

ESI

An Enthalpic Approach to Delineate Interactions of the Cations of Imidazolium-based Ionic Liquids with Molecular Solvents

*Gitanjali Rai and Anil Kumar**

Physical Chemistry Division, National Chemical Laboratory, Pune 411 008, India

E-mail: a.kumar@ncl.res.in

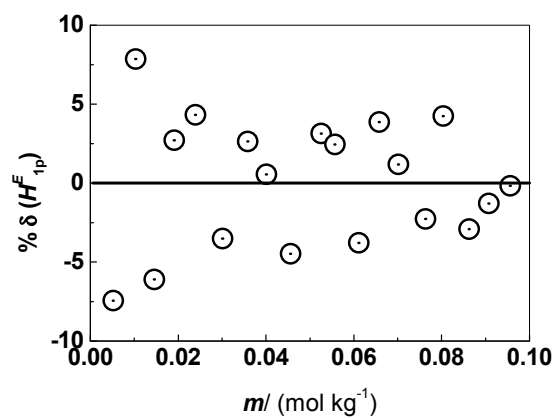


Figure S1: Percent deviation, $\% \delta (H^E_{lp})$ calculated from between ours and the literature data, Ref. 7

Table S1: Experimental H^E_{IL} Data for the Ionic Liquid-Solvent Systems at 298.15 K

x_{IL}	$H^E_{IL}/(\text{J mol}^{-1})$	x_{IL}	$H^E_{IL}/(\text{J mol}^{-1})$	x_{IL}	$H^E_{IL}/(\text{J mol}^{-1})$	x_{IL}	$H^E_{IL}/(\text{J mol}^{-1})$	x_{IL}	$H^E_{IL}/(\text{J mol}^{-1})$
[EMIM]BF ₄ - H ₂ O		[EMIM]BF ₄ - methanol		[EMIM]BF ₄ - ethylene glycol		[EMIM]BF ₄ - formamide		[EMIM]BF ₄ - DMF	
0.04999	521	0.06311	1594	0.26373	626	0.11814	834	0.12096	-1084
0.09522	266	0.11871	737	0.34953	439	0.21132	402	0.21581	-492
0.13634	172	0.16809	456	0.41738	336	0.28669	262	0.29219	-307
0.17389	129	0.21222	308	0.47243	271	0.34891	193	0.35501	-220
0.20830	103	0.25192	264	0.51797	227	0.40115	153	0.40759	-175
0.23997	86	0.28780	200	0.55628	194	0.44562	126	0.45224	-143
0.26920	74	0.32040	185	0.58894	170	0.48395	108	0.49063	-120
0.29626	66	0.35014	151	0.61713	151	0.51732	92	0.52400	-104
0.32139	60	0.37739	124	0.64170	135	0.54664	81	0.55326	-90
						0.57260	73	0.57913	-78
								0.60217	-70
								0.62282	-63
								0.64143	-58
								0.65829	-52

[BMIM]BF ₄ - H ₂ O		[BMIM]BF ₄ - methanol		[BMIM]BF ₄ - ethanol		[BMIM]BF ₄ - 1- propanol		[BMIM]BF ₄ - ethylene glycol	
0.04792	241	0.07556	1264	0.10517	1947	0.10998	2433	0.13504	1066
0.09145	137	0.14050	638	0.19032	957	0.19817	1216	0.23795	574
0.13117	97	0.19692	420	0.26067	626	0.27046	808	0.31898	394
0.16757	75	0.24639	318	0.31978	458	0.33079	598	0.38443	299
0.20104	61	0.29011	255	0.37013	364	0.38190	472	0.43840	240
0.23193	52	0.32904	211	0.41354	299	0.42576	387	0.48367	200
0.26051	46	0.36393	179	0.45136	253	0.46381	325	0.52219	171
0.28704	40	0.39536	156	0.48459	219	0.49713	278	0.55536	149
0.31174	35	0.42383	138	0.51403	191	0.52655	243	0.58422	132
0.33478	32	0.44975	123	0.54028	169	0.55272	215	0.60957	118
0.35633	29	0.47343	111	0.56385	152	0.57615	192	0.63200	107
0.37653	27	0.49516	101	0.58511	137	0.59724	173	0.65199	97
0.39549	24	0.51516	93	0.60440	124	0.61634	157	0.66993	88
0.41334	23	0.53364	86	0.62198	113	0.63370	143	0.68610	82
0.43017	21	0.55077	80	0.63806	103	0.64956	133	0.70077	75

