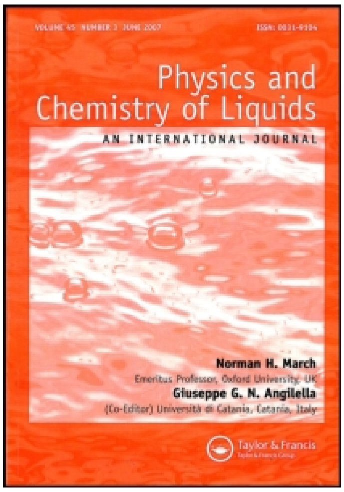

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VAPOUR-LIQUID EQUILIBRIUM OF THE TERNARY SYSTEM (BENZENE + CYCLOHEXANE + HEXANE) AT 40.0 kPa AND 101.3 kPa

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The isobaric vapour-liquid equilibrium has been experimentally studied for the ternary mixture (Benzene + Cyclohexane + Hexane) at pressures of 40.0 kPa and 101.3 kPa. The equilibrium data have been correlated using the equations of Wilson, NRTL and UNIQUAC. They have been also compared with the results obtained from the application of the modified UNIFAC group contribution method. The mixture does not show azeotrope.

KEY WORDS: Isobaric vapour-liquid equilibrium, ternary mixture, Wilson, NRTL, UNIQUAC, UNIFAC.

INTRODUCTION

The knowledge of vapour-liquid equilibrium (VLE) provides information about the behaviour of liquid mixtures and is an essential requirement to design the processes of separation of liquid mixtures by means of distillations. So, there are many binary systems in that respect[1–5]; however, the complexity and difficulty corresponding to the experimental determination of vapour-liquid equilibrium data significantly increase when the number of components goes up. Because of this, the experimental study of the vapour-liquid equilibrium for multicomponent systems and the evaluation of methods to predict it by comparing with the experimental results are important subjects.

The present paper reports experimental data of the isobaric vapour-liquid equilibrium for the ternary mixture (Benzene + Cyclohexane + Hexane) at two different pressures (40.0 and 101.3 kPa). The experimental results are compared with those calculated through the equations of Wilson[6], NRTL[7], UNIQUAC[8] and the modified UNIFAC group contribution method[9].

The vapour-liquid equilibrium for the binary mixtures (Benzene + Cyclohexane), (Benzene + Hexane) and (Cyclohexane + Hexane) have been studied a number of times. On the contrary, only the work of Ridway *et al.*,[10] has been found in literature for the isobaric vapour-liquid equilibrium of the ternary mixture (Benzene + Cyclohexane + Hexane) at a single pressure 101.3 kPa.

EXPERIMENTAL

Benzene and hexane used were provided by Aldrich, while cyclohexane was obtained from Lab. Scan. Their purity is: benzene > 99.9%, cyclohexane > 99.8% and hexane > 99%. The measured physical properties of the pure compounds (densities, speeds of sound and normal boiling points) are gathered in Table 1 along with the corresponding ones found in literature.

The vapour-liquid equilibrium experiments in this study were performed using an all-glass, dynamic recirculating still, equipped with a Cottrell pump. It is a commercial unit (Labodest model) built by Fischer capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. This still allows good mixing of the vapour and liquid phases and a good separation of the phases once they reach equilibrium, and it prevents entrainement of liquid drops and partial condensation in the vapour pressure.

The temperature was measured using a thermometer (model F25) from Automatic System Laboratories, and the accuracy is ±0.01K. Pressure was measured with a pressure transducer Druck PDCR 110/W and pressure indicator PDI201 with an accuracy of ±0.1kPa.

In each experiment, the work pressure was fixed and the heating and shaking system of the liquid mixture was connected. The system was kept at the boiling-point for 15 min. to ensure the stationary state. Once it was reached samples (approximately 2 ml) of liquid and vapour from the Cottrell pump were taken. The composition of the liquid and vapour samples were determined by measuring their densities and speeds of sound at 298.15 K with an Anton Paar DMA-48 vibrating tube densimeter and sound analyser. This was previously calibrated at atmospheric pressure with doubly distilled water and dry air.

