



# Are solubility parameters relevant for the solubility of liquid organic solutes in room temperature ionic liquids?



Yizhak Marcus

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

## ARTICLE INFO

### Article history:

Received 25 October 2015

Accepted 8 November 2015

Available online xxxx

### Keywords:

Liquid organic solutes

Room temperature ionic liquids

Solubility parameters

Solubility prediction

## ABSTRACT

A database for the solubilities of (volatile) liquid organic solutes in (non-volatile) room temperature ionic liquids at 298 K (or thereabouts) was constructed in terms of the infinite dilution activity coefficients,  $\ln\gamma_{i(s)}^\infty$ , from data in the literature. In most cases the fit of these data by the Hildebrand solubility parameter expression  $(V_i/RT)(\delta_{Hi} - \delta_{Hs})^2$  alone is unsuccessful, and in particular this expression cannot account for negative values of  $\ln\gamma_{i(s)}^\infty$ . An (negative) entropic correction term related to the relative sizes of the solute and solvent that was suggested is generally inadequate to cause a better fit. The prediction of the solubilities of organic solutes in RTILs remains a challenge.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The solubility of volatile solutes (subscript  $i$ ) in (the non-volatile) room temperature ionic liquids (RTILs, subscript  $s$ ) is commonly reported in terms of the Henry constant  $H_{i(s)}$ , the mole fraction of the solute at saturation,  $x_i$ , at a (partial) pressure of the solute  $p_i$ :

$$H_{i(s)} = p_i/x_{i(s)}. \quad (1)$$

It is related to the widely reported infinite dilution activity coefficient (obtained from gas chromatography):

$$\gamma_{i(s)}^\infty = H_{i(s)}/p_i^* \quad (2)$$

where  $p_i^*$  is the vapor pressure of the pure liquid solute. Another measure of the solubility is the partition constant:

$$\log K_{i(s)} = \log(RT/\gamma_{i(s)}^\infty p_i^* V_s) = \log(RT/H_{i(s)} V_s) \quad (3)$$

where  $V_s$  is the molar volume of the solvent. Values of  $\log K_{i(s)}$  are also widely reported, having been obtained from gas chromatography too. A database of  $\ln\gamma_{i(s)}^\infty$  values has been assembled in Table 1 [1–13] for 28 volatile liquid organic solutes, including aliphatic and aromatic hydrocarbons and polar organic compounds, pertaining to the 22 RTILs listed in Table 2. The RTILs are identified in Table 1 by their ordinal numbers in Table 2. Where required, values of  $x_{i(s)}$ ,  $H_{i(s)}$ , and  $\log K_{i(s)}$  have been

converted to  $\gamma_{i(s)}^\infty$  values according to the expressions (1), (2), and (3). The auxiliary data (including  $p_i^*$  and  $V_s$ , where employed, Table 3) pertain nominally to 298.15 K, and no corrections have been applied for solubility data reported at  $\approx 303$  K. The solubilities in terms of the mole fraction of the solute in the saturated solution are accordingly inversely proportional to the  $\gamma_{i(s)}^\infty$  values.

Several attempts of description of the solubilities of volatile solutes in RTILs in terms of the regular solution theory have been made [2,5,14,15,16]. Lee [2] suggested that the solubilities of organic solutes in RTILs could be expressed as:

$$\ln \gamma_{i(s)}^\infty = (V_i/RT)(\delta_{Hi} - \delta_{Hs})^2 - \text{correction terms} \quad (4)$$

where the  $\delta_H$  are the total Hildebrand solubility parameters and the *correction terms* pertain to the solute–solvent dispersion-, polar-, and hydrogen-bonding–interaction partial solubility parameters. The  $\delta_{Hi}$  solubility parameters of the 28 solutes in the data base are well known [17] and those of the RTILs,  $\delta_{Hs}$ , are discussed in the present paper. However, the required *correction terms* are generally not available.

A somewhat different approach was suggested recently by Wang et al. [16] and by Ge et al. [5] who set:

$$\ln \gamma_{i(s)}^\infty = (V_i/RT)(\delta_{Hi} - \delta_{Hs})^2 + \left[ \ln(r_i/r_s)^{2/3} + 1 - (r_i/r_s)^{2/3} \right] \quad (5)$$

where the (negative) term in square brackets is due to Kilic et al. [18], describing the entropic effects of the discrepancies in the van der Waals volumes  $r_i$  and  $r_s$  of the solute and solvent.

It is noted (Table 1) that for aliphatic hydrocarbons  $\ln\gamma_{i(s)}^\infty$  is positive, of the order of a few units, for aromatic hydrocarbons it is generally still

E-mail address: [yMarcus@vms.huji.ac.il](mailto:yMarcus@vms.huji.ac.il).

