ELSEVIER

Chemical Engineering Journal 133 (2007) 213–218

Chemical Engineering Journal

www.elsevier.com/locate/cej

Citrus essential oil terpenless by extraction using 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid: Effect of the temperature

A. Arce*, A. Pobudkowska[1], O. Rodríguez, A. Soto

Department of Chemical Engineering, University of Santiago de Compostela, Lope Gómez de Marzoa, s/n, E-15782 Santiago de Compostela, Spain

Received 5 September 2006; received in revised form 15 January 2007; accepted 24 January 2007

Abstract

Ionic liquids have awakened a big interest as solvents in the last years. In this work, the possibility of using an ionic liquid as solvent for the citrus essential oil deterpenation by liquid–liquid extraction has been studied. Citrus essential oil was simulated as the binary mixture (limonene + linalool) and equilibrium data for limonene + linalool + 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO$_4$]) have experimentally been measured at 298.15 and 318.15 K. The experimental technique is based on direct analysis of phases at equilibrium using ^{1}H NMR, which allows quantitative analysis of the three compounds. Linalool distribution ratios and selectivities have been calculated from experimental data. Slightly bigger values of these parameters were found at the lowest temperature. Correlation of the experimental LLE data was done by means of the non-random two-liquid (NRTL) equation. The nonrandomness parameter (α) was fixed to 0.1, 0.2, and 0.3, and the best results were obtained with $\alpha = 0.1$. Correlation is performed for each temperature data set and also for both data sets simultaneously, getting in all the cases an adequate correlation.

Keywords: Essential oil; Ionic liquid; LLE; Solvent extraction

1. Introduction

Room-temperature ionic liquids are electrolytes with low melting temperatures. They have interesting physical and chemical properties which are giving them increasing attention in research and industry. Thus, some ACS meetings were dedicated to ionic liquids [1–4], and also some journal special issues [5], reviews [6,7] and books [8,9] were published collecting the beginning of the research performed on and about ionic liquids. Industrial applications are also appearing, demonstrating the interest of these new chemicals and encouraging further research.

Research on ionic liquids covers different fields. As they are good solvents for many different substances, both organic and inorganic, they are being investigated as reaction media [1–6,9], solvents for separation purposes [10–13], electrolytes [10,14,15], or thermal fluids [2,9]. Ionic liquids' negligible vapor pressure favors their separation from most mixtures, thus application as entrainers for extractive distillations or as solvents for liquid extraction reveals of highest interest [11,12].

Essential oils are important in the food and cosmetic industry because of their characteristic taste and odor. The oil is composed by one or more terpenes and some oxygenated derivatives [16]. The oxygenated compounds usually have better organoleptic properties, so terpene separation is of interest. Nowadays preparation of essential oils with a high content on oxygenated terpenoids presents some difficulties, due to their delicate characteristics. Liquid extraction would be preferred over distillation to avoid heating the essential oil.

Recently, we have proposed the use of ionic liquids to carry out essential oils terpenless [17]. In the same research line, in this work we study the ability of a different ionic liquid to find the objective, moreover analyzing the influence of temperature in the process. Citrus essential oil, as in our previous work [17], is simulated as the binary mixture of its main components, limonene and linalool (a terpene and a terpenoid). The ionic liquid used as solvent for the separation is 1-ethyl-3-methylimidazolium ethylsulfate, [emim][EtSO$_4$]. This ionic liquid, in addition to the

---

* Corresponding author. Tel.: +34 981 563100x16790; fax: +34 981 528050. *E-mail address:* eqaaarce@usc.es (A. Arce).

[1] Present address: Physical Chemistry Division, Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland.

