Influence of Thermophysical Properties of Ionic Liquids in Chemical Process Design†

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It has been proved in the past, with common liquids, that the values of their thermophysical properties have a significant effect on the design of physicochemical processing and reaction units, influencing directly the design parameters and performance of equipment like heat exchangers, distillation columns, and reactors. In this paper we have analyzed the effect of the uncertainty of thermophysical data of ionic liquids (density, heat capacity, thermal conductivity, and viscosity) in the design of some current equipment, used in processes as solvents or heat transfer fluids. Data have been collected from the IL Thermo database for alkylmethylimidazolium ($C_n$mim) liquids, with $[BF_4]$ and $[PF_6]$ anions. Results obtained show that the influence of actual errors in the thermophysical properties of ionic liquids can render any future design as not working or excessively costing. Moreover, the heat storage capacity of these ionic liquids has been analyzed, and it is possible to consider them as possible replacements of current silicon-based heat transfer fluids. The results obtained support that the implementation of those applications needs a careful selection of experimental data, otherwise equipment will be either under- or overdimensioned, with the consequent ill operation or increased capital costs. In addition, they recommend a revision of the present methods of measurement of thermophysical properties of ionic liquids and the establishment of reference data on thermophysical properties with low uncertainty, to avoid the actual status of experimental data.

1. Introduction

Ionic liquids are presently a good challenge to both scientists and chemical companies, not only because of their interesting properties but also for their actual and potential applications in the chemical process industries. It has been proved in the past, with common liquids, that the values of their thermophysical properties have a significant effect on the design of physicochemical processing and reaction units,[1−4] influencing directly the design parameters and performance of equipment like heat exchangers, distillation columns, and reactors. Recently, we have analyzed the same effect for molten alkali nitrates, which have emerged as high-temperature fluids for several technological processes, such as high-temperature energy storage in batteries for solar plants and waste treatment, and demonstrated that the knowledge of accurate data for the transport coefficients of these fluids is very important.[5] Values of the uncertainty found in high temperature properties of molten salts are smaller than those found in the published data on properties of ionic liquids, as their accurate measurement pose some delicate problems.[6]

Professor William Wakeham initiated his fight toward the society awareness of the effect of the uncertainty of the transport properties of fluids in the process plant design for the chemical industry in the late seventies.[7] One of us (C.A.N.C.) was privileged to be at the Imperial College in London, as a postdoc, under his supervision, and to be part of this fight against the traditional way of facing the use of thermophysical properties data without inquiring about the accuracy of those data, making nonapplicable extrapolations, and, when experimental data were not available, using predictive/estimation methods not based in sound theoretical schemes, if available. This last problem was also part of the attempts that were initiated by Professor Wakeham to establish a philosophy of approach to the calculation methods of transport properties, using for the first time the classification of methods in prediction and estimation classes.[8] Now, 30 years later, we can say that, for common fluids, this philosophy is accepted worldwide by all users of scientific data included in databases and interactive online estimation procedures, namely, for common process liquids, including refrigerants, in wide ranges of temperature and pressure (see, for example, ref 9).

In this paper, we have analyzed the effect of the uncertainty of thermophysical data of ionic liquids (density, heat capacity, thermal conductivity, and viscosity) used in processes as solvents or heat transfer fluids, in the design of some current equipment. Data have been collected from IL Thermo[10] for alkylmethylimidazolium ($C_n$mim) liquids, with $[BF_4]$ and $[PF_6]$ anions. Results obtained show that the influence of actual errors in the thermophysical properties of ionic liquids can render any future design as not working or excessively costing. Moreover, the heat storage capacities of these and other ionic liquids, containing anions like $[C_2H_5SO_4]$, $[(CF_3SO_2)_2N]$, $[CF_3SO_3]$, and $[C_8H_{17}SO_4]$, possible replacements of current heat transfer fluids, have been analyzed. Although the actual cost of ionic liquids is higher than these heat transfer fluids, the future production of higher quantities can make their use competitive.

2. Ionic Liquids Properties

Low temperature ionic liquids (LTILs) are innovative fluids for chemical and materials processing, and the recent explosion on their measurement, molecular interpretation, and property prediction, allied to the first industrial processes that started to

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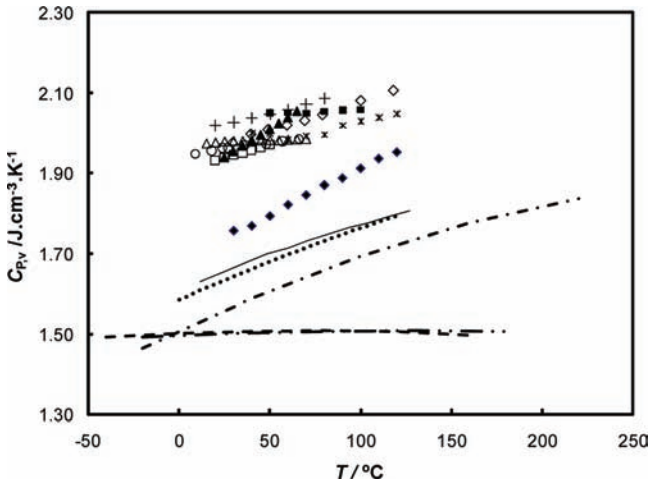

