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

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Isothermal equilibrium data published in [1] were processed by means of the Renon NRTL equation. The values of individual constants of the equation used are given. Furthermore, a procedure for a convenient choice of initial parameters applicable to the iterative calculation of the parameters in the NRTL equation by the Newton method is presented. The results obtained indicate a non-uniqueness of solution of the NRTL equation.

Изотермические равновесные данные, уведенные в I части этой работы [1], были обработаны уравнением NRTL Ренона. Приводятся отдельные константы использованного уравнения. Дан также приём подходящего выбора начальных параметров для вычисления параметров уравнения NRTL итерационным методом Ньютона. Полученные данные указывают на неоднозначность решения уравнения NRTL.

The equation derived by *Renon* [2] was used for processing the experimental data [1] expressing the dependence of γ_i on composition of the solutions containing acetone, vinyl acetate, crotonaldehyde, and acetic acid. Some problems concerning the use of this equation are discussed in this paper.

Renon derived the expression for the dependence of activity coefficients on composition in the general form

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l \tau_{lj} G_{lj} x_l}{\sum_k G_{kj} x_k} \right), \tag{1}$$

where

$$\tau_{ij} = \frac{(g_{ij} - g_{jj})}{RT} \tag{2}$$

and

$$G_{ij} = \exp\left(-\alpha_{ij} \frac{(g_{ij} - g_{jj})}{RT} \right). \tag{3}$$

Renon [3, 4] assumed a linear temperature dependence of the parameters $(g_{ij} - g_{ii})$ and α_{ij} which involves six parameters of the binary NRTL equation in the form

$$C_{ij} = g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^T(T - 273.15), \tag{4}$$

$$C_{ji} = g_{ji} - g_{ii} = C_{ji}^0 + C_{ji}^T(T - 273.15), \tag{5}$$

$$\alpha_{ij} = \alpha_{ij}^0 + \alpha_{ij}^T(T - 273.15), \tag{6}$$

where $C_{ij,ji}^0$ and α_{ij}^0 stand for the values of parameters at °C and $C_{ij,ji}^T$ and α_{ij}^T are the temperature coefficients.

The dependence of parameters on temperature thus obtained enables us to convert the isothermal data into isobaric data or to calculate the data corresponding to a temperature different from that one used for experiment [5].

Calculation of the parameters of the NRTL equation

The procedure recommended by Renon which is based on the Newton method of the solution of non-linear equations was used for the calculation of the parameters of the NRTL equation from experimental liquid—vapour equilibrium data.

According to literature the NRTL equation has a non-unique solution. *Boyarinov* [6] has shown that there are several possible sets of coefficients by means of which it is possible to obtain the sets of practically equal multicomponent equilibrium data. *Greiner et al.* [7] processed some data concerning liquid—liquid equilibrium and came to a similar conclusion.

In order to obtain parameters of the NRTL equation suited for the data given in [1] which show minimum deviations between the calculated and experimental values of the vapour phase composition and of the relative pressure, the following condition has to be fulfilled

$$\left(\frac{\partial Q}{\partial C_i}\right)_{C_j \neq i} = 0 \qquad (i = 1, 2, \qquad k). \tag{7}$$

System (7) has as many equations as the number of parameters of the NRTL equation considered. Equation (20) of Part I of this study [1] was used as a minimization function. The linearization of the system and the calculation of coefficients were performed by the Newton method described elsewhere [4, 8].

Selection of parameters for the first estimate

According to literary data the values of parameters C_i $(C_{12}, C_{21}, \alpha_{12})$ are in the intervals $C_{12} \in (-1000; 2000)$; $C_{21} \in (-1000; 2000)$, and $\alpha_{12} \in (0; 1)$ for most binary systems. The procedure for the first estimate of parameters at a certain temperature was as follows:

a) Choice of arbitrary values of initial parameters C_{12}, C_{21}, and α_{12} and calculation of the refined parameters.

b) Parameter α_{12} is fixed during calculation and the other two parameters are subjected to iteration.

c) Analysis of the network of parameters C_i $(C_{12}, C_{21}, \alpha_{12})$ in which there are two possible procedures:

ca) α_{12} is arbitrary for initial calculation of the network;

cb) α_{12} is constant and selected from physicochemical properties of the substances

while the parameters found for the minimum of function Q serve as data of the first estimate for calculation.

For all binary systems described in Part I of this study [1] the initial values of parameters were assumed to be C_i^0 (800; 800; 0.3) and thus the value of minimization function was calculated. It was found that the result obtained was not satisfactory. The function
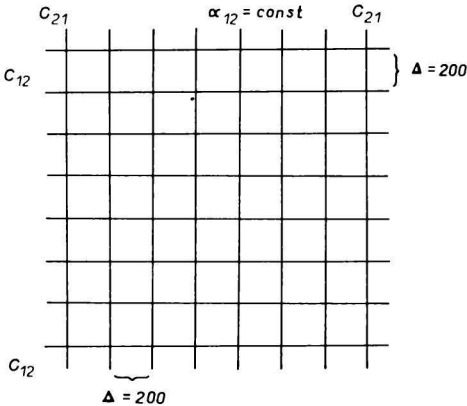

Fig. 1. Network for the determination of parameters of the NRTL equation.