The experimental densities, ρ, and speeds of sound, u, at 298.15 K have been previously reported[11] as a function of composition for this ternary system. The composition dependence of these properties has been established using the following equation:

$$S = \sum_{i=1}^{3} \sum_{j=1}^{m} A_{ij} x_i^j \tag{1}$$

were S is ρ/gcm^{-3} o $u/\mathrm{m\ s}^{-1}$, x_i the mole fraction of component i and A_{ij} adjustable coefficients. As a result of the crossing of density and speed of sound isolines, the

Table 1 Physical properties of the pure compounds.

			Benzene	*Cyclohexane*	*Hexane*
$\rho/(\mathrm{gcm}^{-3})^a$		exp.	0.8736	0.7737	0.6550
		lit.[b]	0.87360	0.77389	0.65484
$u/(\mathrm{ms}^{-1})^a$		exp.	1299.73	1254.45	1077.67
		lit.	1299.08[c]	1253.78[c]	1076.42[d]
$T_b/(\mathrm{K})$	101.3 kPa	exp.	353.26	353.92	341.92
		lit.[b]	353.24	353.88	341.89

[a] at 298.15 K; [b] Reference 21.; [c] Reference 22.; [d] Reference 23.

Table 2 Adjustable coefficients of the Eq. (1) for the densities, ρ, speeds of sound, u, and boiling points, T_b, of liquid phase for the ternary mixture (Benzene + Cyclohexane + Hexane) at 40.0 and 101.3 kPa along with the corresponding standard deviations, σ.

$\rho/(\mathrm{g\,cm^{-3}})^a$	$A_{11} = 0.8232$	$A_{12} = 0.0433$	$A_{13} = -0.0108$	$A_{14} = 0.0178$
	$A_{21} = 0.7822$	$A_{22} = 0.0064$	$A_{23} = -0.0366$	$A_{24} = 0.0218$
	$A_{31} = 0.6222$	$A_{32} = 0.0180$	$A_{33} = 0.0324$	$A_{34} = -0.0175$
				$\sigma = 0.0002$
$u/(\mathrm{m\,s^{-1}})^a$	$A_{11} = 1206.73$	$A_{12} = 101.26$	$A_{13} = -50.66$	$A_{14} = 42.41$
	$A_{21} = 1248.32$	$A_{22} = 51.81$	$A_{23} = -93.01$	$A_{24} = 47.40$
	$A_{31} = 1007.21$	$A_{32} = 107.22$	$A_{33} = -39.87$	$A_{34} = 3.08$
				$\sigma = 0.27$
$T_b/(\mathrm{K})$				
40.0 kPa	$A_{11} = 315.70$	$A_{12} = 13.13$	$A_{13} = -12.63$	$A_{14} = 9.89$
	$A_{21} = 326.01$	$A_{22} = 2.34$	$A_{23} = -5.46$	$A_{24} = 3.29$
	$A_{31} = 307.95$	$A_{32} = 16.25$	$A_{33} = -12.94$	$A_{34} = 4.14$
				$\sigma = 0.07$
101.3 kPa	$A_{11} = 344.16$	$A_{12} = 7.21$	$A_{13} = -1.59$	$A_{14} = 3.57$
	$A_{21} = 354.94$	$A_{22} = -3.08$	$A_{23} = 3.71$	$A_{24} = -1.55$
	$A_{31} = 332.17$	$A_{32} = 25.48$	$A_{33} = -26.66$	$A_{34} = 10.97$
				$\sigma = 0.06$

[a] Reference 11.

composition can be determined from the density, the speed of sound, and the parameters A_{ij}. The estimated error in the determination of both liquid and vapour phase mole fractions is ± 0.001.

RESULTS AND DISCUSSION

The vapour-liquid equilibrium data $(T_b, x_1, x_2, y_1, y_2)$ and the activity coefficients at 40.0 and 101.3 kPa thus obtained are shown in Tables 3 and 4, respectively.

