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Solubility of HFC134a (1,1,1,2-Tetrafluoroethane) in Two Dialkyl Carbonates[†]

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This paper analyzes one of the most important properties in the refrigeration field: the solubility of the refrigerants in lubricants. The experimental solubilities of 1,1,1,2-tetrafluorethane (HFC134a) in dimethyl carbonate and diethyl carbonate are reported and discussed for a temperature range from (263.15 to 308.15) K and 101.33 kPa partial pressure of refrigerant. An experimental device previously adapted for measurements of the same refrigerant in polyethers was used in this work. The mole fraction of the refrigerant was calculated using the $\phi-\gamma$ method and the symmetrical criteria for the components. From the solubility data, the thermodynamic quantities related to the solution process were also obtained. The results achieved show the adequacy of dialkyl carbonates to dissolve properly HFC134a. In addition, solubility parameters were used as a research strategy to anticipate inadequate behavior on the refrigerant/lubricant miscibility.

Introduction

The increasing interest in achieving a desirable sustainable development has directed the efforts of research and innovation in many fields during the last decades. The high demand of more efficient and secure refrigeration systems for industrial and domestic purposes requires special attention. As it is known,[1,2] correct lubrication in the refrigeration equipment can yield high savings in energy and materials and contribute to a longer life and better security. Lubricants in general have an intrinsic main leading role in the development of green chemistry as they minimize energy consumption by reducing the energy waste in mechanical systems and also spare material due to the lesser wear.[1] Besides their efficacy as lubricants, it would be desirable that these products would follow as near as possible other principles of sustainable chemistry, namely, design of safer chemicals and use of molecular structure design to minimize the intrinsic toxicity of the product. Finally, an easy degradability and recyclability must be sought when their service period is finished.[1]

As each type of refrigerant imposes special requirements on the lubricants, the mineral oils used with the classic CFCs are no longer suitable for the HFCs.[3−6] In this context, the alkyl carbonates appear as relevant candidates in the formulation of lubricants suitable for devices using refrigerants based on HFCs. Molecules containing carbonate groups, and aromatic and aliphatic chains, have been proposed as lubricants of the HFC refrigerants.[7−9] The aliphatic chain gives stability to the molecule, and the polar carbonate group enables these oils to adhere strongly to metallic surfaces. In addition, they are generally highly compatible with polymers. Products of thermo-oxidative disintegration of dialkyl carbonates form insignificant amounts of sediments. Organic carbonates exhibit a low toxicity to human beings and the natural environment and are easily biodegradable.[10] It can also be pointed out that dialkyl carbonates have an important industrial interest[11−15] because they are used in the synthesis of pharmaceuticals and agrochemicals, as well as a substitute of phosgene, dimethyl sulfate, chloromethane, etc., in carbonylation or methylation reactions, among others. Dialkyl carbonates are also used as solvents for many synthetic and natural resins and polymers and in lithium battery technology. Furthermore, in the last years, the papers and patents involving dialkyl carbonates have increased because these fluids have been proposed as additives to gasoline as well as components of hydraulic fluids. Thus, dimethyl carbonate was selected very recently[16] as a reactant for exploring a new noncatalytic process for supercritical biodiesel production. Because dialkyl carbonates are environmentally benign and biodegradable, they are expected to gain importance and to find increasing applications as components of the lubricant base stocks.[11]

In the case of refrigeration cycles, the circulating fluid comes into contact with the lubricant used in the compressors, and some of the refrigerant may dissolve into the oil depending on the solubility.[5,17] The solubility of the refrigerant in the lubricant affects to the lubrication properties of the actual oil in the compressor.[3] Thus the decrease in the viscosity of the oil due to the dissolved refrigerant should be taken into account to avoid the wear in shaft and the bearings of the compressor.[18] Moreover, part of the lubricant oil migrates from the compressor to other parts of the system such as the evaporator, condenser, expansion device, and piping.[17] Thus, a small amount of compressor lubricant, as a part of the working fluid, circulates with the refrigerant.[19] The working fluid is changed from a pure refrigerant, with well-defined properties, to a mixture with properties dependent on the lubricant concentration. In fact, migrated oil affects the heat-transfer coefficient, which is an important characteristic of any working fluid, changing the evaporator pressure drop and degrading the performance of both the condenser and the evaporator.[20] The change of the heat-transfer coefficients, due to the presence of lubricant, depends on the lubricant type (POEs, mineral oils, PAGs, or others) and its concentration. Some related problems might also develop as a consequence of the occurrence of phase separation

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(immiscibility) at unforeseen places of a refrigeration cycle. For example, oil accumulation may take place inside the heat exchanger tubes reducing heat transfer capabilities and resulting in an overall decrement of the refrigeration cycle performance. In fact, because at the evaporator the temperature and the pressure are the lowest in a refrigeration cycle, this is the place where most probably phase separation may occur. Thus, as the refrigerant evaporates, it leaves a liquid oil film on the internal cold surface of the evaporator tubing.[17,21] These problems may become more serious in the presence of unforeseen barotropic behavior that may induce a refrigerant-rich phase denser than the lubricant-rich phase. Nevertheless, we should point out that some refrigerant companies are developing HFC blends containing small quantities of hydrocarbons, which enable these products to be used with mineral oils. The hydrocarbons will be absorbed by the oil, reducing its viscosity and improving its flow characteristics to the point where the mineral oil will again flow freely back to the compressor. Hence, for an optimal performance design, both the solubility of the refrigerant in the lubricant and the miscibility of the refrigerant and lubricant must be known.