Figure 1. Heat capacity per unit volume of several ionic liquids. Data for the ionic liquids were taken from ref 10 and for the heat transfer fluids from their Material Safety Data Sheets available online. ◆, $[C_6mim][PF_6]$; ◇, $[C_4mim][PF_6]$; +, $[C_2mim][BF_4]$; ■, $[C_6mim][(CF_3SO_2)_2N]$; ▲, $[C_4mim][C_{18}O_{17}SO_4]$; *, $[C_4mim][CF_3SO_3]$; ●, $[C_4mim][(CF_3SO_2)_2N]$; □, $[C_2mim][PF_6]$; ○, $[C_2mim][(CF_3SO_2)_2N]$; △, $[C_2mim][C_2H_5SO_4]$; - - -, Syltherm 800; - •• -, Syltherm HF; —, Dowtherm A; — • —, Dowtherm MX; ••••, Paratherm HE.

use them as environmentally friendly solvents and reaction fluids, raises very important points to the scientific and industrial community. These points are related with all the available knowledge on the properties of these fluids and its relation with the chemical structure, its quality, and our capacity of using this knowledge for the benefit of society. These liquids possess a unique array of physicochemical properties that make them suitable in numerous task-specific applications in which conventional solvents are nonapplicable or insufficiently effective. Such properties include: high thermal stability, high electrical conductivity, high heat capacity per unit volume, wide range of viscosity and very good solvent properties, and, last but not least, their negligible vapor pressure.[6,11−13] As a result of these properties, ionic liquids are very popular materials, and they enjoy a plethora of applications in various domains of physical science.

The possible use of ionic liquids as heat transfer fluids, for heat exchange in chemical plants and solar thermal power generation, from cryogenic temperatures up to 200 °C, based on the values of heat capacity per unit volume, very low vapor pressures, wide liquid ranges, and thermal stability (some can be used at temperatures up to 500 °C) has been discussed,[14] and its comparison with the properties of synthetic compounds (based on hydrocarbons, polyaromatics, and siloxanes) showed that common imidazolinium systems have higher heat capacities per unit volume than two high performance commercial thermal fluids, Paratherm HE and Dowtherm MX, in all the applicable temperature ranges. This analysis was complemented here for several ionic liquids and Syltherm 800, Syltherm HF, Dowtherm A (trademarks of Dow Chemical Company, USA), and Paratherm HE (registered mark of Paratherm Corporation). Figure 1 shows the results obtained for $[C_2mim][BF_4]$, $[C_2mim][C_2H_5SO_4]$, $[C_2mim][(CF_3SO_2)_2N]$, $[C_4mim][BF_4]$, $[C_4mim][CF_3SO_3]$, $[C_4mim][(CF_3SO_2)_2N]$, $[C_4mim][PF_6]$, $[C_4mim][C_8H_{17}SO_4]$, $[C_6mim][(CF_3SO_2)_2N]$, and $[C_6mim][PF_6]$. Data for the density and heat capacity of the ionic liquids chosen were taken from the IL Thermo database.[10] It is clear that, comparatively, the heat capacity per unit volume ($C_{P,V} = \rho C_P$) of these ionic liquids, between room temperature and 130 °C, is (20 to 40) % higher. These results are highly promising and led us to analyze the existing data for density, heat capacity, viscosity, and thermal conductivity of the same ionic liquids, to have an idea of the uncertainties of the data therein presented, followed by studying the effect of these uncertainties in the design of a heat exchanger.

3. Methodology

Following the methodology described in previous publications,[2,4,5] we will evaluate the changes in the design parameters of a chemical process unit, namely, a heat exchanger, of the shell and tube type, which arise solely from changes made in the thermophysical properties (density, heat capacity, viscosity, and thermal conductivity) of the heat transfer fluid used, here chosen to be an ionic liquid. The degrees of freedom of a heat exchanger may be reduced to two, by selecting a specific type of device and by prescribing its duty to satisfy the external constraints of a particular process, the heat transfer area, and the pressure drop across the fluid ducts. Because this last effect is not usually a major factor in the design, we shall adopt here, as before, the heat transfer area as a sole factor that reflects the changes in the design caused arising from the changes in the thermophysical properties of the ionic liquid process stream. This also permits us to estimate easily the economic consequences of these changes in the design. For the sake of simplicity, we have followed the procedure used in ref 5, with the necessary adaptations. The equipment chosen, also described there,[5] is modern solar power equipment using a molten salt receiver as the thermal energy storage system, which captures the sun's energy and stores it in hot molten sodium nitrate or molten nitrate mixtures, so that power can be generated when needed, not just when the sun is shining. The heat transfer unit uses a molten salt through oil to salt heat exchanger.[15] We replace the molten salt mixture used by an ionic liquid, chose one set of reference conditions for the operation based on a given set of values of the thermophysical properties, and then perturbed the assigned values about their reference values, within ranges commensurate with the actual stage of experimental uncertainty reported in IL Thermo.[10] The heat transfer area can be calculated from the general principles[16,17] and is given by

