

**Equilibrium data of the liquid—vapour systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid. III. Experimental data for isothermal multicomponent systems processed by means of the Wilson and Renon equations
Conversion of isothermal data into isobaric data**

^aW. WARADZIN and ^bJ. SUROVÝ

^aResearch Laboratory of the Establishment "Duslo", n. e.,
927 03 Šala

^bDepartment of Chemical Engineering, Slovak Technical University,
880 37 Bratislava

Received 27 February 1975

Isothermal equilibrium data of the ternary and quaternary systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid are presented. The thermodynamic verification was performed by the Tao method. The experimental data were compared with the data calculated from binary parameters by means of the Wilson and NRTL equations. The known temperature dependence of the parameters of the equations was used for the conversion of isothermal data into isobaric data.

Приведены изотермические равновесные данные для трех- и четырехкомпонентных систем, содержащих ацетон, винилацетат, кротоновый альдегид и уксусную кислоту. Термодинамическая проверка была осуществлена при помощи метода Тао. Экспериментальные данные сравнивались со значениями, рассчитанными по бинарным параметрам уравнений Вильсона и NRTL. Изотермические равновесные значения переводились в изобарные на основании известной зависимости параметров уравнений от температуры.

The liquid—vapour equilibrium data of multicomponent mixtures are frequently required for different separation and rectification processes carried out on industrial scale. Therefore their calculation from binary data is very useful. In this paper the multicomponent liquid—vapour data have been calculated by means of binary parameters of the Wilson equation [1] and the NRTL equation [2]. The data obtained in this way are compared with the experimental isothermal data found for the ternary and quaternary mixtures containing acetone, vinyl acetate, crotonaldehyde, and acetic acid.

Since isobaric data are most frequently used in operation, isothermal data have been converted into isobaric data.

Conversion of isothermal data into isobaric data

The conversion was based on the general equation for liquid—vapour equilibrium of the following form

$$\varphi_i y_i P = \gamma_i x_i f_{is}^0 \exp \frac{v_i^{0L} P}{RT}. \quad (1)$$

The conversion was done for the pressure of 760 Torr and therefore it holds

$$P = \sum y_i P = 760. \quad (2)$$

Table 1

Liquid-vapour equilibrium data for the acetone (1)-vinyl acetate (2)-crotonaldehyde (3) system at 35°C

x_1	x_2	y_1	y_2	P/Torr
0.1835	0.1852	0.4963	0.2529	156.20
0.3176	0.1812	0.6375	0.1941	194.99
0.4737	0.1790	0.7410	0.1580	236.10
0.6183	0.1811	0.8072	0.1379	272.88
0.1179	0.3470	0.3249	0.4543	154.24
0.2307	0.3502	0.4859	0.3678	189.26
0.4344	0.2967	0.6714	0.2490	239.09
0.6075	0.2832	0.7660	0.2039	282.38
0.0995	0.5149	0.2531	0.5921	164.40
0.2107	0.5200	0.4160	0.4891	202.46
0.3440	0.5067	0.5480	0.4056	238.10
0.4460	0.4666	0.6293	0.3452	260.52
0.0774	0.7412	0.1834	0.7416	180.91
0.1730	0.7025	0.3387	0.6159	210.08
0.1972	0.7061	0.3691	0.5973	226.98
0.2109	0.7200	0.3826	0.5912	222.69

Table 2

Liquid-vapour equilibrium data for the acetone (1)-vinyl acetate (2)-crotonaldehyde (3) system at 55°C

x_1	x_2	y_1	y_2	P/Torr
0.2250	0.194	0.527	0.241	385.10
0.4280	0.198	0.691	0.184	501.30
0.5830	0.170	0.782	0.140	573.02
0.6410	0.159	0.811	0.126	598.48
0.1790	0.384	0.397	0.429	401.82
0.3190	0.345	0.557	0.325	476.56
0.3940	0.319	0.621	0.282	511.49
0.5480	0.341	0.704	0.261	596.47
0.1300	0.542	0.292	0.573	406.43
0.2240	0.539	0.415	0.496	465.21
0.3560	0.518	0.539	0.417	537.28
0.4420	0.483	0.605	0.369	575.47
0.0820	0.748	0.186	0.740	418.02
0.1430	0.741	0.285	0.668	458.73
0.1850	0.727	0.340	0.625	482.85
0.2560	0.691	0.422	0.558	519.51

