Application of the Wilson Equation with Binary Parameters to the Prediction of the Isothermal Vapour-Liquid Equilibrium Data of Ternary and Quaternary Systems in the Assessment of the Polar Solvent in Extractive Distillation

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Equilibrium P—x data were measured at a temperature of 69.7 °C for the mixtures hexane—cyclohexane, hexane—benzene—cyclohexane, hexane—cyclohexane—N-methylpyrrolidone, and hexane—benzene—cyclohexane—N-methylpyrrolidone. These equilibrium data along with data of other previously published systems were used in the assessment of the suitability of the Wilson equation for the prediction of vapour-liquid equilibrium for multicomponent mixtures employed in the extractive distillation.

Extractive distillation is very often implemented for the separation of components of liquid mixtures exhibiting an azeotrope or for close boiling mixtures. In the presence of a polar agent called the solvent, which manifests affinity toward one of the components of the original mixture, the azeotropic point disappears and the relative volatility adequately alters. Prerequisites for the choice of a suitable solvent and a suitable ratio of the amount of solvent to the separated mixture are vapour-liquid equilibrium (VLE) data. Experimental equilibrium data of given systems must be first processed prior to their application in form of the relative volatility or the coefficient of selectivity in the assessment of the suitability of selected solvents. In the case of a qualitative reproducibility of equilibrium data a significant position has particularly the dependence of activity coefficients of components on the liquid mixture composition. In our previous works [1, 2] dealing with similar problems we used for this dependence the Wilson equation with binary parameters. Whether it is possible to predict the equilibrium of three- and four-component systems sufficiently precisely by the application of the Wilson equation with binary parameters will be verified by the comparison of measured equilibrium data with calculated values of the total pressure above a solution of known composition. As the object of investigation the quaternary mixture hexane—benzene—cyclohexane—N-methylpyrrolidone, four related three-component systems, and six related two-component systems were used. Measurements of some above-mentioned systems in form of equilibrium P—x data at 69.7 °C were published in our previous papers. The rest of measurements will be given in this contribution.

EXPERIMENTAL

Hexane (component 1) was obtained from technical grade hexane by rectification in a column with a separation efficiency equivalent to 70 theoretical plates. The chromatographic grade of hexane prepared in this manner was 99.6 %. Benzene (component 2) of chromatographic grade was obtained from benzene without thiophene in a rectification column with 70 plates and twofold freezing of distillate. Cyclohexane (component 3) was a product purified by rectification and employed for chromatographic purposes. N-Methylpyrrolidone (component 4) was prepared from technical solvent by twofold rectification at a pressure of 4 kPa. Physical properties of materials prepared in this way and then used in the experimental part of the work are listed in Table 1.

Isothermal P—x equilibrium data were determined by a static method reported by *Renon* [3] and modified by *Surový* [4]. The pressure was measured with an accuracy of ± 25 Pa, the temperature was maintained with an accuracy of ± 0.05 °C. In Tables 2—5 are given vapour pressures P_{exp} measured above solutions of known composition at a temperature of 69.7 °C for mixtures hexane—cyclohexane, hexane—benzene—cyclohexane, hexane—cyclohexane—N-methylpyrrolidone, and hexane—benzene—cyclohexane—N-methylpyrrolidone.

Further mixtures, hexane—benzene, hexane—N-methylpyrrolidone, benzene—cyclohexane, benzene—N-methylpyrrolidone, cyclohexane—N-methylpyrrolidone as well as ternary mixtures hexane—benzene—N-methylpyrrolidone, benzene—cyclohexane—N-methylpyrrolidone, the equilibrium data of which were

Table 1. Physical Properties of Materials Prepared

Component	Refractive index at 20 °C n_D	Density at 25 °C $g\ cm^{-3}$
Hexane	1.3751	0.6550
	1.3749 [5]	0.6548 [5]
Benzene	1.5010	0.8736
	1.0511 [5]	0.8737 [5]
Cyclohexane	1.4262	0.7785*
	1.4262 [5]	0.7786*[5]
N-Methylpyrrolidone	1.4686	1.0284
	1.4680 [5]	1.0280 [5]

*Measured at 20 °C.