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.01.035

Table 1
Density and refraction indices of the pure components

Component	ρ (g cm^{-3})		n_D	
	Experimental	Literature	Experimental	Literature
R-(+)-Limonene	0.83729	0.8383 [19]	1.47029	1.4701 [19]
(±)-Linalool[a]	0.85746	0.85760 [20]	1.45956	–
[emim][EtSO$_4$]	1.23882	1.2296 [21], 1.2423 [22]	1.47889	–

Experimental and literature data at 298.15 K.
[a] ~(1:1) mixture of *cis* and *trans* isomers.

own advantages of ionic liquids, presents an acceptable level of toxicity and it can be easily synthesized in an atom-efficient and halide-free way, with a reasonable cost. Liquid–liquid equilibrium data for the ternary system (limonene + linalool + 1-ethyl-3-methylimidazolium ethylsulfate) are determined. The temperature effect is studied performing the phase equilibrium experiments at 298.15 and 318.15 K. Experimental data are correlated by means of the NRTL equation [18] and solvent is evaluated using the solute distribution ratio and its selectivity.

2. Experimental

2.1. Reagents

R-(+)-Limonene and (±)-linalool were supplied by Fluka, in *purum* grade and >98 and >97 mass% nominal purities, respectively. This purity was checked by gas chromatography and chemicals used without further purification. 1-Ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO$_4$]) was synthesized in our laboratory as described below. Densities and refractive indices of pure components were measured experimentally. Results are shown in Table 1 and compared with values published in the literature for purity verification. Densities were measured with an Anton Paar DMA 60/602 densimeter precise to within $\pm 10^{-2}$ kg m^{-3}. Refractive indices were measured with an Atago RX-5000 refractometer with an accuracy of $\pm 4 \times 10^{-5}$. Table 1 shows experimental values and those from literature [19–22] for comparison. Several differences are found on density for [emim][EtSO$_4$], this is due to the fact of trace amounts of impurities, such as water or ions having a dramatic effect on physical properties of ionic liquids.

2.2. Synthesis of 1-ethyl-3-methylimidazolium ethylsulfate

The ionic liquid was prepared by reaction of equimolecular quantities of 1-methylimidazole (Aldrich, >99%, GC) and diethyl sulfate (Aldrich, >98%, GC) in toluene [21,23]. A solution of 1-methylimidazole in toluene was prepared first and then diethyl sulfate added drop-wise under helium atmosphere. Reaction was done on an ice bath to avoid rising of the temperature over 40 °C. As [emim][EtSO$_4$] is non-soluble in toluene, it separated immediately from reagents and solvent. It was then washed three times with fresh toluene to remove reagents from the ionic liquid-phase. Removal of residual volatile compounds in the ionic liquid was carried out first in a rotary evaporator (75 °C, 30 min) and later under vacuum (10 mmHg) at 80 °C for 48 h.

3. Procedure

Samples whose composition was in the immiscible region were prepared in jacketed cells with septum outlets. Temperature was controlled circulating water from a thermostat (Julabo model F12) through the jacket of the cell. Experimental temperatures selected were 298.15 or 318.15 K, and they were measured with a PT100 PRT probe connected to a digital thermometer from Automatic Systems Laboratories (AΣΔ) model F250 MkII precise to within ±0.02 K. Samples were stirred vigorously for at least 1.5 h and then left to equilibrate for at least 10 h (overnight). Samples of both phases at equilibrium were withdrawn using syringes through the septum outlets. Then they were introduced into the NMR tubes and the analysis was performed.

Direct analysis of phases in equilibrium was used to obtain the ends of the tie-lines. Analytical technique was ^{1}H NMR spectroscopy on a Bruker DRX500 with an 11.74 T magnet (^{1}H resonance: 500 MHz). Samples for analysis were introduced into Wilmad NMR screw-cap tubes, with PTFE/silicone septa to avoid losses by vaporization. In order to avoid immiscibility, deuterated solvent (benzene-d_6, supplied by Aldrich, 99.95 at.% D), was not mixed with the sample, but added on sealed, capillary tubes into the NMR tubes.

