

# Equilibrium data of the liquid—vapour systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid. I. Experimental data for isothermal binary systems processed by means of the Wilson equation

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Isothermal equilibrium data of the binary systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid were measured in the Gillespie circulation equilibrium apparatus modified according to Dvořák—Boublik. For non-associating binary systems the data were verified thermodynamically by means of the Redlich—Kister planary test. For associating systems the differential test was used. The dependence of  $\gamma_i$  on composition was evaluated for binary systems by means of the Wilson equation. The agreement of the measured and calculated data is comparable with the values published for other systems.

Измерены изотермические равновесные данные бинарных систем ацетона, винилацетата, кротонового альдегида и уксусной кислоты при помощи циркуляционного равновесного прибора Джиллеспи, модифицированного по Дворжаку и Бобублику. Данные для неассоциирующих двойных систем были проверены термодинамически на основании критерия Редлих—Кистера в плоскости. В случае ассоциирующих систем использовался дифференциальный критерий. Зависимость  $\gamma_i$  от состава бинарных систем находилась по уравнению Вильсона. Мера совпадения измеренных и рассчитанных значений соответствовала опубликованным данным для других систем.

In the operation of the vinyl acetate production the major problems consist in the separation of monomer from the reaction mixture after condensation. This separation is carried out by means of rectification. The calculation of rectification equipments requires experimental data on liquid—vapour equilibria of the solutions containing acetone, vinyl acetate, crotonaldehyde, and acetic acid.

The data presented in this paper are processed by means of the Wilson equation. The virtue of this equation consists in the fact that it may be applied to multicomponent systems according to literary data by using only binary parameters.

## *Basic relationships*

### *a) Systems without association*

The criterion of liquid—vapour equilibrium enables us to derive the equilibrium condition for the  $i$ -th component of a mixture in the form

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

and

$$f_{is}^0 = \varphi_i^s(T, P_i^s) P_i^s(T) \exp \left( - \frac{v_i^0 P_i^s}{RT} \right), \quad (2)$$

$$\ln \varphi_i^s = \frac{P_i^s B_{ii}^s}{RT}. \quad (3)$$

The calculation of the vapour phase composition  $y_i$  from eqn (1) at pressure  $P$  and temperature  $T$  of the system is based on the fugacity coefficient  $\varphi_i$  defined by the relationship

$$\ln \varphi_i = (2 \sum_j y_j B_{ij} - B^M) \frac{P}{RT}, \quad (4)$$

where it is valid for the virial coefficient of the mixture

$$B^M = \sum_i^n \sum_j^k y_i y_j B_{ij}, \quad (5)$$

while  $B_{ij} = B_{ji}$ .

For the calculation of the virial coefficients  $B_{ii}$  and  $B_{ij}$  it is possible to use the equation proposed by *O'Connell* and *Prausnitz* [1].

By combining eqns (1) to (5) we obtain

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^s} + \frac{(B_{ii} - v_i^0)(P - P_i^s)}{RT} + \frac{P \delta_{ij} y_j^2}{RT}, \quad (6)$$

while

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}.$$

Equation (6) will be used subsequently for the calculation of  $\gamma_i$  from experimental data.

By means of eqn (1) the equilibrium composition of vapour or liquid phase may be calculated provided the dependence of the Gibbs excess energy on the composition of solution is known. In order to express this relationship, we use the equation proposed by *Wilson* [2, 10] in the form

$$\ln \gamma_i = 1 - \ln \left( \sum_j^n x_j \Lambda_{ij} \right) - \sum_k^n \left( \frac{x_k \Lambda_{ki}}{\sum_j^n x_j \Lambda_{kj}} \right), \quad (7)$$

where it holds for the constants  $\Lambda_{ij}$

$$\Lambda_{ij} = \frac{v_j}{v_i} \exp \left( - \frac{\lambda_{ij} - \lambda_{ii}}{RT} \right) \quad (8)$$

provided  $\Lambda_{ij} > 0$ . The parameters of this equation ( $\lambda_{ij} - \lambda_{ii}$ ) are a measure of the interaction between the molecules  $i$  and  $j$  in solution assuming a linear dependence on temperature

$$\lambda_{ij} - \lambda_{ii} = a + bt, \quad (9)$$

$$\lambda_{ji} - \lambda_{jj} = c + dt. \quad (10)$$

*b) Systems with the association of one component*

Systems which are able to form hydrogen bonds and in which these forces prevail over other interactions may be described by the equilibrium constants of this process [3, 4]. The association of components is especially intense in low-molecular organic acids, in our case in acetic acid.

