

## VAPOUR-LIQUID EQUILIBRIUM IN THE BENZENE(1)-PROPIONIC ACID(2)-ACETIC ACID(3) TERNARY SYSTEM\*

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Results of measurement of vapour-liquid equilibria in the benzene-propionic acid-acetic acid ternary system at normal pressure are presented. The activity coefficients were, within the framework of inaccuracies determined on the basis of the law of error propagation, subjected to a test of consistency and correlated by the Wilson equation. The experimental values of activity coefficients are compared with the values calculated on the basis of the Wilson equation with its constants obtained both from the ternary and from the binary data and with the values estimated by the UNIFAC method.

After measuring several binary<sup>1-5</sup> and one ternary<sup>6</sup> systems, the study of strongly associating systems was continued by determining vapour-liquid equilibrium in the benzene-propionic acid-acetic acid ternary system. To calculate the deviations from the ideal behaviour in the vapour phase, the model was used of ideally associating system with six microcomponents: monomer and dimer of both acids, mixed dimer, and benzene monomer.

### EXPERIMENTAL

*Preparation of pure substances.* Benzene (Lachema Brno, plant Neratovice) was predried by means of calcined calcium chloride, and then rectified on a sixty-plate column. Propionic acid (Spolana Neratovice) was predried with calcined sodium sulphate and twice rectified with a small  $\text{KMnO}_4$  addition on a twenty-plate bubble-cup column with outer heating mantle. Acetic acid (Lachema Brno, plant Neratovice) was purified by double rectification with a small addition of chromium oxide on a forty-plate bubble-cup column. The physico-chemical properties of substances used are given in Table I.

*The recirculation equilibrium* still used for measuring the vapour-liquid equilibrium was described previously<sup>4</sup>.

*The analysis of the ternary mixtures* was to be carried out by measuring density and refractive index. To calibrate the dependence  $V_m^E = V_m^E(x_1, x_2)$ , where  $V_m^E$  is the excess volume, and  $n_e = n_e(x_1, x_2)$ , 45 samples of known compositions were measured. The density was measured

\* Part C in the series Liquid-Vapour Equilibrium; Part IC: This Journal 51, 194 (1986).

in 25 ml pycnometers of the Bruin type at  $20 \pm 0.1^\circ\text{C}$  with the accuracy  $s(d) = 1 \cdot 10^{-4}$ , the refractive index was measured with a Pulfrich refractometer illuminated by the green Hg line with the accuracy  $s(n_e) \sim 5 \cdot 10^{-5}$ .

The dependence of excess volume on composition was expressed in the form

$$\begin{aligned} V_m^E &= \frac{M_1 x_1 + M_2 x_2 + M_3 x_3}{d} - \frac{M_1 x_1}{d_1} - \frac{M_2 x_2}{d_2} - \frac{M_3 x_3}{d_3} = \\ &= A_1 x_1 x_2 + A_2 x_2 x_3 + A_3 x_1 x_3 + A_4 x_1 x_3 (x_1 - x_3) + \\ &\quad + A_5 x_1 x_3 (x_1 - x_3)^2 + A_6 x_2 x_3 (x_2 - x_3)^2, \end{aligned} \quad (1)$$

where

$$\begin{aligned} A_1 &= 1.46797, A_2 = 0.399787, A_3 = 3.26148, \\ A_4 &= -0.710044, A_5 = 0.250541, A_6 = -0.078638. \end{aligned}$$

Standard deviation of the correlation has been  $s(V_m^E) = 1 \cdot 10^{-2}$ .