$$Q = U_0 A_0 (\Delta T)_{lm} \tag{1}$$

where Q is the rate of heat transfer; U_0 is the overall heat transfer coefficient; A_0 is the area across which the heat is being transferred; and $(\Delta T)_{lm}$ is the logarithm mean temperature difference between the inlet and outlet stream temperatures of the two fluids. For a particular duty, the only design parameter allowed to depend on thermophysical properties is the area for heat transfer or, in a shell and tube exchanger, the number of tubes and passages of fluid. The overall heat transfer coefficient measures the "barrier resistance" to the heat transfer and includes all the resistances to heat transfer. In this case it includes the contribution due to convection at the tubes inner and outer surfaces and across the tube walls. Convection transfer is determined by the boundary layers developed at the surfaces, thus depending on several properties, like thermal conductivity, viscosity, density, and heat capacity. For circular tubes, the overall heat transfer coefficient may be calculated by

$$\frac{1}{U_0} = \frac{1}{h_o} + \frac{1}{h_i}\frac{D_o}{D_i} + r_w + r_o + r_i\frac{D_o}{D_i} \tag{2}$$

where D_o is the outside tube diameter; D_i is the inside tube diameter; r_w is the thermal resistance of the tube wall; r_i and r_o

Table 1. Values of Heat Transfer Liquid Properties, Reference Area A_0, and Estimated Costs for the Shell and Tube Heat Exchanger

heat transfer fluid	ρ / kg·m^{-3}	C_P / J·kg^{-1}·K^{-1}	η / mPa·s	λ / mW·m^{-1}·K^{-1}	A_0 / m^2	C_E / k$
[C_4mim][PF_6] (50 °C)	1346 ± 1^{25}	1493 ± 30^{20}	68.8 ± 1.8^{25}	146 ± 7^{22}	480.75	738
[C_6mim][PF_6] (50 °C)	1273 ± 3^{19}	1409 ± 61^{20}	111.9 ± 3.2^{21}	146 ± 7^{22}	634.60	891
[C_2mim][BF_4] (50 °C)	1280 ± 2^{19}	1600 ± 25^{23}	15.9 ± 1.1^{24}	196 ± 6^{23}	217.29	430
Dowtherm A (50 °C)	1041	1632	2.12	134	138.60	317
Dowtherm MX (100 °C)	905	1870	2.09	114	159.08	348
Syltherm 800 (80 °C)	882	1711	3.86	124	202.86	410
Syltherm HF (80 °C)	811	1830	0.83	92	135.47	312

are the fouling resistance; and h_i and h_o are the heat transfer coefficients for the inside and outside film of fluids. For our purposes, this can be simplified to

$$\frac{1}{U_0} = \frac{1}{h_o} + \frac{1}{h_i}\frac{D_o}{D_i} + R \tag{3}$$

where R represents the combined resistance of the tube wall and other factors are considered constant. To obtain optimal heat transfer, the flow must be turbulent, and this can be achieved by placing baffles in the shell part of the exchanger and controlling fluid velocity in the tubes.

There are many equations relating the heat transfer coefficients to fluid properties, and for our intents we will adopt one of the most utilized in practice. For the turbulent flow in a smooth circular tube, the Sieder and Tate correlation[17] is

$$\mathrm{Nu} = \frac{h_i D_i}{\lambda} = 0.027\mathrm{Re}^{0.8}\mathrm{Pr}^{1/3}\left(\frac{\eta}{\eta_s}\right)^{0.14} \tag{4}$$

where Re is the Reynolds number; Pr is the Prandtl number; λ is the thermal conductivity of the fluid; and η is its viscosity, all the properties being evaluated at mean bulk temperature of the fluid. η_s is the fluid viscosity at wall temperature. The ratio at the left-hand side of the equation is known as the Nusselt number. The Prandtl and the Reynolds numbers are given by

$$\mathrm{Pr} = \frac{C_P \eta}{\lambda} \tag{5}$$

$$\mathrm{Re} = \frac{\rho u D}{\eta} \tag{6}$$

where C_P is the heat capacity; ρ is the fluid density; and u is the mean fluid velocity over the tube cross section. Since viscosity, thermal conductivity, heat capacity, and density are functions of the fluid, only the fluid velocity must be fixed, which for the calculations of the total area of tubes will be considered the same. For the heat transfer coefficients on the shell side of the heat exchanger tube, referred to as the outside area, h_o is given by

$$\frac{h_o D_e}{\lambda} = 0.36\mathrm{Re}^{0.55}\mathrm{Pr}^{1/3}\left(\frac{\eta}{\eta_w}\right)^{0.14} \tag{7}$$

where D_e is the equivalent diameter between the tubes.