In a mixture containing an associating substance it is necessary to distinguish every molecular species or constituent of mixture. From this point of view monomer, dimer, and higher units represent two and more constituents of mixture whereas according to thermodynamics they must be regarded merely as one component [5]. Therefore it is necessary to distinguish between the real molar fractions of constituents and the stoichiometric (gross) molar fractions of components of a mixture. The definition of these quantities is given by *Marek* [6].

The gross molar fractions of component *A* may be determined from the relationship valid for a binary mixture involving association to tetramer by means of the following expression

$$y_A = \frac{y_1 + 2y_2 + 3y_3 + 4y_4}{1 + y_2 + 2y_3 + 3y_4} = \frac{y_1 + 2K_2 P y_1^2 + 3K_3 P^2 y_1^3 + 4K_4 P^3 y_1^4}{1 + K_2 P y_1^2 + 2K_3 P^2 y_1^3 + 3K_4 P^3 y_1^4}, \quad (11)$$

where it holds

$$y_1 + y_2 + y_3 + y_4 + y_B = y_1 + K_2 P y_1^2 + K_3 P^2 y_1^3 + K_4 P^3 y_1^4 + y_B = 1. \quad (12)$$

*Prigogine* and *Defay* [7] deduced the subsequent relation for reacting system containing an associating component in equilibrium in two phases

$$\mu_{A1}^L = \mu_A^G. \quad (13)$$

*Francesconi* and *Trevisoi* [8] generalized this assumption for real equilibrium systems and obtained for gross chemical potentials of a component

$$\mu_{A1} = \mu_A^G = \mu_A^L. \quad (14)$$

By applying this equation and eqn (1) to the equilibrium in systems with an associating component, rearranging, and assuming that vapour phase is not an ideal solution, *i.e.*  $\delta_{ij} = 0$  [9], we obtain the expression for the activity coefficient of a gross component in the form

$$\ln \gamma_A = \ln \frac{P y_1}{x_A P_A^0 y_1 (y_{A=1})} + \frac{(B_1 + v_A^0)(P - P_A^0)}{RT}, \quad (15)$$

which is similar to eqn (6) where  $\delta_{ij} = 0$ .

For  $y_1(y_{A=1})$ , *i.e.* a pure associating component subjected, for instance, to dimerization where  $y_A = 1$  it holds

$$y_1(y_{A=1}) = \frac{\sqrt{1 + 4K_2 P_A^0} - 1}{2K_2 P_A^0}. \quad (16)$$

*Thermodynamic verification of data*

The Redlich—Kister test is most frequently used for isothermal binary data. This test was also applied in the present case. Assuming the validity of symmetrical

convention for activity coefficients, this planary test may be considered to be fulfilled according to the condition formulated by *Praussnitz* [4].

For isothermal binary systems with association we used the so-called differential test recommended by *Francesconi* [8, 23], in the form

$$I + I(B) = \int_{Y_{A1}}^{Y_{A2}} \frac{x_A}{P y_1} d(P y_1) + \int_{Y_{A1}}^{Y_{A2}} \frac{1 - x_A}{P y_1'} d(P y_1') + \frac{1}{RT} \int_{P_1}^{P_2} (x_A B_1 + (1 - x_A) B_1') dP = 0, \text{ where it holds } v_i^{0L} \ll B. \quad (17)$$

## Experimental

### Preparation of pure substances

*Acetone*: The analytical grade chemical (SLZ Hnúšťa-Likier) was mixed with an aqueous solution of  $\text{AgNO}_3$  and after adding a 10% solution of  $\text{NaOH}$  it was stirred for 10 min. Then the solution was filtered and dried with copper(II) sulfate. Finally, it was distilled in a column with 40 plates and 1 : 60 reflux [12].

