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Liquid–liquid equilibria of limonene + linalool + diethylene glycol system at different temperatures

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Abstract

We report liquid–liquid equilibrium data for the ternary system limonene + linalool + diethylene glycol at 298.15, 308.15 and 318.15 K. The experimental data have been correlated using UNIQUAC and NRTL equations to obtain the binary interaction parameters. These data were also compared to those predicted using the UNIFAC group contribution method.

Keywords: LLE; Limonene; Linalool; Correlation

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1. Introduction

Lemon oil is an essential oil of considerable importance in both perfumery, food and taste applications. In general terms the essential oil is based on one large component, limonene, a monoterpene which accounts for over 60% of the constituents. The other oxygenated components are generally preferable due to their odour. In order to improve the quality of essential oils, some processes have therefore been developed to enrich the mixture in oxygenated compounds, linalool being one important component of this class. The separation of mixtures containing these components is frequently carried out by solvent extraction.

To design the extraction equipment for the separation of a homogeneous liquid mixture of two components using a third component, it is necessary to know the liquid–liquid equilibrium data of the ternary system formed by these components. In this work, liquid–liquid equilibria for the system limonene + linalool + diethylene glycol at 298.15, 308.15 and 318.15 K have been studied. The experimental data were correlated using the UNIQUAC and NRTL equations and the energetic parameters of these models at each temperature are obtained. The LLE data have also been predicted with the UNIFAC method and they were compared with the experimental data.

2. Experimental

2.1. Chemicals

The chemicals used were supplied by Fluka and were of chromatographic quality. The purities are >99 mass% for diethylene glycol, 98 mass% for limonene and 97 mass% for linalool. The purities were verified with gas chromatography and the chemicals were used without further purification.

The densities and refractive indices of pure substances were measured and compared with other recent literature values [1,2] at 293.15 K and atmospheric pressure (Table 1). The densities were measured with an Anton Paar DMA 60/602 densimeter precise to within $\pm 10^{-2}$ kg m^{-3}, and the refractive indices were measured with an Atago RX-5000 refractometer with an accuracy of $\pm 4 \times 10^{-5}$.

2.2. Procedure

First, the solubility curves at 298.15, 308.15 and 318.15 K were determined by the cloud point method [3]. These curves were employed for calibrating the gas chromatograph using an internal standard calibration method; the technique is explained in detail elsewhere [4]. The chromatograph used was a Hewlett-Packard 5890 Series II equipped with a TCD. A capillary column (HP5: 30 m × 0.32 mm × 0.25 μm) was used. Helium was used as the mobile phase and the injection volume was 0.3 μl with a split ratio of 1:200. Separation was made to 393.15 K under isothermal conditions. The greatest errors in determining the mole fraction

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Table 1
Densities (ρ) and refractive indices (n_D) of the pure components at 293.15 K and atmospheric pressure

Component	ρ (g cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature
Limonene	0.84115	0.8403 [1]	1.4726	1.4732 [1]
Linalool	0.86245	–	1.46202	–
Diethylene glycol	1.11644	1.1164 [1]	1.44728	1.4472 [2]

composition using the calibration curves were of ±0.004 in the limonene-rich phase, and ±0.003 in the diethylene glycol-rich phase.

The tie-line data were determined by the analysis of two layers of a heterogeneous mixture. A mixture with partial miscibility was placed inside an equilibrium cell, where it was agitated for 1 h in order to allow an intimate contact between the phases, and the thermodynamic equilibrium was finally achieved by letting the mixture rest for 6 h. The complete process was carried out at constant temperature using a thermostatic bath. When the thermodynamic equilibrium was achieved, samples of both the liquid phases were collected and analysed by gas chromatography.

3. Results and discussion

3.1. Experimental data

The experimental tie-lines data for limonene + linalool + diethylene glycol at the three temperatures are listed in Table 2.