Table 3

Liquid-vapour equilibrium data for the vinyl acetate (2)-crotonaldehyde (3)-acetic acid (4) system at 50°C

x_2	x_3	y_2	y_3	P/Torr
0.1645	0.5936	0.4498	0.4746	155.41
0.1492	0.4620	0.4519	0.4017	145.29
0.1422	0.2948	0.4656	0.2731	133.22
0.1276	0.1648	0.4398	0.1691	125.18
0.3243	0.4783	0.6478	0.3040	198.01
0.3063	0.3585	0.6424	0.2556	187.92
0.2936	0.2413	0.6697	0.1700	183.29
0.2814	0.1405	0.6658	0.1039	180.68
0.5096	0.3359	0.7813	0.1869	243.23
0.4986	0.2567	0.8083	0.1291	238.00
0.4839	0.1726	0.8055	0.0971	232.41
0.4488	0.0988	0.7919	0.0635	224.39
0.7008	0.1921	0.8896	0.0912	279.20
0.6973	0.1462	0.8952	0.0730	276.93
0.6941	0.1074	0.9032	0.0488	275.39
0.6943	0.0657	0.9052	0.0366	274.61

Table 4

Liquid-vapour equilibrium data for the vinyl acetate (2)-crotonaldehyde (3)-acetic acid (4) system at 70°C

x_2	x_3	y_2	y_3	P/Torr
0.1588	0.6164	0.4046	0.5110	330.91
0.1388	0.4424	0.3812	0.4196	298.81
0.1305	0.2804	0.4197	0.2615	284.02
0.1244	0.1444	0.4384	0.1347	273.20
0.3243	0.4862	0.6182	0.3163	401.91
0.3083	0.3680	0.6164	0.2699	395.89
0.2879	0.2650	0.6242	0.1972	381.40
0.3293	0.1369	0.6468	0.1017	370.42
0.4915	0.3672	0.7544	0.2084	494.03
0.5387	0.2496	0.7854	0.1528	483.59
0.5441	0.1764	0.8083	0.1111	474.60
0.5236	0.0910	0.7886	0.0621	464.02
0.7626	0.1722	0.8904	0.0973	582.61
0.7401	0.1319	0.8957	0.0718	579.60
0.7644	0.0904	0.9299	0.0466	578.31
0.7537	0.0586	0.9230	0.0312	573.18

From the known temperature dependence of the parameters of the Wilson and Renon equations presented in Part I and Part II of this study [1, 2] the values of activity coefficients were calculated. After inserting in eqn (1) for a given x_i at a certain temperature (temperature for which γ_i is to be determined), the pressure of saturated vapour of pure component is calculated by means of the Antoine equation and subsequently it is inserted in eqn (1). Then it is possible to calculate the compo-

Table 5

Liquid-vapour equilibrium data for the acetone (1)-vinyl acetate (2)-acetic acid (4) system at 45°C

x_1	x_2	y_1	y_2	P/Torr
0.1271	0.1298	0.363	0.401	143.63
0.3128	0.1522	0.614	0.278	224.22
0.4944	0.1895	0.734	0.222	318.62
0.6647	0.1668	0.833	0.150	397.14
0.1071	0.2753	0.240	0.598	180.78
0.2929	0.3382	0.488	0.446	269.80
0.3898	0.3255	0.590	0.367	310.10
0.5859	0.3852	0.679	0.302	369.02
0.1031	0.4746	0.193	0.709	226.09
0.2174	0.4876	0.363	0.581	274.80
0.2785	0.5022	0.438	0.525	306.14
0.3818	0.4915	0.548	0.434	354.60
0.0682	0.6784	0.127	0.810	251.84
0.1274	0.7082	0.229	0.734	284.01
0.1704	0.7008	0.296	0.677	303.42
0.2739	0.6440	0.431	0.555	342.53