*Vinyl acetate*: Pure vinyl acetate suitable for polymerization (Duslo, n.e., Šaľa, activity 20 min [13, 14]), stabilized with hydroquinone against polymerization was three times shaken with distilled water (ratio 10 : 1) for removing water-soluble impurities. Then it was dried with calcined  $\text{CaCl}_2$  and distilled in a column with 40 plates at normal pressure in an inert atmosphere ( $\text{N}_2$ ) at the 1 : 60 reflux [15]. Vinyl acetate obtained was stabilized with diphenylamine (0.03%) and hydroquinone (0.01%) [16].

*Crotonaldehyde*: Crude crotonaldehyde obtained in the production of acetic acid (Duslo, n.e., Šaľa) was frozen out at  $-30^\circ\text{C}$ . The non solidified portion was dried with calcined  $\text{CaCl}_2$  and rectified in a column with 30 plates at normal pressure. The fraction going in the interval between 100.5 and 102.5°C was taken. The distillate was frozen out again, dried, and rectified in a column with 30 plates and 1 : 60 reflux. The clear, colourless distillate was stabilized with hydroquinone (0.05%) against polymerization and oxidation [17].

Table 1

Some physicochemical properties of the prepared substances

Substance		$d^{20}$ g cm <sup>-3</sup>	B.p. °C	$n_D^{20}$
Acetone	exp	0.7903	56.10	1.3588
	publ	0.7905–0.792	56.05–56.67	1.3588–1.35911
Vinyl acetate	exp	0.9303	72.55	1.3953
	publ	0.9312–0.9321	72.5–73.0	1.395–1.3958
Crotonaldehyde	exp	0.8483	102.15*	1.4361
	publ	0.8477–0.8516	102.1–105	1.436–1.4737
Acetic acid	exp	1.0492	118.05	1.3719
	publ	1.049–1.0516	117.72–118.7	1.3715–1.3721

exp — experimental data, publ — data presented in [9].

\*At 759. 83 Torr.

Table 2

Coefficients in eqn (18) for individual binary systems

System	A	B	C	D	Max. rel. error %
Acetone—vinyl acetate	0.9320	-0.3411	0.5384	-0.3431	2.55
Acetone—crotonaldehyde	0.8487	-0.0303	-0.0559	0.0280	0.18
Acetone—acetic acid	1.0496	-0.2873	0.0164	0.0118	0.28
Vinyl acetate—crotonaldehyde	0.8485	0.1150	-0.0674	0.0342	0.16
Vinyl acetate—acetic acid	1.0490	-0.2017	0.1254	-0.0421	0.15
Crotonaldehyde—acetic acid	1.0499	-0.2531	0.0754	-0.0234	0.21

Table 3

Coefficients in eqn (19) for individual binary systems

System	A	B	Max. rel. error %
Acetone—vinyl acetate	79.4599	67.3332	0.02
Acetone—crotonaldehyde	92.3367	39.9842	0.04
Acetone—acetic acid	62.6509	12.7342	0.03
Vinyl acetate—crotonaldehyde	-137.7113	-115.3272	0.01
Vinyl acetate—acetic acid	236.6256	-118.5449	0.21
Crotonaldehyde—acetic acid	35.6406	-12.1677	0.06

Table 4

Liquid—vapour equilibrium data for the system acetone (1)—vinyl acetate (2)

25°C			35°C			50°C		
$x_1$	$y_1$	P/Torr	$x_1$	$y_1$	P/Torr	$x_1$	$y_1$	P/Torr
0.907	0.942	221.95	0.902	0.936	333.96	0.971	0.979	608.25
0.768	0.851	208.96	0.850	0.904	328.12	0.924	0.947	598.26
0.719	0.823	205.18	0.745	0.828	315.32	0.872	0.909	588.07
0.714	0.817	204.07	0.587	0.721	292.95	0.834	0.882	580.52
0.646	0.773	196.65	0.511	0.660	281.28	0.752	0.827	563.33
0.584	0.725	190.10	0.358	0.532	256.95	0.698	0.784	552.67
0.559	0.708	188.02	0.288	0.460	242.87	0.675	0.768	546.47
0.382	0.565	166.15	0.217	0.378	228.06	0.624	0.730	533.93
0.276	0.459	155.29	0.148	0.284	216.29	0.619	0.728	531.10
0.219	0.388	148.52	0.140	0.272	215.10	0.457	0.610	495.36
0.143	0.289	136.05	0.066	0.147	200.12	0.369	0.525	474.50
0.068	0.157	126.51				0.328	0.493	458.07
0.063	0.144	125.50				0.297	0.463	450.27
						0.226	0.377	427.75
						0.115	0.232	388.93

*Acetic acid:* The analytical grade chemical (Lachema, Brno) was frozen out and  $\text{Cr}_2\text{O}_3$  (2%) and acetic anhydride were added. Then it was distilled in a column with 40 plates and 1 : 60 reflux [12].