On the other hand, gas solubility data are frequently needed in many application-oriented areas like chemical process design, geochemistry, environmental science, or biomedical technology. Thus, for example, dissolved gases are a key component of many industrial chemical processes, such as in the case of refrigeration, in catalytic hydrogenation of vegetable oils, or in removal of acid gases from emissions due to the combustion. Furthermore, solubility data play a special role from the fundamental point of view, providing information about solute−solvent interactions in solutions or the organization of the solvent around a solute.[22]

Following, we report the solubilities of the refrigerant 1,1,1,2-tetrafluoroethane (HFC134a) in dimethyl carbonate (DMC) and diethyl carbonate (DEC) at 101.33 kPa partial pressure of gas and several temperatures, (263.15 to 308.15) K. Using the experimental solubility data, three thermodynamical quantities related to the solution process, namely, the Gibbs energy, the enthalpy, and the entropy of solution, were calculated. Previously, solubility parameters were used as a research strategy to anticipate the miscibility of the refrigerant HFC134a with the dialkyl carbonate.

Experimental Section

Materials. 1,1,1,2-Tetrafluoroethane (mole fraction > 0.997) was supplied by Air Liquide. Dimethyl carbonate (Fluka, mole fraction ≥ 0.99) and diethyl carbonate (Fluka, mole fraction ≥ 0.995) were used without any chemical purification.

Apparatus and Procedures. The solubility measurements were carried out by means of a volumetric method with an apparatus[23] similar to that of Ben-Naim and Baer,[24] made of glass with Teflon valves, which has been redesigned for measurements of HFC134a in polyethers. Details of the technique and the procedure were published previously.[25]

In brief, the experimental method is a saturation one based on the determination of the volume of the gas phase dissolved in a known mass or volume of a degassed liquid. The gas phase is a wet gas, that is, a gas mixed with vapor of the solvent. The gas dissolved into the liquid phase is replaced by mercury introduced in the graduated burets in such a way that the pressure of the gas phase, controlled through the mercury manometer, is kept constant during the measuring process.

The volume of mercury introduced, that is, the volume of wet gas dissolved, is measured with an uncertainty of ± 0.01 cm^3. The pressure is determined with an uncertainty of ± 3 Pa by using a cathetometer (Wild KM 338). Temperature is controlled within ± 0.05 K. The mean values for the relative expanded uncertainties in the solubility measurements, expressed as mole fractions and Ostwald coefficients, were about 1 %.

Before every experiment, alkyl carbonates were degassed under vacuum. Densities of the solvents were determined using an Anton Paar DMA-58 vibrating tube density meter, the uncertainty being ± 0.01 $\text{kg}\cdot\text{m}^{-3}$.

Results and Discussion

Parameters of Solubility. Previous to performing the solubility measurements, our purpose was to know if the refrigerant−lubricant pair selected showed any immiscibility region. For this purpose, we selected semiempirical approximations because of their simplicity in providing enough information about the behavior of the systems.

In the first half of the last century, Hildebrand and Scott[26,27] published (in the frame of the regular solution theory) the expression that relates the so-called solubility parameter with the mixing enthalpy. However, this theory is not valid for all the systems, so mixtures containing polar and associated compounds (nonregular systems) required a most complex treatment. To overcome this lack, Hansen[28] divided the solubility parameter, δ_T, into three contributions: dispersive, δ_D, polar, δ_P, and hydrogen bond, δ_H, relating to the respective interactions, as follows

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \qquad (1)$$

On the other hand, one of the more useful aspects of this approach, named the Hansen three-parameter model, is that the parameters can be visualized in three-dimensional space (δ_P, δ_H, δ_P axis). So, the distance between these solubility parameter points for the solute and for the solvent can be determined as follows

$$D_{ij} = [(\delta_{D,i} - \delta_{D,j})^2 + (\delta_{P,i} - \delta_{P,j})^2 + (\delta_{H,i} - \delta_{H,j})^2]^{1/2} \qquad (2)$$

As it is known, the closer the total solubility parameters of the solute and solvent are, the higher its mutual miscibility is.

To determine the solubility parameters, we have used the method given by Martin and Hoy.[29] Table 1 gathers the values obtained at 298.15 K for HFC134a, dialkyl carbonates, TEGDME, and TrEGDME, along with other lubricants (polyolesters and glycols) found in the literature[30−32,49] for comparative purposes. In Figure 1, the values obtained for δ_P, δ_H, and δ_D were plotted in a three-dimensional space with their projections in the δ_H−δ_D plane. The distances from the HFC134a solubility point to those corresponding to every lubricant are also listed in Table 1.

The experimental study of Remigy et al.[30] shows that HFC134a is immiscible at 298.15 K in a synthetic poly-α-olefin (PAO), an alkylbenzene (AB), and in two polyolesters (PE-nC9 and DiPE-nC7). We have also tested the adequacy of this method with other lubricants found in the literature.[32] For instance, the solubility of HFC134a in glycol-type compounds increases following the series TEGDME > TrEGDME > HEXG > TETG > TRIG. The higher values of D_{ij} obtained for TETG and TRIG [(10.5 and 15.3) $\text{MPa}^{1/2}$, respectively] indicate potential immiscibility, which is in agreement with the LLE behavior found by Tseregounis and Riley.[32] These results are very useful to establish the minimum or critical distance (≈ 10