Table 2. Measured and Calculated Values of Vapour Pressure in the System Hexane—Cyclohexane at a Temperature of 69.7 °C

x_1	P_{exp}/kPa	P_{calc}/kPa
0	72.17	–
0.0900	75.71	75.69
0.1779	78.99	78.94
0.2640	81.95	81.98
0.3512	84.94	84.94
0.4344	87.57	87.66
0.5163	90.30	90.25
0.5983	92.77	92.77
0.6774	95.07	95.13
0.7616	97.58	97.59
0.8371	99.86	99.74
0.9235	102.24	102.16
1	104.27	–

Average deviation of pressure equals ± 0.052 %.

x_1 – mole fraction of hexane, P – vapour pressure above the solution.

Table 3. Measured and Calculated Values of Vapour Pressure in the System Hexane—Benzene—Cyclohexane at a Temperature of 69.7 °C

x_1	x_2	P_{exp}/kPa	P_{calc}/kPa
0.1610	0.6385	86.50	86.62
0.1187	0.4708	84.47	84.63
0.0923	0.3660	82.69	82.87
0.0410	0.1623	77.71	77.99
0.3152	0.4824	92.07	92.21
0.2362	0.3614	88.02	88.30
0.1575	0.2411	83.59	83.83
0.0772	0.1182	78.25	78.45
0.4784	0.3243	95.86	96.13
0.3630	0.2461	91.71	91.15
0.2350	0.1595	85.02	85.14
0.1207	0.0818	79.02	79.21
0.6373	0.1585	97.91	98.11
0.4896	0.1218	92.61	92.75
0.3222	0.0801	86.21	86.29
0.1602	0.0398	79.57	79.51

Average deviation of pressure equals ± 0.23 %.

x_1, x_2 – mole fractions of hexane and benzene, P – vapour pressure above the solution.

Table 4. Measured and Calculated Values of Vapour Pressure in the System Hexane—Cyclohexane—*N*-Methylpyrrolidone at a Temperature of 69.7 °C

x_1	x_3	P_{exp}/kPa	P_{calc}/kPa
0.1567	0.6394	73.35	74.04
0.1170	0.4773	71.09	71.86
0.0782	0.3188	67.22	67.85
0.0396	0.1616	54.66	55.68
0.3085	0.4931	80.25	80.19
0.2292	0.3663	77.06	78.09
0.1533	0.2450	74.23	74.61
0.0788	0.1261	62.33	63.49
0.4734	0.3158	85.81	86.26
0.3553	0.2371	83.66	84.30
0.2345	0.1565	81.06	81.03
0.1206	0.0805	69.47	70.47
0.6413	0.1631	91.46	91.71
0.5163	0.1313	89.55	89.97
0.3238	0.0823	87.47	86.70
0.1528	0.0389	74.31	75.38

Average deviation of pressure equals ± 0.90 %.

x_1, x_3 – mole fractions of hexane and cyclohexane, P – vapour pressure above the solution.

measured by the same technique, can be found in papers [1, 2].

The saturated vapour pressure measured above the solution was calculated by the relation

$$P = \sum_i P_i^{\circ} x_i \gamma_i / \Phi_i \tag{1}$$

where the correction coefficient for individual components Φ_i is given by the equation

$$\Phi_i = \frac{\varphi_i^{g}}{\varphi_{is}^{o} \exp\left[\frac{v_i^{ol}}{RT}\left(P - P_i^{o}\right)\right]} \tag{2}$$

In the case of a real vapour phase and low pressure, Φ_i can be considered dependent solely on the properties of pure components at given pressure and given temperature of the system. Correlations for its calculation were taken from the paper published by *O'Connell* and *Prausnitz* [6].