First, the technique was tested by analysis of samples of known composition. Samples of the three components whose composition laid in the homogeneous region were prepared by weight on a balance (Mettler-Toledo, precise to within $\pm 10^{-7}$ kg). The samples were analyzed by ^{1}H NMR spec-

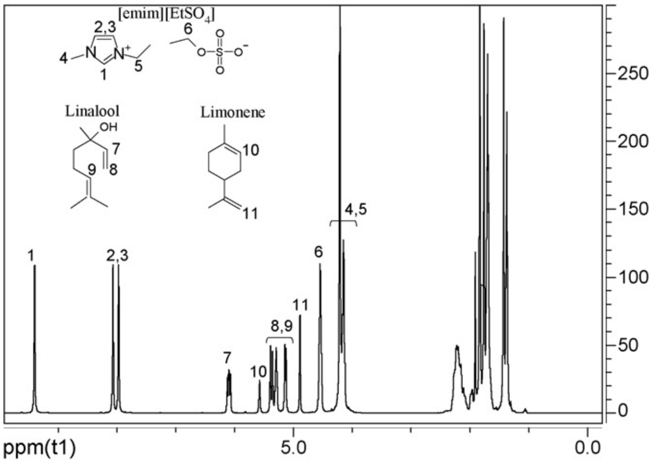

Fig. 1. Example of a ^{1}H NMR spectrum for a ternary mixture, with chemical structures and peaks identification. Peaks in bold were integrated for analysis.

Table 2
Experimental tie-lines, linalool distribution ratio, β_{linalool}, and [emim][EtSO$_4$] selectivity, S, for the system limonene (x_1) + linalool (x_2) + [emim][EtSO$_4$] ($1-x_1-x_2$)

T (K)	Ionic liquid-rich phase		Limonene-rich phase		β_{linalool}	S
	x_1	x_2	x_1	x_2		
298.15	0.0087	0.0000	1.0000	0.0000	–	–
	0.0100	0.0278	0.9574	0.0426	0.65	62.67
	0.0140	0.0607	0.9162	0.0838	0.72	47.40
	0.0196	0.1049	0.8594	0.1402	0.75	32.85
	0.0217	0.1239	0.8324	0.1670	0.74	28.40
	0.0276	0.1557	0.8073	0.1922	0.81	23.71
	0.0426	0.1990	0.7778	0.2210	0.90	16.46
	0.0754	0.2727	0.7403	0.2577	1.06	10.39
	0.1370	0.3551	0.6976	0.2986	1.19	6.06
	0.2018	0.4019	0.6580	0.3356	1.20	3.91
	0.3183	0.4641	0.5558	0.4259	1.09	1.90
	0.3735	0.4745	0.5158	0.4533	1.05	1.45
318.15	0.0006	0.0000	1.0000	0.0000	–	–
	0.0116	0.0275	0.9483	0.0517	0.53	43.64
	0.0174	0.0830	0.8602	0.1395	0.59	29.45
	0.0289	0.1564	0.7715	0.2285	0.68	18.24
	0.0496	0.2234	0.7227	0.2756	0.81	11.81
	0.0885	0.3031	0.6772	0.3195	0.95	7.26
	0.1453	0.3745	0.6331	0.3601	1.04	4.53
	0.2042	0.4252	0.5852	0.4040	1.05	3.02
	0.3231	0.4992	0.4673	0.4843	1.03	1.49

Compositions in molar fraction.

troscopy, peaks were identified and errors in composition were verified. Maximum error found was ±0.005 in molar fraction. Fig. 1 shows a ^{1}H NMR spectrum of the ternary system together with the chemical structure of the components and the peaks selected for integration and composition determination. A deeper explanation of the technique can be found in previous articles [12].

4. Results and data correlation

LLE data were obtained experimentally at 298.15 and 318.15 K. Ends of the tie-lines are presented in Table 2 and Fig. 2. Mutual solubility of the immiscible pair (limonene + [emim][EtSO$_4$]) is low, specially ionic liquid solubility in limonene. This produces a big heterogeneous region, with maximum of the bimodal curve close to 0.5 linalool molar fraction. Moreover, representation on a molar fraction basis lets observe a solutropic phenomenon, this is, slope of the tie-lines changes from negative to positive values as the linalool composition increases. This change happens around 0.25 linalool molar fraction at 298.15 K and around 0.35 linalool molar fraction at 318.15 K. Thus, temperature affects slopes of the tie-lines, but produces nearly no effect on size of the heterogeneous region.