Table 1. Solubility Parameters, δ_T, and the Dispersive, δ_D, Polar, δ_P, and Hydrogen Bond, δ_H, Contributions from Several Compounds at 298.15 K[a]

compound	δ_T / MPa$^{1/2}$	δ_D / MPa$^{1/2}$	δ_P / MPa$^{1/2}$	δ_H / MPa$^{1/2}$	D_{ij} [f] / MPa$^{1/2}$
HFC134a	13.6 14.9[b] 13.8[c]	8.9 8.1[b] 8.4[c]	7.8 8.7[b] 8.0[c]	6.7 9.2[b] 7.5[c]	
DMC	20.5 20.3[d]	12.1	11.9	11.5	5.6
DEC	17.8 17.8[d]	12.6	9.5	8.3	4.6
tetraethylene glycol dimethyl ether, TEGDME	13.1	9.5	5.9	6.9	3.9
triethylene glycol dimethyl ether, TrEGDME	16.7	12.3	7.5	8.5	4.4
poly-α-olefin, PAO[b]	17.2	17.2	0.0	0.0	15.6
alkylbenzene, AB[b]	18.2	17.8	3.6	0.8	13.8
pentaerythritol tetrapentanoate, PE-nC5[b]	15.4	14.1	4.7	4.3	8.7
pentaerythritol tetraheptanoate, PE-nC7[b]	15.3	14.5	3.3	3.7	10.0
pentaerythritol tetranonanoate, PE-nC9[b]	15.2	14.8	2.5	3.0	11.0
pentaerythritol tetraisooctanoate, PE-iC8[b]	15.1	14.1	3.8	3.7	9.5
pentaerythritol tetraisononanoate, PE-iC9[b]	14.6	14.2	3.1	2.8	10.5
dipentaerythritol hexapentanoate, DiPE-nC5[b]	15.4	14.2	4.6	4.4	8.8
dipentaerythritol hexaheptanoate, DiPE-nC7[b]	15.7	14.8	3.8	3.5	10.1
dipentaerythritol hexaisononanoate, DiPE-iC9[b]	15.3	14.4	3.6	4.0	9.6
trimethyolpropane heptanoate, TMP-nC7[b]	15.0	13.5	4.4	5.1	8.0
neopentylglycol heptanoate, NPG-nC7[b]	16.3	13.1	6.5	7.2	5.8
hexaethylene glycol, HEXG[e]	24.1	12.6	11.4	17.1	9.5
triethylene glycol, TRIG[e]	29.2	13.2	12.0	23.2	15.3
tetraethylene glycol, TETG[e]	24.9	12.9	11.0	18.2	10.5

[a] Last column includes the distances between solute and solvent, D_{ij}. [b] Extrapolated from Remigy et al.[30] [c] Values from Corr.[49] [d] Values from Marcus.[31] [e] Values from Tseregounis and Riley.[32] [f] Calculated using the experimental values of HFC134a from Remigy et al.[30]

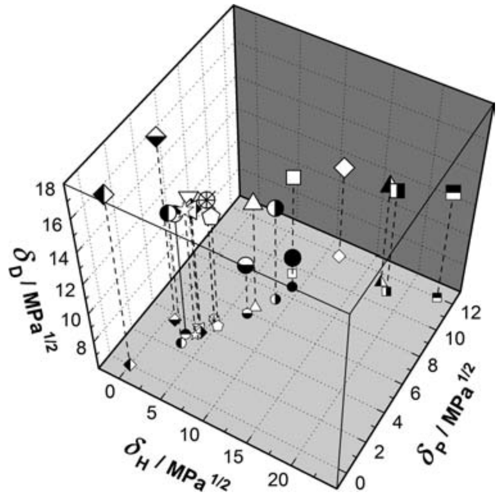

Figure 1. Three-dimensional plot of the contributions to the solubility parameter: dispersive, δ_D, polar, δ_P, and hydrogen bond, δ_H, for HFC134a and several solvents at 298.15 K. The plot also includes the $\delta_H-\delta_P$ projections of the points. ●, HFC134a; ◒, TEGDME; ◑, TrEGDME; □, DEC; ◇, DMC; left-filled diamond, PAO; bottom-filled diamond, AB; ○, PE-nC5; ☆, PE-Nc7; ◐, PE-nC9; open triangle pointing right, PE-iC8; ◓, PE-iC9; *, DiPE-nC5; ▽, DiPE-nC7; right-filled diamond, DiPE-iC9; ⬠, TMP-nC7; Δ, NPG-nC7; ◭, HEXG; ⬒, TRIG; ◨, TETG.

MPa$^{1/2}$) from which immiscibility phenomena could occur at 298.15 K. In our case, the values of D_{ij} found for DMC and DEC (5.6 and 4.6, respectively, clearly lower than 10 MPa$^{1/2}$) indicate a potential miscibility between the refrigerant and dialkyl carbonates.

Solubility of HFC134a in Dialkyl Carbonates. Once the study on the solubility parameter was performed, experimental measurements of the refrigerant in dialkyl carbonates were carried out. Mole fraction of the refrigerant was determined using the $\phi-\gamma$ method and the symmetrical criteria for the standard states of both the solute and the solvent.

First, the mole fraction of gas at total pressure P (close to 101.33 kPa) and at working temperature T was calculated using the second virial coefficients for the gas phase and considering ideal gas behavior in the zeroth-order iteration.[33] Then, the activities of the components in the liquid phase were estimated through the isofugacity condition for both components.

$$P \cdot y_i \cdot \phi_i^V(T, P, y_i) = x_i \cdot \gamma_i(T, P, x_i) P_{s,i} \cdot \phi_{s,i}^{*v} \cdot P_i(T, P) \tag{3}$$

where x_i and y_i are the mole fractions of the liquid and gas phases, respectively; ϕ_i^V is the fugacity coefficient of component i; $\phi_{s,i}^{*v}$ is the fugacity coefficient of saturated pure component i; $P_{s,i}$ is the vapor pressure of component i; P_i is the Poynting correction; and γ_i is the activity coefficient of liquid component i according to the Lewis−Randall rule.

Finally, from the mole fraction of gas at the given total pressure, the solubility values at 101.33 kPa partial pressure of gas were inferred, again using the isofugacity condition for both components.

Several simplifications were made during the trial and error procedure: (i) A one-parameter Margules equation was used to describe the behavior of the liquid phase. (ii) The fugacity coefficients were estimated from a virial equation truncated after the second term, except for the fugacity coefficient of the saturated vapor of the refrigerant, which was calculated using the REFPROP software package.[34] (iii) The Poynting corrections were obtained using the molar volumes of the pure components and Zellner's method for HFC134a.[35] In previous works,[25,36] the reduction method was described in detail taking into account the specific features of our device.