The activity coefficients, γ_i, were calculated from the equation of Van Ness and Abbott[12]:

$$\ln \gamma_i = \ln\left(\frac{y_i P}{x_i p_i^0}\right) + (B_{ii} - v_i^0)\left(\frac{P - p_i^0}{RT}\right) + \left(\frac{P}{2RT}\right)\sum_1^n \sum_1^n y_i y_k (2\delta_{ji} - \delta_{jk}) \tag{2}$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \tag{3}$$

In Eq. (2), x_i and y_i are the mole fractions of component i in the liquid phase and in the vapour phase respectively, P is the total pressure, p_i^0 the vapour pressure of pure i component that we have calculated from the Antoine equation taking the coefficients A, B, and C from Gmehling[13], B_{ii} are the second virial coefficients of component i obtained from the expressions included in the TRC Tables[14], while B_{ij} are the cross second virial coefficients estimated by means of the Amdur-Mason equation[15]. The molar volumes of the saturated liquids, v_i^0, were determined by the method of Yen and Woods[16].

Table 3 Experimental vapour-liquid equilibrium data for the ternary mixture ((x_1) Benzene + (x_2) Cyclohexane + ($1 - x_1 - x_2$) Hexane) at 40.0 kPa.

T_b/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
316.23	0.103	0.108	0.102	0.082	1.431	1.089	0.995
316.33	0.229	0.093	0.209	0.069	1.310	1.061	1.021
316.65	0.336	0.085	0.302	0.055	1.272	0.916	1.053
317.18	0.459	0.056	0.391	0.040	1.182	0.992	1.090
317.88	0.572	0.037	0.473	0.025	1.116	0.926	1.163
317.81	0.031	0.286	0.020	0.223	0.849	1.047	1.009
317.63	0.106	0.271	0.109	0.206	1.400	1.032	1.005
317.55	0.230	0.239	0.223	0.180	1.327	1.025	1.030
317.81	0.343	0.210	0.319	0.157	1.259	1.003	1.065
318.36	0.478	0.163	0.417	0.130	1.155	1.049	1.125
319.17	0.604	0.121	0.517	0.104	1.100	1.092	1.193
320.17	0.718	0.085	0.612	0.078	1.052	1.124	1.319
321.63	0.810	0.055	0.703	0.055	1.014	1.149	1.428
319.73	0.036	0.480	0.038	0.384	1.331	1.001	1.012
319.23	0.159	0.423	0.167	0.337	1.339	1.015	1.026
319.19	0.258	0.379	0.257	0.303	1.276	1.019	1.049
319.29	0.274	0.321	0.351	0.265	1.199	1.047	1.086
319.71	0.505	0.256	0.452	0.223	1.126	1.089	1.154
320.32	0.607	0.204	0.533	0.189	1.078	1.133	1.223
321.08	0.710	0.152	0.618	0.154	1.040	1.209	1.325
322.09	0.800	0.105	0.705	0.118	1.012	1.292	1.452
323.23	0.874	0.065	0.792	0.081	0.997	1.389	1.541
324.67	0.950	0.019	0.903	0.032	0.991	1.792	1.479
321.78	0.028	0.691	0.037	0.592	1.534	0.993	1.042
321.18	0.127	0.622	0.147	0.526	1.379	1.001	1.049
320.97	0.226	0.552	0.240	0.470	1.274	1.014	1.062
320.92	0.431	0.410	0.410	0.368	1.143	1.072	1.133
321.30	0.540	0.331	0.496	0.314	1.087	1.116	1.186
321.70	0.643	0.261	0.579	0.262	1.051	1.165	1.302
322.41	0.747	0.184	0.671	0.205	1.019	1.259	1.390
323.35	0.844	0.114	0.772	0.142	1.002	1.370	1.502
323.95	0.058	0.848	0.052	0.805	0.968	1.016	1.109
323.53	0.124	0.790	0.154	0.720	1.350	0.991	1.084
322.96	0.221	0.703	0.252	0.637	1.267	1.005	1.105
322.62	0.325	0.607	0.345	0.557	1.195	1.030	1.109
322.48	0.443	0.501	0.442	0.475	1.129	1.070	1.145

The boiling points of the ternary mixtures have been fitted to a polynomial according to the Eq. (1). The coefficients A_{ij} for the fitting of $\rho/(\mathrm{gcm}^{-3})$, $u/(\mathrm{ms}^{-1})$ and $T_b/(\mathrm{K})$ to the Eq. (1) at 40.0 and 101.3 kPa are listed in Table 2. Figures 1 and 2 show the isolines corresponding to the boiling points of the liquid phase at 40.0 and 101.3 kPa, respectively.