Q had a too high value for the finite solution and α_{ij} almost always converged to a value approximating one unit for the number of iterations equalling 70. Since these results were not satisfactory, we fixed α_{ij} = const during calculation while the initial values of other two parameters used for starting iteration were C_i^0 (800; 800). The values of the minimization function Q and the corresponding parameters C_i thus calculated were also unsatisfactory and for this reason we proceeded to the so-called analysis of parameter network. The detailed results of these solutions are presented in full in [8]. The procedure was as follows: For various combinations of parameters C_{12} and C_{21} varying by the value $\varDelta C = 200$ (Fig. 1) at a constant value of α_{12} the value of the minimization function Q was calculated. For each temperature the smallest three values of Q and the corresponding parameters C_{12}, C_{21}, and α_{12} were selected. From these results the parameters of eqns (4—6) $C_{12}^0, C_{12}^T, C_{21}^0, C_{21}^T, \alpha_{12}^0, \alpha_{12}^T$ were determined for individual systems by the method of least squares. The parameters thus obtained were used as parameters for the first estimate allowing to solve the NRTL equation of binary mixtures (eqn (1)) by the Newton method. The values of these parameters applied to individual systems are listed in Table 1.

It is worth mentioning that the selected three least values of the minimization function Q, though not quite equal, do not give substantial differences between $\varDelta y$ and $\varDelta P_{\text{rel}}$. In some cases two values of the function Q are equal or very near but the corresponding values of parameters are rather different.

The detailed procedure with particular steps of solution and complete results is presented in full extent in [8].

Discussion

The values of $\varDelta y$ and $\varDelta P_{\text{rel}}$ obtained for individual binary systems by means of the parameters calculated by the above procedure are presented in Table 1.

A comparison of the results obtained by means of the NRTL equation involving six parameters with the results obtained by means of the Wilson equation involving

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Table 1

Values of Δy and ΔP_{rel} for binary systems calculated by means of the six parameter NRTL equation

System	C_{ij}^0	C_{ij}^T	C_{ji}^0	C_{ji}^T			$\Delta y \cdot 10^2$	$\Delta P_{rel} \cdot 10^2$
Acetone—vinyl acetate	−324.35	4.8592	413.15	−2.202	−0.0641	0.0115	0.36	0.47
	156.96	1.1435	−95.19	1.6239	0.5378	−0.011	0.43	0.79
	1100.0	−76.4	−1170	87.1	0.0545	−0.0007	0.28	0.75
	2211.1	−138.7	−2391.4	152.86	0.0192	−0.0002	0.37	0.67
	−499.63	18.582	606.50	−16.77	1.5760	−0.0315	0.34	0.83
	475.81	−38.77	−524.7	48.434	0.1229	−0.0013	0.33	0.68
	1079.1	−85.86	−1159.3	96.298	0.0261	−0.0002	0.30	0.71
	140.29	−27.63	−120.5	34.218	0.1085	−0.0011	0.34	0.51
Acetone—crotonaldehyde	−23.95	−26.98	724.69	14.925	0.3474	−0.0063	2.94	8.04
	−834.0	17.3	943.0	−13.1	−0.677	0.0305	0.92	2.24
	−3003	55.872	3321.4	−55.31	−0.146	0.0069	0.65	1.36
	−578.6	12.321	768.95	−10.66	−0.4625	0.0266	1.07	2.86
	−1453.9	28.699	1589.0	−24.46	−0.5693	0.0238	0.61	1.27
	−3364.9	61.934	3770.9	−62.92	−0.1134	0.0056	0.49	1.31
	−3509.1	64.537	3897.7	−65.35	−0.1025	0.0051	0.63	1.36
	−3049.7	56.844	3350.8	−55.93	−0.1528	0.0072	0.67	1.48
Acetone—acetic acid	−421.75	−8.42	591.13	9.81	0.4424	−0.005	2.54	10.2
	483.98	−3.879	−365.4	0.966	0.7499	−0.0077	2.00	8.97
	−386.54	−0.18	379.68	0.921	0.2950	0.0020	2.15	9.41
	−172.77	−0.43	188.96	−0.027	0.739	−0.008	2.56	10.4
	−217.90	−0.347	234.96	−0.676	0.559	−0.003	2.58	10.5
	580.11	−7.238	−366.9	2.598	1.0133	−0.0004	1.89	8.48
	−1053.9	−0.068	1016.0	7.243	−0.052	0.0045	1.75	8.23
	−123.72	−6.93	361.79	2.09	1.272	−0.023	2.43	10.2
	365.09	−1.82	−399.3	1.544	0.0986	−0.0004	2.15	9.44

