Solubilities of Cinnamic Acid Esters in Ionic Liquids

Eleni K. Panteli and Epaminondas K. Voutsas*

Laboratory of Thermodynamics and Transport Phenomena, School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Str., Zographou Campus, 15780 Athens, Greece

The solubilities of three cinnamic acid esters, namely, methyl ferulate, methyl *p*-coumarate, and methyl sinapate, in eight imidazolium-based ionic liquids composed of the PF_6^- and BF_4^- anions have been measured at (30, 39, and 48) °C. Higher solubilities of the three esters were observed in the ionic liquids composed of the BF_4^- anion than those composed of the PF_6^- anion. Also, higher solubilities are observed in alkyl-substituted (on the imidazolium cation moiety) ILs than in polar-substituted ILs, whereas, as the alkyl chain length on the cation moiety increases, the solubility increases as well. Moreover, using the van't Hoff equations, the apparent Gibbs energy, enthalpy, and entropy of solution were calculated. Positive values of the three thermodynamic functions were found in all cases. Finally, successful correlations of the experimental data were achieved with the UNIQUAC and the NRTL activity coefficient models.

Introduction

Antioxidants are compounds whose presence in small quantities on an oxidized substrate can retard or prevent its oxidation. Consequently, such compounds are widely used in several application fields, especially in the food and drug industry. Cinnamic acids and their derivatives, cinnamic acid esters (CAEs), belong to this class of compounds.[1] Cinnamic acids are natural components of the plant cell wall that are covalently linked to polysaccharides through ester linkages.[2] Such examples are ferulic acid that is abundant in wheat bran, sugar beet pulp, and maize bran,[3−5] *p*-coumaric acid that is found in maize bran,[5] and sinapic acid. Because of their acidic structure, cinnamic acids cannot be properly used in oil-based processes, which are often encountered in industrial applications. CAEs, like methyl ferulate, methyl *p*-coumarate, and methyl sinapate, can be used in such applications because of their lipophilic character. Moreover, CAEs have been utilized in the production of phenolic acid sugar esters,[6] which have antitumoric activity as well as the potential to be used in the formulation of antimicrobial, antiviral, and anti-inflammatory agents.[7−9]

In recent years, ionic liquids (ILs) have been extensively evaluated as environmentally friendly or "green" alternatives to conventional organic solvents for a broad range of applications. ILs are molten salts (melting point less than 100 °C) that show some unique characteristics that distinguish them from conventional organic solvents, such as no measurable vapor pressure, good thermal stability, high polarity, hydrophobic or hydrophilic character, unique solvating properties for both organic and inorganic compounds, and so on. More importantly, by simply changing the cation, the anion, or both, a wide range of tunable properties can be obtained, for example, density, viscosity, hydrophobicity, solvation, and so on. Several studies have shown that ILs can be successfully used as solvents in chemical reactions, as entrainers in special distillations, as extractive agents, as absorption media for gas separations, as heat transfer fluids, as the working fluid in a variety of electrochemical applications, as pharmaceutical reservoirs, and so on.[10−18]

Although much experimental work has been conducted so far through measurement of thermophysical properties of the pure ILs and the phase equilibrium in systems containing ILs, solubility data of solids in ILs are very scarce. Most of the latter concern solubility data of inorganic salts in ILs,[19−21] whereas some other papers have reported solubility data in ILs of taurine,[21] dibasic carboxylic acids,[22] drugs,[23] and flavonoids.[24]

This article presents experimental solubility measurements of three CAEs, namely, methyl *p*-coumarate, methyl ferulate, and methyl sinapate, in eight imidazolium (IM)-based ILs composed of the PF_6^- and BF_4^- anions. Moreover, by utilizing the van't Hoff equations, we have calculated the apparent thermodynamic functions relative to the solution of the three CAEs. Finally, the capability of the UNIQUAC and the NRTL activity coefficient models to correlate the obtained data is also tested.

Experimental Section

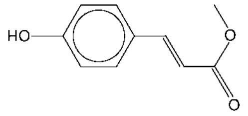
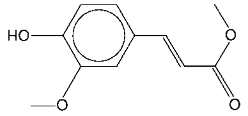
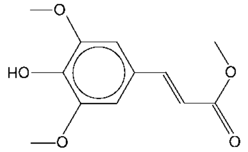
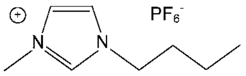
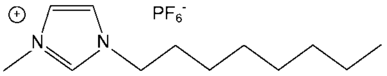
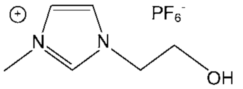
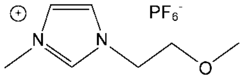
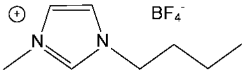
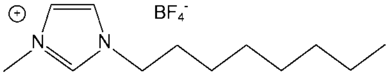
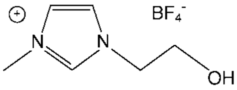
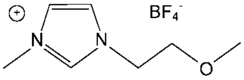
Materials. Methyl *p*-coumarate (MpCA, > 98 % purity, CAS no. 3943-97-3), methyl ferulate (MFA, > 98 % purity, CAS no. 2309-07-1), and methyl sinapate (MSA, 98.5 % purity, CAS no. 20733-94-2) were purchased from Apin Chemicals. 1-Butyl-3-methyl-imidazolium hexafluorophosphate (IL1, [BMIM][PF_6], 99 % purity, CAS no. 174501-64-5), 1-methyl-3-octyl-imidazolium hexafluorophosphate (IL2, [OMIM][PF_6], 99 % purity, CAS no. 304680-36-2), 1-(2-hydroxyethyl)-3-methyl-imidazolium hexafluorophosphate (IL3, [C_2OHMIM][PF_6], 99 % purity, CAS no. 444723-80-2), 1-(2-methoxyethyl)-3-methyl-imidazolium hexafluorophosphate (IL4, [C_3OMIM][PF_6], > 98 % purity, CAS no. 474972-47-9), 1-butyl-3-methyl-imidazolium tetrafluoroborate (IL5, [BMIM][BF_4], 99 % purity, CAS no. 174501-65-6), 1-methyl-3-octyl-imidazolium tetrafluoroborate (IL6, [OMIM][BF_4], 99 % purity, CAS no. 244193-52-0), 1-(2-hydroxyethyl)-3-methyl-imidazolium tetrafluoroborate (IL7, [C_2OHMIM][BF_4], 99 % purity, CAS no. 374564-83-7), and 1-(2-methoxyethyl)-3-methyl-imidazolium tetrafluoroborate (IL8,