4. Results and Discussion

The values for the operation of the heat exchanger were prescribed before,[5] $u = 0.5$ m·s^{-1}, $D_i = 0.018$ m, $D_o = 0.020$ m, $D_e = 0.020$ m, $R = 0$ (ideal flow), $(\Delta T)_{lm} = 20$ K, $Q = 1$ MW, and $h_o = 2000$ W·m^{-2}·K^{-1}. The temperature was 50 °C for the ionic liquids. Data for the thermophysical properties for the ionic liquids were taken from IL Thermo.[10] When more than one reference was available, the data used were those of smaller uncertainty, only if purity and water content were assigned unambiguously, as in the literature low water content does not mean necessarily low uncertainty, depending on the methods of measurement used. From all the ionic liquids, three were chosen, attempting to have a wide range of viscosity and of heat capacity vs temperature data. The values of the properties used can be found in Table 1, together with the reference area values, $A_{0,ref}$, obtained for the ionic liquids chosen, [C_2mim][BF_4], [C_4mim][PF_6], and [C_6mim][PF_6], and also for Dowtherm A, Dowtherm MX, Syltherm 800, and Syltherm HF (Dowtherm Co., http://www.dow.com/heattrans/prod/synthetic/dowtherm.htm; http://www.dow.com/heattrans/prod/synthetic/syltherm.htm). This table shows that the reference area is higher for the ionic liquids, except for [C_2mim][BF_4], with a reference area similar to Syltherm 800.

The effect of the uncertainties of the thermophysical properties of the ionic liquids can be calculated by calculating the new heat transfer area A_0 and its variation ΔA as a function of the variation in percentage of the thermophysical properties, $\Delta\rho$, $\Delta\eta$, $\Delta\lambda$, and ΔC_P.

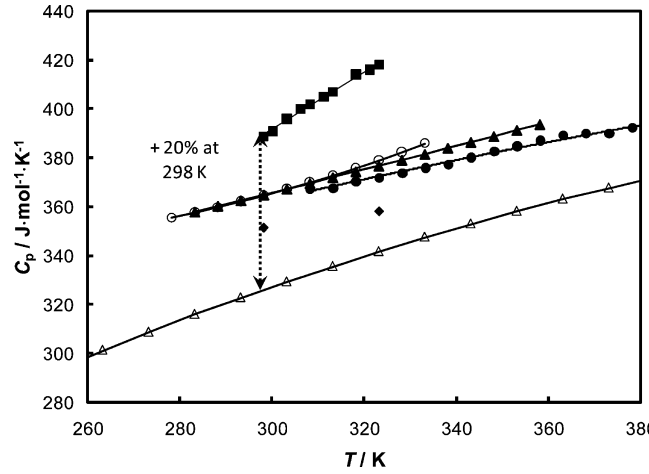

Figure 2. Existing values of the heat capacity for [C_4mim][BF_4]. △, ref 23; ○, ref 31; ■, ref 32; ◆, ref 33; ▲, ref 34; ●, ref 35. The arrow at 300 K illustrates the difference (20 %) between the extreme values at this temperature.

$$\Delta A_0 = \left(\frac{A_0 - A_{0,\mathrm{ref}}}{A_{0,\mathrm{ref}}}\right) \cdot 100 \qquad (8)$$

The results discussed below can be easily minimized in an industrial application of an impure ionic liquid but of known thermophysical properties in processing conditions. If this was easily obtainable and a pilot plant could be constructed, the uncertainty in the equipment design will be only depending on the real performance of the in situ measuring instruments. However, this situation is far from being achieved nowadays.

In previous publications, we have only studied the effect of the uncertainties of the transport properties because the reported uncertainties in the measurements of densities and heat capacities of the fluids studied were very small. This is not the situation in the ionic liquids, where errors up to 3 % in density and 25 % in heat capacity can be found, as shown in Figure 2 for [C_4mim][BF_4]. Therefore, we decided to study also the effect of the uncertainties in these properties. As a result, we have a 5D surface that can only be visualized in 2D or 3D, at the most. Table 2 displays the perturbation in the area values as a function of the perturbation in viscosity and the maximum and minimum values of thermal conductivity, heat capacity, and density (± 30 %). Figure 3 shows the effect of $\Delta\eta$ and $\Delta\lambda$ in ΔA for [C_6mim][PF_6], using the uncertainty in viscosity as a parameter for the curves. As an example, if we use the thermal conductivity 10 % higher and the viscosity 20 % lower (explained by the presence of water, p. ex.), the calculated area will decrease by 15 %, with the corresponding effect on the "bad-functioning" of the heat exchanger. A fortiori, if we use thermal conductivity 10 % lower and viscosity 20 % higher (explained by nonreported systematic errors in the measurement), we obtain a 20 % increase in the area, with the corresponding effect on the capital and operational costs of the equipment. Figure 4 shows the effect of $\Delta\rho$ and ΔC_P in ΔA for [C_6mim][PF_6], using the uncertainty in heat capacity as a parameter for the curves. Here the effect is greater, especially for the underestimation of density, a fact that can be easily found if the ionic liquid has impurities with smaller densities. For an error of +10 % in density and +20 % in heat capacity, an error of −10 % in area can be found, and

