1·266	0·11
40	358·80	0·335	0·344	0·716	0·192	2·071	0·03	1·393	0·08	1·321	0·17
41	356·42	0·370	0·407	0·711	0·230	2·005	0·03	1·464	0·07	1·298	0·26
42	363·88	0·122	0·689	0·583	0·370	4·266	0·18	1·064	0·03	0·906	0·23
43	367·26	0·090	0·743	0·525	0·429	4·864	0·27	1·031	0·03	0·896	0·23
44	373·56	0·068	0·674	0·454	0·451	4·792	0·35	1·021	0·03	0·997	0·13
45	362·63	0·152	0·604	0·612	0·326	3·677	0·12	1·123	0·04	0·957	0·19
46	365·46	0·104	0·715	0·554	0·394	4·581	0·22	1·037	0·03	0·989	0·23
47	372·35	0·081	0·605	0·501	0·385	4·484	0·28	1·020	0·03	1·021	0·12
48	363·06	0·159	0·539	0·633	0·292	3·530	0·11	1·139	0·04	0·947	0·15
49	366·09	0·110	0·661	0·571	0·363	4·373	0·20	1·036	0·03	0·974	0·18
50	364·10	0·117	0·702	0·572	0·380	4·367	0·19	1·058	0·03	0·955	0·23
51	360·56	0·163	0·658	0·619	0·340	3·671	0·12	1·124	0·04	0·918	0·26

the molar volume of i-th component. The subscript $i1$ denotes the monomer of i-th component, the subscripts l and o denote the liquid phase and pure component, respectively, and * denotes the value for the monomer of i-th component (for a non-associating component, $f_{i1}^* = f_i^o$).

Since even for binary systems the corrections to the real behaviour of the true components are swamped by inaccuracies in the measured quantities, activity coefficients for this ternary system were calculated using a model of an ideally associating system, namely

$$\gamma_i = \frac{y_{i1}P}{x_i y_{i1}^* P_i^o} \exp\left[1/RT \int_P^{P_i^o} \mathscr{V}_i^{ol}\, dP\right], \qquad (2)$$

where y is the mole fraction of a component in the vapour phase.

In order to calculate the mole fractions of the monomers of the individual components in the vapour phase, mass balance equations (*3*), (*4*), and (*5*) must be solved simultaneously with chemical equilibrium equations (*6*), (*7*), and (*8*).

$$1 = y_C + y_{A1} + y_{A2} + y_{P1} + y_{P2} + y_{AP} \qquad (3)$$

$$y_A = (y_{A1} + 2y_{A2} + y_{AP})/(1 + y_{A2} + y_{P2} + y_{AP}) \qquad (4)$$

$$y_P = (y_{P1} + 2y_{P2} + y_{AP})/(1 + y_{A2} + y_{P2} + y_{AP}) \qquad (5)$$

$$K_A = y_{A2}P_{st}/y_{A1}^2 P \qquad (6)$$

$$K_P = y_{P2}P_{st}/y_{P1}^2 P \qquad (7)$$

$$K_{AP} = y_{AP}P_{st}/y_{A1}y_{P1}P \qquad (8)$$

The values for pure acids were obtained from Eqs (*9*) and (*10*).

$$1 = y_{j1}^* + y_{j2}^* \qquad (9)$$

$$K_j = y_{j2}^* P_{st}/y_{j1}^{*2} P_j^o\,, \quad j = \text{A, P} \qquad (10)$$

where K denotes the equilibrium constant of dimerization, the subscripts A, P, AP, and C relate to acetic acid, propionic acid, mixed dimer, and cyclohexane, respectively, and the subscript st denotes the quantity in the standard state.

In the calculations we used the constants of Antoine's equation listed in Table III and the following temperature dependences of the equilibrium constants of dimerization (standard state: pure substance in the ideal gas state at a pressure of 1 Pa)[6,7]

$$\ln K_A = 7\,425{\cdot}837/T - 29{\cdot}2449$$

and

$$\ln K_P = 7\,635{\cdot}370/T - 29{\cdot}8390\,.$$

For the mixed dimer, we used the approximation

$$K_{AP} = 2(K_A K_P)^{1/2}\,.$$

The measured vapour-liquid equilibrium data are listed in Table II, along with the calculated activity coefficients and their standard deviations.

In Fig. 1, the coexisting vapour and liquid compositions are connected by arrows pointing towards the vapour phase composition.