Activity coefficients of components in the liquid solution at T = const practically depend only on the composition of the solution. For their calculation we can use the Wilson equation [7]. This equation was modified for a multicomponent system with n compo-

Table 5. Measured and Calculated Values of Vapour Pressure in the System Hexane—Benzene—Cyclohexane—*N*-Methylpyrrolidone at a Temperature of 69.7 °C

x_1	x_2	x_3	P_{exp}/kPa	P_{calc}/kPa
0.2527	0.2806	0.2604	82.37	82.75
0.1903	0.2113	0.1961	77.61	78.39
0.1254	0.1392	0.1292	70.83	71.46
0.0583	0.0647	0.0600	55.52	53.96
0.3114	0.1584	0.3204	82.83	83.44
0.2301	0.1171	0.2368	79.35	80.00
0.1626	0.0828	0.1673	74.90	75.66
0.0752	0.0383	0.0775	58.18	60.32
0.0779	0.0396	0.0802	59.32	61.17
0.2011	0.4069	0.2025	82.19	81.59
0.1472	0.2979	0.1482	74.93	75.35
0.0977	0.1976	0.0983	66.55	66.77
0.0494	0.1000	0.0497	48.54	49.98
0.1919	0.2075	0.3826	78.47	78.98
0.1473	0.1592	0.2935	74.26	75.25
0.0963	0.1041	0.1919	68.27	68.66
0.0473	0.0512	0.0947	51.52	53.17
0.1569	0.3196	0.3071	77.85	78.41
0.1212	0.2470	0.2373	73.41	73.69
0.0785	0.1600	0.1538	65.19	65.28
0.0399	0.0813	0.0781	47.88	49.25
0.3925	0.1989	0.1973	86.83	87.39
0.3007	0.1524	0.1512	83.95	84.23
0.1986	0.1007	0.0999	79.05	78.95
0.0956	0.0484	0.0481	63.02	64.10
0.5171	0.1419	0.1305	91.11	90.93
0.3808	0.1045	0.0961	88.37	87.85
0.2595	0.0712	0.0655	85.13	83.76
0.1190	0.0326	0.0300	67.77	68.99

Average deviation of pressure equals ± 1.24 %.

x_1, x_2, x_3 – mole fractions of hexane, benzene, and cyclohexane, P – vapour pressure above the solution.

nents by *Orye* and *Prausnitz* [8] in the following form

$$\ln \gamma_i = 1 - \ln\left(\sum_{j=1}^{n} x_j \Lambda_{ij}\right) - \sum_{k=1}^{n}\left(\frac{x_k \Lambda_{ki}}{\sum_{j=1}^{n} x_j \Lambda_{kj}}\right) \quad (3)$$

In this equation parameters Λ_{ii} have a value equal to one. Parameters Λ_{ij} have a binary character and for their calculation experimental P—x data of binary mixtures were used. The form of the Wilson equation for a binary mixture is as follows

$$\ln \gamma_i = -\ln(x_i + x_j \Lambda_{ij}) + + x_j\left(\frac{\Lambda_{ij}}{x_i + x_j \Lambda_{ij}} - \frac{\Lambda_{ji}}{x_j + x_i \Lambda_{ji}}\right) \quad (4)$$

Equation for the calculation of $\ln \gamma_j$ is obtained by replacement of index i by index j and *vice versa*. In eqn (*4*) index i is always related to a component with a lower serial number and index j to a higher serial number.

RESULTS AND DISCUSSION

Parameters of the Wilson equation Λ_{ij} and Λ_{ji} were calculated by the Gauss—Newton iteration method using the following objective function

$$F = \sum_h \left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}}\right)_h^2 \quad (5)$$

where P_{exp} is the value of the total pressure measured above the solution and P_{calc} is the calculated value of the h-th measurement.

Calculated values of Wilson parameters for the mixture hexane—cyclohexane are given in Table 6, which includes also values of parameters of other binary mixtures, which had been reported in the previous papers.