3.2. Correlation

The correlation of the experimental data was made with NRTL [5] and UNIQUAC [6] equations, as they are two of the most used in the literature. The value of the nonrandomness parameter of the NRTL equation, α, was previously assigned as 0.3. The structural parameters for UNIQUAC,

Table 2
Experimental tie-lines of the limonene (1) + linalool (2) + diethyleneglycol (3) system (compositions in molar fraction)

Diethylene glycol phase			Limonene phase		
x_1	x_2	x_3	x_1	x_2	x_3
$T = 298.15$ K					
0.0118	0.0000	0.9882	0.9868	0.0000	0.0132
0.0145	0.0195	0.9660	0.9597	0.0290	0.0113
0.0237	0.0582	0.9181	0.8756	0.0947	0.0297
0.0360	0.0782	0.8858	0.8078	0.1341	0.0580
0.0496	0.0987	0.8515	0.7428	0.1673	0.0899
0.0813	0.1330	0.7857	0.6125	0.2130	0.1745
$T = 308.15$ K					
0.0119	0.0000	0.9881	0.9897	0.0000	0.0103
0.0155	0.0185	0.9660	0.9511	0.0316	0.0173
0.0200	0.0321	0.9479	0.9266	0.0559	0.0175
0.0221	0.0446	0.9333	0.8898	0.0820	0.0281
0.0278	0.0613	0.9109	0.8491	0.1138	0.0371
0.0405	0.0854	0.8741	0.7726	0.1558	0.0716
0.0740	0.1267	0.7993	0.6199	0.2209	0.1592
0.0913	0.1398	0.7689	0.5674	0.2336	0.1990
$T = 318.15$ K					
0.0100	0.0000	0.9900	0.9892	0.0000	0.0108
0.0152	0.0375	0.9473	0.9004	0.0784	0.0212
0.0262	0.0641	0.9097	0.8152	0.1340	0.0508
0.0492	0.1008	0.8501	0.7069	0.1984	0.0947
0.0689	0.1227	0.8084	0.6061	0.2294	0.1645
0.0947	0.1493	0.7560	0.5060	0.2451	0.2489

r and q, were taken from literature [8] or calculated from group contribution data [9].

The binary interaction parameters for both NRTL and UNIQUAC equations were obtained using a computer program described by Sørensen [7], who used two objective functions. First, F_a does not require any previous knowledge of parameters, and after convergence the parameters are used in the second function to fit the experimental concentrations, F_b:

$$F_a = \sum_k \sum_i \sum_j \left[\frac{a^{\mathrm{I}}_{ijk} - a^{\mathrm{II}}_{ijk}}{a^{\mathrm{I}}_{ijk} + a^{\mathrm{II}}_{ijk}} \right]^2 + Q \sum_n P_n^2 \quad (1)$$

Table 3
LLE data correlation; root mean square deviations (r.m.s.d., in %) for each model and each temperature, defining or not the solute distribution ratio at infinite dilution β_∞

Model	r.m.s.d.	Temperature (K)					
		298.15		308.15		318.15	
UNIQUAC[a]	β_∞		1.31		1.58		1.96
	$\Delta\beta$ (%)	4.00	1.43	2.18	1.15	1.85	0.87
	F (%)	0.1859	0.1924	0.1443	0.1473	0.2962	0.2989
NRTL ($\alpha = 0.3$)	β_∞		1.64		1.74		2.31
	$\Delta\beta$ (%)	10.00	5.48	7.15	1.78	4.89	2.34
	F (%)	0.2151	0.3091	0.1941	0.2110	0.2291	0.2483

[a] Structural parameters for the UNIQUAC equation: limonene [9]: $r = 6.278$, $q = 5.208$; linalool [9]: $r = 6.506$, $q = 5.476$; diethylene glycol [8]: $r = 4.001$, $q = 3.168$.

Table 4
LLE data correlation; binary interaction parameters for NRTL ($\alpha = 0.3$) and UNIQUAC equations for each temperature, specifying the optimal value of the solute distribution ratio at infinite dilution β_∞

Temperature (K)		NRTL		UNIQUAC	
		a_{ij} (J mol^{-1})	a_{ji} (J mol^{-1})	b_{ij} (J mol^{-1})	b_{ji} (kJ mol^{-1})
298.15	1–2	−416.16	−1076.50	−846.86	−367.24
	1–3	8910.11	8420.42	3830.34	369.50
	2–3	−1183.08	1021.46	−1662.80	1312.70
308.15	1–2	4390.46	−2526.62	−1608.76	421.38
	1–3	8777.09	9063.09	3825.19	346.89
	2–3	493.32	2096.46	−1322.51	796.80
318.15	1–2	3190.50	−2563.04	−1427.01	209.70
	1–3	9220.23	9593.52	4324.28	396.08
	2–3	425.68	1724.32	−1554.72	1297.82