Table 2. A_i Coefficients and Standard Deviations, σ, for Equation 4

	DMC	DEC
A_0/g·cm^{-3}	1.39639	1.23608
-10^3A_1/g·cm^{-3}·K^{-1}	0.90649	0.67357
-10^6A_2/g·cm^{-3}·K^{-2}	0.70705	0.74334
$10^4\sigma$/g·cm^{-3}	2.5	1.9

Table 3. Second Virial Coefficients of Pure Components, B_{ii} and B_{jj}, and Cross Second Virial Coefficients, B_{ij}, of Mixtures used in This Work

Dimethyl Carbonate (i) - HFC134a (j)				Diethyl Carbonate (i) - HFC134a (j)			
$\frac{T}{\mathrm{K}}$	$\frac{B_{ii}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{B_{jj}{}^{a}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{B_{ij}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{T}{\mathrm{K}}$	$\frac{B_{ii}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{B_{jj}{}^{a}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$	$\frac{B_{ij}\cdot 10^{-6}}{\mathrm{m^3\cdot mol^{-1}}}$
308.15	−1772	−459.1	−972.0	298.15	−3484	−501.3	−1542
298.15	−1966	−501.3	−1072	288.15	−3903	−549.2	−1714
293.15	−2075	−524.5	−1128	278.15	−4396	−603.6	−1914
288.15	−2194	−549.2	−1188	273.15	−4677	−633.7	−2027
283.15	−2322	−575.5	−1253	268.15	−4984	−665.9	−2150
278.15	−2461	−603.6	−1322	263.15	−5319	−700.4	−2283

[a] From Beckermann and Kohler.[46]

Table 4. Solubilities at 101.33 kPa of HFC134a in DMC and DEC Expressed as Mole Fraction, x_r, and as the Ostwald Coefficient, L, along with the Refrigerant Activity Coefficients, γ_r

dimethyl carbonate				diethyl carbonate			
T/K	x_r	γ_r	L	T/K	x_r	γ_r	L
308.15	0.1125	1.211	37.3	298.15	0.1540	1.138	36.5
298.15	0.1432	1.223	48.2	288.15	0.2217	1.042	55.8
293.15	0.1729	1.158	59.7	278.15	0.3115	1.005	86.6
288.15	0.2063	1.121	73.4	273.15	0.3684	1.001	110.4
283.15	0.2514	1.065	93.7	268.15	0.4449	0.985	149.5
278.15	0.3098	1.010	123.8	263.15	0.5364	0.979	212.9

To apply the calculation method, new values of density for DEC at (268.15 and 273.15) K were measured, being, respectively, (1001.69 and 996.17) kg·m^{-3}. These values were correlated with the previous ones found in the literature.[37−41]

$$\rho(T, 0.1\ \mathrm{MPa}) = \sum_{i=0}^{m} A_i T^i \tag{4}$$

The A_i values for the two carbonates and the standard deviations σ are listed in Table 2.

The values of the vapor pressures needed were also found in the literature.[42−44] The second virial coefficients were obtained using the method proposed by Tsonopoulos[45] for the dialkyl carbonates, whereas for HFC134a they were taken from Beckermann and Kohler.[46] Table 3 gathers the coefficients used in this work.

The experimental solubility results are given in Table 4 in terms of the mole fraction of the gas in the liquid phase and as Ostwald coefficients at several temperatures and 101.33 kPa partial pressure of the gas. Ostwald coefficients, $L = (V_g/V_s)_T$, were determined from the volume of gas dissolved, V_g, and the volume of the pure solvent used, V_s, at the temperature of the vessel, T, and 101.33 kPa. Volumes from (39 to 193) cm^3 of the gas phase were dissolved in the dialkyl carbonates depending on the temperatures. Refrigerant activity coefficients, γ_r, determined from experimental solubilities are also included in Table 4.

The data indicate that the solubility of the refrigerant in the two dialkyl carbonates is similar. In the overlapping temperature region, HFC134a is slightly more soluble in diethyl carbonate than in dimethyl carbonate [see also Figure 2]. As it has been pointed out previously, given a series of solvents with the same functional group, the bigger the size of a molecule, the better the solubility.[47] Particularly, we have previously found this trend for the solubilities of several nonpolar gases in DMC and DEC.[33,48]

As usual for gases having high solubility, the solubility of HFC134a decreases when the temperature rises, for both liquids.

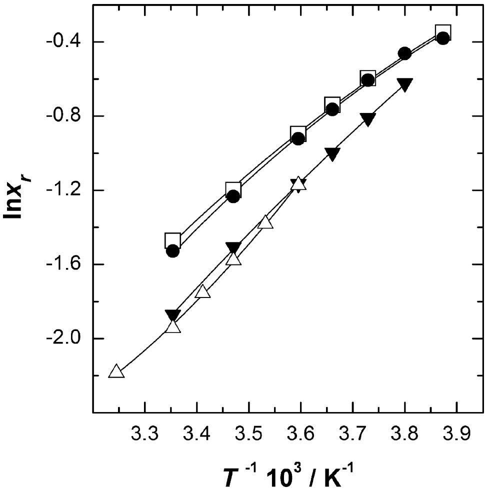

Figure 2. Temperature dependence of the HFC134a solubility (ln x_r) in dialkyl carbonates and in polyethers[25] at 101.3 kPa. □, TEGDME; ●, TrEGDME; ▼, DEC; Δ, DMC.