Solute distribution ratio, β, and solvent selectivity, S, are important parameters for extraction processes. They are calculated directly from experimental data as follows:

$$\beta_{\text{linalool}} = \frac{(x_{\text{linalool}})^{\text{solvent}}}{(x_{\text{linalool}})^{\text{limonene}}} \qquad (1)$$

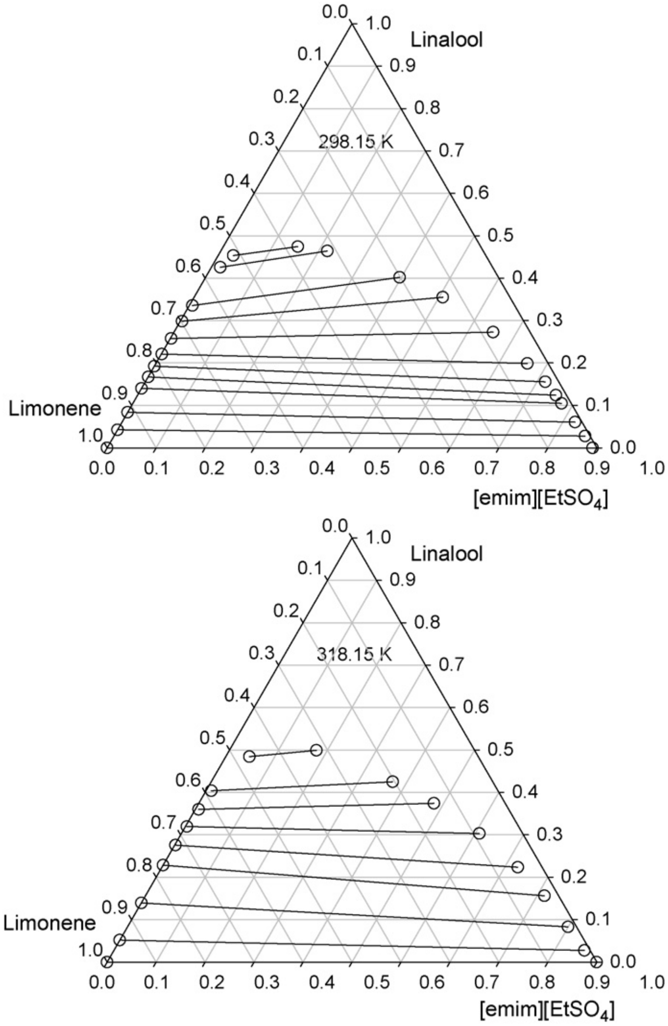

Fig. 2. Experimental tie-lines (○) for limonene + linalool + [emim][EtSO$_4$] at 298.15 K (top) and 318.15 K (bottom).

$$S = \frac{(x_{\text{linalool}})^{\text{solvent}}(x_{\text{limonene}})^{\text{limonene}}}{(x_{\text{linalool}})^{\text{limonene}}(x_{\text{limonene}})^{\text{solvent}}} = \frac{\beta_{\text{linalool}}}{\beta_{\text{limonene}}} \qquad (2)$$

where x refers to compositions in molar fraction, subscripts to components and superscripts to phases (solvent-rich phase and limonene-rich phase). Both parameters were calculated from experimental data and they are presented in Table 2.

Fig. 3 shows solute distribution ratios and selectivities for the system with [emim][EtSO$_4$] and with 1-ethyl-3-methylimidazolium methanesulfonate according data previously published [17]. To make comparison, both parameters are represented on a mass fraction basis. Solutropy disappears when the concentrations are computed in mass, rather than molar, fractions for system with [emim][EtSO$_4$].