---

* To whom correspondence should be addressed. E-mail: evoutsas@chemeng.ntua.gr.

10.1021/je800596c CCC: $40.75

Table 1. List of Investigated Compounds: Names, Structures, and Abbreviations of Names

Name	Structure	Abbreviation
methyl p-coumarate		MpCA
methyl ferulate		MFA
methyl sinapate		MSA
1-Butyl-3-Methyl-Imidazolium Hexafluorophosphate (IL1)		[BMIM][PF$_6$]
1-Octyl-3-Methyl-Imidazolium Hexafluorophosphate (IL2)		[OMIM][PF$_6$]
1-(2-Hydroxyethyl)-3-Methyl-Imidazolium Hexafluorophosphate (IL3)		[C$_2$OHMIM][PF$_6$]
1-(2-Methoxyethyl)-3-Methyl-Imidazolium Hexafluorophosphate (IL4)		[C$_3$OMIM][PF$_6$]
1-Butyl-3-Methyl-Imidazolium Tetrafluoroborate (IL5)		[BMIM][BF$_4$]
1-Octyl-3-Methyl-Imidazolium Tetrafluoroborate (IL6)		[OMIM][BF$_4$]
1-(2-Hydroxyethyl)-3-Methyl-Imidazolium Tetrafluoroborate (IL7)		[C$_2$OHMIM][BF$_4$
1-(2-Methoxyethyl)-3-Methyl-Imidazolium Tetrafluoroborate (IL8)		[C$_3$OMIM][BF$_4$]

[C$_3$OMIM][BF$_4$], 99 % purity, CAS no. 388095-13-4) were purchased from Solchemar Lda., Portugal. Methanol, acetonitrile, and water, all HPLC grade, were purchased from SDS-Carlo Erba Reactifs, France. All materials were used as they were. ILs [BMIM][PF$_6$], [OMIM][PF$_6$], and [OMIM][BF$_4$] have a water content of less than 0.01 % w/w, [BMIM][BF$_4$], [C$_3$OMIM][PF$_6$], and [C$_3$OMIM][BF$_4$] have a water content of less than 0.1 % w/w, and [C$_2$OHMIM][PF$_6$] and [C$_2$OHMIM][BF$_4$] have a water content of less than 0.5 % w/w. The molecular structures of the methyl esters and the ILs are illustrated in Table 1. Some pure compound thermophysical properties, pertinent to this work, are presented in Table 2.

Apparatus. The equilibrium runs were performed in a Thermomixer Comfort (Eppendorf). This apparatus combines stirring up to 1400 r·min^{-1} and heating (up to 99 °C) or cooling (13 °C below room temperature). The temperature readings of the thermomixer have been checked using an external thermometer calibrated with the Isocal-6 Venus$^{\text{Plus}}$ 2140 calibrator of temperature sensors. The accompanied thermoblock can accommodate 24 micro test tubes for 2 mL volumes.

Procedure. Approximately 200 μL of the solvent was placed in the 2 mL volume safe-lock micro test tube. An excess quantity of each methyl ester was then added. At constant temperature, measured with an uncertainty of ± 0.1 K, the solutions were stirred at 1400 r·min^{-1}. Solution samples were then withdrawn using adjustable micropipettes. The sampling tips of the pipettes were preheated at the temperature of the experiment to avoid solid precipitation. Before sampling, each solution was centri-

Table 2. Thermophysical Property Values of the Compounds Involved in This Study

compound	MW / g·mol^{-1}	ρ / kg·m^{-3}	T_m / K	$\Delta_{fus}H$ / J·mol^{-1}	R^d	Q^d
methyl *p*-coumarate	178.18		410.71[a]	30 216[a]	6.7834	5.315
methyl ferulate	208.21		335.71[a]	25 836[a]	7.7623	6.123
methyl sinapate	238.24		361.79[a]	29 858[a]	8.7412	6.931
[BMIM][PF$_6$]	284.18	1310[b]	283.15[b]		11.0340	6.958
[OMIM][PF$_6$]	340.29	1190[b]	203.15[c]		14.2300	8.935
[C$_2$OHMIM][PF$_6$]	272.13	1480[b]	201.15 (T_g)[b]		10.4585	6.770
[C$_3$OMIM][PF$_6$]	286.06	1400[b]	299.15[b]		10.6035	6.658
[BMIM][BF$_4$]	226.02	1210[b]	192.15[b]		10.0570	6.368
[OMIM][BF$_4$]	282.13	1080[b]	192.65 (T_g)[b]		13.1870	8.357
[C$_2$OHMIM][BF$_4$]	213.97	1330[b]	189.15 (T_g)[b]		9.4815	6.180
[C$_3$OMIM][BF$_4$]	228.00	1260[b]	185.15 (T_g)[b]		9.6265	6.068