Table 5. A, B, C and A', B', C' Coefficients and Standard Deviations, σ, for Equations 5 and 6, Respectively

solvent	A	B	C	σ^a
DMC	−313.290	16141.1	45.1469	0.0144
DEC	92.4503	−1596.80	−15.6136	0.010
solvent	A'	B'	C'	σ^a
DMC	−52.0720	4232.51	6.34198	0.0012
DEC	−54.8819	4353.42	6.76409	0.0002

[a] $\sigma = [(\Sigma \ln(x_r, a_r)_{\mathrm{exp}} - \ln(x_r,a_r)_{\mathrm{cal}})^2/(N - N_P)]^{1/2}$.

The experimental solubility data were correlated using a polynomial depending on T

$$\ln x_r = A + \frac{B}{T} + C \ln T \tag{5}$$

where x_r is the mole fraction of the refrigerant. A similar equation could be used to describe the dependence of activity with temperature

$$\ln a_r = \ln(x_r \gamma_r) = A' + \frac{B'}{T} + C' \ln T \tag{6}$$

For both systems, the sets of parameters of eqs 5 and 6, determined by the least-squares method, are gathered in Table 5, together with the standard deviation, σ.

The temperature dependence of the solubilities expressed as refrigerant mole fraction is shown in Figure 2 together with the correlated values using eq 5 and the parameters

Table 6. Gibbs Energy, $\Delta\bar{G}^0_{\mathrm{r,sol}}$, Enthalpy, $\Delta\bar{H}^0_{\mathrm{r,sol}}$, and Entropy of Solution, $\Delta\bar{S}^0_{\mathrm{r,sol}}$, of the Refrigerant HFC134a in Both Dialkyl Carbonates at 101.33 kPa

Dimethyl Carbonate				Diethyl Carbonate			
T / K	$\Delta\bar{G}^0_{\mathrm{r,sol}}$ / kJ·mol^{-1}	$\Delta\bar{H}^0_{\mathrm{r,sol}}$ / kJ·mol^{-1}	$\Delta\bar{S}^0_{\mathrm{r,sol}}$ / J·mol^{-1}·K^{-1}	T / K	$\Delta\bar{G}^0_{\mathrm{r,sol}}$ / kJ·mol^{-1}	$\Delta\bar{H}^0_{\mathrm{r,sol}}$ / kJ·mol^{-1}	$\Delta\bar{S}^0_{\mathrm{r,sol}}$ / J·mol^{-1}·K^{-1}
308.15	5.11	−18.94	−78.04	298.15	−4.32	−19.43	−79.64
298.15	4.32	−19.47	−79.78	288.15	−3.51	−19.99	−81.56
293.15	3.92	−19.73	−80.67	278.15	−2.69	−20.55	−83.55
288.15	3.51	−20.00	−81.58	273.15	−2.27	−20.83	−84.57
283.15	3.10	−20.26	−82.50	268.15	−1.84	−21.12	−85.61
278.15	2.69	−20.52	−83.44	263.15	−1.41	−21.40	−86.67

reported in Table 5. Figure 2 also includes the solubilities of HFC134a + tetraethylene glycol dimethyl ether (TEGDME) and + triethylene glycol dimethyl ether (TrEGDME) measured previously in our laboratory.[25] As can be seen, the refrigerant HFC134a is more soluble in these glycol-type compounds than in dialkyl carbonates, although these last systems are far from having small solubility. This result is not similar to that obtained with a series of nonpolar gases of small solubility. Thus, in a previous study with several nonpolar gases including noble gases, light hydrocarbons and sulfur hexafluoride, almost all of them were more soluble in DEC than in TrEGDME.[33,48] In this sense, as Corr[49] pointed out, it is often the case that when a solvent and solute are only sparingly soluble in each other the dominant solute−solvent intermolecular interactions are based on dispersion forces, embodied in the dispersion Hansen parameter. This makes some sense since if any of the relatively strong specific solvent−solute interactions are present the mutual solubility is likely to be higher.[49] Thus, in the recent studies about the solvent capabilities of room-temperature ionic liquids (RTILs) for HFCs, Shiflett et al.[50] and Shiflett and Yokozeki[51] have concluded that the trends of the solubilities of HFCs in the same RTIL should be explained in terms of hydrogen bonding capability instead of HFC dipole moments.

The activity coefficients decrease when the temperature increases, as can be seen in Table 4. It can be also observed that the activity coefficients are higher than 1 (except for HFC134a−diethyl carbonate at (268.15 and 263.15) K). Thus, except in these last cases, both mixtures at the temperatures studied present positive deviations from ideality. Comelli and Francesconi[52] also reported positive deviations from Raoult's law for the mixtures DMC + 1,1,1-trichloroethane, showing that an increase of the number of halogen atoms in the alkyl halide molecule provides a sign inversion in the excess molar Gibbs energy and in the excess molar enthalpy. The positive deviations indicate that the solution of refrigerant produces a breaking of the important specific and van der Waals forces of the pure carbonates.[35,53−56] In comparison with the above-mentioned polyethers, the affinity between the HFC134a and the dialkyl carbonate molecules is lower than that between HFC134a and polyether molecules.[25]

Standard Changes in the Thermodynamic Functions of Solution. The solubility of a gas in a liquid is directly related to the standard changes in thermodynamic functions of solution such as the so-called change of the Gibbs energy of the solution process[57,58] and enthalpy and entropy of solution. The last two properties are obtained from the Gibbs energy of solution using well-known relationships of classical thermodynamics. The three functions are associated to a dissolution process that consists of the transference of the solute particles from the pure perfect gas state to a hypothetical solution of mole fraction of solute equal to one at a given temperature and standard pressure.