NRTL equation [18] was used for data correlation. Nonrandomness parameter, α, was fixed to 0.1, 0.2 and 0.3, and the best result was selected. Binary interaction parameters for NRTL were obtained using a program as that described by Sørensen and Arlt [24], which uses two objective functions. First, F_a, does not require any previous guess for parameters, and after convergence the obtained parameters are used in the second objective

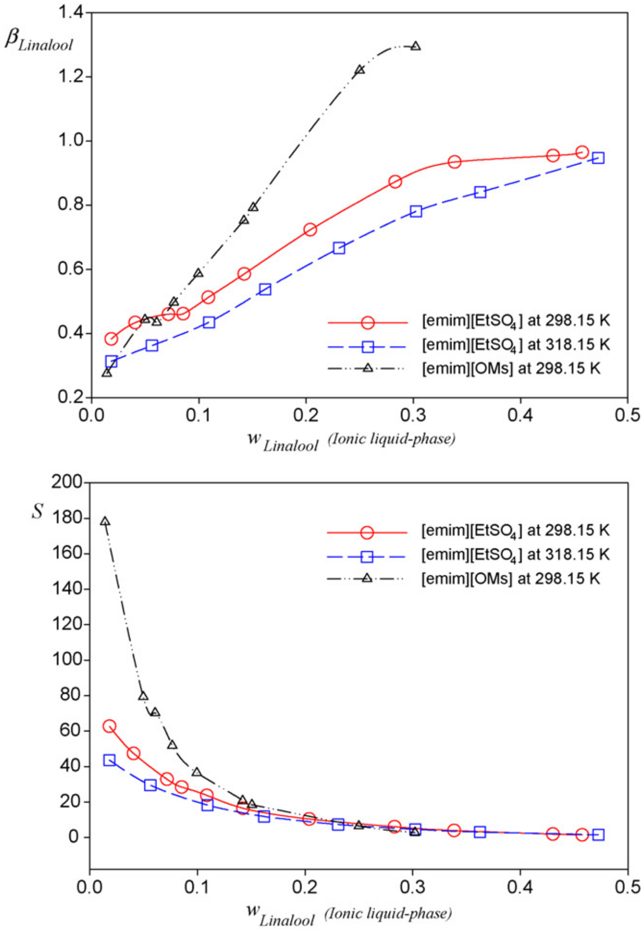

Fig. 3. Solute distribution ratio and selectivity for the systems limonene + linalool + [emim][EtSO$_4$] (○, 298.15 K; 318.15 K) and limonene + linalool + [emim][OMs] (△, 298.15 K) as a function of the mass fraction of solute in the ionic liquid-rich phase. Lines are shown merely to facilitate identification, without physical meaning.

function, F_b, to fit the experimental concentrations:

$$F_a = \sum_k \sum_i \left[\frac{a_{ik}^{\mathrm{I}} - a_{ik}^{\mathrm{II}}}{a_{ik}^{\mathrm{I}} + a_{ik}^{\mathrm{II}}} \right]^2 + Q \sum_n P_n^2 \tag{3}$$

$$F_b = \sum_k \min \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum P_n^2 + \left[\ln \left(\frac{\hat{\gamma}_{\mathrm{S},\infty}^{\mathrm{I}}}{\hat{\gamma}_{\mathrm{S},\infty}^{\mathrm{II}}} \beta_\infty \right) \right]^2 \tag{4}$$

Table 3
NRTL ($\alpha = 0.1$) correlation residuals (F and $\Delta\beta$, in %) fixing or not β_∞ for system limonene + linalool + [emim][EtSO$_4$]

T (K)	β_∞	F	$\Delta\beta$
298.15	–	0.6825	8.1
	0.67	0.3886	3.9
318.15	–	0.6411	8.08
	0.56	0.3024	2.89
Simultaneous correlation			
298.15	–	0.9508	11.01
318.15	–	1.1086	11.02

where x is the experimental mole fraction, $\wedge$ stands for the calculated properties, a the activity, i the components of the mixture, j the phases and k are the tie-lines. Both functions include a penalization term (the second 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 ensure that the parameters give a solute distribution ratio at infinite dilution which approximates to a value previously defined by the user, β_∞, and $\hat{\gamma}_{\mathrm{S},\infty}^{\mathrm{I}}$ and $\hat{\gamma}_{\mathrm{S},\infty}^{\mathrm{II}}$ represent the solute activity coefficients calculated at infinite dilution in both phases.