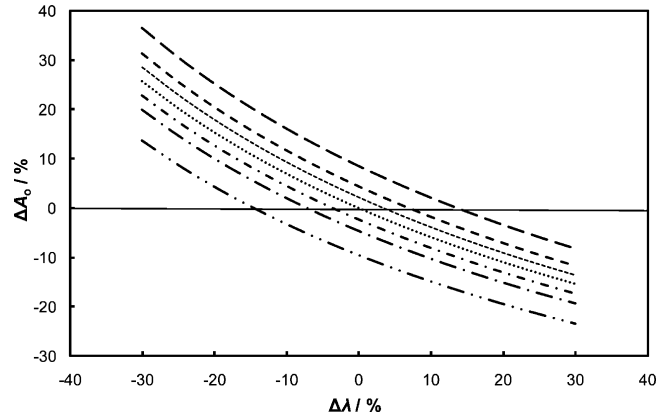

Figure 3. Effect of uncertainty of thermal conductivity $\Delta\lambda$ and viscosity $\Delta\eta$ of [C_6mim][PF_6] on the area (ΔA) of a shell and tube heat exchanger, as a function of $\Delta\lambda$, for $\Delta\eta$ values: -••-, 20 %; -•-, 10 %; −•−, 5 %; ••••, 0 %; - - - -, +5 %; − − −, +10 %; − − − + 20%.

Table 2. Maximum and Minimum Area Variation for Each Thermophysical Property Perturbation

			Dowtherm A	Dowtherm MX	Syltherm 800	Syltherm HF	[C_2mim][BF_4]	[C_4mim][PF_6]	[C_6mim][PF_6]
$\Delta\eta = -20$ %	$\Delta\lambda$	Δmax	−19.96	−20.52	−21.35	−19.86	−21.55	−23.08	−23.39
		Δmin	1.22	1.25	1.30	1.21	1.32	1.41	1.43
	ΔC_P	Δmax	−14.29	−14.70	−15.29	−14.22	−15.43	−16.53	−16.75
		Δmin	16.28	16.74	17.42	16.20	17.58	18.83	19.08
	$\Delta\rho$	Δmax	−22.09	−22.71	−23.63	−21.98	−23.85	−25.55	−25.89
		Δmin	17.01	17.50	18.20	16.93	18.37	19.68	19.94
$\Delta\eta = -10$ %	$\Delta\lambda$	Δmax	−16.45	−16.92	−17.60	−16.37	−17.77	−19.03	−19.28
		Δmin	5.92	6.09	6.33	5.89	6.39	6.85	6.94
	ΔC_P	Δmax	−10.47	−10.76	−11.20	−10.41	−11.30	−12.11	−12.27
		Δmin	21.83	22.45	23.36	21.72	23.57	25.25	25.59
	$\Delta\rho$	Δmax	−18.71	−19.24	−20.01	−18.61	−20.20	−21.64	−21.92
		Δmin	19.54	20.10	20.90	19.44	21.10	22.60	22.90
$\Delta\eta = -5$ %	$\Delta\lambda$	Δmax	−14.78	−15.20	−15.81	−14.70	−15.96	−17.09	−17.32
		Δmin	8.16	8.40	8.73	8.12	8.81	9.44	9.57
	ΔC_P	Δmax	−8.64	−8.88	−9.24	−8.60	−9.33	−9.99	−10.13
		Δmin	24.49	25.18	26.19	24.36	26.44	28.32	28.70
	$\Delta\rho$	Δmax	−17.09	−17.57	−18.28	−17.00	−18.45	−19.77	−20.03
		Δmin	22.00	22.62	23.54	21.89	23.75	25.45	25.79
$\Delta\eta = 0$ %	$\Delta\lambda$	Δmax	−13.15	−13.52	−14.07	−13.09	−14.20	−15.21	−15.41
		Δmin	10.35	10.64	11.07	10.29	11.17	11.97	12.13
	ΔC_P	Δmax	−6.86	−7.06	−7.34	v6.83	v7.41	−7.94	−8.04
		Δmin	27.06	27.83	28.95	26.93	29.22	31.30	31.72
	$\Delta\rho$	Δmax	−15.52	−15.96	−16.60	−15.44	v16.75	−17.95	−18.19
		Δmin	24.40	25.09	26.10	24.27	26.34	28.22	28.59
$\Delta\eta = +5$ %	$\Delta\lambda$	Δmax	−11.57	−11.90	−12.37	−11.51	−12.49	−13.38	−13.56
		Δmin	12.47	12.83	13.34	12.41	13.47	14.43	14.62
	ΔC_P	Δmax	−5.13	−5.28	−5.49	−5.11	−5.54	−5.94	−6.02
		Δmin	29.58	30.41	31.64	29.43	31.93	34.21	34.66
	$\Delta\rho$	Δmax	−13.99	−14.38	−14.96	−13.92	−15.10	−16.18	−16.39
		Δmin	26.73	27.49	28.59	26.59	28.86	30.92	31.33
$\Delta\eta = +10$ %	$\Delta\lambda$	Δmax	−10.02	−10.31	−10.72	−9.97	−10.82	−11.59	−11.75
		Δmin	14.55	14.96	15.56	14.47	15.71	16.82	17.05
	ΔC_P	Δmax	−3.45	−3.55	−3.69	−3.43	−3.72	−3.99	−4.04
		Δmin	32.02	32.93	34.26	31.86	34.58	37.04	37.53
	$\Delta\rho$	Δmax	−12.50	−12.85	−13.37	−12.43	−13.49	−14.45	−14.65
		Δmin	31.23	32.12	33.41	31.08	33.72	36.13	36.61
$\Delta\eta = +20$ %	$\Delta\lambda$	Δmax	−7.04	−7.24	−7.53	−7.01	−7.60	−8.14	−8.25
		Δmin	18.55	19.07	19.84	18.45	20.02	21.45	21.74
	ΔC_P	Δmax	−0.19	−0.20	−0.21	−0.19	−0.21	−0.22	−0.23
		Δmin	36.75	37.79	39.31	36.56	39.68	42.50	43.07