We have calculated these three thermodynamic functions related to the hypothetical solution process using the following expressions[25]

$$\Delta\bar{G}^0_{\mathrm{r,sol}} = -RT\ln[x_{\mathrm{r}}\gamma_{\mathrm{r}}] = -RT\left(A' + \frac{B'}{T} + C'\ln T\right) \tag{7}$$

$$\Delta\bar{H}^0_{\mathrm{r,sol}} = -T^2\left[\frac{\partial(\Delta\bar{G}^0_{\mathrm{r,sol}}/T)}{\partial T}\right]_p = -RB' + RTC' \tag{8}$$

$$\Delta\bar{S}^0_{\mathrm{r,sol}} = \frac{\Delta\bar{H}^0_{\mathrm{r,sol}} - \Delta\bar{G}^0_{\mathrm{r,sol}}}{T} = RA' + RC'(1 + \ln T) \tag{9}$$

where A', B', and C' are the coefficients of eq 6, which are tabulated in Table 3. The obtained values are shown in Table 6. These values for the standard thermodynamic functions associated to the solution process are in agreement with the high solubility that presents the refrigerant in the dialkyl carbonates. For both systems, the results are similar. Furthermore, there is a high similitude among the values obtained for the standard thermodynamic functions of HFC134a + dialkyl carbonate systems and those of HFC134a + polyether systems, although the solubilities of HFC134a in polyethers are higher. This is due to the fact that these higher solubilities are compensated by the lower activity coefficients of HFC134a in the systems containing polyethers, resulting in practically identical activities for HFC134a in the four solvents.

Conclusions

In conclusion, we can state that HFC134a and dialkyl carbonates are compatible enough; that is, the refrigerant dissolves properly in both carbonates. Its solubility seems to not be high enough to reduce severely the viscosity and other lubrication properties of a commercial lubricant, which would contain these carbonates. Thus, dialkyl carbonates seem to be adequate candidates in the formulation of new synthetic lubricants, as additives to increase the miscibility of the refrigerants HFCs, or as a starting reagent to prepare lubricating compounds based on the carbonate group.

Moreover, the determination of the solubility parameters is able to predict correctly the miscibility order of the refrigerant in the solvents considered by us: TEGDME > TrEGDME > DEC > DMC. In light of this result, Martin and Hoy's method appears as an appropriate strategy to select or discard the potential systems before experimentation. On the other hand, the adverse barotropic effects could be avoided because liquid phase separation between HFC134a and carbonates is not expected.

Two of the green aspects in refrigeration cycles could be achieved by using dialkyl carbonates as components of the lubricants, long-term refrigeration compressor use and optimal cycle performances, although to verify this point other studies and trials are required.

Literature Cited

(1) Boyde, S. Green lubricants. Environmental Benefits and Impacts of Lubrication. *Green Chem.* **2002**, *4*, 293–307.

(2) Rudnick, L. R.; Shubkin, R. L., Eds. *Synthetic Lubricants and High-Performance Functional Fluids*, 2nd ed.; M. Dekker: New York, 1999; Vol. 77.

(3) Randles, S. J. *Refrigeration Lubricants, in Synthetics, Mineral Oils, and Biobased Lubricants and High-Performance Functional Fluids*; CRC Press, Taylor and Francis: New York, 2006; pp 493−516.

(4) Chaudhari, S. K.; Salavera, D.; Esteve, X.; Coronas, A. Vapour-Liquid Equilibria of the System 1,1,1,2-Tetrafluoroethane + Monoethylene-Glycol Dimethylether from 283.15 to 353.15 K: New Modified UNIFAC Parameters. *Fluid Phase Equilib.* **2008**, *271*, 28–33.

(5) Spauschus, H. O. Lubricants for Refrigeration Compressors: a 1996 Status Report. *Bull. Int. Inst. Refrig.* **1997** (1), 2.

(6) Marchi, P.; Scalabrin, G.; Ihmels, E. C.; Fischer, K.; Gmehling, J. Bubble Pressure Measurements for the (1,1,1,2-Tetrafluoroethane + Triethylene Glycol Dimethyl Ether) System. *J. Chem. Thermodyn.* **2006**, *38*, 1247–1253.

(7) Takeno, T.; Mizui, K.; Takahata, K. New Type Lube Oil for HFC-134a Compressor System. In *Proceedings of the International Compressor Engineering Conference*; Purdue, USA, 1992; pp 1045−1054.

(8) Takahata, K.; Tanaka, M.; Hayashi, T.; Mizui, K.; Sakamoto, N. New Lube Oil for Stationary Air Conditioner. In *Proceedings of 1994 International Refrigeration Conference*; Purdue, USA, 1994; pp 141−146.

(9) Hayashi, T.; Tanaka, M.; Takeuchi, K.; Takahata K.; Sakamoto, N. Carbonate Oils for Unitary Air Conditioners with R-410A. In *Proceedings of 1996 International Refrigeration Conference*; Purdue, USA,1996; pp 285−290.

(10) Gryglewicz, S.; Oko, F. A.; Gryglewicz, G. Synthesis of Modern Synthetic Oils Based on Dialkyl Carbonates. *Ind. Eng. Chem. Res.* **2003**, *42*, 5007–5010.

(11) Rudnick, L. R. *Dialkyl Carbonates, in Synthetics, Mineral Oils, and Biobased Lubricants and High-Performance Functional Fluids*; CRC Press, Taylor and Francis: New York, 2006; pp 235−245.

(12) Tundo, P.; Perosa, A. Green Organic Syntheses: Organic Carbonates as Methylating Agents. *Chem. Record* **2002**, *2*, 13–23.

(13) Bhanage, B. M.; Fujita, S. I.; Ikushima, Y.; Torii, K.; Arai, M. Synthesis of Dimethyl Carbonate and Glycols from Carbon Dioxide, Epoxides and Methanol Using Heterogeneous Mg Containing Smectite Catalysts: Effect of Reaction Variables on Activity and Selectivity Performance. *Green Chem.* **2003**, *5*, 71–75.

(14) Veldurthy, B.; Clacens, J.-M.; Figueras, F. New highly Active and Selective Heterogeneous Catalytic System for the Synthesis of Unsymmetrical Organic Carbonates: A Green Protocol. *Eur. J. Org. Chem.* **2005**, (10), 1972–1976.

