High-Pressure Phase Equilibria in Systems Containing CO_2 and Ionic Liquid of the $[C_n mim][Tf_2N]$ Type*

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Review
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In this review, we present a comparison of the high-pressure phase behaviour of binary systems constituted of CO_2 and ionic liquids of the $[C_n(m)mim][Tf_2N]$ type. The comparative study shows that the solubility of CO_2 in ionic liquids of the $[C_n mim][Tf_2N]$ type generally increases with increasing pressure and decreasing temperature, but some peculiarities have been observed. The solubility of CO_2 in ionic liquid solvents was correlated using the Soave–Redlich–Kwong equation of state. The results of the correlation were analysed by methods of mathematical gnostics. It was proved that the application of this equation of state is sufficient for testing the mutual agreement or disagreement of experimental data of the solubility of carbon dioxide in ionic liquids.

Key words:
Carbon dioxide solubility, imidazolium-based ionic liquids, high-pressure data, correlation, equation of state

Introduction

The interest in sustainable (green) chemistry[1] began approximately twenty years ago. There is a will to replace volatile organic solvents such as aromatics with water, supercritical carbon dioxide or ionic liquids. This fact is confirmed by the constant increase in the number of papers dealing with ionic liquids over the same period.

Room-temperature ionic liquids (RTIL) are molten salts that exist in a liquid state within a broad temperature range from 223 to 473 K; moreover, they exhibit high thermal stability. The basic properties of an ionic liquid can be radically changed (e.g. melting point, viscosity etc.) if its substituent is modified. Ionic liquids could also be used as a reaction medium[2,3] instead of other volatile organic compounds. Furthermore, they could be exploited in the separation of carbon dioxide from gas mixtures.[4,5] 'Newly green' applications of ionic liquids include hydrogen purification[6] or carbon-dioxide capture and sequestration,[7] using RTIL in a mixture with amine solutions. Since ionic liquids exhibit rather low vapour pressure,[8] they do not pollute the atmosphere but can contaminate water.

High-pressure phase equilibrium data in systems containing supercritical CO_2 and ionic liquids are considered as industrially important, primarily for their use in the modelling and design of supercritical extraction processes.[9,10] The knowledge of carbon-dioxide solubility in ionic liquids is of interest for extractions,[9] property modifications, selectivity enhancement, enantiomeric resolution,[11] catalysis in ionic liquids with supercritical carbon dioxide[9,10,12–15] and their applications. The viscosity of ionic liquids decreases as the melting point is depressed if carbon dioxide is used as a property modifier.

State-of-the-art

The studied binary mixtures[16–27] of CO_2 with imidazolium-based ionic liquids with bis(trifluoromethylsulfonyl)imide anion ($[C_n(m)mim][Tf_2N]$) are presented in Table 1. The ionic liquids consist of 1-alkyl-3-methylimidazolium cation (a positive charge is located in the imidazolium cycle) and bis(trifluoromethylsulfonyl)imide anion (see Fig. 1). One of these ionic liquids consists of a thrice-substituted cation, namely the 2,3-dimethyl-1-hexylimidazolium cation. A partial comparison of the published data for those systems is summarised in the references.[17–21]

The convex shape of the solubility curve is common for non-polar solvents because of the presence of fluoroalkyl groups; such Tf_2N anion-based ionic liquids are 'CO_2-philic'.[21] The RTIL and CO_2 systems were investigated within a temperature range from 280 to 450 K and at pressures from very low to 60 MPa. The solvents $[C_2mim][Tf_2N]$ and $[C_4mim][Tf_2N]$ have been studied most frequently as the two first studied members of the ionic liquids

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Table 1 – *Investigated systems of CO_2 with imidazolium-based ionic liquids containing bis(trifluoromethylsulfonyl)imide anion*

Binary system	Cation	Temperature range/K	Pressure range/MPa	References
CO_2 + [C_2mim][Tf_2N]	1-ethyl-3-methylimidazolium	293–450	0.2–47.9	16–20
CO_2 + [C_4mim][Tf_2N]	1-butyl-3-methylimidazolium	280–449	0.3–50.0	20–25
CO_2 + [C_5mim][Tf_2N]	1-pentyl-3-methylimidazolium	298–363	0.6–59.8	17
CO_2 + [C_6mim][Tf_2N]	1-hexyl-3-methylimidazolium	282–413	0.01–39.0	18–21, 26–27
CO_2 + [C_6mmim][Tf_2N]	2,3-dimethyl-1-hexylimidazolium	298–333	1.5–11.8	21
CO_2 + [C_8mim][Tf_2N]	1-octyl-3-methylimidazolium	298–344	0.7–34.8	20–21