TABLE III
Constants of Antoine's equation[a]

Compound	A	B	C
Cyclohexane[3]	20·667105	2 778·6003	−49·917
Acetic acid[4]	23·939051	5 199·7434	27·820
Propionic acid[5]	22·204615	3 670·9490	−70·545

[a] $\ln P = A - B/(T + C)$, where T is the thermodynamic temperature, and P is in units of Pa.

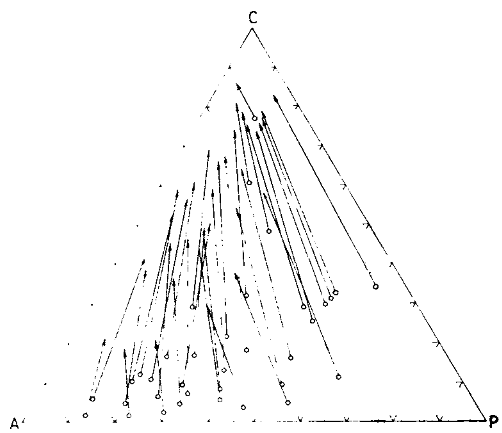

FIG. 1
Vapour-liquid equilibrium in the system cyclohexane(1)-acetic acid(2)-propionic acid-(3); circles denote the liquid phase compositions, arrowheads the vapour phase compositions

The calculated activity coefficients were subjected to a consistency test in the form[8]

$$\sum_{i=1}^{3}(x_{ic} + x_{id})(\ln \gamma_{id} - \ln \gamma_{ic}) = D\,, \qquad (11)$$

where c and d denote a chosen pair of experimental points for which Δx_1 and $\Delta x_2 \leqq 0{\cdot}1$ and $\Delta T \leqq 3$ K, and D is the mean quadratic deviation obtained by the method of error propagation.

The calculation of the standard deviation in the activity coefficient was based on the following errors in the input quantities: $s(x_1) = s(y_1) = 0{\cdot}005$, $s(x_2) = s(y_2) = 0{\cdot}01$, $s(T) = 0{\cdot}05$ K, $s(P) = 50$ Pa, $s(P_i^\circ)/P_i^\circ = 0{\cdot}003$, $s(K_A)/K_A = 0{\cdot}05$, $s(K_P)/K_P = 0{\cdot}1$, and $s(K_{AP})/K_{AP} = 0{\cdot}1$.

No suitable partners for the consistency test were found within the above defined ranges of Δx_1, Δx_2, and ΔT for points No. 9, 11, 14, 15, 20, 21, and 22; the other experimental points passed the test.

The activity coefficients were correlated with composition by the Wilson equation

$$\ln \gamma_i = -\ln \sum_{s=1}^{3} x_s \Lambda_{is} + 1 - \sum_{r=1}^{3} \left(x_r \Lambda_{ri} / \sum_{s=1}^{3} x_s \Lambda_{rs}\right), \qquad (12)$$

where

$$\Lambda_{ij} = \mathscr{V}_j^\circ / \mathscr{V}_i^\circ \exp\left(-k_{ij}/T\right). \qquad (13)$$

The objective function was the sum of weighted squares of the deviations in the logarithms of activity coefficients. In this way, we obtained the following set of constants:

$$k_{12} = 318{\cdot}833 \quad k_{13} = 44{\cdot}137 \quad k_{23} = 546{\cdot}617$$

$$k_{21} = 822{\cdot}554 \quad k_{31} = 811{\cdot}009 \quad k_{32} = -326{\cdot}378\,.$$

The standard deviation of the correlation

$$s = \left(\sum_{i=1}^{N} \sum_{j=1}^{3} w_{ij} (\ln \gamma_{ij}^{\text{exp}} - \ln \gamma_{ij}^{\text{cal}})^2 / (3N - 6)\right)^{1/2} \qquad (14)$$

was $s = 1{\cdot}2$, where N is the number of experimental points, w is the weight, and the superscripts cal and exp denote the calculated and experimental values, respectively.

By calculating the vapour composition and temperature with the use of the constants of the Wilson equation as obtained by the ternary data correlation, we found the average errors $\Delta\bar{y} = 0{\cdot}007$ and $\Delta\bar{T} = 0{\cdot}6$ K. The same back calculation using constants of the Wilson equation obtained from binary data[9] yielded the average errors $\Delta\bar{y} = 0{\cdot}009$ and $\Delta\bar{T} = 1{\cdot}9$ K.

A better agreement with experimental data than one might have expected was obtained by the use of the UNIFAC prediction method, which yielded the average errors $\Delta\bar{y} = 0{\cdot}01$ and $\Delta\bar{T} = 0{\cdot}6$ K.

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