[a] Experimentally measured in our laboratory.[25] [b] Data taken from SOLCHEMAR Lda. T_g is the glass-transition temperature. [c] Experimental value taken from Sun et al.[26] [d] van der Waals volume (R) and van der Waals area (Q) parameters for MpCA, MFA, and MSA have been calculated from the UNIFAC table.[27] R and Q parameters for [BMIM][PF$_6$], [OMIM][PF$_6$], [BMIM][BF$_4$], and [OMIM][BF$_4$] have been taken from Banerjee et al.,[28] whereas those for [C$_2$OHMIM][PF$_6$], [C$_3$OMIM][PF$_6$], [C$_2$OHMIM][BF$_4$], and [C$_3$OMIM][BF$_4$] have been calculated by utilizing the values given by Banerjee et al. and some group parameter values from the UNIFAC tables.

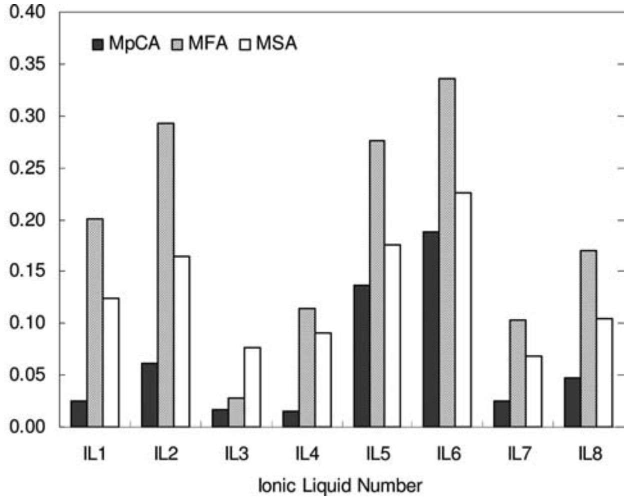


Figure 1. Mole fraction solubility, *x*, of methyl *p*-coumarate (MpCA), methyl ferulate (MFA), and methyl sinapate (MSA) in different ionic liquids at 303.15 K.

Table 3. Mole Fraction Solubilities (x) of Methyl *p*-Coumarate, Methyl Ferulate, and Methyl Sinapate in Different Ionic Liquids at Different Temperature

		methyl *p*-coumarate		methyl ferulate		methyl sinapate	
solvent	T/K	x	± SD	x	± SD	x	± SD
[BMIM][PF$_6$]	303.15	0.026	0.0020	0.201	0.0012	0.124	0.0005
	312.15	0.042	0.0040	0.245	0.0022	0.175	0.0062
	321.15	0.056	0.0002	0.394	0.0056	0.197	0.0052
[OMIM][PF$_6$]	303.15	0.061	0.0024	0.292	0.0009	0.165	0.0057
	312.15	0.071	0.0070	0.348	0.0087	0.209	0.0077
	321.15	0.092	0.0008	0.466	0.0091	0.252	0.0151
[C$_2$OHMIM][PF$_6$]	303.15	0.017	0.0007	0.028	0.0002	0.077	0.0047
	312.15	0.027	0.0019	0.055	0.0028	0.124	0.0009
	321.15	0.037	0.0021	0.096	0.0000	0.163	0.0016
[C$_3$OMIM][PF$_6$]	303.15	0.016	0.0016	0.114	0.0027	0.091	0.0027
	312.15	0.025	0.0001	0.206	0.0197	0.127	0.0003
	321.15	0.033	0.0014	0.272	0.0131	0.182	0.0004
[BMIM][BF$_4$]	303.15	0.136	0.0074	0.276	0.0142	0.176	0.0059
	312.15	0.159	0.0062	0.326	0.0149	0.196	0.0018
	321.15	0.198	0.0122	0.410	0.0048	0.225	0.0016
[OMIM][BF$_4$]	303.15	0.188	0.0040	0.336	0.0177	0.226	0.0147
	312.15	0.208	0.0047	0.364	0.0067	0.234	0.0036
	321.15	0.220	0.0116	0.492	0.0270	0.287	0.0031
[C$_2$OHMIM][BF$_4$]	303.15	0.024	0.0007	0.103	0.0052	0.068	0.0019
	312.15	0.028	0.0006	0.120	0.0045	0.086	0.0069
	321.15	0.050	0.0013	0.227	0.0027	0.131	0.0030
[C$_3$OMIM][BF$_4$]	303.15	0.048	0.0013	0.170	0.0056	0.105	0.0065
	312.15	0.063	0.0001	0.238	0.0091	0.135	0.0042
	321.15	0.092	0.0049	0.348	0.0026	0.184	0.0096

fuged for a short time (60 s) to enhance the physical separation of the two phases, liquid and solid, and to ensure that no precipitated solute was also drawn away during sampling because of the high viscosities of the ILs.

To determine the time required to reach equilibrium, a preliminary measurement of the solubility of the most soluble ester (MFA) in the most viscous IL [OMIM][PF$_6$] was performed. Samples were taken and analyzed after (12, 24, 48, 72, and 96) h of stirring. It was found that the difference among the solubility values measured after (48, 72, and 96) h was less than 2 %, which led to the conclusion that a time frame of 48 h is sufficient for achieving equilibrium for all ILs and esters.

The effect of the IL impurities on the ester solubility was also investigated. For this purpose, solubility measurements were performed using dried (at 80 °C under vacuum for 48 h) ILs, and when they were compared with those obtained in the ILs used as purchased, no difference was found.

All experiments were performed at least in duplicate.