The thermodynamic consistency of the experimental data has been checked by means of the point to point test of Van Ness[17], modified by Fredenslund[18] and extended to multicomponent mixtures using the following equation proposed by Prausnitz[19] in order to determine the activity coefficient, γ_i, of any component i:

$$\ln \gamma_i = Q + \left(\frac{\partial Q}{\partial x_i}\right)_{T,P,x_{j \neq i}} - \sum_{j=1}^{k-1} x_j \left(\frac{\partial Q}{\partial x_j}\right)_{T,P,x_{i \neq j}} \tag{4}$$

Table 4 Experimental vapour-liquid equilibrium data for the ternary mixture ((x_1) Benzene + (x_2) Cyclohexane + ($1 - x_1 - x_2$) Hexane) at 101.3 kPa.

T_b/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
351.17	0.085	0.812	0.105	0.752	1.321	1.001	1.065
349.75	0.071	0.721	0.083	0.641	1.295	1.004	1.061
348.14	0.063	0.591	0.071	0.506	1.307	1.014	1.025
346.56	0.050	0.462	0.055	0.379	1.353	1.019	1.017
351.13	0.310	0.668	0.353	0.615	1.213	0.997	1.127
349.61	0.272	0.612	0.308	0.527	1.265	0.975	1.138
348.27	0.230	0.543	0.242	0.470	1.222	1.020	1.060
347.07	0.196	0.468	0.205	0.394	1.257	1.029	1.034
346.00	0.160	0.389	0.179	0.295	1.398	0.957	1.039
344.94	0.121	0.301	0.122	0.240	1.299	1.042	1.014
344.03	0.084	0.222	0.084	0.174	1.329	1.056	1.008
343.34	0.050	0.158	0.049	0.123	1.344	1.075	1.005
350.53	0.503	0.472	0.516	0.444	1.113	1.035	1.277
348.88	0.442	0.440	0.442	0.392	1.140	1.031	1.158
347.35	0.374	0.389	0.370	0.326	1.183	1.016	1.100
346.26	0.320	0.337	0.314	0.275	1.213	1.020	1.062
345.18	0.260	0.278	0.257	0.216	1.265	1.006	1.041
344.49	0.214	0.233	0.207	0.185	1.264	1.049	1.025
343.88	0.166	0.186	0.161	0.145	1.290	1.052	1.016
343.18	0.107	0.133	0.100	0.105	1.313	1.087	1.009
342.68	0.052	0.087	0.052	0.069	1.368	1.119	1.003
350.54	0.693	0.283	0.657	0.300	1.028	1.166	1.436
348.15	0.607	0.263	0.558	0.254	1.063	1.133	1.198
346.81	0.519	0.232	0.479	0.193	1.122	1.023	1.149
345.60	0.445	0.200	0.413	0.152	1.170	0.969	1.108
344.65	0.366	0.166	0.335	0.133	1.190	1.054	1.054
343.89	0.293	0.138	0.281	0.089	1.280	0.872	1.048
343.34	0.227	0.112	0.219	0.076	1.310	0.937	1.026
342.81	0.153	0.084	0.146	0.067	1.313	1.101	1.011
351.79	0.878	0.105	0.835	0.130	0.993	1.309	1.648
349.18	0.792	0.100	0.713	1.067	1.017	1.222	1.363
347.32	0.705	0.088	0.618	0.080	1.049	1.103	1.253
345.70	0.605	0.070	0.527	0.052	1.096	0.943	1.167

where k is the number of components in the mixture, x_i is the mole fraction of component i in the mixture and Q is the reduced excess Gibbs free energy, $Q = G^E/RT$. We have used an equation of Redlich-Kister type extended to a multicomponent mixture in order to establish the relationship between Q and the liquid phase composition:

$$Q = \sum_{i=1}^{k} \sum_{j=i+1}^{k} x_i x_j \sum_{p=0}^{p} A_p (x_i - x_j)^p + x_1 x_2 (1 - x_1 - x_2)(B_1 + B_2 x_1 + B_3 x_2) \quad (5)$$

Table 5 Coefficients of the Antoine equation log (P/ mmHg) = A − B/(C + t(°C)) for the vapour pressures of the pure components.