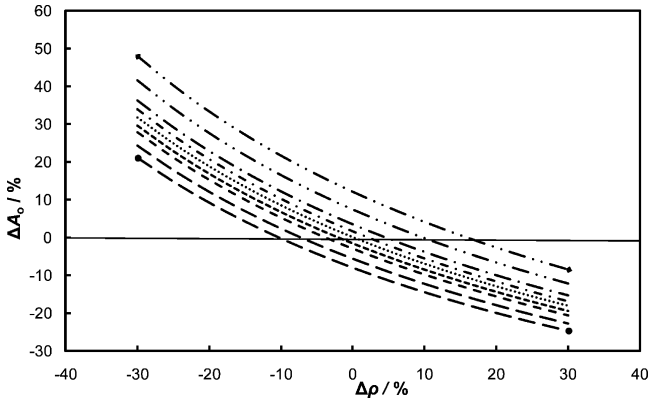

Figure 4. Effect of uncertainty of density ($\Delta\rho$) and heat capacity (ΔC_P) of [C_6mim][PF_6] on the area (ΔA) of a shell and tube heat exchanger, as a function of $\Delta\rho$, for ΔC_P values: •— —•, 30 %; — —, 20 %; — — —, 10 %; - - -, 5 %; ••••, 0 %; -•-, +5 %; —•—, +10 %; -••-, +20 %; ■—••—■, +30 %.

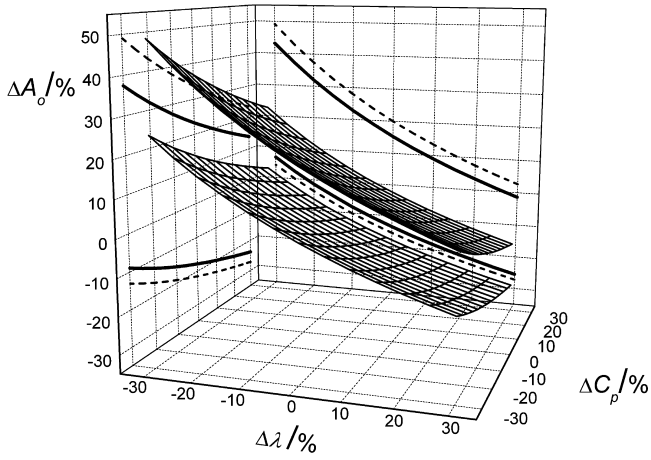

Figure 5. 3D plot of the effect of uncertainty of heat capacity (ΔC_P) and thermal conductivity ($\Delta\lambda$) for [C_2mim][BF_4] on the area (ΔA) of a shell and tube heat exchanger, using viscosity uncertainty, $\Delta\eta$, as a parameter for the surfaces (upper, +20 %; lower, −20 %). The lines in the planes represent the maximum and minimum values of the area variation for ± 20 %, —, and ± 30 %, - - -, in $\Delta\lambda$ and ΔC_P (similar lines generate the two-dimensional plots shown as examples in Figures 3 and 4).

for an error of −5 % in density and − 30 % in heat capacity, the effect is +18 % in the area of the heat exchanger.

Figure 5 shows in a 3D plot the effect of ΔC_P and $\Delta\lambda$ in ΔA for [C_2mim][BF_4], using again the viscosity uncertainty, $\Delta\eta$, as a parameter for the surfaces. Density is not shown, as this is the property known with less uncertainty. Not using extreme values, whereby the area can be overestimated by 50 %, an error of +20 % in viscosity, −20 % in thermal conductivity, and −10 % in heat capacity generates an error of +20 % in the area of the heat exchanger.