The dependence of refractive index on composition was expressed in the form

$$\begin{aligned} n_e &= n_{e1}^0 x_1 + n_{e2}^0 x_2 + n_{e3}^0 x_3 + B_1 x_1 x_3 + B_2 x_1 x_2 + \\ &\quad + B_3 x_1 x_3 (x_1 - x_3) + B_4 x_1 x_2 (x_1 - x_2) + B_5 x_1 x_2 x_3, \end{aligned} \quad (2)$$

where

$$\begin{aligned} n_{e1}^0 &= 1.50490, n_{e2}^0 = 1.38773, n_{e3}^0 = 1.37295, \\ B_1 &= 0.027101, B_2 = 0.003260, B_3 = -0.002961, \\ B_4 &= -0.003574, B_5 = 0.009359. \end{aligned}$$

Standard deviation of the correlation has been  $s(n_e) \sim 1 \cdot 10^{-4}$ . The result of correlation was subjected to an analysis.

For standard deviation in composition, one can write

$$s(x_i) = \left[ \left( \frac{\partial x_i}{\partial n_e} \right)_{x_j \neq i}^2 s^2(n_e) + \left( \frac{\partial x_i}{\partial V^E} \right)_{x_j \neq i}^2 s^2(V^E) \right]^{1/2}. \quad (3)$$

TABLE I

Physico-chemical constants of substances used

Substance	$n_D^{20}$	$d^{20}$
Benzene	1.5006	0.8787
	1.5009—1.50115 <sup>a</sup>	0.87888—0.87910 <sup>a</sup>
Propionic acid	1.3863	0.9934
	1.3865 <sup>b</sup>	0.9934 <sup>b</sup>
Acetic acid	1.3714	1.0492
	1.3717—1.3719 <sup>a</sup>	1.04910—1.04926 <sup>a</sup>

<sup>a</sup> Ref. 7; <sup>b</sup> ref. 8.

Considering only random errors, the error in the determination of benzene concentration would be lower than  $1 \cdot 10^{-3}$  in the whole concentration region for the given variances in refractive index and excess volume. With the same accuracy it is therefore possible to determine also the total amount of acids. With regard to the close values of quantities measured for both the acids, the error in the mole fraction determination of the individual acids is, however, higher. In the regions with lower benzene concentration, the error in the mole fraction determination of acids does not reach the value of  $1 \cdot 10^{-2}$ , in the region richer in benzene increases with a maximum in the vicinity of  $x_1 \sim 0.8$ .

In the regions where one can expect  $s(x_2) \geq 1 \cdot 10^{-2}$ , gas chromatography was used for the determination of the acid concentration. A GC-ALPHA chromatograph with a thermal-conductivity detector was employed. Its column packing was a polymer sorbent Separon SDA. The temperature of thermostat and injection port was 190°C, that of the detector 140°C. The hydrogen flow rate was 40 ml/min.

One  $\mu\text{l}$  sample was injected into the apparatus using simultaneously an external standard (a mixture of known composition close to the analysed sample) and internal standard (a known amount of benzene in the analysed sample). The peak areas were established by quadrature. On statistical treating, the accuracy in the acid determination as much as  $s(x_2) \sim 5 \cdot 10^{-3}$  was attained.

## RESULTS AND DISCUSSION

Activity coefficients were calculated from the measured equilibrium data using the relation

$$\gamma_i = y_{i1}P/(x_i y_{i1}^* P_i^0), \quad (4)$$

where  $\gamma$  denotes the activity coefficient,  $P$  pressure,  $y$  the composition of the vapour phase,  $x$  the composition of the liquid phase, subscript  $i$  refers to a macroscopic component,  $il$  its monomer, superscript<sup>0</sup> refers to a pure substance, and\* the value of a microscopic quantity in a pure macroscopic substance.

For the calculations, we used the Antoine constants given in Table II and the following dependences of equilibrium dimerization constants (standard state: pure substance in an ideal gas state at the pressure of 1 Pa) on temperature: for propionic acid<sup>4</sup>

$$\ln K_2 = 8\,858.32/T - 33.3563$$

and for acetic acid<sup>10</sup>

$$\ln K_3 = 7\,425.84/T - 29.2449.$$

For the mixed dimer, the approximation was used

$$K_{23} = (K_2 K_3)^{1/2}.$$

The measured equilibrium data along with the calculated activity coefficients and their standard deviation are given in Table III. The coexisting vapour and

liquid phases are connected in Fig. 1 with arrows whose arrow-heads denote the compositions of the vapour phase.