Some physicochemical properties of the substances thus prepared (Table 1) were measured and compared with the literary data of several authors which are quoted in the whole extent in [9].

### Apparatus

All measurements were carried out in a Gillespie circulation apparatus modified according to *Dvořák–Boublík* [18] with electromagnetic stirring. A Cottrel pump was heated with electric coil. The bumping boil was prevented by crest heating. The vacuum in the system was achieved by means of a vacuum pump and controlled with a contact mercury manostat. The thermostatic control of the receivers of equilibrium still was done by means of a cooling NBE thermostat accurate to  $\pm 1^\circ\text{C}$ . The pressure was read on a mercury manometer by means of a cathetometer accurate to  $\pm 0.01$  Torr. The temperature was measured with an Anschütz thermometer accurate to  $\pm 0.01^\circ\text{C}$ .

### Composition of binary mixtures

The composition of binary equilibrium mixtures was determined by means of an empirical relationship between refractive index  $n_D^{20}$  or density  $\rho^{20}$  and composition. For density, the calibration relationships were processed mathematically into the form of polynomial

$$\rho^{20} = A + Bx + Cx^2 + Dx^3 \text{ (g cm}^{-3}\text{)}. \quad (18)$$

For the refractive index we used the equation according to *Lama and Lu* [19] in the form

$$A + Bx_2 = \frac{x_1 x_2}{n_D - n_{D_1} x_1 - n_{D_2} x_2}. \quad (19)$$

The coefficients of these equations are listed in Tables 2 and 3.

Table 5

Liquid–vapour equilibrium data for the system acetone (1)–crotonaldehyde (2)

25°C			40°C			55°C		
$x_1$	$y_1$	$P/\text{Torr}$	$x_1$	$y_1$	$P/\text{Torr}$	$x_1$	$y_1$	$P/\text{Torr}$
0.902	0.9771	212.42	0.9275	0.983	399.36	0.9390	0.9790	700.87
0.8437	0.962	203.96	0.8440	0.959	373.99	0.8830	0.9590	675.84
0.7735	0.944	190.82	0.771	0.9411	349.54	0.8020	0.9360	638.02
0.6795	0.92	174.88	0.6882	0.9163	324.16	0.7599	0.9220	618.28
0.6155	0.8985	163.39	0.6117	0.8910	300.43	0.6598	0.8868	573.20
0.525	0.8685	147.77	0.5505	0.866	281.71	0.6055	0.8680	544.84
0.433	0.831	132.26	0.429	0.809	240.31	0.4955	0.8280	493.31
0.3472	0.779	118.73	0.3572	0.7585	217.20	0.3605	0.7581	421.45
0.2845	0.734	104.76	0.297	0.721	194.90	0.2810	0.7026	376.86
0.1757	0.630	84.17	0.219	0.6378	167.42	0.2240	0.6500	338.88
0.13	0.557	73.61	0.147	0.5264	139.15	0.1627	0.5730	292.25
0.047	0.312	51.30	0.084	0.3822	113.23	0.0925	0.4310	234.18

Table 6

Liquid—vapour equilibrium data for the system vinyl acetate (2)—crotonaldehyde (3)