These plots show similar trends for any pair or trio of variables chosen, allowing us to state that the effect of the uncertainty of the thermophysical properties of ionic liquids, namely, when difficulties are still observed in the quality of the methods of measurement of these properties,[6] is a limiting factor in the correct design of a heat exchanger.

As an additional comment, it can be said that the variations induced in the area with λ and C_p if η and ρ are constant are similar for all the fluids herein considered. This is caused by the form of the Sieder and Tate correlation.[17] It can be easily shown that the exponents in the heat transfer coefficients for the thermal conductivity and heat capacity are equal and symmetrical, while those for density and viscosity are very different

$$h_i \alpha \lambda^{-1/3} \eta^{-0.47} C_P^{1/3} \rho^{0.80} \tag{9}$$

$$h_o \alpha \lambda^{-1/3} \eta^{-0.22} C_P^{1/3} \rho^{0.55} \tag{10}$$

From the results presented, we can conclude that the effects of the uncertainty in the thermophysical properties of RTILs are high and that the heat transfer areas (see Table 1) are higher than those obtained with the used heat transfer oils, except for [C_2mim][BF_4]. These effects can render equipment obsolete and/or induce additional operational costs, well above those estimated by design. When a heat exchanger is built, its cost will be weakly dependent on the size/length of the pipes but highly dependent on the heat transfer area, and the operational costs will increase significantly with size. However, to increase the capacity of the unit after having been built would represent an additional cost, possibly smaller when replacing it with a new unit. Therefore, the wise approach would be to obtain good experimental measurements of the fluids needed and proceed with better technological designs.

The results obtained for these three ionic liquids would be similar for other ionic liquids since the magnitude of the effects in the heat transfer area depends on their thermophysical properties.

The main question to answer would then be: Are the ionic liquids prepared to replace efficiently and economically the actual heat transfer fluids? If the answer to the first part of this question has been proved to be affirmative, from a technical/scientific point of view, to answer the second part one needs a quick digression through the economy of the chemical processes, namely, to the costs of heat transfer equipment. A good view of the nature of the chemical processes and the process economics can be found in ref 25. As stated there, the role of the chemical processes is to make money, the understanding of the process economics being critical for process design. Decision making on using ionic liquids as heat transfer liquids in chemical processes is not the purpose of this paper. However, it will be interesting to estimate the total cost of a new heat exchanger, to understand if RTILs are in the present or can be in the future good alternatives to actual heat transfer liquids used in industry. We shall only discuss the total cost for the design of a new heat exchanger, leaving aside the financial costs and management.

The total cost required for a new design can be broken in five parts,[26] the battery limits investment, the utility investment, the off-site investment, the engineering fees, and the working capital. From these, we will be concerned first with the battery limit investment, which is the cost of individual plant items and their installation to form a working process. The cost of a heat exchanger will be a function of its size (where the type of heat exchanger and the heat transfer area will be critical), the materials of its construction (materials compatibility between metal parts and heat transfer fluids), design pressure, and temperature, and it can be given by[26]

$$C_E = C_B \left(\frac{X}{X_B} \right)^m \tag{11}$$

where C_E represents the cost of the equipment with a given capacity X (here the heat transfer area, A_0); C_B is the base cost of a reference equipment with a capacity X_B; and m is

a constant depending on the equipment type ($m = 0.68$ for a shell and tube heat exchanger). The installation cost will be 3 to 4 times the value of C_E. The cost of the reference equipment, if obtained for a given year, must be corrected by accepted indexes, like the Chemical Engineering Indexes (1957 to 1959 index = 100) or the Nelson−Farrar Cost Indexes for refinery construction.[27] The Chemical Engineering Indexes are the most useful for these types of heat exchangers and were used here on the basis of January 2000 costs, as we are going to use the values for comparative purposes, and therefore any recent year is adequate. The base cost of a carbon steel shell and tube heat exchanger, with a heat transfer area of 80 m^2 would be $3.28 \cdot 10^4$ US$. Equation 11 has to be corrected with factors arising from the type of materials used and pressure and temperature operational values

$$C_E = C_B' \left(\frac{X}{X_B}\right)^m f_M f_P f_T \tag{12}$$

where C_B' is now the equipment cost for carbon steel and moderate pressure and temperature ranges with capacity X_B; f_M is the correction factor for materials of construction different from carbon steel; f_P is the correction factor for design pressure; and f_T is the correction factor for design temperature.[25] For the sake of simplicity, we shall considerer that all the ionic liquids and the synthetic oils based on hydrocarbons, polyaromatics, and siloxanes will utilize the same construction materials, although actual technology allows the use of different components from different materials, making more complex the analysis, appropriate to the materials compatibility with the ionic liquids. We will assume high grade stainless steel, and therefore $f_M = 3.4$. The pressure used in the pipes and in the shell will also be considered to be the same and smaller than 50 bar, although the dynamic operation of the heat exchanger could justify different values of pressure and of pressure drops, and therefore $f_P = 1.5$. Finally, the design temperature will be smaller than 200 °C, and therefore $f_T = 1.3$. C_B' was assumed to be $3.28 \cdot 10^4$ US($).[26] Equation 11 reduces then to

$$C_E = 3.28 \cdot 10^4 \left(\frac{A_0}{80}\right)^{0.68} 3.4 \cdot 1.5 \cdot 1.3 = 2.18 \cdot 10^5 \left(\frac{A_0}{80}\right)^{0.68} \tag{13}$$