Consistency of the measured data was tested by the McDermott–Ellis method<sup>9</sup> with all the point pairs whose  $\Delta x_1$  and  $\Delta x_2 \leq 0.1$  and  $T \leq 3$ . As consistent were accepted, within the framework of the accuracy given, those experimental points which satisfied the condition

$$\sum_{i=1}^3 (x_{ic} + x_{id}) (\ln \gamma_{id} - \ln \gamma_{ic}) = D, \quad (5)$$

TABLE II  
Antoine constants of substances used<sup>a</sup>

Substance	<i>A</i>	<i>B</i>	<i>C</i>
Benzene <sup>11</sup>	20.7343	2 755.64	−53.989
Propionic acid <sup>8</sup>	22.2749	3 724.09	−67.480
Acetic acid <sup>11</sup>	22.2994	3 785.56	−39.626

<sup>a</sup>  $\ln P = A - B/(T + C)$ , where *T* is thermodynamic temperature and *P* pressure in Pa.

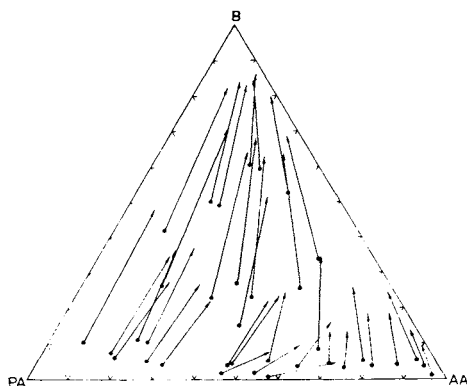


FIG. 1  
Vapour–liquid equilibrium in the system benzene (1)–propionic acid(2)–acetic acid(3); circles denote the liquid phase compositions, arrow-heads the vapour phase compositions

TABLE III  
 Experimental data on vapour-liquid equilibrium in the system benzene(1) - propionic acid(2) - acetic acid(3) at the pressure of 101.325 kPa

No	$t, ^\circ\text{C}$	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1 \pm s(\gamma_1)$	$\gamma_2 \pm s(\gamma_2)$	$\gamma_3 \pm s(\gamma_3)$
1	123.97	0.009	0.420	0.049	0.282	2.47 ± 0.28	0.990 ± 0.054	1.043 ± 0.025
2	126.87	0.014	0.539	0.077	0.382	2.25 ± 0.16	0.979 ± 0.039	1.021 ± 0.032
3	114.48	0.017	0.025	0.093	0.015	3.20 ± 0.19	1.09 ± 0.86	0.997 ± 0.015
4	124.36	0.021	0.448	0.096	0.300	1.988 ± 0.098	0.979 ± 0.049	1.009 ± 0.027
5	112.90	0.026	0.030	0.134	0.020	3.07 ± 0.12	1.26 ± 0.77	0.993 ± 0.016
6	117.49	0.030	0.329	0.151	0.197	2.578 ± 0.089	1.023 ± 0.073	1.035 ± 0.023
7	113.35	0.033	0.152	0.170	0.083	2.946 ± 0.092	1.02 ± 0.15	1.012 ± 0.019
8	112.10	0.036	0.097	0.185	0.046	3.020 ± 0.086	0.91 ± 0.23	1.005 ± 0.018
9	116.68	0.037	0.225	0.167	0.124	2.349 ± 0.066	0.96 ± 0.10	0.994 ± 0.020
10	123.02	0.043	0.667	0.215	0.457	2.083 ± 0.051	1.043 ± 0.031	1.049 ± 0.054
11	117.85	0.044	0.498	0.221	0.315	2.426 ± 0.058	1.081 ± 0.049	1.036 ± 0.034
12	114.74	0.048	0.260	0.221	0.130	2.446 ± 0.053	0.914 ± 0.090	1.016 ± 0.022
13	118.18	0.048	0.486	0.238	0.276	2.353 ± 0.052	0.965 ± 0.049	1.063 ± 0.033
14	113.43	0.053	0.398	0.259	0.247	2.621 ± 0.052	1.177 ± 0.068	1.010 ± 0.029
15	107.95	0.054	0.030	0.253	0.015	2.972 ± 0.057	1.07 ± 0.80	0.993 ± 0.017
16	109.50	0.054	0.169	0.254	0.089	2.846 ± 0.055	1.09 ± 0.15	1.020 ± 0.021
17	121.45	0.055	0.684	0.269	0.449	2.065 ± 0.041	1.044 ± 0.031	1.045 ± 0.060
18	125.17	0.060	0.763	0.279	0.520	1.762 ± 0.032	0.999 ± 0.024	1.022 ± 0.084
19	116.05	0.070	0.450	0.304	0.210	2.110 ± 0.033	0.841 ± 0.053	1.091 ± 0.033
20	122.37	0.076	0.760	0.350	0.480	1.812 ± 0.027	1.002 ± 0.026	1.009 ± 0.092
21	107.65	0.088	0.259	0.349	0.126	2.387 ± 0.030	1.07 ± 0.11	1.032 ± 0.026