0.44605	20	0.56668	74	0.65283	95	0.66411	123	0.71412	70
0.46108	18	0.58150	69	0.66644	89	0.67750	114	0.72634	65
0.47531	17	0.59534	65	0.67902	82	0.68986	106	0.73755	61
0.47982	16	0.60830	61	0.69069	77	0.70130	99	0.74788	57
		0.62045	58	0.70154	72	0.71194	94	0.75743	54
		0.63187	55	0.71165	68	0.72184	88	0.76628	51
		0.64262	52	0.72110	64	0.73108	83	0.77451	48
		0.65277	49	0.72996	61	0.73973	79	0.78218	46
		0.66235	47	0.73826	57	0.74784	74	0.78934	43
		0.67142	44						
		0.68001	42						
[BMIM]BF ₄ -formamide		[BMIM]BF ₄ -DMF		[BMIM]BF ₄ -CHCl ₃		[BMIM]BF ₄ -D ₂ O		[HMIM]BF ₄ -H ₂ O	
0.10472	750	0.13513	-1343	0.78633	-329	0.10320	197	0.02707	-635
0.18958	369	0.23809	-567	0.81109	87	0.14720	101	0.05272	-269
0.25975	245	0.31915	-337	0.8307	84	0.18708	64	0.07705	-163
0.31874	180	0.38461	-239	0.84663	78	0.22341	54	0.10016	-112

0.36902	143	0.43859	-184	0.85982	70	0.25662	46	0.12214	-83
0.41239	118	0.48387	-142	0.87091	64	0.28711	38	0.14307	-66
0.45018	100	0.52239	-117	0.88038	59	0.31520	33	0.16303	-53
0.48340	86	0.55555	-97	0.88856	54	0.38759	29	0.18208	-44
0.51284	74	0.58441	-83	0.89569	50	0.40843	27	0.20028	-37
				0.90196	46	0.42790	25	0.21769	-31
				0.90752	43	0.44613	23	0.23436	-27
				0.91249	41	0.46324	22	0.25033	-24
				0.91694	38	0.47932	20	0.26565	-22
				0.92097	37	0.49446	19	0.28035	-21
				0.92462	35	0.50875	17		
				0.92796	33	0.52226	16		
				0.931	30	0.52341	15		
				0.93639	26				
[HMIM]BF ₄ - methanol		[HMIM]BF ₄ - ethanol		[HMIM]BF ₄ - 1-propanol		[HMIM]BF ₄ - ethylene glycol		[HMIM]BF ₄ - formamide	
0.03851	446	0.10139	196	0.06934	-1615	0.17547	86	0.07267	765

0.07416	260	0.14474	161	0.12970	-726	0.24197	70	0.13549	379
0.10726	179	0.18411	131	0.18270	-385	0.29855	56	0.19034	251
0.13808	133	0.22001	114	0.22961	-231	0.34727	45	0.23864	184
0.16684	105	0.25288	98	0.27143	-147	0.38966	37	0.28151	144
0.19374	87	0.28310	87	0.30895	-97	0.42688	31	0.31980	119
0.21896	75	0.31096	74	0.34279	-63	0.45982	26	0.35422	99
0.24265	65	0.33674	67	0.37347	-42	0.48918	23	0.38533	86
0.26495	58	0.36066	60	0.40141	-27	0.51552	19	0.41357	75
0.28597	51	0.38292	54	0.42697	-17	0.53927	16	0.43934	66
0.30582	46	0.40368	49	0.45044	-11	0.56080	13	0.46293	59
0.32460	41	0.42309	46	0.47206	-7	0.58041	11	0.48462	53
0.34239	39	0.44127	41	0.49204	-5	0.59834	10	0.50463	48
0.35926	35			0.51056	-3			0.52314	44
[HMIM]BF ₄ - dmf		[HMIM]BF ₄ - CHCl ₃		[OMIM]BF ₄ - H ₂ O		[OMIM]BF ₄ - methanol		[OMIM]BF ₄ - ethanol	
0.09759	-1246	0.00341	3471	0.00802	-539	0.01143	-1394	0.01716	-7787