Analysis. All samples were analyzed by reverse phase high-performance liquid chromatography (HPLC). The HPLC system was equipped with a Jusco PU-1580 pump, an ICI LC 1200 UV/vis detector set at 280 nm, and a BDS Hypersil C18 column ((250·4.6) mm^2, particle size 5 μm, Thermo Scientific). The eluent solution used was a mixture of acetonitrile/water (80/20 v/v) with 0.1 % acetic acid. The flow rate was adjusted to 1 mL·min^{-1}, the column temperature was kept constant at 30 °C, and the injection volume was 50 μL. The eluent solution was degassed with Helium.

Results and Discussion

Table 3 presents the measured solubilities of the three CAEs in the various ILs at the temperatures of (30, 39, and 48) °C, which are averages of at least two agreeing independent experiments. The corresponding standard deviation (SD) for each mean value is also reported. Moreover, Figure 1 graphically presents the solubilities measured at 30 °C. The following comments summarize the results: (a) The ranking of the solubilities of the three solids in the ILs is: MFA > MSA > MpCA. This can be explained by the fact that MFA has the lowest melting temperature (T_m) of the three esters, followed by MSA, whereas MpCA has the highest T_m (Table 2). In addition, MFA has the lowest enthalpy of fusion value ($\Delta_{fus}H$) among the three CAEs, whereas MSA and MpCA have similar values (Table 2). The only exception in the ranking presented above is IL3, where MSA has higher solubility than MFA and,

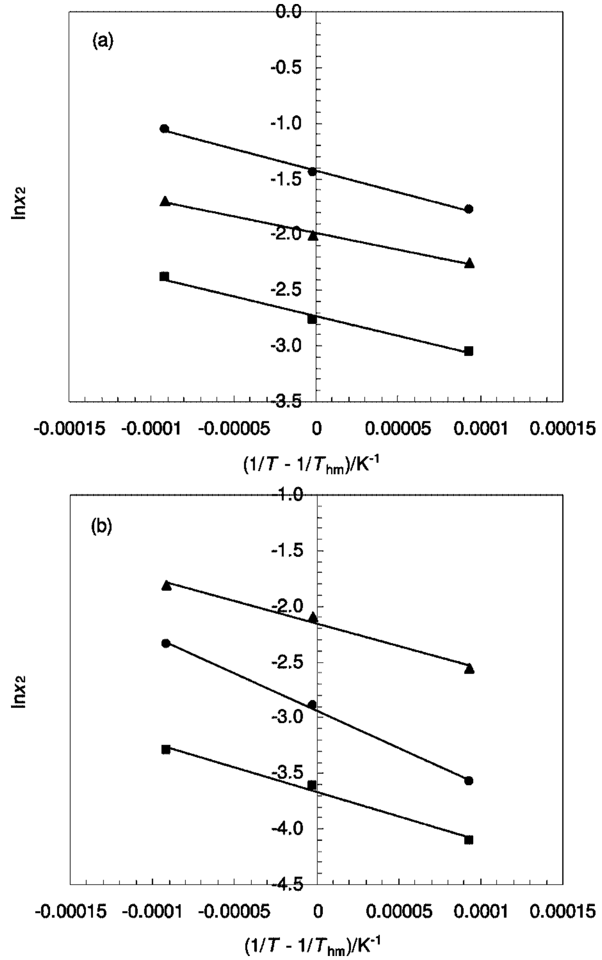


Figure 2. Temperature dependence of the solubility x of ▲, methyl sinapate; ●, methyl ferulate; and ■, methyl *p*-coumarate in (a) [C_2OHMIM][PF_6] and (b) [C_3OMIM][BF_4].

of course, MpCA. However, it should be taken into account that the solid compound' solubility is affected by not only its T_m and $\Delta_{fus}H$ (actually, this is the case only when the chemical nature of the solute and solvent are similar, i.e., the solute behaves ideally in the solution) but also its activity coefficient in the solution, which is a function of the intermolecular forces between solute and solvent. In this case, the activity coefficient of MSA in IL3 (equal to 13.2, as determined through eq 6 from the experimental solubility value) is much lower than the corresponding activity coefficient of MFA (equal to 1.9), thus compensating its higher T_m and $\Delta_{fus}H$. (b) The comparison of the CAE solubilities between ILs composed of the PF_6^- anion and the corresponding ILs composed of the BF_4^- anion shows that higher solubilities are observed in the latter. As shown by Anderson et al.,[29] ILs composed of the BF_4^- anion, which is hydrophilic, have a much stronger tendency to create hydrogen bonds, for example, with the hydroxyl or the methoxy group of the CAEs, than the ILs composed of the PF_6^- anion (hydrophobic). (c) Among the alkyl-substituted (nonpolar) (on the IM cation moiety) ILs (1, 2, 5, and 6) and the polar-substituted ILs (3, 4, 7, and 8), higher solubilities are observed in the first class. This is due to the fact that the alkyl, lipophilic, part of the IL is a good solvent for the ester part of the CAEs. This behavior is also supported by the fact that as the chain length of the alkyl substitute on the IM cation moiety of the ILs increases, the solubility of the CAE increases as well.