**Table 1**  
 $\ln\gamma_i^\infty$  of the listed solutes in RTILs identified by their numbers in Table 2.

Solute RTIL	1	2	2a	3	3a	4	5	5a	6	7	8	9	10	10a	11	12	13	14	15	16	17	18	19	20	21	22	
Reference	1	2	3	1	4	1	1	4	5	6	1	7	1	4	8	9	4	7	10	11	12	12	11	13	12	13	
<i>n</i> -Pentane																			2.14		2.13	3.93		2.37		2.69	
<i>n</i> -Hexane		3.30	3.31		4.19				2.72	1.93	4.16			2.11			2.15		2.50	2.74	2.46	4.04	3.35	2.70		2.98	
<i>n</i> -Heptane		3.74	3.74		4.42				3.11	2.79	4.66			2.42			2.40		2.73	3.10	2.84	4.26	3.53	3.04	5.19	3.32	
<i>n</i> -Octane		4.18	4.21		4.76				3.51	3.48	5.13			2.79			2.78		2.88	3.51	3.23	4.35	3.77	3.40	5.60	3.72	
<i>n</i> -Decane		5.16	5.18						4.17	4.20			4.53	3.46							4.28	3.98	5.28	4.38	4.10	6.42	4.47
<i>c</i> -Hexane		2.74	2.74		3.12				2.22	4.03	3.39		2.47	1.76					1.87	2.37	2.12	3.28	2.73	2.20	3.77	2.84	
Benzene	0.74	0.16	0.16	0.52	0.41	0.47	-0.12	-0.16	1.83	0.62	0.43		-0.30	-0.27	0.72	0.60	-0.36		-0.06	0.34	-0.60	0.33	-0.13	-0.25	0.50	-0.18	
Toluene		0.54	0.55		0.92				0.35	2.73	1.13			0.01	1.09	1.01	0.00		0.34	0.66	-0.21	0.79	0.24	-0.16	1.07	0.12	
Ethylbenzene		1.06	1.03						0.79		1.71		1.48	0.45	1.41	1.45			0.72	1.01	0.09	1.20	0.58	0.44	1.60	0.47	
<i>o</i> -Xylene		0.86	0.87							3.19	1.46		1.41		1.26	1.29			1.06	0.56	0.93	-0.03	1.06	0.42	0.33	1.39	0.33
<i>m</i> -Xylene		0.99	1.04							3.48	1.69		1.63	0.34	1.43	1.45			1.23	0.70	1.00	0.03	1.28	0.50	0.40	1.59	0.48
<i>p</i> -Xylene		1.00	0.96		-0.22					3.41	1.62		1.54	0.35	1.42	1.41			1.29	0.68	1.01	0.06	1.20	0.49	0.37	1.60	0.39
Methanol		0.23	0.21		0.10				0.25		-1.14			0.39	-2.30	-0.99	-1.20		-1.35	0.70	1.25	-0.35	0.55	0.50	-1.13	0.18	
Ethanol		0.52	0.52						0.62		-0.58			0.74	-1.56	-0.51	-0.69		-0.97		1.24	0.05	0.79	0.71	-0.52	0.51	
<i>n</i> -Propanol		0.84	0.87						1.02		-0.26		0.91	0.97	-1.08	-0.34			1.29	-0.87	1.28	1.60	0.32	1.02	0.95	0.74	
<i>i</i> -Propanol		0.77	0.78						0.73					0.64		-0.20			0.64	-0.82	1.14	1.39	0.23	0.94		-0.04	0.67
<i>n</i> -Butanol		1.21	1.29						1.16					1.07		-0.04			0.44		2.07	1.93	0.67	1.46	1.29	0.24	1.07
Diethyl ether																				0.55	0.34		1.11	0.76	0.08	0.86	
Tetrahydrofuran					0.34					1.68			0.98		0.67	0.65	-0.36		0.61	0.03	-0.22	-0.96	0.25	-0.30	-0.49	0.65	-0.53
1,4-Dioxane												0.81		0.65	0.30				1.18		-0.10	-0.93	0.07	-0.39	-0.53	0.38	-0.78
Acetone	0.19	-0.94	-0.94	-0.08		-0.92	-0.94	-1.00	1.46	0.10	-0.26		-0.99	-1.06	0.52	0.26			0.11	-0.17		-1.40		-0.72	-0.82	0.30	-0.81
2-Pentanone			0.72																			0.05					
Ethyl acetate		-0.14			0.59				2.54	1.08			1.37		0.97	1.05	-0.10		0.63	0.50							
Dichloromethane		-0.03	-0.03						0.85	-0.78		-0.25			-0.45	-0.69			-0.42	-1.14	0.18						
Chloroform		-0.06	-0.06						0.75	-1.27		-0.63		-0.42	-2.53	-1.24			-0.76	-1.77	0.17						
Tetrachloromethane		1.18	0.68						2.72	0.74		1.52		-0.48	0.77				0.85	0.15	0.77						
Acetonitrile		-0.82	-0.81					-0.74	0.67	-0.51		0.66		-0.76	0.01	-0.14			-0.27	-0.51	-0.35	-1.14					
Pyridine																					-0.90			-0.69	0.57	-0.71	

Download English Version:

<https://daneshyari.com/en/article/5410217>

Download Persian Version:

<https://daneshyari.com/article/5410217>

[Daneshyari.com](https://daneshyari.com)