Table 6

Liquid-vapour equilibrium data for the acetone (1)-vinyl acetate (2)-acetic acid (4) system at 65°C

x_1	x_2	y_1	y_2	P/Torr
0.1616	0.1449	0.3571	0.2801	272.80
0.3338	0.1519	0.5185	0.3165	357.01
0.4881	0.1709	0.7002	0.2561	489.09
0.6918	0.1813	0.8155	0.1736	753.92
0.1367	0.3328	0.1604	0.6483	362.53
0.2740	0.3381	0.3524	0.5507	445.38
0.4090	0.3321	0.5292	0.4303	546.40
0.5163	0.3373	0.6409	0.3514	683.31
0.1145	0.5390	0.1433	0.7537	447.83
0.1954	0.5180	0.2297	0.7177	493.01
0.2830	0.5269	0.3728	0.5896	585.58
0.3982	0.5019	0.4906	0.4996	699.19
0.0750	0.7713	0.1040	0.8670	537.71
0.1270	0.7174	0.1734	0.7978	555.50
0.1880	0.7176	0.2608	0.7112	619.81
0.2159	0.6909	0.2938	0.6994	634.88

sition of the vapour phase y_i by an approximative solution of eqns (1) and (2). A similar method was used for the solution of systems with association of one component, however, it was necessary to consider the relationships presented in Part I of this study [1]. A more detailed procedure of calculation as well as the block diagram for the solution on a computer is described in [3].

Experimental

The apparatus used was the same as described in Part I of this study [1].

The samples of vapour or liquid phase were analyzed on a chromatograph with a thermal conductivity detector and polymeric separation packing (Porapak Q) [3]. The composition was determined by a direct calibration with respect to major components. The method of linear relation [4, 5] was applied to calculation.

Table 7

Liquid-vapour equilibrium data for the acetone (1)-crotonaldehyde (3)-acetic acid (4) system at 35°C

<i>x</i> ₁	<i>x</i> ₃	<i>y</i> ₁	<i>y</i> ₃	<i>P/Torr</i>
0.1796	0.5936	0.6024	0.3576	112.20
0.1727	0.4275	0.5958	0.3011	101.31
0.1671	0.2777	0.6005	0.2165	90.69
0.1463	0.1706	0.5725	0.1431	78.82
0.3563	0.4678	0.7894	0.1979	167.50
0.3616	0.3414	0.8126	0.1491	155.78
0.3295	0.2355	0.8083	0.1157	140.83
0.3132	0.1358	0.8174	0.0689	126.10
0.5375	0.3290	0.8910	0.1004	218.51
0.5335	0.2450	0.8962	0.0830	209.92
0.5160	0.1719	0.8962	0.0820	198.39
0.4848	0.0919	0.9012	0.0523	183.10
0.7453	0.1626	0.9414	0.0439	266.01
0.7374	0.1380	0.9610	0.0333	270.49
0.7315	0.0939	0.9067	0.0232	265.32
0.8093	0.0453	0.9787	0.0146	285.13

Table 8

Liquid-vapour equilibrium data for the acetone (1)-crotonaldehyde (3)-acetic acid (4) system at 55°C

<i>x</i> ₁	<i>x</i> ₃	<i>y</i> ₁	<i>y</i> ₃	<i>P/Torr</i>
0.1837	0.5898	0.5328	0.4162	224.81
0.1774	0.4307	0.5076	0.3760	206.23
0.1669	0.2826	0.4894	0.2840	190.39
0.1573	0.1546	0.4485	0.1821	153.58
0.3434	0.4548	0.7306	0.2480	310.80
0.3370	0.3263	0.7268	0.2129	288.22
0.3036	0.2405	0.6888	0.1905	254.01
0.3304	0.1429	0.7394	0.1022	248.32
0.5458	0.3052	0.8612	0.1267	426.39
0.5483	0.2362	0.8622	0.1193	399.10
0.5278	0.1598	0.8716	0.0843	379.91
0.5083	0.0888	0.8816	0.0665	340.32
0.7965	0.1440	0.9452	0.0491	609.88
0.8105	0.0802	0.9613	0.0349	600.17
0.8087	0.0732	0.9623	0.0298	598.90
0.7967	0.0466	0.9682	0.0203	579.80