Table 4. Apparent Thermodynamic Functions Relative to Solution of Methyl *p*-Coumarate, Methyl Ferulate, and Methyl Sinapate in Different ILs and Corresponding Standard Deviations

	ΔG°_{soln}		ΔH°_{soln}		ΔS°_{soln}	
solvent	$kJ\cdot mol^{-1}$	SD	$kJ\cdot mol^{-1}$	SD	$J\cdot mol^{-1}\cdot K^{-1}$	SD
			Methyl *p*-Coumarate			
[BMIM][PF_6]	8.42	0.06	35.2	2.5	85.9	7.7
[OMIM][PF_6]	6.76	0.03	18.1	1.5	36.3	4.7
[C_2OHMIM][PF_6]	9.51	0.04	36.6	1.8	86.7	5.7
[C_3OMIM][PF_6]	9.73	0.05	33.0	2.0	74.6	6.3
[BMIM][BF_4]	4.71	0.02	16.7	1.0	38.4	3.0
[OMIM][BF_4]	4.11	0.01	7.0	0.6	9.2	1.8
[C_2OHMIM][BF_4]	8.91	0.15	32.1	6.5	74.2	20.4
[C_3OMIM][BF_4]	7.08	0.04	29.8	1.6	72.8	5.0
			Methyl Ferulate			
[BMIM][PF_6]	3.41	0.09	30.3	3.8	86.2	11.9
[OMIM][PF_6]	2.64	0.04	21.0	1.7	58.8	5.2
[C_2OHMIM][PF_6]	7.62	0.03	55.3	1.2	152.8	3.8
[C_3OMIM][PF_6]	4.37	0.09	39.0	3.7	111.0	11.7
[BMIM][BF_4]	2.86	0.02	17.8	1.0	47.8	3.1
[OMIM][BF_4]	2.43	0.07	17.1	3.0	47.0	9.5
[C_2OHMIM][BF_4]	5.08	0.15	35.2	6.5	96.6	20.5
[C_3OMIM][BF_4]	3.69	0.02	32.3	0.8	91.6	2.5
			Methyl Sinapate			
[BMIM][PF_6]	4.72	0.06	21.0	2.7	52.2	8.6
[OMIM][PF_6]	4.10	0.01	19.1	0.5	48.1	1.6
[C_2OHMIM][PF_6]	5.59	0.05	33.8	2.2	90.4	6.9
[C_3OMIM][PF_6]	5.34	0.01	31.1	0.6	82.6	1.9
[BMIM][BF_4]	4.21	0.01	11.0	0.5	21.9	1.5
[OMIM][BF_4]	3.62	0.05	10.5	2.3	22.1	7.2
[C_2OHMIM][BF_4]	6.20	0.06	29.6	2.5	75.1	7.9
[C_3OMIM][BF_4]	5.15	0.02	25.1	1.0	64.1	3.2

Thermodynamic Functions of Solution. According to van't Hoff analysis, the apparent standard enthalpy change in solution is obtained from the slope of an ln x_2 versus $1/T$ plot, where x_2 is the solute solubility in mole fraction. In recent thermodynamic treatments, some modifications have been introduced to the van't Hoff treatment to transform the intercept facilitating their use in thermodynamic calculations. According to the Krug et al.[30] approach, the following modified van't Hoff expression is used

$$\left[\frac{\partial \ln x_2}{\partial\left(\frac{1}{T}-\frac{1}{T_{hm}}\right)}\right]_P = -\frac{\Delta H^{o}_{soln}}{R} \tag{1}$$

In eq 1, $\Delta_{soln}H^o/R$ is the apparent standard enthalpy energy change for the solution process, and T_{hm} is the harmonic mean of the experimental temperatures, which is calculated to be

$$T_{hm} = \frac{n}{\sum_{i=1}^{n}\frac{1}{T_i}} \tag{2}$$

where n is the number of temperatures studied.[30] In the present study, T_{hm} is equal to 312 K.

The application of linear regression models of the modified van't Hoff plots using the experimentally measured solubilities in this work yielded very high correlation coefficient values (r^2). For this reason it is considered that the van't Hoff equation is useful for estimating the enthalpies of solution in these systems. Figure 2 presents two such examples for the solubilities of the three CAEs in ILs 3 and 8.

The apparent standard Gibbs energy change for the solution process ($\Delta_{soln}G^o$), considering the approach proposed by Krug et al., is calculated at T_{hm} by

$$\Delta_{soln}G^o = -R\cdot T_{hm}\cdot K \tag{3}$$

in which, the intercept K used is the one obtained in the analysis by treatment of ln x_2 as a function of $((1/T) - (1/T_{hm}))$ (eq 1).

Finally, the standard apparent entropy change for the solution process ($\Delta_{\text{soln}}S^{\text{o}}$) is obtained from

$$\Delta_{\text{soln}}S^{\text{o}} = \frac{\Delta_{\text{soln}}H^{\text{o}} - \Delta_{\text{soln}}G^{\text{o}}}{T_{\text{hm}}} \tag{4}$$

Table 4 summarizes the apparent standard thermodynamic functions for the solution process of the three esters in all ILs. The standard Gibbs energy of solution is positive in all cases; that is, the solution process apparently is not spontaneous, which may be explained in terms of the concentration scale used (mole fraction), where the reference state is the ideal solution having the unity as the concentration of the CAEs, that is, the solid pure solute. Also, the enthalpy of solution is positive in all cases, which suggests that the solution process is always endothermic. Finally, the entropy change is also positive in all cases, indicating that the entropy of solubilization is unfavorable for all esters in the ILs examined.