TABLE III  
(Continued)

	$t, ^\circ\text{C}$	$x_1$	$x_2$	$y_1$	$y_2$	$\gamma_1 \pm s(\gamma_1)$	$\gamma_2 \pm s(\gamma_2)$	$\gamma_3 \pm s(\gamma_3)$
22	119.41	0.103	0.812	0.477	0.455	1.857 $\pm$ 0.021	0.992 $\pm$ 0.026	0.87 $\pm$ 0.17
23	116.40	0.104	0.660	0.425	0.368	1.831 $\pm$ 0.021	1.034 $\pm$ 0.034	0.983 $\pm$ 0.069
24	115.46	0.115	0.678	0.464	0.360	1.819 $\pm$ 0.019	1.021 $\pm$ 0.034	0.987 $\pm$ 0.079
25	104.57	0.152	0.416	0.514	0.171	2.026 $\pm$ 0.016	1.034 $\pm$ 0.073	1.069 $\pm$ 0.043
26	100.26	0.231	0.446	0.647	0.146	1.777 $\pm$ 0.011	0.993 $\pm$ 0.076	1.126 $\pm$ 0.066
27	98.07	0.232	0.342	0.631	0.117	1.853 $\pm$ 0.011	1.08 $\pm$ 0.10	1.071 $\pm$ 0.050
28	94.11	0.260	0.219	0.637	0.068	1.870 $\pm$ 0.010	1.08 $\pm$ 0.17	1.115 $\pm$ 0.044
29	100.86	0.261	0.547	0.702	0.171	1.634 $\pm$ 0.009	0.985 $\pm$ 0.063	1.21 $\pm$ 0.12
30	96.68	0.273	0.359	0.679	0.112	1.724 $\pm$ 0.009	1.06 $\pm$ 0.10	1.106 $\pm$ 0.062
31	89.85	0.335	0.132	0.687	0.033	1.734 $\pm$ 0.008	1.01 $\pm$ 0.32	1.185 $\pm$ 0.048
32	92.81	0.417	0.461	0.826	0.103	1.439 $\pm$ 0.006	1.02 $\pm$ 0.10	1.52 $\pm$ 0.25
33	88.68	0.491	0.290	0.829	0.060	1.384 $\pm$ 0.006	1.06 $\pm$ 0.18	1.45 $\pm$ 0.15
34	88.74	0.501	0.305	0.837	0.069	1.362 $\pm$ 0.006	1.17 $\pm$ 0.18	1.41 $\pm$ 0.17
35	85.19	0.527	0.111	0.795	0.022	1.396 $\pm$ 0.006	1.04 $\pm$ 0.48	1.462 $\pm$ 0.089
36	84.06	0.594	0.139	0.842	0.032	1.329 $\pm$ 0.005	1.36 $\pm$ 0.44	1.54 $\pm$ 0.14
37	84.17	0.608	0.161	0.855	0.024	1.307 $\pm$ 0.005	0.91 $\pm$ 0.38	1.76 $\pm$ 0.16