Table 9

Liquid-vapour equilibrium data for the acetone (1)-vinyl acetate (2)-crotonaldehyde (3)-acetic acid (4) system at 60°C

x_1	x_2	x_3	y_1	y_2	y_3	P/Torr
0.2947	0.4353	0.1297	0.4298	0.4872	0.0639	484.40
0.4636	0.3143	0.0972	0.6203	0.3256	0.0446	575.31
0.6621	0.2110	0.0664	0.7918	0.1766	0.0280	690.08
0.8299	0.1034	0.0363	0.9018	0.0820	0.0138	757.02
0.2540	0.3453	0.2820	0.4191	0.4250	0.1471	462.41
0.4803	0.2453	0.1865	0.6662	0.2451	0.0837	572.14
0.6469	0.1623	0.1232	0.8144	0.1359	0.0454	652.09
0.8300	0.0865	0.0598	0.9005	0.0735	0.0240	764.00
0.2651	0.2380	0.4245	0.4728	0.3096	0.2056	469.11
0.4905	0.1706	0.2794	0.6965	0.1776	0.1149	564.28
0.6726	0.1123	0.1775	0.8210	0.1041	0.0702	681.80
0.8392	0.0574	0.0796	0.9126	0.0498	0.0353	749.73
0.2257	0.1068	0.6188	0.5048	0.1534	0.3312	385.62
0.4808	0.0912	0.4250	0.7332	0.0947	0.1676	546.87
0.7006	0.0652	0.2121	0.8712	0.0612	0.0762	689.21
0.8363	0.0347	0.1144	0.9220	0.0309	0.0453	758.40
0.2385	0.3307	0.1496	0.3831	0.4615	0.0928	375.80
0.4095	0.2352	0.0982	0.6511	0.2750	0.0521	488.41
0.6448	0.1520	0.0724	0.8029	0.1487	0.0331	514.58
0.8111	0.0867	0.0426	0.8946	0.0808	0.0161	735.32
0.1918	0.2210	0.3211	0.3866	0.3750	0.1891	361.24
0.4215	0.1762	0.2120	0.6518	0.2191	0.1040	465.50
0.6431	0.1117	0.1270	0.8115	0.1206	0.0539	600.91
0.8189	0.0618	0.0631	0.9146	0.0555	0.0248	739.32
0.2150	0.1511	0.4506	0.4494	0.2489	0.2635	336.59
0.4473	0.1298	0.2935	0.6765	0.1515	0.1566	491.81
0.6208	0.1012	0.2074	0.8179	0.0926	0.0811	593.10
0.8260	0.0505	0.0912	0.9102	0.0446	0.0401	733.40
0.1948	0.0835	0.6146	0.4935	0.1509	0.3377	326.61
0.4073	0.0588	0.4523	0.7124	0.0698	0.2083	461.32
0.6390	0.0525	0.2582	0.8373	0.0544	0.1021	625.20
0.8221	0.0284	0.1212	0.9212	0.0265	0.0498	731.01
0.1977	0.1974	0.1451	0.3643	0.3780	0.1064	300.50
0.4153	0.1469	0.1088	0.6434	0.2239	0.0687	408.51
0.6197	0.1009	0.0724	0.8174	0.1163	0.0331	526.38
0.8143	0.0574	0.0362	0.9256	0.0509	0.0136	706.73
0.1694	0.1293	0.2985	0.3750	0.2808	0.2279	285.31
0.4194	0.1229	0.2074	0.6716	0.1705	0.1212	410.32
0.6294	0.0857	0.1305	0.8148	0.1012	0.0640	573.21
0.8137	0.0468	0.0641	0.9233	0.0430	0.0243	698.12
0.1870	0.0939	0.4488	0.4479	0.1925	0.2914	296.74
0.3764	0.0905	0.3352	0.6612	0.1246	0.1755	402.50
0.6055	0.0581	0.2092	0.8224	0.0679	0.0924	563.71
0.7898	0.0366	0.1071	0.9209	0.0338	0.0390	699.20
0.1791	0.0486	0.6180	0.4680	0.1054	0.3925	288.30
0.4053	0.0465	0.4372	0.7091	0.0626	0.2108	451.00
0.6316	0.0385	0.2510	0.8306	0.0397	0.1196	589.11
0.8267	0.0280	0.1111	0.9281	0.0255	0.0438	719.39
0.1625	0.0813	0.1455	0.3659	0.2302	0.1286	242.41
0.3626	0.0819	0.1036	0.6747	0.1371	0.0676	361.60
0.5900	0.0515	0.0678	0.8427	0.0726	0.0335	462.32