Thermodynamic Modeling. The solubility x_2 of a solid, in mole fraction, in a solvent is calculated by the following standard thermodynamic equation

$$\ln \gamma_2 x_2 = -\left\{\frac{\Delta_{\text{fus}}H(T_{\text{m}})}{RT}\left[1 - \frac{T}{T_{\text{m}}}\right] + \frac{\Delta C_p}{R}\left[1 - \frac{T_{\text{m}}}{T}\right] + \frac{\Delta C_p}{R}\ln\frac{T_{\text{m}}}{T}\right\} \tag{5}$$

where γ_2, $\Delta_{\text{fus}}H$, and T_{m} stand for the activity coefficient, the enthalpy of fusion, and the melting temperature of the solid solute, whereas ΔC_p is the difference between the heat capacity of the solid and that of the subcooled liquid at the corresponding temperature. By neglecting the terms that include ΔC_p because their contribution to the calculated solubility is very small, eq 5 becomes

$$\ln x_2 = -\ln \gamma_2 - \frac{\Delta_{\text{fus}}H(T_{\text{m}})}{RT}\left[1 - \frac{T}{T_{\text{m}}}\right] \tag{6}$$

In this study, two classical local composition activity coefficient models were used for the correlation of the solubility data, the NRTL[31] and the UNIQUAC[32] models. We determined temperature-independent binary interaction parameters per binary mixture for both models by minimizing the following objective function (OF)

$$\text{OF} = \sqrt{\frac{\sum_i^n \left(\frac{x_2 \cdot \gamma_{2,\text{calcd}}}{x_2 \cdot \gamma_2} - 1\right)^2}{\text{NP}}} \tag{7}$$

In eq 7, NP is the number of experimental points, x_2 and γ_2 are the experimental solubility and the corresponding activity coefficient values, and $\gamma_{2,\text{calcd}}$ is the activity coefficient calculated with the NRTL or UNIQUAC equation at $x = x_{2,\text{exptl}}$.

The interaction parameters determined for the two models along with the obtained errors in solubility calculations are presented in Table 5, whereas typical results are also presented graphically in Figure 3. It is concluded that very good correlation of the experimental data is obtained by both models, with UNIQUAC being slightly better than NRTL. Because the two parameters of the models per binary system were fitted to only three experimental data, it is advised that they not be used far from the temperature range over which they were been determined. It should be also noted that the use of the modified combinatorial, proposed by Larsen et al.,[33] with the UNIQUAC model does not lead to better results than those obtained with the original combinatorial.

Table 5. Interaction Parameters for NRTL and UNIQUAC Models and Respective Average Relative Deviations for the Solubility of CAE (2) in Ionic Liquid (1)

	NRTL[a]			UNIQUAC		
solvent	$(\Delta g_{12}/R)$/K	$(\Delta g_{21}/R)$/K	ARD (%)[b]	$(\Delta u_{12}/R)$/K	$(\Delta u_{21}/R)$/K	ARD (%)
			Methyl *p*-Coumarate			
$[\text{BMIM}][\text{PF}_6]$	1377.6	−716.91	5.1	−1.836	0.816	5.2
$[\text{OMIM}][\text{PF}_6]$	−526.74	3143.1	2.7	−325.13	804.69	2.5
$[\text{C}_2\text{OHMIM}][\text{PF}_6]$	1382.9	−669.21	3.9	48.956	−17.372	4.4
$[\text{C}_3\text{OMIM}][\text{PF}_6]$	−16.481	424.07	3.6	45.101	−17.332	3.6
$[\text{BMIM}][\text{BF}_4]$	1436.2	−955.60	1.5	−355.69	549.82	1.6
$[\text{OMIM}][\text{BF}_4]$	−963.25	3428.6	4.0	−422.59	2000.0	2.4
$[\text{C}_2\text{OHMIM}][\text{BF}_4]$	1544.0	−755.93	11.6	683.26	−338.96	10.6
$[\text{C}_3\text{OMIM}][\text{BF}_4]$	1113.6	−690.36	2.5	−82.186	50.543	2.7
			Methyl Ferulate			
$[\text{BMIM}][\text{PF}_6]$	−313.72	1048.9	5.4	−192.52	323.97	5.3
$[\text{OMIM}][\text{PF}_6]$	−568.92	1565.5	2.3	−257.42	471.74	2.3
$[\text{C}_2\text{OHMIM}][\text{PF}_6]$	804.23	43.170	5.2	326.89	−160.38	6.1
$[\text{C}_3\text{OMIM}][\text{PF}_6]$	10.195	591.39	9.2	−123.69	215.04	7.1
$[\text{BMIM}][\text{BF}_4]$	−551.26	2100.4	1.3	−292.26	665.44	1.2
$[\text{OMIM}][\text{BF}_4]$	−647.68	1806.5	4.6	−284.67	569.33	4.7
$[\text{C}_2\text{OHMIM}][\text{BF}_4]$	−27.358	859.69	9.8	−113.89	237.65	9.7
$[\text{C}_3\text{OMIM}][\text{BF}_4]$	−260.49	1017.8	0.2	−188.39	329.13	0.1
			Methyl Sinapate			
$[\text{BMIM}][\text{PF}_6]$	−557.21	1871.7	4.9	−272.69	483.93	5.1
$[\text{OMIM}][\text{PF}_6]$	−310.63	4872.0	0.8	−291.89	523.49	1.1
$[\text{C}_2\text{OHMIM}][\text{PF}_6]$	−126.69	449.26	4.2	270.54	−187.74	4.8
$[\text{C}_3\text{OMIM}][\text{PF}_6]$	−308.69	764.87	0.8	−157.50	196.71	0.6
$[\text{BMIM}][\text{BF}_4]$	−517.01	3253.0	5.4	−352.28	1279.7	0.7
$[\text{OMIM}][\text{BF}_4]$	−634.64	3343.7	5.5	−357.20	1088.9	3.7
$[\text{C}_2\text{OHMIM}][\text{BF}_4]$	−291.19	1140.4	4.1	−178.98	297.60	3.9
$[\text{C}_3\text{OMIM}][\text{BF}_4]$	−477.70	1468.2	1.7	−241.77	396.68	1.4

[a] Nonrandomness parameter of the NRTL model was set equal to 0.2. [b] ARD $= 1/3(\sum_{i=1}^{3} |x_{\text{exptl}} - x_{\text{calcd}}|/x_{\text{exptl}})$.