(15) Aresta, M.; Dibenedetto, A.; Fracchiolla, E.; Giannoccaro, P.; Pastore, C.; Papai, I.; Schubert, G. Mechanism of Formation of Organic Carbonates from Aliphatic Alcohols and Carbon Dioxide under Mild Conditions Promoted by Carbodiimides. DFT Calculation and Experimental Study. *J. Org. Chem.* **2005**, *70*, 6177–6186.

(16) Ilham, Z.; Saka, S. Dimethyl Carbonate as Potential Reactant in Non-Catalytic Biodiesel Production by Supercritical Method. *Bioresour. Technol.* **2009**, *100*, 1793–1796.

(17) Marsh, K. N.; Kandil, M. E. Review of Thermodynamic Properties of Refrigerants + Lubricant Oils. *Fluid Phase Equilib.* **2002**, *199*, 319–334.

(18) Hauk, A.; Weidner, E. Thermodynamic and Fluid-Dynamic Properties of Carbon Dioxide with Different Lubricants in Cooling Circuits for Automobile Application. *Ind. Eng. Chem. Res.* **2000**, *39*, 4646–4651.

(19) McMullan, J. T.; Hewitt, N. J.; Masson, A. L.; Murphy, N. E. The Influence of Oil Viscosity and Refrigerant Quality on Evaporator Performance. *Int. J. Energy Res.* **1992**, *16*, 567–581.

(20) Youbi-Idrissi, M.; Bonjour, J.; Marvillet, C.; Meunier, F. Impact of Refrigerant-Oil Solubility on an Evaporator Performances Working with R-407C. *Int. J. Refrig.* **2003**, *26*, 284–292.

(21) Quiñones-Cisneros, S. E.; García, J.; Fernández, J.; Monsalvo, M. A. Phase and Viscosity Behaviour of Refrigerant-Lubricant Mixtures. *Int. J. Refrig.* **2005**, *28*, 714–724.

(22) Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes de Azevedo, E. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: NJ, 1999.

(23) Carnicer, J.; Gibanel, F.; Urieta, J. S.; Gutiérrez Losa, C. Aparato para la Medida de Solubilidades de Gases en Líquidos. Solubilidades de Helio, Deuterio, Nitrógeno y Hexafluoruro de Azufre en p-Xileno. *Rev. Acad. Cienc. Zaragoza* **1979**, *34*, 115–122.

(24) Ben Naim, A.; Baer, S. Method for Measuring Solubilities of Slightly Soluble Gases in Lliquids. *Trans. Faraday Soc.* **1963**, *59*, 2735–2738.

(25) López, E. R.; Mainar, A. M.; García, J.; Urieta, J. S.; Fernández, J. Experimental and Predicted Solubilities of HFC134a (1,1,1,2-Tetrafluoroethane) in Polyethers. *Ind. Eng. Chem. Res.* **2004**, *43*, 1523–1529.

(26) Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-Electrolytes*, 3rd ed.; Reinhold Publ. Corp: New York, 1950.

(27) Hildebrand, J. H.; Scott, R. L. *Regular Solutions*; Prentice Hall: Englewood Cliff, NJ, 1962.

(28) Hansen, C. M. Universality of the Solubility Parameter. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 2–11.

(29) Martin, R. A.; Hoy, K. L. *Tables of Solubility Parameters*; Research and Development Department, Union Carbide: Tarrytown, NY, 1975.

(30) Remigy, J.-C.; Nakache, E.; Brechot, P. D. Computer-Aided Method for the Determination of Hansen Solubility Parameters. Application to the Miscibility of Refrigerating Lubricant and New Refrigerant. *Ind. Eng. Chem. Res.* **1999**, *38*, 4470–4476.

(31) Marcus, Y. *The Properties of Solvents*; John Wiley & Sons Ltd.: Chichester, 1998.

(32) Tseregounis, S. I.; Riley, M. J. Solubility of HFC-134a Refrigerant in Glycol-type Compounds: Effects of Glycol Structure. *AIChE J.* **1994**, *40*, 726–737.

(33) De la Iglesia, O.; Mainar, A. M.; Pardo, J. I.; Urieta, J. S. Solubilities of Nonpolar Gases in Triethylene Glycol Dimethyl Ether, Tetraethylene Glycol Dimethyl Ether, Dimethyl Carbonate, and Diethyl Carbonate at 298.15 K and 101.33 kPa Partial Pressure of Gas. *J. Chem. Eng. Data* **2003**, *48*, 657–661.

(34) McLinden, M. O.; Klein, S. A.; Lemmon E. W.; Peskin, A. P. REFPROP v 6.01, Thermodynamic and Transport Properties of Refrigerants and Refrigerant Mixtures, 1998.

(35) Zellner, M. G.; Claitor, L. C.; Prausnitz, J. M. Prediction of Vapor-Liquid Equilibriums and Enthalpies of Mixtures at Low Temperatures. *Ind. Eng. Chem. Fundam.* **1970**, *9*, 549–564.

(36) Mainar, A. M.; Pardo, J. I.; Santafé, J.; Urieta, J. S. Solubility of Gases in Binary Liquid Mixtures: an Experimental and Theoretical Study of Noble Gas + Trifluoroethanol + Water. *Ind. Eng. Chem. Res.* **2003**, *42*, 1439–1450.

(37) Comuñas, M. J. P.; Baylaucq, A.; Boned, C.; Fernández, J. High-Pressure Measurements of the Viscosity and Density of Two Polyethers and Two Dialkyl Carbonates. *Int. J. Thermophys.* **2001**, *22*, 749–768.