Compound	*A*	*B*	*C*
Benzene	6.87987	1196.76	219.161
Cyclohexane	6.85146	1206.47	223.136
Hexane	6.91058	1189.64	226.280

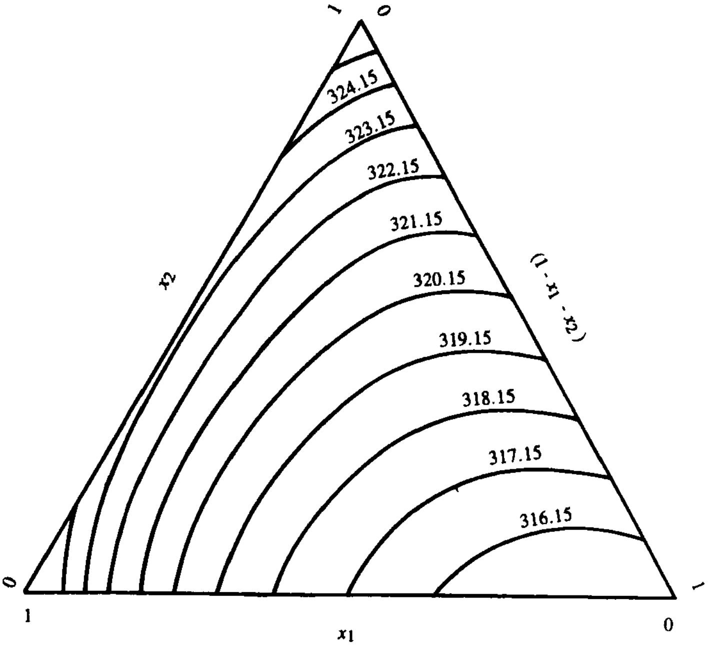

Figure 1 Isolines showing the variation of the liquid phase boiling point with respect to the composition for the ternary mixture ((x_1) Benzene + (x_2) Cyclohexane + ($1 - x_1 - x_2$) Hexane) at 40.0 kPa.

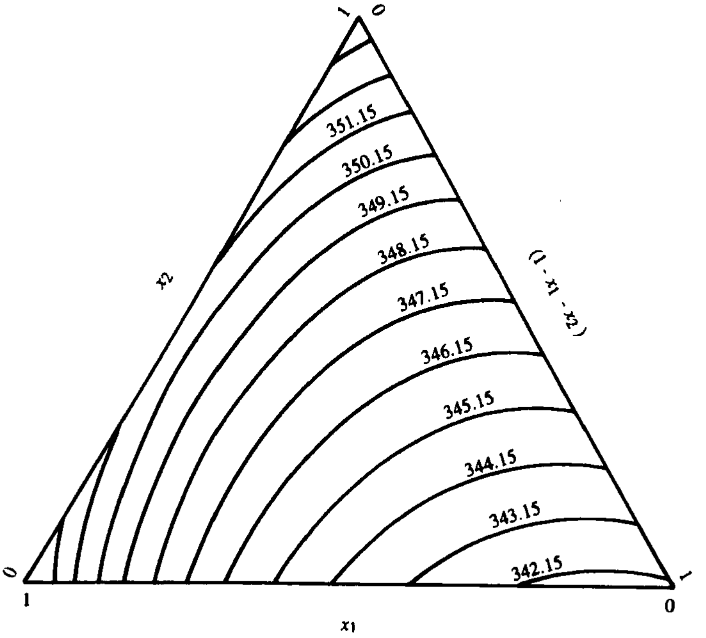

Figure 2 Isolines showing the variation of the liquid phase boiling point with respect to the composition for the ternary mixture ((x_1) Benzene + (x_2) Cyclohexane + ($1 - x_1 - x_2$) Hexane) at 101.3 kPa.

According to this consistency test, the experimental data are considered thermodynamically consistent when the average deviation for the vapour phase composition (Δy) is less than 0.01. The values of Δy calculated for our system when the test is applied fulfil satisfactorily that condition at the two studied pressures as can be seen in Table 6.