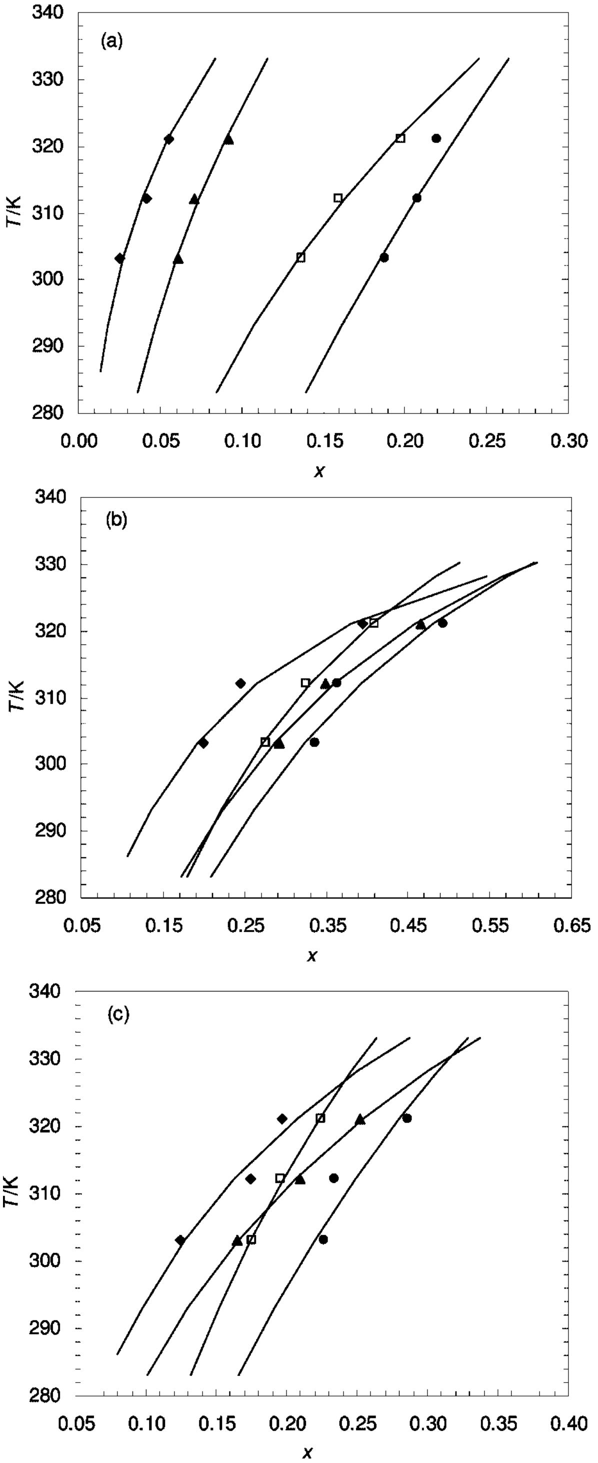


Figure 3. Solubilities of (a) methyl *p*-coumarate, (b) methyl ferulate, and (c) methyl sinapate in: ◆, [BMIM][PF_6]; □, [BMIM][BF_4]; ▲, [OMIM][PF_6]; and ●, [OMIM][BF_4]. Solid lines calculated by the UNIQUAC model.

Conclusions

The solubilities of three CAEs have been measured in IM-based ILs composed of the PF_6^- and the BF_4^- anions. The results showed that the BF_4^--based ILs are better solvents than the corresponding PF_6^--based ILs. Furthermore, it is noticed that the alkyl-substituted (on the IM moiety) ILs are better solvents for the CAEs than the polar-substituted ILs, whereas as the chain length of the alkyl substitution on the IM moiety increases, the solubility increases. By utilizing the experimental solubilities, we determined the thermodynamic functions of solutions. The results indicated that the solution process is not spontaneous and is always endothermic and that the entropy of solubilization is unfavorable for all systems studied. Finally, successful correlation with the NRTL and UNIQUAC models was obtained for all systems studied, with UNIQUAC being slightly better than NRTL.

Acknowledgment

Dr. P. Christakopoulos and Dr. Ch. Vafiadi, Biotechnology Laboratory, NTUA, are kindly thanked for their help and the many stimulating discussions.