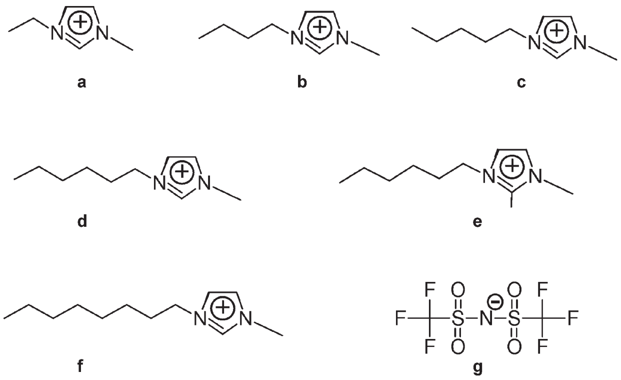

Fig. 1 – *Structural formulas of imidazolium-based ionic liquids of [C_2(m)mim][Tf_2N] type.*
a) 1-ethyl-3-methylimidazolium cation, b) 1-butyl-3-methylimidazolium cation, c) 1-pentyl-3-methylimidazolium cation, d) 1-hexyl-3-methylimidazolium cation, e) 2,3-dimethyl-1-hexylimidazolium cation, f) 1-octyl-3-methylimidazolium cation, g) bis(trifluoromethylsulfonyl)imide anion.

series, because they are cheaper than the other commercial products.

High-pressure vapour-liquid equilibrium (VLE) binary data of CO_2 with ionic liquids are scarce; moreover, there are significant discrepancies between the data from different sources. The ionic liquid [C_6mim][Tf_2N] was selected as the IUPAC standard in order to eliminate difficulties occurring in both the theoretical and experimental studies. The critical data of carbon dioxide (304.25 K and 7.39 MPa) delimit the super- and sub-critical region. CO_2 is soluble in ionic liquids, but ionic liquids are not soluble in CO_2. The comparative study showed that the solubility of CO_2 in ionic liquids of the [$C_n$mim][Tf_2N] type generally increases with increasing pressure and decreasing temperature. The solubilites of CO_2 in ionic liquids are rather similar at low pressures, while differing considerably at elevated pressures. The equilibrium pressure increases slowly with the mole fraction of CO_2 at lower concentrations, whereas the dependence becomes steeper at a higher concentration range. The ionic liquid [C_2mim][Tf_2N] exhibits different behaviour at higher pressures: carbon dioxide is less soluble in [C_6mmim] than in [C_6mim].