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

$$F = \left[\sum_k \min \sum_i \sum_j \frac{x_{ijk} - \hat{x}_{ijk}}{6M} \right]^{0.5} \times 100 \tag{5}$$

$$\Delta\beta = \left[\sum_k \frac{((\beta_k - \hat{\beta}_k)/\beta_k)^2}{M} \right]^{0.5} \times 100 \tag{6}$$

where M is the total number of tie-lines.

Correlation was done in two ways, as suggested by Sørensen and Arlt [24]: without defining a value for β_∞, and then specifying an optimal value of this parameter. Optimum β_∞ was found with a trial and error procedure considering the minimization of $\Delta\beta$ as the optimality criterion. The obtained residuals are shown in Table 3. It can be seen that fixing β_∞ at its optimum allowed to reduce both residuals, F and $\Delta\beta$. Parameters for this correlation are presented in Table 4. In order to get parameters valid in the whole range of temperatures, a simultaneous correlation was performed using data sets at both temperatures. The residuals obtained are shown in Table 3 and parameters in Table 4.

Table 4
NRTL ($\alpha = 0.1$) correlation parameters (J mol^{-1}) using the optimal β_∞ value for single data sets, and not defining β_∞ for simultaneous correlation

Components		T = 298.15 K		T = 318.15 K		Simultaneous	
i	j	Δg_{ij}	Δg_{ji}	Δg_{ij}	Δg_{ji}	Δg_{ij}	Δg_{ji}
1	2	19,241	−13,626	20,731	−14,471	−2053.0	2694.4
1	3	38,243	5429.0	40,084	5367.5	37,293	2692.1
2	3	11,232	−10,350	12,434	−10,324	−4158.7	7341.2

System: limonene (1) + linalool (2) + [emim][EtSO$_4$] (3).

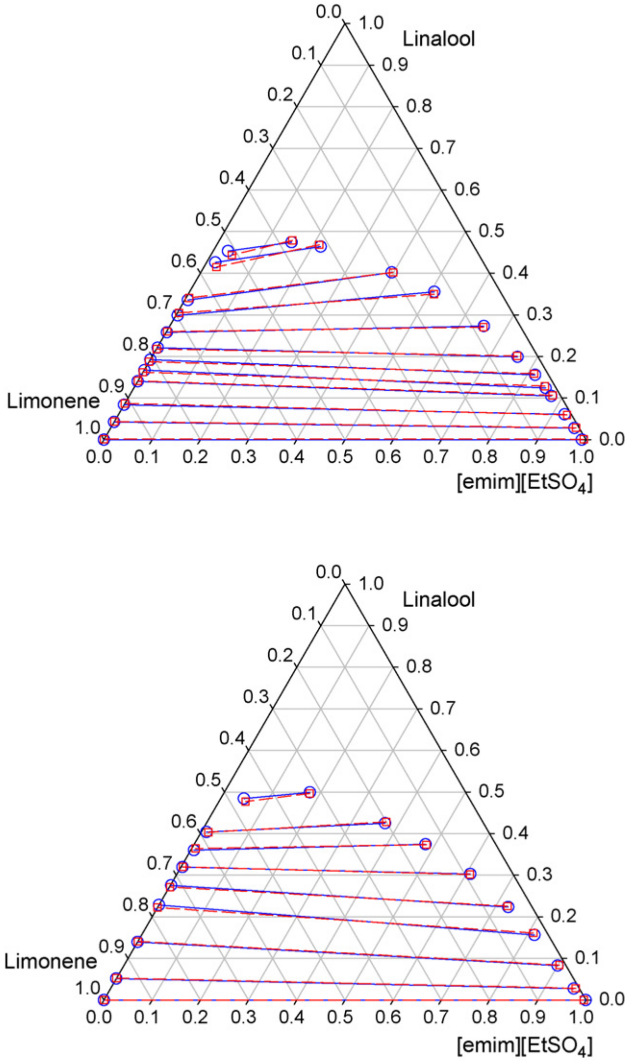

Fig. 4. Experimental tie-lines (◯) and NRTL correlation with $\alpha = 0.1$ (☐) for limonene + linalool + [emim][EtSO$_4$] at 298.15 K (top) and 318.15 K (bottom).