We report also in Table 1 the estimated costs for the shell and tube heat exchangers using the different heat transfer fluids. It can be seen that the heat exchangers for the RTILs are, other factors being constant, more expensive, except that of [C_2mim][BF_4], as a greater heat transfer area is required. Depending on the process, it is possible to obtain savings in the IL equipment, either by changing other design variables (D_e, D_i, pressure drops, materials, temperatures of the cold and hot streams, etc.) or by using other ionic liquids than the ones tested, especially with low viscosity (will enhance the contribution of heat transfer by convection). However, another problem makes yet unfavorable the use of the ILs: the working capital, namely, the raw materials for the heat exchanger start up. If we take as an example [C_2mim][BF_4], this liquid is not produced at industrial scale, as Syltherm 800, although the resistance to thermal degradation with time is higher. Therefore, although having similar values of heat transfer area and capital cost, it would be nearly 1000 times more expensive to fill it with [C_2mim][BF_4] than with Syltherm 800, at actual selling prices.[28] This comparison would change completely with an industrial production of the ionic liquid to prices that cannot be foreseen now.

5. Conclusions

The current investigations on the properties of ionic liquids and the search for possible applications framed with environmental or green chemistry requirements lead us to investigate the effect of the uncertainty of thermophysical data of ionic liquids (density, heat capacity, thermal conductivity, and viscosity) in the design of some current equipment, used in processes as solvents or heat transfer fluids. This was justified by the fact that the thermophysical properties of ionic liquids, measured in different laboratories and by different methods, do not agree within their mutual uncertainties, probably caused by incorrect methods of measurement and/or purity problems. Although knowing that industrial applications will not use ionic liquids as pure as academia would like to measure, the results obtained can be easily generalized to measurement and control in the industry, whatever the degree of purity used. Furthermore, as said above, the effect of the uncertainties could be easily minimized in an industrial application of an impure ionic liquid but of known thermophysical properties in processing conditions. If this was easily obtainable and a pilot plant could be constructed, the uncertainty in the equipment design will be only depending on the real performance of the in situ measuring instruments. However, this situation is far from being achieved nowadays.

From the calculations performed, and in agreement with previous results obtained for other liquids and pioneered in the group of Professor William Wakeham, the actual uncertainties in properties like density and heat capacity are well above those for current liquids, even at room temperature. The same, but usually more acceptable, is obtained for viscosity and thermal conductivity, properties more difficult to measure accurately[29] and where the effects of minor impurities are more important. The effect in the most important design parameter of a shell and tube heat exchanger, the heat transfer area, is very significant, with repercussions in the capital costs and operation (energy balances) of the chemical processes or in the workability of the equipment.

To analyze the possibility of using ionic fluids as replacement heat transfer liquids in heat transfer, a comparison of heat storage capacity and heat transfer areas with current heat transfer fluids, including total costs of a heat exchanger, showed that although the heat capacity per unit volume of ionic liquids is significantly larger that these liquids [(20 to 50) %] the heat transfer areas may be comparable or bigger (keeping all the other design parameters constant), which makes the cost of the equipment possibly larger. Additionally, the cost of filling a heat exchanger with an ionic liquid is actually prohibitive because these liquids are not yet produced in an industrial scale and therefore their costs per kilogram are still a factor of 10^3 greater.

The results presented justify an international program of measuring accurately the properties of well chosen reference ionic liquids, that can be proposed as reference fluids, as it was started with the IUPAC project on [C_6mim][$(CF_3SO_2)_2N$],[30] which can be used for testing and calibrating equipment and also to support the development of accurate prediction/estimation of thermophysical properties, where it is impossible to have only theoretical property input. The cost of such a program will probably be much smaller than the total savings in heat transfer equipment construction within the next few years by the

industry, as a requirement of current regulations and green chemistry approaches.

Finally, these results also justify the production of ionic liquids at an industrial scale, where one of the future applications will be their use as heat transfer/heat storage liquids.

Final Note. The composition of the proprietary heat transfer fluids can be seen in the homepages mentioned, not always detailed. However, for the sake of consistency they are included here: Dowtherm A is a eutectic mixture of two very stable compounds, biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$); Dowtherm MX is a mixture of alkylated aromatics; Paratherm HE is a paraffinic hydrocarbon (Single Cut, $M = 445$ g·mol^{-1}) (http://www.paratherm.com/_engineering/HEEngBul.pdf); Syltherm 800 and Syltherm HF are dimethyl polysiloxanes.

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