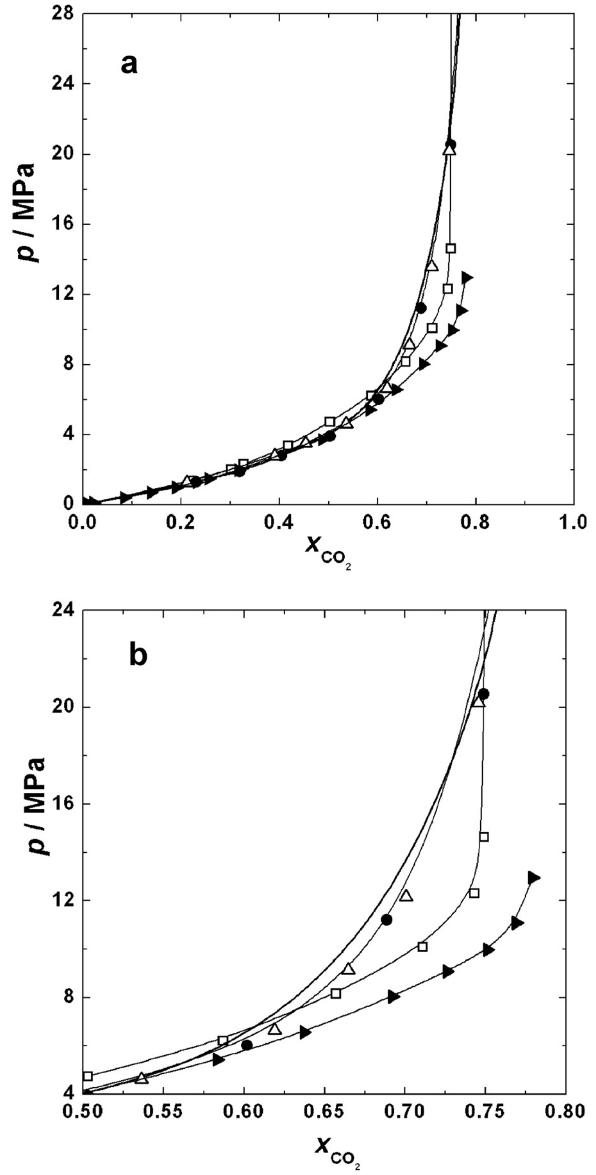

Fig. 2 – *a) Solubility of CO_2 in the selected ionic liquids at 323 K; b) Enlarged region of CO_2 solubility in the selected ionic liquids at 323 K. Binary systems: CO_2 + [C_2mim][Tf_2N] (□), CO_2 + [C_4mim][Tf_2N] (●), CO_2 + [C_5mim][Tf_2N] (△), CO_2 + [C_6mim][Tf_2N] (▶). (– – –) correlation.*

Fig. 2 shows the comparison of carbon-dioxide solubility in ionic liquids at a temperature of 323 K.

It is obvious that the increase of the alkyl-chain length from butyl to hexyl has resulted in an increase of the CO_2 solubility. The solubility data for butyl and pentyl are very similar in contrast to ethyl, which exhibits a different behaviour.

The literature reviews available state that the carbon-dioxide solubility increases with the length of the alkyl chain. However, when we compare all of the published data, some peculiarities can be observed, such as curve crossing. This observation usually occurs for the first members of the homologue series.

Data processing

Equations of state (EOS) are often used[28] for correlation at high-pressure VLE. The Soave modification[29] of the Redlich–Kwong equation

$$P = (RT)/(V-b)-(a\alpha)/[V(V+b)] \tag{1}$$

is applied in this work with the parameters a and b defined as follows

$$a = 0.42747\ R^2T_c^{\,2}/P_c \tag{2}$$

$$b = 0.08664\ RT_c/P_c \tag{3}$$

and parameter α as expressed by Graboski and Daubert[30]

$$\alpha = [1+(0.48508+1.55171\omega - 0.15613\omega^2)(1-T_r^{0.5})]^2, \tag{4}$$

where

$$T_r = T / T_c \tag{5}$$

For mixtures, the classical mixing rules are applied

$$a = \sum_i \sum_j x_i x_j (1-k_{ij})(a_i a_j)^{0.5} \tag{6}$$

$$b = \sum_i x_i b_i, \tag{7}$$

where the interaction parameter $k_{ij} = k_{ji}$ and $k_{ii} = 0$. The data for pure components used for the calculation are summarised in Table 2.

All of the available data within the temperature range for each binary system from Table 1 were correlated simultaneously with no prior analysis for possible outliers. Phase equilibrium correlation usually uses overdetermined data, which is not the case of incomplete T–p–x data for ionic liquid systems. Therefore, the objective function (OF) cannot include deviations in all of the variables. If that were the case, the minimum of the OF would be very flat and difficult to determine. For this reason, the following objective function was used:

Table 2 – *Critical properties of carbon dioxide and ionic liquids. The critical properties of ionic liquid were calculated by the modified Lydersen–Joback–Reid group contribution method.*[38,39]

Compound	T_c/K	P_c /MPa	ω	Reference
CO_2	304.10	7.375	0.239	37
$[C_2mim][Tf_2N]$	1244.90	3.260	0.182	38
$[C_4mim][Tf_2N]$	1265.00	2.760	0.266	38
$[C_5mim][Tf_2N]$	1281.10	2.560	0.344	39
$[C_6mim][Tf_2N]$	1287.30	2.390	0.354	38
$[C_6mmim][Tf_2N]$	1286.10	2.150	0.439	40
$[C_8mim][Tf_2N]$	1311.90	2.100	0.445	38

$$\mathrm{OF} = \sum_{m=1}^{N} (x_m^{\,\mathrm{exp}} - x_m^{\,\mathrm{calc}})^2, \tag{8}$$

where N is the number of experimental points, and m denotes the m-th experimental point. The use of deviations in pressure would be an inappropriate choice due to the high slope of the bubble-point curve at elevated pressures. The optimisation algorithm used in the interaction parameter estimation was the Generalised Controlled Random Search with Alternating Heuristics.[31–33] The optimised interaction parameters are presented in Table 3, along with the resulting average deviations in the compositions of carbon dioxide.