β_∞ optimization was not done for the simultaneous correlation. Despite residuals for this correlation are higher, its parameters are valid in a wider range of temperature.

5. Conclusions

Liquid–liquid equilibrium data for the system limonene + linalool + [emim][EtSO$_4$] were obtained experimentally at 298.15 and 318.15 K. The heterogeneous region is big with little miscibility of the pair limonene + [emim][EtSO$_4$] (see Fig. 2). On a molar fraction basis system shows solutropy, with change of the sign in the tie-lines' slopes around 0.25 linalool molar fraction at 298.15 K and around 0.35 linalool molar fraction at 318.15 K.

With the aim to analyze the viability of using the 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid to perform citrus oil terpenless, solute distribution ratio, β, and solvent selectivity, S, were calculated from experimental data. As the system is solutropic in molar basis, solute distribution ratio presents values below 1 in the low-linalool region, and higher in the rich-linalool region. Temperature has some effect, and solute distribution gives smaller values at the higher temperature. Selectivity gives also acceptable results (up to 60 in molar basis at 298.15 K and 60 at 318.15 K), smaller at the higher temperature.

Thermodynamic behavior is very similar to that found for 1-ethyl-3-methylimidazolium methanesulfonate (Fig. 3), nonetheless solutropy disappears when the concentrations are computed in mass, rather than molar, fractions for system with 1-ethyl-3-methylimidazolium ethylsulfate. Solute distribution ratios and selectivities were lower for [emim][EtSO$_4$], not being influence of temperature enough to improve results considerably. This appoint at the 1-ethyl-3-methylimidazolium methanesulfonate as a more interesting ionic liquid, from thermodynamic point of view, to carry out terpenless of citrus essential oil.

LLE data correlation was done by means of the NRTL equation. It was performed for each temperature data set and also with both data sets simultaneously. The nonrandomness parameter, α, was fixed to 0.1, 0.2 and 0.3. The best results were obtained with $\alpha = 0.1$ and results are showed for this value only. Optimization of β_∞ improves the values of the residuals, thus this correlation is preferred. Residuals obtained are low and the system can be well represented by this model (see Fig. 4). Simultaneous correlation at both temperatures gets higher values for the residuals, but also provides parameters with a wider range of validity (see Table 3). Despite NRTL is intended for non-electrolytes, it is the most used model for ionic liquids' LLE data correlation and provides satisfactory results [12,25,26].

Acknowledgement

The authors are grateful to the Ministerio de Educación y Ciencia (Spain) for financial support through project PPQ2003-01326.

References

[1] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids: Industrial Applications to Green Chemistry, ACS Symposium Series 818, American Chemical Society, Washington, DC, 2002.
[2] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symposium Series 856, American Chemical Society, Washington, DC, 2003.
[3] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids IIIA: Fundamentals, Progress, Challenges, and Opportunities: Properties and Structure, ACS Symposium Series 901, American Chemical Society, Washington, DC, 2005.
[4] R.D. Rogers, K.R. Seddon (Eds.), Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities: Transformations and Processes, ACS Symposium Series 902, American Chemical Society, Washington, DC, 2005.
[5] J. Brennecke, T. Letcher, A.R.H. Goodwin (Eds.), Preface, J. Chem. Thermodyn. 37 (2005) 523–626.
[6] M.J. Earle, K.R. Seddon, Ionic liquids. Green solvents for the future, Pure Appl. Chem. 72 (2000) 1391–1398.
[7] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, Room temperature ionic liquids and their mixtures—a review, Fluid Phase Equil. 219 (2004) 93–98.
[8] R.D. Rogers, K.R. Seddon, S. Volkov (Eds.), Green Industrial Applications of Ionic Liquids, Kluwer, Dordrecht, 2002.
[9] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley/VCH, Weinheim, 2003.