where  $c$  and  $d$  denote the selected pair of experimental points and

$$D = [2(\ln \gamma_{1d} - \ln \gamma_{1c})^2 s^2(x_1) + 2 \sum_{i=2}^3 (\ln \gamma_{id} - \ln \gamma_{ic})^2 \cdot s^2(x_2) + \sum_{i=1}^3 (x_{ic} + x_{id})^2 (s^2(\ln \gamma_{id}) + s^2(\ln \gamma_{ic}))]^{1/2}. \quad (6)$$

For the calculations, it was taken  $s(x_1) = 0.001$ ,  $s(x_2) = 0.01$ , and  $s(\ln \gamma_i)$  (given in Table III) were calculated for the errors in composition given above and for  $s(y_1) = 0.001$ ,  $s(y_2) = 0.01$ ,  $s(T) = 0.05$  K,  $s(P) = 50$  Pa,  $s(P_i^0)/P^0 = 0.003$ ,  $s(K_3)/K_3 = 0.05$ ,  $s(K_2)/K_2 = 0.1$ , and  $s(K_{23})/K_{23} = 0.1$  on the basis of the law of error propagation.

The input conditions of the test of consistency were not satisfied by points 1, 6, 7, 14, 15, 21, 25, 26, 28, 29, 31, and 32 which consequently were not tested. The test of consistency was not passed by point 19 with  $x_1 = 0.070$  and  $x_2 = 0.450$  which was excluded from further treatment.

The experimental data were then correlated in dependence on composition by the Wilson equation

$$\ln \gamma_i = -\ln \left( \sum_{s=1}^3 x_s A_{is} \right) + 1 - \sum_{r=1}^3 (x_{ri} / \sum_{s=1}^3 x_s A_{rs}), \quad (7)$$

where

$$A_{ij} = V_{mj}/V_{mi} \exp(-k_{ij}/T), \quad (8)$$

and  $V_m$  denotes molar volume.

The sum of weighted sums of squares of deviations in logarithms of activity coefficients was chosen as an objective function.

The result is the following set of constants

$$\begin{aligned} k_{12} &= -139.7 & k_{21} &= 673.0 \\ k_{13} &= 676.6 & k_{31} &= 676.6 \\ k_{23} &= -309.1 & k_{32} &= 438.2 \end{aligned}$$

with the variance of correlation  $s^2 = 69.8$  which gives evidence that this six-constant equation is not able to represent the correlated data with the experimental accuracy.

Table IV summarizes the activity coefficients calculated on the basis of correlation of the ternary data,  $\gamma^W$ , further the values predicted by the UNIFAC method<sup>12</sup>,  $\gamma^{UNIF}$ , and the values calculated from the Wilson equation on the basis of constants obtained from the measurement of binary systems,  $\gamma^{WB}$ .

TABLE IV  
Activity coefficients in the system benzene(1) – propionic acid(2) – acetic acid(3)