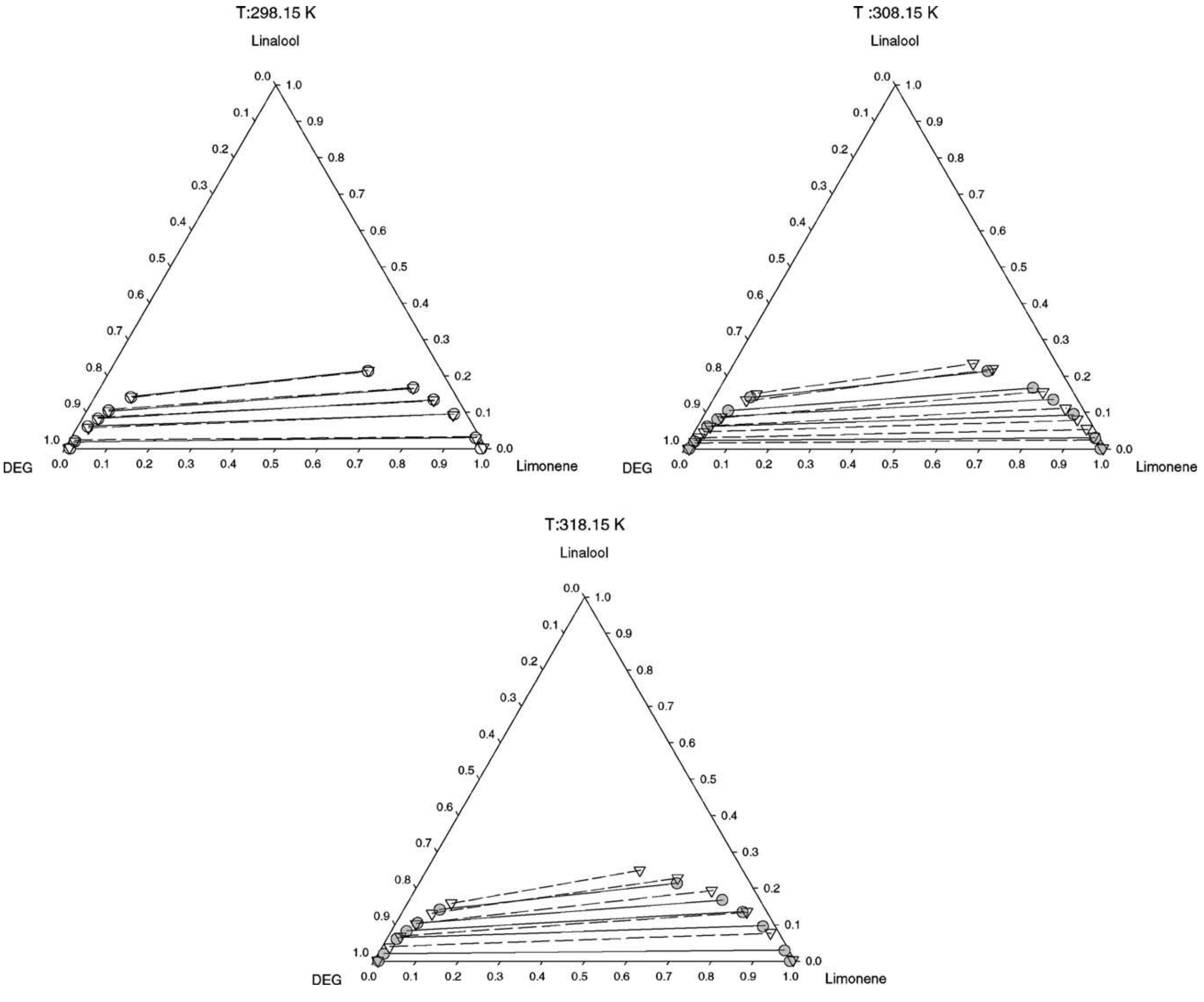

Fig. 1. Experimental tie-lines (—○) and the corresponding UNIQUAC correlation using the optimal value of the solute distribution ratio at infinite dilution (− − −▽) at different temperatures.