Table 6. Calculated Values of the Wilson Equation Parameters Λ_{ij} and Λ_{ji} from Binary P—x Data at a Temperature of 69.7 °C

System i—j	Λ_{ij}	Λ_{ji}	Ref.
1—2	0.5668	1.0550	[1]
1—3	0.8276	1.1103	This paper
1—4	0.1899	0.1118	[1]
2—3	0.8780	0.7768	[2]
2—4	1.8657	0.2783	[1]
3—4	0.3939	0.1088	[2]

Values of calculated pressures according to eqn (*1*) are always given in the last column in Tables 2—5. At the bottom of these tables are given also values of the average relative deviation in the vapour pressure

$$\bar{d} = \frac{100}{n} \sum \frac{|P_{\text{exp}} - P_{\text{calc}}|}{P_{\text{exp}}} \quad (6)$$

where n represents the number of equilibrium measurements.

In Table 7 are presented values of average deviations in vapour pressures $\bar{d}$ and the number of measured equilibrium data n of the studied four-component system, which form a comprehensive and mutually interconnected set of information.

From the gained results it follows that the Wilson equation with binary parameters is a suitable tool for the expression of the activity coefficients of the liquid mixture in predicting of the isothermal VLE data so for three-component systems as for four-component systems containing aliphatic, aromatic and/or cyclanic hydrocarbons and a polar solvent.

While isothermal equilibrium P—x data are mainly used in the investigation of the influence of the polar solvent on alterations of the relative volatility

Table 7. Summary of Values of Average Relative Deviations in Vapour Pressure ($\bar{d}$) and the Number of Measurements (n) for Individual Systems

System	$\frac{\bar{d}}{\%}$	n	Ref.
1—2	0.12	13	[1]
1—3	0.052	11	This paper
1—4	0.69	12	[1]
2—3	0.21	12	[2]
2—4	0.22	13	[1]
3—4	0.64	13	[2]
1—2—3	0.23	16	This paper
1—2—4	1.36	16	[1]
1—3—4	0.90	16	This paper
2—3—4	1.09	16	[2]
1—2—3—4	1.24	29	This paper

of components of the original (hydrocarbon) mixture, isobaric equilibrium t—x, y data are necessary for the calculation of the separation effect on the plates of the rectification column. It can be supposed that also for the isobaric VLE data Wilson's equation will be an equally suitable relation. The procedure for the treatment of t—x, y data, however, will be different and different will be also Wilson's parameters having the form of energy differences of interactions $\lambda_{ij} - \lambda_{ii}$ and $\lambda_{ji} - \lambda_{jj}$.

The possibilities of application of the Wilson equation in predicting equilibrium for the purposes of extractive distillation are extensive in the light of the availability of a great number of binary parameters of the Wilson equation assembled in the DECHEMA Data Bibliography [9].

SYMBOLS

$\bar{d}$	average relative deviation in vapour pressure
F	objective function
n	number of measured data
P_{calc}	calculated saturated vapour pressure above the solution
P_{exp}	measured saturated vapour pressure above the solution
P_i^{o}	saturated vapour pressure of the pure component
P	pressure above the solution, pressure of the system
R	gas constant
T	absolute temperature
v_i^{ol}	molar volume of the pure liquid component
x_i	mole fraction of component in the liquid solution
γ_i	activity coefficient of component in the liquid solution
Λ_{ij}, Λ_{ji}	binary parameters of the Wilson equation
φ_i^{g}	fugacity coefficient of component in the vapour phase
$\varphi_{\text{is}}^{\text{o}}$	fugacity coefficient of pure component in the saturation state
Φ_i	correction coefficient for the real behaviour of component in the vapour phase

Subscripts

h	serial number of the experiment
i	arbitrary component
l, g	liquid or vapour phase
1, 2, 3, 4	components of the system (1 - hexane, 2 - benzene, 3 - cyclohexane, 4 - *N*-methylpyrrolidone)

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