40°C			55°C			70°C		
$x_2$	$y_2$	$P/\text{Torr}$	$x_2$	$y_2$	$P/\text{Torr}$	$x_2$	$y_2$	$P/\text{Torr}$
0.952	0.9765	217.31	0.975	0.988	401.39	0.977	0.988	686.14
0.885	0.945	210.05	0.924	0.964	391.06	0.942	0.971	674.27
0.777	0.893	196.94	0.879	0.941	380.36	0.859	0.924	646.03
0.731	0.870	192.25	0.835	0.919	370.18	0.836	0.914	637.69
0.656	0.832	181.74	0.779	0.892	358.29	0.794	0.891	626.06
0.587	0.797	172.57	0.708	0.857	342.25	0.708	0.847	593.88
0.519	0.760	165.33	0.680	0.839	334.71	0.618	0.798	562.88
0.46	0.716	157.48	0.609	0.804	316.38	0.589	0.775	551.85
0.419	0.694	151.07	0.548	0.766	304.87	0.44	0.682	494.66
0.339	0.625	140.36	0.509	0.744	297.31	0.389	0.642	475.05
0.285	0.575	131.64	0.482	0.717	288.75	0.313	0.575	439.13
0.22	0.497	119.53	0.406	0.669	272.80	0.226	0.478	398.19
0.151	0.396	107.80	0.293	0.558	242.14	0.140	0.362	350.54
0.108	0.314	98.78	0.229	0.485	223.41	0.112	0.307	335.77
0.0503	0.175	87.85	0.149	0.379	198.39	0.043	0.140	290.83

Table 7

Liquid—vapour equilibrium data for the system acetone (1)—acetic acid (4)

35°C			45°C			55°C		
$x_1$	$y_1$	$P/\text{Torr}$	$x_1$	$y_1$	$P/\text{Torr}$	$x_1$	$y_1$	$P/\text{Torr}$
0.921	0.9983	320.2	0.9340	0.9985	476.6	0.9670	0.9993	675.66
0.8795	0.9971	305.2	0.896	0.998	456.4	0.932	0.9975	631.07
0.6755	0.9695	235.1	0.837	0.9948	426.8	0.778	0.9885	497.2
0.5967	0.9508	207.85	0.738	0.985	375.3	0.750	0.9845	476.1
0.5231	0.928	182.82	0.645	0.966	325.92	0.651	0.9649	408.6
0.4445	0.8968	157.65	0.558	0.9375	284.3	0.569	0.938	354.7
0.3685	0.8499	135.2	0.412	0.8488	216.7	0.499	0.904	313.2
0.2781	0.7714	108.64	0.280	0.713	154.6	0.407	0.8265	258.8
0.2245	0.7056	92.35	0.232	0.661	134.3	0.322	0.729	215.3
0.1682	0.6157	73.72	0.162	0.551	106.5	0.154	0.466	136.4
0.1050	0.4700	55.05	0.056	0.256	66.3	0.106	0.374	116.3
0.0508	0.2735	40.1						

The experimental data of binary equilibrium mixtures obtained at different temperatures are presented in Tables 4—9. Individual systems without association fulfill the condition of consistence. The systems with the association of one component evaluated according to eqn (17) also give consistent data provided the formation of dimer is taken into consideration [9].

#### Calculation of coefficients of the Wilson equation

The solution of the Wilson eqn (7) for binary systems was performed on a computer Minsk-22. The principle of the computational method consisted in a minimization of the function in the form proposed by *Renon* [11]

Table 8

Liquid—vapour equilibrium data for the system vinyl acetate (2)—acetic acid (4)

35°C			50°C			70°C		
$x_2$	$y_2$	$P/\text{Torr}$	$x_2$	$y_2$	$P/\text{Torr}$	$x_2$	$y_2$	$P/\text{Torr}$
0.8730	0.977	162.62	0.797	0.955	279.38	0.941	0.986	656.19
0.731	0.940	145.84	0.685	0.918	255.01	0.884	0.970	622.85
0.628	0.908	132.79	0.472	0.824	209.97	0.833	0.962	594.76
0.587	0.888	126.36	0.453	0.811	206.39	0.774	0.943	561.58
0.476	0.845	114.50	0.411	0.782	197.48	0.693	0.905	525.18
0.390	0.799	101.46	0.359	0.748	182.31	0.594	0.865	480.53
0.350	0.772	97.22	0.303	0.702	168.40	0.437	0.746	415.29
0.220	0.653	77.03	0.156	0.503	123.88	0.285	0.621	346.86
0.137	0.519	63.85	0.125	0.443	109.56	0.184	0.522	295.28
0.053	0.298	42.43	0.120	0.435	107.36	0.097	0.357	234.87
			0.113	0.412	103.33			
			0.056	0.244	81.62			