[10] J.F. Brennecke, E.J. Maginn, Ionic liquids: innovative fluids for chemical processing, AIChE J. 47 (2001) 2384–2389.

[11] M. Seiler, C. Jork, A. Kavarnou, W. Arlt, R. Hirsch, Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids, AIChE J. 50 (2004) 2439–2454.

[12] A. Arce, O. Rodríguez, A. Soto, *Tert*-amyl ethyl ether separation from its mixtures with ethanol using the 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid: liquid–liquid equilibrium, Ind. Eng. Chem. Res. 43 (2004) 8323–8327.

[13] R.E. Baltus, R.M. Counce, B.H. Culbertson, H. Luo, D.W. DePaoli, S. Dai, D.C. Duckworth, Examination of the potential of ionic liquids for gas separations, Sep. Sci. Technol. 40 (2005) 525–541.

[14] J. Ding, D. Zhou, G. Spinks, G. Wallace, S. Forsyth, M. Forsyth, D. MacFarlane, Use of ionic liquids as electrolytes in electromechanical actuator systems based on inherently conducting polymers, Chem. Mater. 15 (2003) 2392–2398.

[15] J.N. Barisci, G.G. Wallace, D.R. MacFarlane, R.H. Baughman, Investigation of ionic liquids as electrolytes for carbon nanotube electrodes, Electrochem. Commun. 6 (2004) 22–27.

[16] R.E. Kirk, D.F. Othmer (Eds.), Encyclopaedia of Chemical Technology, 4th ed., John Wiley and Sons Inc., New York, 1996.

[17] A. Arce, A. Marchiaro, O. Rodríguez, A. Soto, Citrus essential oil terpenless by liquid–liquid extraction using organic solvents or ionic liquids, AIChE J. 52 (2006) 2089–2097.

[18] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixtures, AIChE J. 14 (1968) 135–144.

[19] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Physical Properties and Methods of Purification, 4th ed., John Wiley and Sons, New York, 1986.

[20] F. Comelli, S. Ottani, R. Francesconi, C. Castellari, Densities, viscosities, and refractive indices of binary mixtures containing *n*-hexane + components of pine resins and essential oils at 298.15 K, J. Chem. Eng. Data 47 (2002) 93–97.

[21] J.-Z. Yang, X.-M. Lu, J.-S. Gui, W.-G. Xu, A new theory for ionic liquids—the interstice model. Part 1. The density and surface tension of ionic liquid EMISE, Green Chem. 6 (2004) 541–543.

[22] M. Krummen, P. Wasserscheid, J. Gmehling, Measurement of activity coefficients at infinite dilution in ionic liquids using the dilutor technique, J. Chem. Eng. Data 47 (2002) 1411–1417.

[23] J.D. Holbrey, W.M. Reichert, R.P. Swatloski, G.A. Broker, W.R. Pitner, K.R. Seddon, R.D. Rogers, Efficient, halide free synthesis of new low cost ionic liquids: 1,3-dialkylimidazolium salts containing methyl- and ethyl-sulfate anions, Green Chem. 4 (2002) 407–413.

[24] J.M. Sørensen, W. Arlt, Liquid–Liquid Equilibrium Data Collection. Binary Systems, DECHEMA Chemistry Data Series, vol. 5, Frankfurt, 1979.

[25] M.S. Selvan, M.D. McKinley, R.H. Dubois, J.L. Atwood, Liquid–liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide, J. Chem. Eng. Data 45 (2000) 841–845.

[26] T.M. Letcher, P. Reddy, Ternary liquid–liquid equilibria for mixtures of 1-hexyl-3-methylimidazolium (tetrafluoroborate or hexafluorophosphate) + ethanol + an alkene at $T = 298.2$ K, Fluid Phase Equil. 219 (2004) 107–112.