Table 3 – *Estimated interaction parameters of the Soave–Redlich–Kwong equation of state for binary systems containing CO_2 (1) + $[C_n(m)mim][Tf_2N]$ (2)*

Binary system	k_{12}	Average absolute deviation in x_1
CO_2 + $[C_2mim][Tf_2N]$	– 0.2245	0.0094
CO_2 + $[C_4mim][Tf_2N]$	– 0.0573	0.0098
CO_2 + $[C_5mim][Tf_2N]$	0.0369	0.0130
CO_2 + $[C_6mim][Tf_2N]$	0.0245	0.0078
CO_2 + $[C_6mmim][Tf_2N]$	0.0101	0.0270
CO_2 + $[C_8mim][Tf_2N]$	0.0179	0.0120

As an example, the solubility of CO_2 in the ionic liquid $[C_6mim][Tf_2N]$ is used to illustrate both the experimental and correlated data. Fig. 2 presents the comparison of the experimental data published by Aki *et al.*,[21] Kim *et al.*,[18] and Ren *et al.*[19] at 298 K including Shiflett and Yokozeki[26] at 297 K with the data calculated from our correlation at 298 K. Analogous calculations have been performed for isotherms 323 and 333 K; the results are shown in Figs. 4 and 5. Good agreement between the calculated and experimental data within the experimental errors is clear from Figs. 3–5.

The residuals (deviations in the mole fraction) were further analyzed by the method of mathematical gnostics.[34,35] This method makes no prior assumption on the kind of distribution. Instead, the distribution function is obtained from the data analysis. Statistical methods suffer from problems in the selection of proper bandwidth. It may lead to an overfitting if a small bandwidth is used or underfitting in case of a large bandwidth. Mathematical gnostics provides us with an objective criterion for determining the correct bandwidth.

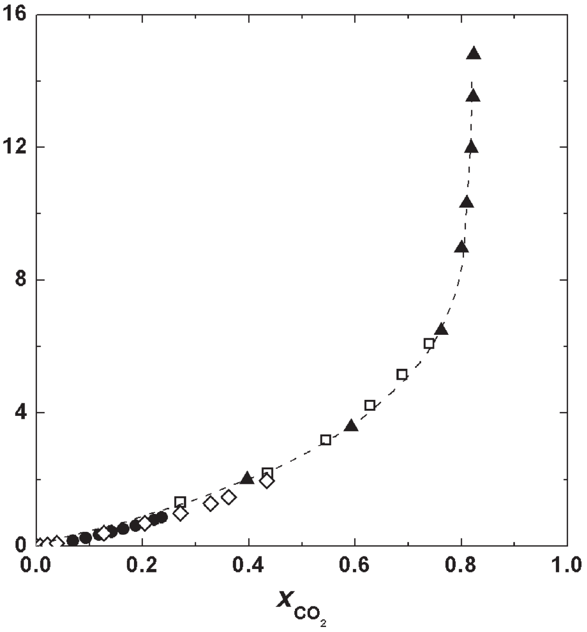

Fig. 3 – *Comparison of CO_2 solubility in $[C_6mim][Tf_2N]$ at 298 K. Literature data: Ref. 18 (●), ref. 19 (▲), ref. 21 (□), ref. 26 at 297 K (◇). (– – –) correlation.*