Table 9

Liquid—vapour equilibrium data for the system crotonaldehyde (3)—acetic acid (4)

50°C			75°C			100°C		
$x_3$	$y_3$	$P/\text{Torr}$	$x_3$	$y_3$	$P/\text{Torr}$	$x_3$	$y_3$	$P/\text{Torr}$
0.8950	0.9679	111.78	0.9050	0.9625	290.36	0.9720	0.9912	688.54
0.7795	0.9008	105.48	0.822	0.9137	279.59	0.816	0.9016	652.17
0.6943	0.8442	100.50	0.709	0.8338	264.48	0.734	0.8370	637.96
0.563	0.7253	91.49	0.612	0.7549	249.62	0.637	0.7724	612.10
0.4965	0.6701	86.32	0.515	0.6615	236.46	0.545	0.6832	585.22
0.426	0.5878	84.86	0.434	0.5706	225.76	0.506	0.6333	573.14
0.3025	0.4430	77.78	0.361	0.4847	216.78	0.421	0.5345	548.07
0.2796	0.4104	75.20	0.290	0.3949	207.82	0.359	0.4692	531.48
0.2012	0.2998	69.99	0.206	0.2812	197.17	0.265	0.3419	502.26
0.151	0.2186	66.58	0.158	0.2172	191.56	0.196	0.2473	480.65
0.0955	0.1486	61.82	0.119	0.1636	186.41	0.161	0.2011	470.64
0.043	0.0669	60.82	0.102	0.1404	184.27	0.080	0.1017	445.30

$$Q = \sum 100^2 (y_1^{\text{calc}} - y_1^{\text{exp}})^2 + \sum \left( \frac{100}{P^{\text{exp}}} \right)^2 (P^{\text{calc}} - P^{\text{exp}})^2. \quad (20)$$

The minimization was performed by approximating the coefficients  $A_{ij}$  of eqn (13) according to the gradient method. The more detailed computational procedure as well as the block diagram of computation is presented in [9].

### Results and discussion

The values of coefficients of the Wilson equation (eqn (7)) calculated from binary data are presented in Table 10. This table also contains the mean quadratic deviations



Table 10

Values of the coefficients in the Wilson equation

System	$T$ °C	$A_{12}$	$A_{21}$	$\Delta y \cdot 10^2$	$\Delta P_{\text{rel}} \cdot 10^2$
Acetone—vinyl acetate	25	0.700	1.125	0.47	0.50
	35	0.668	1.137	0.27	0.57
	50	0.625	1.137	0.35	0.28
Acetone—crotonaldehyde	25	0.488	1.232	0.32	0.57
	40	0.870	0.887	0.27	0.23
	55	0.756	0.753	0.22	0.29
Acetic acid—acetone	35	1.183	0.908	0.64	1.08
	45	0.465	1.945	1.30	1.00
	55	0.376	2.841	1.79	4.82
Vinyl acetate—crotonaldehyde	40	0.870	0.818	0.32	0.42
	55	0.763	0.974	0.41	0.39
	70	0.720	0.945	0.28	0.20
Acetic acid—vinyl acetate	35	0.762	0.613	0.65	1.31
	50	0.587	0.869	0.59	1.01
	70	1.077	0.419	0.97	0.27
Acetic acid—crotonaldehyde	50	0.283	1.463	0.78	1.37
	75	0.332	1.382	0.13	0.45
	100	0.158	1.555	0.72	0.32

Table 11

Temperature dependence of the parameters in the Wilson equation

System	$a$ cal mol <sup>-1</sup>	$b$ cal mol <sup>-1</sup> K <sup>-1</sup>	$c$ cal mol <sup>-1</sup>	$d$ cal mol <sup>-1</sup> K <sup>-1</sup>
Acetone—vinyl acetate	128.730	6.617	-184.590	-0.910
Acetone—crotonaldehyde	618.956	-8.011	-430.791	10.232
Acetic acid—acetone	-1195.044	37.747	1186.457	-37.734
Vinyl acetate—crotonaldehyde	-149.480	4.182	278.977	-2.490
Acetic acid—vinyl acetate	771.199	-5.872	-406.808	8.086
Acetic acid—crotonaldehyde	340.787	11.942	-333.697	-2.498