$x_1$	$x_2$	$\gamma_1^W$	$\gamma_1^{UNIF}$	$\gamma_1^{WB}$	$\gamma_2^W$	$\gamma_2^{UNIF}$	$\gamma_2^{WB}$	$\gamma_3^W$	$\gamma_3^{UNIF}$	$\gamma_3^{WB}$
0.009	0.420	2.404	2.313	2.475	1.030	1.006	1.042	1.002	1.006	1.011
0.014	0.539	2.222	2.222	2.305	1.027	1.003	1.031	1.008	1.010	1.023
0.017	0.025	3.182	2.595	3.064	1.004	1.021	1.056	1.001	1.000	1.001
0.021	0.448	2.320	2.259	2.390	1.026	1.003	1.036	1.006	1.008	1.016
0.026	0.030	3.117	2.562	3.007	0.996	1.018	1.050	1.001	1.001	1.001
0.030	0.329	2.475	2.321	2.521	1.019	1.005	1.040	1.006	1.007	1.011
0.033	0.152	2.794	2.442	2.769	1.004	1.010	1.044	1.004	1.003	1.005
0.036	0.097	2.899	2.475	2.842	0.996	1.012	1.043	1.004	1.003	1.004
0.037	0.225	2.624	2.368	2.633	1.010	1.007	1.042	1.006	1.005	1.008
0.043	0.667	2.007	2.089	2.080	1.015	1.000	1.014	1.034	1.020	1.059
0.044	0.498	2.188	2.183	2.260	1.018	1.000	1.026	1.015	1.014	1.029
0.048	0.260	2.519	2.315	2.540	1.006	1.004	1.036	1.010	1.008	1.012
0.048	0.486	2.190	2.177	2.258	1.017	1.000	1.026	1.016	1.015	1.029
0.053	0.398	2.293	2.223	2.350	1.012	1.001	1.029	1.013	1.013	1.022
0.054	0.030	2.963	2.474	2.864	0.972	1.011	1.033	1.005	1.003	1.004
0.054	0.169	2.666	2.370	2.652	0.991	1.006	1.034	1.009	1.006	1.009
0.055	0.684	1.964	2.055	2.030	1.013	1.000	1.012	1.043	1.023	1.070
0.060	0.763	1.891	2.000	1.943	1.009	1.000	1.006	1.071	1.028	1.102
0.076	0.760	1.860	1.970	1.907	1.008	1.001	1.006	1.079	1.032	1.113



0-088	2-374	2-212	2-390	0-987	1-000	1-022	1-032	1-015	1-023
0-103	1-782	1-895	1-806	1-006	1-004	1-005	1-128	1-044	1-168
0-104	1-873	1-957	1-919	1-010	1-001	1-010	1-064	1-037	1-096
0-115	1-837	1-927	1-877	1-009	1-002	1-009	1-075	1-042	1-111
0-152	1-980	1-968	2-011	0-994	1-001	1-013	1-058	1-042	1-069
0-231	1-768	1-783	1-779	1-001	1-016	1-017	1-110	1-080	1-134
0-232	1-850	1-820	1-857	0-981	1-012	1-012	1-101	1-073	1-110
0-260	1-892	1-807	1-883	0-948	1-013	1-004	1-110	1-079	1-109
0-261	1-643	1-689	1-642	1-020	1-030	1-027	1-148	1-106	1-202
0-273	1-743	1-727	1-743	0-990	1-024	1-019	1-134	1-098	1-149
0-335	1-777	1-677	1-756	0-923	1-035	1-004	1-161	1-121	1-156
0-417	1-438	1-449	1-407	1-076	1-112	1-091	1-291	1-236	1-400
0-491	1-394	1-372	1-367	1-081	1-163	1-118	1-383	1-312	1-440
0-501	1-375	1-356	1-346	1-098	1-176	1-130	1-400	1-329	1-473
0-527	1-408	1-350	1-388	1-011	1-183	1-101	1-425	1-343	1-423
0-594	1-302	1-259	1-279	1-109	1-282	1-183	1-582	1-477	1-602
0-608	1-278	1-240	1-253	1-147	1-309	1-210	1-621	1-513	1-660

The binary constants and the references corresponding to them are given below:

$$\begin{array}{ll} k_{12} = -57.0 \text{ (ref.}^1) & k_{32} = 404.0 \text{ (ref.}^5) \\ k_{21} = 441.7 \text{ (ref.}^1) & k_{13} = 0.5 \text{ (ref.}^{11}) \\ k_{23} = -283.9 \text{ (ref.}^5) & k_{31} = 664.3 \text{ (ref.}^{11}). \end{array}$$

It is evident from the table that the behaviour of both acids which does not differ too much from the ideal one and the positive deviations from the Lewis relation in case of benzene are very well described by the UNIFAC method and excellently predicted from binary measurements.

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