Table 1 (Continued)

System	C_{ij}^0	C_{ij}^T	C_{ji}^0	C_{ji}^T	α_{ij}^0		$\Delta y \cdot 10^2$	$\Delta P_{rel} \cdot 10^2$
Vinyl acetate—	897.22	−12.09	−771.7	13.88	0.5033	0.0126	0.53	1.28
—crotonaldehyde	−249.0	3.87	385.0	−2.2	−0.253	0.0092	0.55	0.75
	2188.2	−29.27	−1787	27.18	−0.956	0.0239	0.99	2.72
	789.0	−10.3	−671.0	12.2	−0.54	0.0135	0.53	0.85
	−477.0	7.73	547.0	−5.36	−1.26	0.0323	0.56	0.61
	1183.7	−14.06	−944.5	13.11	1.4861	0.0331	1.27	2.50
	719.92	−9.668	−592.0	11.42	0.4914	0.0123	0.53	0.89
	−190.69	2.94	323.89	−1.23	−0.35	0.0100	0.54	0.79
	192.83	−2.54	−61.05	4.085	2.1249	−0.0282	0.61	0.79
Vinyl acetate—acetic	−151.20	−0.905	225.39	1.064	−0.084	0.0026	1.34	2.18
acid	−79.51	1.007	489.84	1.02	0.1906	0.0007	1.35	2.14
	141.32	2.530	339.09	−4.11	1.3466	−0.0191	1.49	2.22
	204.96	−0.134	210.91	−0.08	0.569	−0.002	1.45	2.22
	161.49	−9.577	199.42	10.77	0.0963	−0.0006	1.22	2.19
	−13.098	−4.489	574.22	5.901	0.3829	−0.0022	2.75	5.02
	147.23	−0.315	246.46	0.256	0.0672	0.0003	1.30	2.21
	61.283	−4.747	337.08	5.079	0.1407	−0.0007	1.25	2.12
	535.42	−20.51	−128.4	24.29	0.3734	−0.0039	1.75	3.13
Crotonaldehyde—acetic	573.89	1.3738	−178.0	−1.19	0.3074	−0.0008	1.29	1.76
acid	424.35	56.728	−196.4	−46.38	0.0454	−0.0002	0.83	1.45
	560.73	48.092	−283.5	−38.93	0.0564	−0.0003	0.75	1.37
	238.07	8.9486	73.779	−7.024	0.334	−0.002	1.19	1.56
	507.91	12.727	−111.7	−9.323	0.3208	0.0019	0.77	1.41
	−44.48	8.5553	334.75	−6.849	0.3793	0.0022	1.61	2.13
	717.82	1.56	−328.5	−1.36	0.228	−0.0005	1.29	2.04
	413.20	54.581	−181.4	−44.54	0.0478	−0.0003	0.83	1.43
	1407.8	3.8	−646.2	−3.13	0.2369	−0.0008	1.22	2.24

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the dependence of parameters on temperature (see Table 12 in Part I of this study [1]) shows that the NRTL equation is unambiguously more suited for the acetone—vinyl acetate and acetone—crotonaldehyde systems. The Wilson equation is without doubt more suited for the acetone—acetic acid and vinyl acetate——crotonaldehyde systems. For the vinyl acetate—acetic acid and crotonalde-hyde—acetic acid systems the value of Δy calculated according to the Wilson equation is smaller, but the value of ΔP_{rel} is smaller if it is calculated according to the NRTL equation.

Conclusion

In presented paper the isothermal binary liquid—vapour equilibrium data obtained for the acetone—vinyl acetate — crotonaldehyde—acetic acid systems are processed by means of the Renon NRTL equation. The results are compared with the results obtained by means of the Wilson equation for the systems investigated, but it is not possible to decide unambiguously which of these two equations is more serviceable.

A precedure for the selection of the parameters for the first estimate allowing to proceed to the iterative solution of the NRTL equation by the Newton method is briefly described. It was found that more solutions of the NRTL equation were possible on the basis of which it could be concluded that the parameters were more of a mathematical than of an exact physical importance.

Symbols

C difference between the parameters of the NRTL equation (cal mol^{-1})
G coefficient in eqn (1)
g parameter of the NRTL equation (cal mol^{-1})
Q minimization function
R universal gas constant (cal mol^{-1} K^{-1})
T temperature (K)
x composition of liquid phase
α nonrandomness parameter
γ activity coefficient
τ coefficient in eqn (1)

Bottom-indices

i, j, k designation of a component

Top-indices

0 designation of zero temperature
T designation of temperature T

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