Table 5
Simultaneous correlation of the three different temperature data; binary interaction parameters and root mean square deviations (r.m.s.d.) of the models

Model		Parameters		r.m.s.d. (%)	Temperature (K)		
		a_{ij} (J mol^{-1})	a_{ji} (J mol^{-1})		298.15	308.15	318.15
UNIQUAC	1–2	−1240.78	−40.41				
	1–3	4100.88	478.45	$\Delta\beta$	6.94	2.20	7.92
	2–3	−1744.69	1471.83	F	0.4691	0.2825	0.5698
NRTL	1–2	−174.08	−1429.51				
	1–3	9498.75	8600.00	$\Delta\beta$	18.73	7.64	8.88
	2–3	−840.30	1108.42	F	0.7297	0.3044	0.8313

$$F_\mathrm{b}=\sum_k \min \sum_i \sum_j (x_{ijk}-\hat{x}_{ijk})^2 + Q\sum P_n^2 + \left[\ln\left(\frac{\hat{\gamma}_{S\infty}^{\mathrm{I}}}{\hat{\gamma}_{S\infty}^{\mathrm{II}}}\beta_\infty\right)\right]^2 \tag{2}$$

where x is the experimental mole fraction, $\hat{x}$ the mole fraction of the calculated tie-line considered, a is the activity, i are the components of the mixture, j are the phases and k are the tie-lines. Both the functions include a penalisation term to reduce the risks of multiple solutions associated with parameters of high value, in which Q is a constant and P_n are the adjustable parameters. F_b also includes a term to correctly fit experimental results when working with low solute concentrations, in which $\hat{\gamma}_{S\infty}^{\mathrm{I}}$ and $\hat{\gamma}_{S\infty}^{\mathrm{II}}$ represent the solute activity coefficients calculated at infinite dilution in