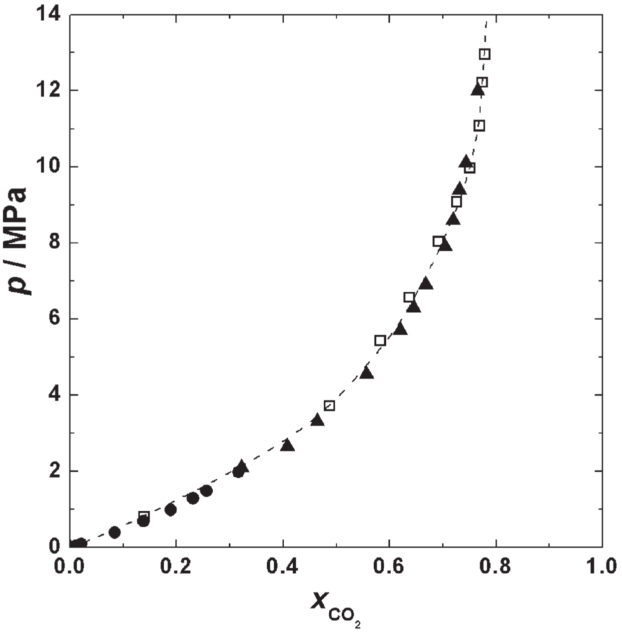

Fig. 4 – *Solubility of CO_2 in $[C_6mim][Tf_2N]$ at approximately 323 K. Literature data: Ref. 19 (□), ref. 20 (▲), ref. 26 (●). (– – –) correlation.*

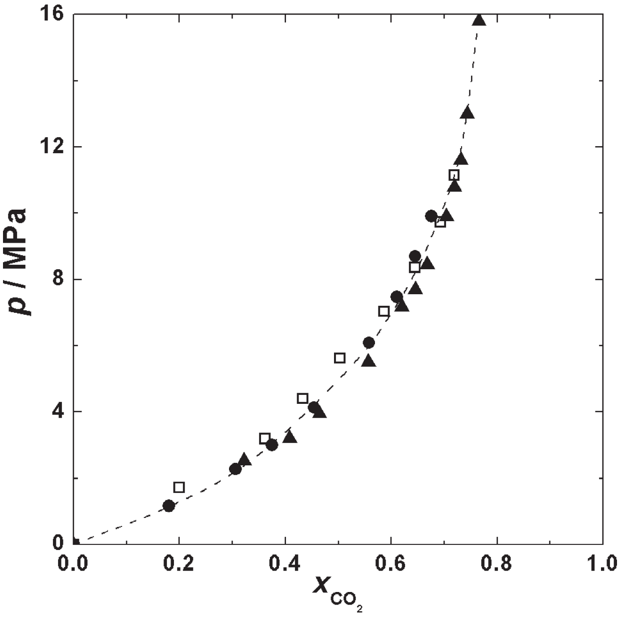

Fig. 5 – *Solubility of CO_2 in $[C_6mim][Tf_2N]$ at approximately 333 K. Literature data: Ref. 20 (▲), ref. 21 (□), ref. 27 (●). (– – –) correlation.*

It is usually assumed that the measurement errors have normal distribution. Strictly speaking, this assumption is based on the central limit theorem saying that, under certain conditions, the sum of random variables is normally distributed. Unfortunately, experimental techniques are often complex and the experimental error need not be the result of a great number of small random errors. Even in case of errors that are not normally distributed, regression can be carried out and the results may be satisfactory. However, the knowledge of the distribution function can provide us with useful additional information. Statistical tests of normality can only accept or reject the hypothesis at a selected significance level. Mathematical gnostics does not test data normality but determines the distribution function.

Two types of gnostic distribution functions are available, global and local. The global distribution function was derived under the assumption that the data are members of the same data set, the properties of which can be described by common parameters. This should be the case of all properly measured experimental data. If the measurement is not subject to systematic errors or gross errors, the residuals of any regression will have some (not necessarily normal) distribution with zero mean. As shown in literature,[34,35] the global distribution function need not exist for arbitrary experimental data. Existence of the global distribution function is thus evidence of good data quality regardless of whether or not their distribution is normal. In contrast, the local distribution function can describe the neat structure of data. In regression analysis, this distribution function is used in case the global distribution function does not exist. The local distribution function is often multimodal and the data can thus be split into clusters. These clusters contain additional information. If the data are split into clusters according to temperature, the temperature dependence of parameters may be assumed. If the data are split according to authors, discrepancies between authors could be suspected.