Literature Cited

(1) Kroon, P. A.; Williamson, G. Hydroxycinnamates in plants and food: current and future perspectives. *J. Sci. Food Agric.* **1999**, *79*, 355–361.
(2) Ishii, T. Structure and functions of feruloylated polysaccharides. *Plant Sci.* **1997**, *127*, 111–127.
(3) Lequart, C.; Nuzillard, J. M.; Kurek, B.; Debeire, P. Hydrolysis of wheat bran and straw by an endoxylanase: production and structural characterization of cinnamoyl-oligosaccharides. *Carbohydr. Res.* **1999**, *319*, 102–111.
(4) Micard, V.; Renard, C.; Colquhoun, I. J.; Thibault, J. F. End-products of enzymic saccharification of beet pulp, with a special attention to feruloylated oligosaccharides. *Carbohydr. Polym.* **1997**, *32*, 283–292.
(5) Saulnier, L.; Thibault, J. F. Ferulic acid and diferulic acids as components of sugar-beet pectins and maize bran heteroxylans. *J. Sci. Food Agric.* **1999**, *79*, 396–402.
(6) Vafiadi, C.; Topakas, E.; Wong, K. K. Y.; Suckling, I. D.; Christakopoulos, P. Mapping the hydrolytic and synthetic selectivity of a type C feruloyl esterase (StFaeC) from *Sporotrichum thermophile* using alkyl ferulates. *Tetrahedron: Assymetry* **2005**, *16*, 373–379.
(7) Tawata, S.; Taira, S.; Kobamoto, N.; Zhu, J.; Ishihara, M.; Toyama, S. Synthesis and Antifungal Activity of Cinnamic Acid Esters. *Biosci., Biotechnol., Biochem.* **1996**, *60*, 909–910.
(8) Chen, X.; Martin, B. D.; Neubauer, T. K.; Linhardt, R. J.; Dordick, J. S.; Rethwisch, D. G. Enzymatic and chemoenzymatic approaches to synthesis of sugar-based polymer and hydrogels. *Carbohydr. Polym.* **1995**, *28*, 15–21.
(9) Patil, N. S.; Dordick, J. S.; Rethwisch, D. G. Macroporous poly(sucrose acrylate) hydrogel for controlled release of macromolecules. *Biomaterials* **1996**, *17*, 2343–2350.
(10) Earle, M. J.; Seddon, K. R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398.
(11) van Rantwijk, F.; Lau, M. R.; Sheldon, R. Biocatalytic transformations in ionic liquids. *Trends Biotechnol.* **2003**, *21*, 131–138.
(12) Zhao, J.; Dong, C. C.; Li, C. X.; Meng, H.; Wang, Z. H. Isobaric vapor−liquid equilibria for ethanol−water system containing different ionic liquids at atmospheric pressure. *Fluid Phase Equilib.* **2006**, *242*, 147–153.
(13) Yan-Ying, Y.; Wei, Z.; Shu-Wen, C. Extraction of ferulic acid and caffeic acid with ionic liquids. *Chin. J. Anal. Chem* **2007**, *35*, 1726–1730.
(14) Brennecke, J. F.; Maginn, E. J. Ionic liquids: innovative fluids for chemical processing. *AIChE J.* **2001**, *47*, 2384–2389.
(15) Wasserscheid, P.; Keim, W. Ionic liquids: new "solutions" for transition metal catalysis. *Angew. Chem., Int. Ed.* **2000**, *39*, 3773–3789.
(16) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.
(17) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.
(18) Jaitely, V.; Karatas, A.; Florence, A. T. Water-immiscible room-temperature ionic liquids (RTILs) as drug reservoirs for controlled release. *Int. J. Pharm.* **2008**, *354*, 168–173.
(19) Yang, J. Z.; Wang, B.; Zhang, Q. G.; Tong, J. Study on solid−liquid phase equilibria in ionic liquid. 1. The solubility of alkali chloride (MCl) in ionic liquid EMISE. *Fluid Phase Equilib.* **2007**, *251*, 68–70.
(20) Wang, B.; Zhang, Q. G.; Yang, J. Z. Study on solid−liquid phase equilibria in ionic liquid. 2. The solubility of alkali bromide in ionic liquid 1-ethyl-3-methylimidazolium ethyl sulphate. *Fluid Phase Equilib.* **2007**, *254*, 163–166.
(21) Gu, Y.; Shi, F.; Yang, H.; Deng, Y. Leaching separation of taurine and sodium sulfate solid mixture using ionic liquids. *Sep. Purif. Technol.* **2004**, *35*, 153–159.

(22) Lin, H. M.; Tien, H. Y.; Hone, Y. T.; Lee, M. J. Solubility of selected dibasic carboxylic acids in water, in ionic liquid of [Bmim][BF_4], and in aqueous [Bmim][BF_4] solutions. *Fluid Phase Equilib.* **2007**, *253*, 130–136.

(23) Mizuuchi, H.; Jaitely, V.; Murdan, S.; Florence, A. T. Room-temperature ionic liquids and their mixtures: potential pharmaceutical solvents. *Eur. J. Pharm. Sci* **2008**, *33*, 326–331.

(24) Guo, Z.; Lue, B. M.; Thomasen, K.; Meyerb, A. S.; Xu, X. Predictions of flavonoid solubility in ionic liquids by COSMO-RS: experimental verification, structural elucidation, and salvation characterization. *Green Chem.* **2007**, *9*, 1362–1373.

(25) Saratsioti, P. Solubility Measurements of Methyl Esters of Cinnamic Acids in Organic Solvents at Three Different Temperatures. Diploma Thesis, National Technical University of Athens, 2007.

(26) Sun, N.; He, X.; Dong, K.; Zhang, X.; Lu, X.; He, H.; Zhang, S. Prediction of the melting points for two kinds of room temperature ionic liquids. *Fluid Phase Equilib.* **2006**, *246*, 137–142.

(27) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC: a Group Contribution Method*; Elsevier Scientific Publishing Company: New York, 1977.

(28) Banerjee, T.; Singh, M. K.; Sahoo, R. K.; Khanna, A. Volume, surface and UNIQUAC interaction parameters for imidazolium based ionic liquids via polarizable continuum model. *Fluid Phase Equilib.* **2005**, *234*, 64–76.

(29) Anderson, J.; Ding, J.; Welton, T.; Armstrong, D. Characterizing ionic liquids on the basis of multiple interactions. *J. Am. Chem. Soc.* **2002**, *124*, 14247–14254.

(30) Krug, R. R.; Hunterlib, W. G.; Grlegerl, R. A. Enthalpy−entropy compensation. 2. Separation of the chemical from the statistical effect. *J. Phys. Chem.* **1976**, *80*, 2341–2351.

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

(32) Abrams, D.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(33) Larsen, B. L.; Rasmussen, P.; Fredenslund, A. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274–2286.

Received for review July 31, 2008. Accepted November 24, 2008. The financial support of the National Technical University of Athens, Greece (program “LEFKIPPOS”) is gratefully acknowledged.

JE800596C