Table 12

Values of  $\Delta y$  and  $\Delta P_{\text{rel}}$  for binary systems

System	$\Delta y \cdot 10^2$	$\Delta P_{\text{rel}} \cdot 10^2$
Acetone—vinyl acetate	0.78	1.07
Acetone—crotonaldehyde	1.05	3.13
Vinyl acetate—crotonaldehyde	0.42	0.81
Acetic acid—acetone	1.70	4.07
Acetic acid—vinyl acetate	0.94	2.69
Acetic acid—crotonaldehyde	0.59	1.63

between the measured and calculated values of the composition,  $\Delta y$ , and of the relative pressure,  $\Delta P_{\text{rel}}$ . These deviations were calculated by means of eqns (21) and (22)

$$\Delta y = \sqrt{\frac{\sum (y_{\text{exp}} - y_{\text{calc}})^2}{n}} \quad (21)$$

$$\Delta P_{\text{rel}} = \sqrt{\frac{\sum \left( \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)^2}{n}} \quad (22)$$

Assuming a linear dependence of parameters on temperature, the values of coefficients in eqns (9) and (10) have been calculated (Table 11). Using these coefficients, all binary data have been processed regardless of temperature and the values of  $\Delta y$  and  $\Delta P_{\text{rel}}$  are given in Table 12. The agreement of the measured and calculated data thus achieved is not so good as in the case when the calculation was performed by means of the coefficients obtained immediately for a given temperature (Table 10). The values of the calculated data are consistent with analogous data processed by means of the Wilson equation and published in literature.

### Conclusion

This paper presents isothermal data for the binary liquid–vapour equilibria in systems containing acetone, vinyl acetate, crotonaldehyde, and acetic acid which are important for the technology of the production of vinyl acetate.

The data presented were verified by means of the common relationships valid for systems without association as well as with association of one component. It was found that the association had to be respected, otherwise the results appeared to be thermodynamically inconsistent.

The equilibrium data were processed by means of the Wilson equation. The coefficients in the equation were ascertained by the gradient method. On the basis of the measurements at different temperatures the temperature dependence of parameters of the Wilson equation was determined.

### Symbols

$A, B, C, D$	empirical coefficients in eqns (18) and (19)
$a, b, c, d$	empirical coefficients in eqns (9) and (10)
$B$	virial coefficient ( $\text{cm}^3 \text{mol}^{-1}$ )
$f$	fugacity (pressure)
$I$	value of integral (eqn (17))
$I(B)$	value of integral (eqn (17)) if the virial coefficient is considered
$K$	equilibrium constant of association
$n$	number of experimental points
$n_D$	refractive index
$P$	pressure of system $\left( \text{Torr}; 1 \text{ Torr} = \frac{101\,325}{760} \text{ Pa} \right)$
$Q$	minimization function
$R$	universal gas constant ( $\text{cal mol}^{-1} \text{K}^{-1}$ )
$T$	temperature (K)

$v$	molar volume ( $\text{cm}^3 \text{mol}^{-1}$ )
$x$	molar fraction of liquid phase
$Y$	integration limits in terms of molar fraction (eqn (17))
$y$	molar fraction in vapour phase
$\gamma$	activity coefficient
$\Delta$	mean quadratic deviation
$\delta$	difference between virial coefficients (eqn (6))
$\Lambda$	coefficient in the Wilson equation
$\lambda$	parameter in the Wilson equation ( $\text{cal mol}^{-1}$ )
$\mu$	chemical potential
$\rho$	density ( $\text{g cm}^{-3}$ )
$\varphi$	fugacity coefficient

*Bottom-indices*

$i, j, k$	designation of a component
1, 2, 3, 4	designation of monomer, dimer, trimer, and tetramer
$B$	designation of inert component
$A$	designation of associating component (acetic acid)

*Top-indices*

0	pure component in standard state
$s$	pure component in the state of saturation
$M$	designation of mixture
$L$	designation of liquid state
$G$	designation of gaseous state
calc	calculated
exp	experimental
20	designation of the temperature of 20°C

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