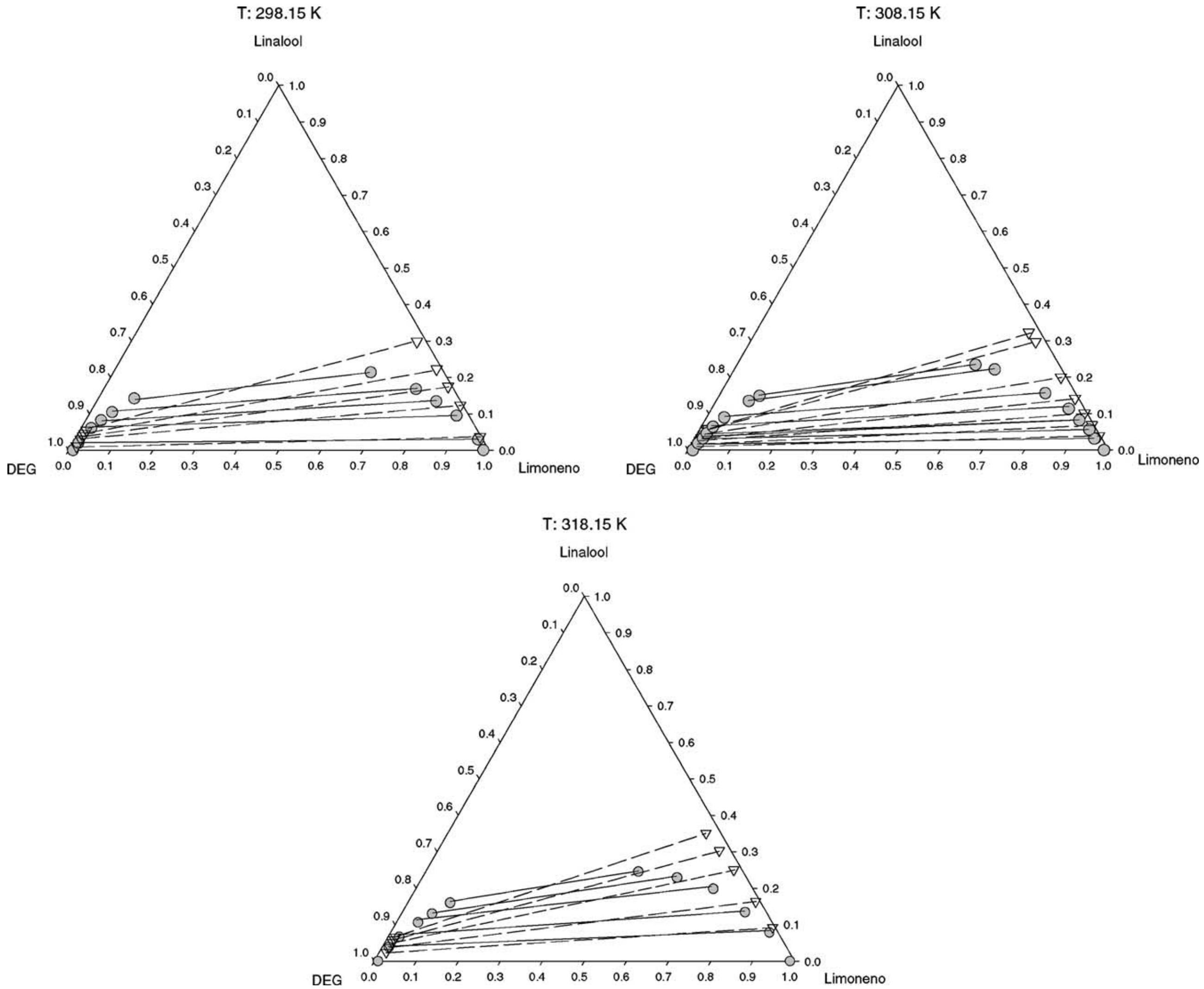

Fig. 2. Experimental (—○) and predicted tie-lines using the UNIFAC method (– – –▽) at different temperatures.

both phases and β_∞ is the solute molar distribution ratio at infinite dilution.

The quality of correlation is measured by the residual function F and by the mean error of the solute distribution ratio, $\Delta\beta$:

$$F = 100\left[\sum_k \min \sum_i \sum_j \frac{(x_{ijk} - \hat{x}_{ijk})^2}{6M}\right]^{0.5} \quad (3)$$

$$\Delta\beta = 100\left[\sum_k \frac{(\beta_k - \hat{\beta}_k)/\beta_k}{M}\right]^{0.5} \quad (4)$$

The correlation of the experimental data was made without defining a value for β_∞ and also using the optimal value of this parameter. In the latter case the optimal β_∞ was found by trial-and-error with $\Delta\beta$ as optimality criterion. Table 3 lists the root mean square deviations found with both models NRTL ($\alpha = 0.3$) and UNIQUAC obtained for each temperature defining β_∞ and without defining it. The correlation defining β_∞ is the best fit of the experimental data.

Table 4 lists the NRTL and UNIQUAC parameters obtained for each temperature when using the optimal value of β_∞. Fig. 1 shows a comparison of experimental tie-lines and those calculated with UNIQUAC for each temperature. Table 5 lists the results (binary parameters and residuals) obtained with the simultaneous correlation of the three different temperature data for both correlation equations.

3.3. Prediction

The experimental data were compared with those predicted by UNIFAC method [10]. The interaction and structural parameters were taken from literature [11]. The quality of prediction is evaluated with the residual F (Eq. (3)), this value was 6.0571 at 298.15 K, 6.2522 at 308.15 K and 8.0236 at 318.15 K. Fig. 2 shows a comparison of the predicted and the experimental tie-lines for each temperature.

The LLE data predicted with the UNIFAC method gives too great a value of the residual F, this method is undesirable for the LLE prediction of the limonene+linalool+diethylene glycol system.

4. Conclusions

Liquid–liquid equilibrium of the limonene + linalool + diethylene glycol system has been measured at different temperatures. The LLE data were correlated using the NRTL and UNIQUAC activity models, without defining a value to the solute distribution ratio at infinite dilution and also using the optimal value to this parameter. As is frequently found in the open literature, the correlation using the optimal β_∞ normally has a slightly larger value of the residual F than the correlation without defining β_∞, but the value of the residual $\Delta\beta$ is much smaller. Thus, this method of correlation was selected in this work.

New UNIQUAC and NRTL interaction parameters between solvent, terpene and oxygenated compounds were found. The correlation with the UNIQUAC equation gives the best results, and the NRTL equation with a value of the nonrandomness parameter optimised at $\alpha = 0.3$ fits the experimental data satisfactorily. The simultaneous correlation of the three different temperature data gives common parameters in the range of the temperature considered, increasing their application in this way. As was expected, the residuals were higher than when the individual correlation at each temperature was made.

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