Table 9 (Continued)

x_1	x_2	x_3	y_1	y_2	y_3	P/Torr
0.7944	0.0300	0.0404	0.9393	0.0326	0.0156	643.60
0.1676	0.0641	0.2940	0.5262	0.1662	0.1458	291.19
0.3261	0.0561	0.2216	0.6601	0.1033	0.1491	340.68
0.5267	0.0442	0.1647	0.8306	0.0589	0.0785	477.31
0.7957	0.0266	0.0723	0.9240	0.0286	0.0325	668.86
0.1950	0.0457	0.4491	0.4879	0.1021	0.3268	277.83
0.3353	0.0461	0.3544	0.6547	0.0766	0.2215	375.32
0.6404	0.0352	0.1857	0.8489	0.0410	0.0898	559.90
0.8113	0.0281	0.0915	0.9251	0.0290	0.0376	700.21
0.1907	0.0306	0.5879	0.5114	0.0566	0.3947	286.18
0.3367	0.0286	0.4694	0.6833	0.0452	0.2499	397.63
0.6108	0.0258	0.2778	0.8491	0.0283	0.1095	578.14
0.8102	0.0192	0.1293	0.9261	0.0185	0.0500	716.80

Table 10

Values of Δy and ΔP_{rel} for multicomponent isothermal liquid-vapour equilibrium data calculated from binary data by means of the Wilson equation

System	t °C	$\Delta y_i \cdot 10^2$				$\Delta P_{\text{rel}} \cdot 10^2$
		y_1	y_2	y_3	y_4	
Acetone (1) — vinyl acetate (2) — — crotonaldehyde (3)	35	0.54	0.62	0.40	—	1.74
	55	0.54	0.20	0.32	—	0.64
Acetone (1) — vinyl acetate (2) — — acetic acid (4)	45	1.43	1.87	—	2.40	3.98
	65	3.09	3.47	—	1.11	2.99
Acetone (1) — crotonaldehyde (3) — acetic acid (4)	35	0.82	—	0.78	0.57	1.83
	55	0.72	—	0.96	0.71	5.45
Vinyl acetate (2) — crotonal- dehyd (3) — acetic acid (4)	50	—	1.07	0.84	0.73	4.95
	70	—	1.79	0.96	1.39	2.93
Acetone (1) — vinyl acetate (2) — — crotonaldehyde (3) — — acetic acid (4)	60	2.44	0.73	1.98	1.14	5.79

The experimental liquid-vapour equilibrium data obtained at different temperatures are presented in Tables 1-8 for ternary mixtures and in Table 9 for the quaternary system at 60°C.

Results and discussion

The experimental equilibrium data were thermodynamically verified by means of the general Tao method [6]. The total deviation from thermodynamic consistence defined according to Tao exceeded 5% only in the case of two systems.

Using the temperature dependence of binary parameters of the Wilson equation, the composition of vapour phase as well as the total pressure of individual multicomponent systems was calculated. A comparison with experimental data is given

Table 11

Values of Δy and ΔP_{rel} for multicomponent isothermal liquid-vapour equilibrium data calculated from binary data by means of the Renon equation
(The same systems and the same order as in Table 10)