The boiling points obtained by K. Ridgway *et al.*,[10] at 101.3 kPa for the ternary mixture (Benzene + Cyclohexane + Hexane) are in good agreement with those yielded by the coefficients A_{ij} of Table 2 (derived from our experimental data) for the same compositions.

The activity coefficients, γ_i, determined by means of the Eq. (2) have been fitted to the equations of Wilson, NRTL, and UNIQUAC. The adjustable parameters for these equations have been obtained through a least squares method using the Simplex method to minimize an objective function F which is expressed in terms of experimental and calculated γ_i values. For a ternary mixture F can be written:

$$F = \sum_{i=1}^{N}\left[\left(\frac{\gamma_1^{\mathrm{exp}} - \gamma_1^{\mathrm{cal}}}{\gamma_1^{\mathrm{exp}}}\right)^2 + \left(\frac{\gamma_2^{\mathrm{exp}} - \gamma_2^{\mathrm{cal}}}{\gamma_2^{\mathrm{exp}}}\right)^2 + \left(\frac{\gamma_3^{\mathrm{exp}} - \gamma_3^{\mathrm{cal}}}{\gamma_3^{\mathrm{exp}}}\right)^2\right]_i \tag{6}$$

where N is the number of experimental data.

Wilson uses the following expression to determine the activity coefficient of any k-component in a multicomponent mixture:

$$\ln \gamma_k = -\ln\left[\sum_{j=1}^{n} x_j \Lambda_{kj}\right] + 1 - \sum_{i=1}^{n}\left[\frac{x_i \Lambda_{ik}}{\sum_{j=1}^{n} x_j \Lambda_{ij}}\right] \tag{7}$$

where Λ_{ij} are the adjustable parameters.

NRTL propose the following equation to determine the activity coefficient of an i component of a multicomponent mixture:

$$\ln \gamma_i = \frac{\sum_{j=1}^{n} x_j \tau_{ji} G_{ji}}{\sum_{m=1}^{n} x_m G_{mi}} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{m=1}^{n} x_m G_{mj}}\left(\tau_{ij} - \frac{\sum_{r=1}^{n} x_r \tau_{rj} G_{rj}}{\sum_{m=1}^{n} x_m G_{mj}}\right) \tag{8}$$

where

$$G_{ij} = \exp(-\alpha_{ji}\tau_{ji}) \tag{9}$$

and τ_{ij} are adjustable parameters. The parameter $\alpha_{ij} = \alpha_{ji}$ is a constant which characterizes the trend of the components to mix up in a nonrandom manner. Its value is included between 0.2 and 0.5 and commonly increases when the complexity of the ij molecular interaction rises. Given the nature of our mixture we have considered adequate a value of $\alpha_{ij} = 0.3$.

Table 6 Results of the thermodynamical consistency test. Average deviations ΔP and Δy.

Pressure/kPa	$\Delta P/kPa$	Δy
40.0	1.2	0.008
101.3	3.0	0.005

UNIQUAC provides the following expression to determine the activity coefficients in a multicomponent mixture:

$$\ln\gamma_i = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{1}{2} Z q_i \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \left(\frac{\phi_i}{x_i}\right)\sum_{j=1}^{n} x_j l_j$$
$$+ q_i - q_i \ln\left(\sum_{j=1}^{n} \theta_j \tau_{ji}\right) - q_i \sum_{j=1}^{n} \frac{\theta_j \tau_{ij}}{\sum_{k=1}^{n} \theta_k \tau_{kj}} \qquad (10)$$

where θ_i and ϕ_i are defined by the equations:

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^{n} x_j q_j} \qquad (11)$$

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^{n} x_j r_j} \qquad (12)$$

$$l_i = \frac{1}{2} Z (r_i - q_i) - (r_i - 1) \qquad (13)$$

r_i and q_i are UNIQUAC parameters, Z is the coordination number of the molecule (authors recommend to use a value $Z = 10$) and τ_{ij} are adjustable parameters.

Parameters resulting from the fitting along with the average deviations of both the temperature (ΔT) and the composition of the vapour phase (Δy) are collected in Table 7 for all the equations considered. It can be seen that all of these equations correlates well the activity coefficients.