(38) López, E. R.; Lugo, L.; Comuñas, M. J. P.; García, J.; Fernández, J. Temperature Dependence of the Excess Molar Volume of (Dimethyl Carbonate, or Diethyl Carbonate + Toluene) from $T = 278.15$ K to 323.15 K. *J. Chem. Thermodyn.* **2000**, *32*, 743–754.

(39) Pardo, J. M.; Tovar, C. A.; Cerdeiriña, C. A.; Carballo, E.; Romaní, L. Excess Molar Volumes and Excess Molar Heat Capacities of (Dimethyl Carbonate, or Diethyl Carbonate + n-Heptane) at Several Temperatures. *J. Chem. Thermodyn.* **1999**, *31*, 787–796.

(40) González, J. A.; García, I.; Cobos, J. C.; Casanova, C. Thermodynamics of Binary Mixtures Containing Organic Carbonates. 4. Liquid-Liquid Equilibria of Dimethyl Carbonate + Selected n-Alkanes. *J. Chem. Eng. Data* **1991**, *36*, 162–164.

(41) Francesconi, R.; Comelli, F. Excess Molar Enthalpies, Densities, and Excess Molar Volumes of Diethyl Carbonate in Binary Mixtures with Seven n-Alkanols at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 45–48.

(42) Negadi, L.; Delepine, H.; Ait-Kaci, A.; Jose, J. Static Measurements of the Total Vapor Pressure of Binary Mixtures of Dimethyl Carbonate + Hex-1-yne, Hex-2-yne, Hex-3-yne, Cyclohexane, Hex-1-ene, or Heptane at Temperatures Between 263 and 373 K. *ELDATA Int. Electron. J. Phys.-Chem. Data* **1999**, *5*, 197–210.

(43) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A. Vapor Pressure, Heat Capacity, and Density along the Saturation Line. Measurements for Dimethyl Isophthalate, Dimethyl Carbonate, 1,3,5-Triethylbenzene, Pentafluorophenol, 4-tert-Butylcatechol, a-Methylstyrene, and N,N′-Bis(2-hydroxyethyl)ethylenediamine. *J. Chem. Eng. Data* **1997**, *42*, 1008–1020.

(44) Choi, J. K.; Joncich, M. J. Heats of Combustion, Heats of Formation, and Vapor Pressures of Some Organic Carbonates. Estimation of Carbonate Group Contribution to Heat of Formation. *J. Chem. Eng. Data* **1971**, *16*, 87–90.

(45) Tsonopoulos, C. Second Virial Coefficients of Water Pollutants. *AIChE J.* **1978**, *24*, 1112–1115.

(46) Beckermann, W.; Kohler, F. Acoustic Determination of Ideal-Gas Heat Capacity and Second Virial Coefficients of Some Refrigerants Between 250 and 420 K. *Int. J. Thermophys.* **1995**, *16*, 455–464.

(47) Wilhelm, E.; Battino, R. Thermodynamic Functions of the Solubilities of Gases in Liquids at 25°C. *Chem. Rev.* **1973**, *73*, 1–9.

(48) Terrado, E. M.; Pardo, J. I.; Urieta, J. S.; Mainar, A. M. Solubilities of Nonpolar Gases in Dimethyl Carbonate and Diethyl Carbonate. *J. Chem. Eng. Data* **2005**, *50*, 512–516.
(49) Corr, S. 1,1,1,2-Tetrafluoroethane; from Refrigerant and Propellant to Solvent. *J. Fluorine Chem.* **2002**, *118*, 55–67.
(50) Shiflett, M. B.; Harmer, M. A.; Junk, C. P.; Yokozeki, A. Solubility and Diffusivity of Difluoromethane in Room-Temperature Ionic Liquids. *J. Chem. Eng. Data* **2006**, *51*, 483–495.
(51) Shiflett, M. B.; Yokozeki, A. Solubility and Diffusivity of Hydrofluorocarbons in Room-Temperature Ionic Liquids. *AIChE J.* **2006**, *52*, 1205–1219.
(52) Comelli, F.; Francesconi, R. Isothermal Vapor-Liquid Equilibria, Densities, Refractive Indices, Excess Molar Volumes, and Excess Molar Enthalpies of Dimethyl Carbonate + 1,2-Dichloroethane and + 1,1,1-Trichloroethane. *J. Chem. Eng. Data* **1994**, *39*, 560–564.
(53) Wang, Y.; Balbuena, P. B. Associations of Alkyl Carbonates: Intermolecular C-H···O Interactions. *J. Phys. Chem. A* **2001**, *105*, 9972–9982.
(54) Moreiras, A. F.; García, J.; Lugo, L.; Comuñas, M. J. P.; López, E. R.; Fernández, J. Experimental Densities and Dynamic Viscosities of Organic Carbonate + n-Alkane or p-Xylene Systems at 298.15 K. *Fluid Phase Equilib.* **2003**, *204*, 233–243.
(55) Lugo, L.; Comuñas, M. J. P.; López, E. R.; García, J.; Fernández, J. Pressure and Temperature Dependence of the Excess Thermodynamic Properties of Binary Dimethyl Carbonate + n-Octane Mixtures. *Can. J. Chem.* **2003**, *81*, 840–849.
(56) Lugo, L.; Comuñas, M. J. P.; López, E. R.; Fernández, J. (p, Vm, T, x) Measurements of Dimethyl Carbonate + Octane Binary Mixtures I. Experimental Results, Isothermal Compressibilities, Isobaric Expansivities and Internal Pressures. *Fluid Phase Equilib.* **2001**, *186*, 235–255.
(57) Clever, H. L.; Battino, R. *The solubility of Gases in liquids, Techniques of Chemistry*; J. Wiley & Sons Ed: New York, 1975.
(58) Wilhelm, E.; Battino, R.; Wilcock, R. J. Low-Pressure Solubility of Gases in Liquid Water. *Chem. Rev.* **1977**, *77*, 219–262.

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