$\Delta y_t \cdot 10^2$				$\Delta P_{\text{rel}} \cdot 10^2$	Note
y_1	y_2	y_3	y_4		
0.92	1.37	0.54	—	1.80	Minimum Q total
0.94	0.86	0.73	—	1.76	minimum Q for $\alpha_{\text{init}} = 0.3$
0.74	0.74	0.89	—	2.14	minimum Q for $\alpha_{\text{init}} = 0.4$
0.97	0.88	0.59	—	1.75	minimum Q for $\alpha_{\text{init}} = 0.2$
1.10	0.93	0.44	—	0.43	Minimum Q total
1.01	0.85	0.29	—	0.49	minimum Q for $\alpha_{\text{init}} = 0.3$
1.25	1.17	0.51	—	2.80	minimum Q for $\alpha_{\text{init}} = 0.4$
1.61	0.87	0.32	—	0.27	minimum Q for $\alpha_{\text{init}} = 0.2$
3.30	2.91	—	2.00	6.69	Minimum Q total
3.21	2.81	—	2.24	6.23	minimum Q for $\alpha_{\text{init}} = 0.3$
3.27	3.56	—	3.00	7.03	minimum Q for $\alpha_{\text{init}} = 0.4$
3.30	2.92	—	2.00	6.69	minimum Q for $\alpha_{\text{init}} = 0.2$
8.03	6.62	—	2.70	17.7	Minimum Q total
8.16	7.01	—	2.73	18.0	minimum Q for $\alpha_{\text{init}} = 0.3$
7.42	6.01	—	2.02	13.1	minimum Q for $\alpha_{\text{init}} = 0.4$
8.64	7.21	—	2.98	20.3	minimum Q for $\alpha_{\text{init}} = 0.2$
1.87	—	1.22	1.52	4.75	Minimum Q total
1.68	—	0.99	1.38	4.26	minimum Q for $\alpha_{\text{init}} = 0.3$
2.38	—	1.77	1.77	4.83	minimum Q for $\alpha_{\text{init}} = 0.4$
1.92	—	1.24	1.51	4.66	minimum Q for $\alpha_{\text{init}} = 0.2$
3.32	—	2.56	2.67	6.90	Minimum Q total
3.02	—	1.50	1.80	8.81	minimum Q for $\alpha_{\text{init}} = 0.3$
3.00	—	1.38	1.89	7.56	minimum Q for $\alpha_{\text{init}} = 0.4$
3.35	—	2.61	2.74	7.00	minimum Q for $\alpha_{\text{init}} = 0.2$
—	1.69	1.44	0.91	2.22	Minimum Q total
—	1.65	1.43	0.93	2.35	minimum Q for $\alpha_{\text{init}} = 0.3$
—	1.46	1.37	0.87	2.21	minimum Q for $\alpha_{\text{init}} = 0.4$
—	1.85	1.52	0.96	2.39	minimum Q for $\alpha_{\text{init}} = 0.2$
—	3.47	2.26	2.46	5.30	Minimum Q total
—	2.74	1.49	2.08	4.06	minimum Q for $\alpha_{\text{init}} = 0.3$
—	2.74	1.32	1.92	3.84	minimum Q for $\alpha_{\text{init}} = 0.4$
—	3.12	3.52	2.23	4.36	minimum Q for $\alpha_{\text{init}} = 0.2$
4.36	1.34	2.78	1.49	13.8	Minimum Q total
5.10	2.08	2.29	1.37	14.6	minimum Q for $\alpha_{\text{init}} = 0.3$
5.59	3.18	2.05	1.23	12.7	minimum Q for $\alpha_{\text{init}} = 0.4$
4.37	1.44	2.88	1.46	13.7	minimum Q for $\alpha_{\text{init}} = 0.2$

in Table 10. We selected the parameters corresponding to the least value of the minimization function Q from the whole set used as well as the parameters corresponding to the least minimization function of individual initial levels α_{12} (i.e. 0.2; 0.3; 0.4) lest it should be necessary to consider a great number of combinations of the parameters of binary systems for the NRTL equation. A comparison of the calculated and experimental values of y_i and P is given in Table 11.

The comparison of the experimental values with those obtained by means of the Wilson and the NRTL equations, respectively, showed a better agreement with data obtained by means of the Wilson equation.