First, the unimodality of the distribution function of the residuals was tested by determining their global distribution function. If the test had failed, the local distribution function would have been determined using the algorithm described by Ždímal *et al.*[36]

Examples of the estimation of the residual-distribution densities for $[C_2mim][Tf_2N]$ and $[C_4mim][Tf_2N]$ are presented in Figs. 6 and 7, respectively. It can be seen that the distribution density of the residuals for $[C_2mim][Tf_2N]$ is unimodal. It means that the data of all the authors at all temperatures are in good mutual agreement. In contrast, the distribution density for $[C_4mim][Tf_2N]$ exhibits three modes, indicating that all the data cannot be described properly using a single value of the interaction parameter. Multimodality can be observed even when analysing data from one literature source. For instance, the distribution density of the residuals of the data for $[C_4mim][Tf_2N]$ by Aki *et al.*[21] possesses three modes, while the distribution densities of the data for $[C_6mim][Tf_2N]$, $[C_6mmim][Tf_2N]$ and $[C_8mim][Tf_2N]$ by the same authors are unimodal and moreover for $[C_6mim][Tf_2N]$ are in good agreement with the data of the other authors.

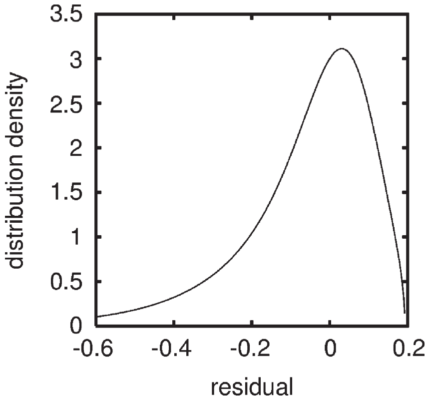

Fig. 6 – *Distribution density of the residuals for the CO_2 + $[C_2mim][Tf_2N]$ system*

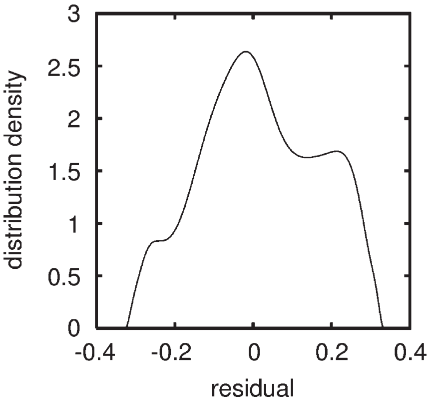

Fig. 7 – *Distribution density of the residuals for the CO_2 + $[C_4mim][Tf_2N]$ system*

The residuals for $[C_4mim][Tf_2N]$ are not split into clusters according to temperature, even the data for a single isotherm of a single author possess three modes. The hypothesis of the temperature-dependent interaction coefficient can thus be neglected. As can be seen from Fig. 2, the results of this binary system do not behave strictly as could be expected in a homologous series. The bubble-point line crosses the bubble-point line of CO_2 + $[C_2mim][Tf_2N]$. The problems in regression thus stem rather from the abnormalities of the behaviour of this particular system.

The results of the analysis prove that even a cubic equation of state with classical mixing rules could be utilised for testing the mutual agreement or disagreement of the experimental data of the solubility of carbon dioxide in ionic liquids. Although discrepancies have been observed, it could be stated that the agreement between the data from different literature sources is fair, and the interaction parameter could be considered as temperature-independent.

Conclusion

It was found that CO_2 solubility increases with increasing length of the substituent on the cation. The behaviour of the first member of the series $[C_2mim][Tf_2N]$ does not comply with this observation, and in addition the solubility curve crosses the curves for the other ionic liquids. The solubilities of liquids with butyl and pentyl substituents are very close.

The literature data available were correlated with the use of the Soave–Redlich–Kwong EOS, and the interaction parameters were evaluated. The results of the correlation served as a basis for the intercomparison of the experimental data from different literature sources. Fair agreement was found, although some discrepancies were observed.

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List of symbols

a – parameter, J m^3 mol^{-2}
b – parameter, m^3 mol^{-1}
k – interaction parameter
N – number of experimental points
P – pressure, Pa
R – gas constant, J K^{-1} mol^{-1}
T – temperature, K
V – volume, m^3
x – molar fraction
α – parameter
ω – acentric factor

Subscripts

c – critical value
i – component
j – component
m – m-th experimental point
r – reduced value

Superscripts

calc – calculated
exp – experimental

Abbreviations

[C$_n$mim][Tf$_2$N] – 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C$_n$mmim][Tf$_2$N] – 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
EOS – equation of state
OF – objective function
RTIL – room-temperature ionic liquid
VLE – vapour-liquid equilibrium

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