The modified UNIFAC group contribution method has been also employed to predict the vapour-liquid equilibrium of the ternary system under study. Compared with the original UNIFAC method[20], only the van der Waals properties have been slightly modified. At the same time, parameters depending on the temperature are introduced in order to achieve a better description of the real behaviour of the system as a function of temperature.

According to the modified UNIFAC model, the activity coefficient is given by the sum of a combinatorial and a residual part:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (14)$$

Table 7 Correlation parameters for the activity coefficients according to the equations of Wilson, NRTL and UNIQUAC. Average deviations of temperature (ΔT) and average deviations of the vapour phase composition (Δy).

Equation	*Pressure /kPa*	A_{12}	A_{13}	A_{21}	A_{23}	A_{31}	A_{32}	$\Delta T/K$	Δy
Wilson^a	40.0	1.752	1.293	0.245	1.330	0.381	0.627	0.28	0.008
	101.3	1.225	1.366	0.536	0.780	0.318	1.167	0.14	0.004
NRTL^b	40.0	−1.860	−1.692	1.401	0.120	1.427	−0.018	0.31	0.008
	101.3	0.597	0.459	−0.404	−0.263	−0.002	0.300	0.13	0.006
UNIQUAC^b	40.0	0.890	0.961	0.978	1.796	0.896	0.408	0.24	0.007
	101.3	0.773	0.715	1.127	1.253	1.161	0.764	0.15	0.004

$^a A_{ij} = \Lambda_{ij}$; $^b A_{ij} = \tau_{ij}$

The combinatorial part can be obtained through the relationship:

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - 5q_i\left(1 - \frac{V_i}{F_i} + \ln\left(\frac{V_i}{F_i}\right)\right) \tag{15}$$

The parameters V_i', V_i and F_i can be calculated using the relative van der Waals volumes, R_k, the molecular surface areas, Q_k, corresponding to the different groups.

$$V_i' = \frac{r_i^{3/4}}{\sum_{j=1}^{n} x_j r_j^{3/4}} \tag{16}$$

$$V_i = \frac{r_i}{\sum_{j=1}^{n} x_j r_j} \tag{17}$$

$$r_i = \sum_{k=1}^{n} v_k^{(i)} R_k \tag{18}$$

$$F_i = \frac{q_i}{\sum_{j=1}^{n} x_j q_j} \tag{19}$$

$$q_i = \sum_{k=1}^{n} v_k^{(i)} Q_k \tag{20}$$

The residual part can be obtained making use of the following relationships:

$$\ln \gamma_i^R = \sum_{k=1}^{n} v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \tag{21}$$

$$\ln \Gamma_k = Q_k\left(1 - \ln\left(\sum_m \theta_m \Psi_{mk}\right) - \sum_m \frac{\theta_m \Psi_{km}}{\sum_n \theta_n \Psi_{nm}}\right) \tag{22}$$

where the group area fraction, θ_m, the group mole fraction, X_m, and the parameters depending on the temperature, Ψ_{nm}, are given by the following equations:

$$\theta_m = \frac{\theta_m X_m}{\sum_n Q_n X_n} \tag{23}$$

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j} \tag{24}$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm} T + c_{nm} T^2}{T}\right) \tag{25}$$

a_{nm}, b_{nm} and c_{nm} are group interaction parameters.

The van der Waals properties and the group interaction parameters used in UNIFAC calculations are collected in Table 8. Table 9 shows the average deviation of both the temperature (ΔT) and the vapour phase composition (Δy) corresponding to application of the UNIFAC method to the two work pressures.

Table 8 Van der Waals properties for the different subgroups and group interaction parameters used in the modified UNIFAC model.

	Group	*Subgroup*	*N° of subgroups in the molecule*			R_k	Q_k
			Benzene	*Cyclohexane*	*Hexane*		
1.	"CH_2"	CH_3	0	0	2	0.6325	1.0608
		CH_2	0	6	4	0.6325	0.7081
2.	"ACH"	ACH	6	0	0	0.3763	0.4321
n	m	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
1	2	114.20	0.09330	0	16.070	−0.2998	0

Table 9 Predictions of the UNIFAC model. Average deviation of the temperature (ΔT) and average deviation of the vapour phase composition (Δy).

Pressure/kPa	$\Delta T/K$	Δy
40.0	0.72	0.013
101.3	0.64	0.011

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