A comparison of the experimental isobaric $y-x$ data with the data obtained by conversion from the isothermal data could be done only for binary equilibrium data because multicomponent isobaric data of the substances investigated were not available in literature. This conversion was also performed for multicomponent systems, however, it is not presented in this paper since the results were given in [3]. As to the binary equilibrium data, only the data for the vinyl acetate—crotonaldehyde system were not found in the literature. As to other binary systems investigated, at least one piece of information enabling us to compare the $y-x$ values was found in the literature. For the acetone—vinyl acetate system the deviations between the published [10] and calculated compositions of vapour phase amount to 3–4 mole % of acetone while in liquid phase these deviations reach up to 50 mole % of acetone. For the acetone—crotonaldehyde system [9] this difference approximates 35 mole % of acetone in liquid phase. As to the acetone—acetic acid system, the results are in a good agreement with the data published by York [7], Othmer [8, 11], and Polyanskii [9, 12] and this agreement depends on the parameters of the equation used. As regards the vinyl acetate—acetic acid system, there is a great difference in the composition of the vapour phase between the data published by different authors [12–16]. The recalculated data are within the experimental data. For the crotonaldehyde—acetic acid system there is a good agreement of the calculated data with the equilibrium data published by Polyanskii [9].

The agreement between the $y-x$ and $t-x$, y values of the published and calculated isobaric systems may be considered to be relatively good though not excellent. It is described in more detail in [3].

Conclusion

The isothermal data of the ternary and quaternary liquid—vapour equilibria in the systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid are presented in this paper. These substances are of importance for the separation of vinyl acetate in technology of the production of monomer vinyl acetate.

The isothermal multicomponent liquid—vapour equilibrium data were calculated from the binary data by means of the Wilson equation and of the NRTL equation and subsequently they were compared with experimental equilibrium data. It was found that the accuracy was up to the standard of the values of Δy and ΔP_{rel} published for other systems.

The isothermal data were converted into isobaric data on the basis of the known temperature dependence of the parameters of the equations used and the results were compared with the data published for binary mixtures.

Symbols

<i>f</i>	fugacity (pressure)
<i>P</i>	pressure of a system $\left(\text{Torr}; 1 \text{ Torr} = \frac{101\,325}{760} \text{ Pa} \right)$
<i>R</i>	universal gas constant ($\text{cal mol}^{-1} \text{ K}^{-1}$)
<i>T</i>	temperature (K)
<i>v</i>	molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
<i>x</i>	molar fraction in liquid phase
<i>y</i>	molar fraction in vapour phase
<i>γ</i>	activity coefficient
<i>φ</i>	fugacity coefficient

Bottom-indices

- i* designation of a component
- s* state of saturation

Top-indices

- 0 pure component in standard state
- L designation of liquid phase

References

1. Waradzin, W. and Surový, J., *Chem. Zvesti* **29**, 783 (1975).
2. Waradzin, W. and Surový, J., *Chem. Zvesti* **30**, 124 (1976).
3. Waradzin, W., *Thesis*. Slovak Technical University, Bratislava, 1974.
4. Janík, A., *J. Chromatogr.* **54**, 321 (1971).
5. Janík, A. and Hetper, J., *J. Chromatogr.* **54**, 327 (1971).
6. Tao, L. C., *Ind. Eng. Chem., Fundam.* **1**, 119 (1962).
7. York, R. and Holmes, R. C., *Ind. Eng. Chem.* **34**, 345 (1942).
8. Othmer, D. F., *Ind. Eng. Chem.* **35**, 614 (1943).
9. Polyaneskii, N. G., Akchurina, R. A., and Kyimova, L. P., *Zh. Prikl. Khim.* (Leningrad) **40**, 23 (1967).
10. Serafimov, L. A., Tikhonova, V. K., and Lvov, S. V., *Zh. Fiz. Khim.* **38**, 2065 (1964).
11. Timmermans, J., *The Physico-Chemical Constants of Binary Systems in Concentrated Solutions*, Vol. 2. Interscience, New York, 1959.
12. Blout, E. R., Hohenstein, W. P., and Mark, H., *Monomers*. Interscience Publishers, New York, 1949.
13. Morrison, G. D. and Shaw T. P. G., *Trans. Electrochem. Soc.* **63**, 425 (1933).
14. Čapková, A. and Fried, V., *Collect. Czech. Chem. Commun.* **28**, 2235 (1963).
15. Tikhonova, V. K., Timofeev, V. S., Serafimov, L. A., and Tolkacheva, N. L., *Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* **13**, 175 (1970).
16. Rudoi-Kolker, V. M. and Grigoryan, Kh. A., *Zh. Prikl. Khim.* (Leningrad) **37**, 1843 (1964).

Translated by R. Domanský