0.17783	-583	0.00680	1444	0.01591	-354	0.02259	-649	0.03362	-3771
0.24496	-368	0.01017	889	0.02367	-298	0.03351	-395	0.04959	-2441
0.30196	-273	0.01352	617	0.03131	-221	0.04419	-293	0.06505	-1771
0.35095	-217	0.01684	493	0.03884	-173	0.05463	-219	0.08001	-1355
0.39352	-179	0.02014	394	0.04625	-137	0.06485	-171	0.09456	-1047
0.43085	-151	0.02342	329	0.05354	-115	0.07485	-139	0.10854	-831
0.46385	-128	0.02667	282	0.06073	-98	0.08463	-115	0.12215	-691
0.49323	-111	0.02991	246	0.06780	-86	0.09422	-98	0.13535	-598
0.51956	-97	0.03312	221	0.07477	-74	0.10361	-84	0.14817	-534
0.54329	-87	0.03631	194	0.08164	-67	0.11279	-73	0.16066	-485
0.56479	-79	0.03948	178	0.08841	-60	0.12181	-65	0.17268	-443
0.58435	-73	0.04263	159	0.09507	-55	0.13062	-58	0.18442	-408
0.60223	-67	0.04576	149	0.10164	-49	0.13927	-52	0.19583	-376
[OMIM]BF ₄ - 1-propanol		[OMIM]BF ₄ - ethylene glycol		[OMIM]BF ₄ - formamide		[OMIM]BF ₄ - DMF		[OMIM]BF ₄ - CHCl ₃	
0.02232	-3734	0.0304	-384	0.02378	389	0.03107	1294	0.07909	8279
0.04364	-1619	0.059	-149	0.04645	187	0.06027	748	0.14658	3797

0.06406	-960	0.08597	-79	0.06814	122	0.08777	551	0.20486	2498
0.08362	-661	0.11143	-47	0.08878	87	0.1137	428	0.25569	1803
0.10239	-498	0.13552	-29	0.10857	68	0.13819	345	0.30041	1394
0.12040	-385	0.15833	-18	0.12751	57	0.16137	287	0.34006	1146
0.13770	-311	0.17997	-14	0.14567	50	0.18333	238	0.37545	967
0.15434	-259	0.20052	-8	0.16309	42	0.20418	199	0.40725	830
0.17035	-220	0.22007	-7	0.17981	37	0.22398	179	0.43596	733
0.18576	-191	0.23869	-6	0.19587	33	0.24283	168	0.46202	654
0.20061	-166	0.25643	-3	0.21132	32	0.26078	157	0.48578	589
0.21492	-146	0.27337	-3	0.22619	28	0.2779	143	0.50753	544
0.22874	-129	0.28956	-4	0.24051	24	0.29424	133	0.52751	494
0.24207	-116	0.30504	-2	0.25431	23	0.30986	125	0.54593	444

Table S2: The Values of Fitting Parameters of eq 1 for Ionic Liquids in Different Solvents, Average Root Mean Squares Deviation for all the calculations < 4%

Solvents	[EMIM][BF ₄]		[BMIM][BF ₄]		[HMIM][BF ₄]		[OMIM][BF ₄]	
Water	q ₁	-2882±33	q ₁	-847 ±6	q ₁	3609±13	q ₁	3504±41
	q ₂	2424±63	q ₂	568±10	q ₂	-3618±26	q ₂	-4817±141
	$H^{E,\infty}_{IL}$	916±43	$H^{E,\infty}_{IL}$	332±14	$H^{E,\infty}_{IL}$	-922±69	$H^{E,\infty}_{IL}$	-1050±23
MeOH	q ₁	-9253±156	q ₁	-4249±16	q ₁	-1936±17	q ₁	10212±43
	q ₂	7320±269	q ₂	2494±20	q ₂	1528±30	q ₂	-14479±124
	$H^{E,\infty}_{IL}$	3056±140	$H^{E,\infty}_{IL}$	1854±76	$H^{E,\infty}_{IL}$	648±25	$H^{E,\infty}_{IL}$	-1858±142
EtOH	q ₁	-	q ₁	-7161±28	q ₁	-394±3	q ₁	4828±23
	q ₂	-	q ₂	3956±34	q ₂	-32±6	q ₂	-4815±45
	$H^{E,\infty}_{IL}$	-	$H^{E,\infty}_{IL}$	3294±117	$H^{E,\infty}_{IL}$	310±6	$H^{E,\infty}_{IL}$	-1236±82
1-propanol	q ₁	-	q ₁	-8867±36	q ₁	8097±8	q ₁	-22418±79
	q ₂	-	q ₂	4813±44	q ₂	-5769±11	q ₂	-24239±170
	$H^{E,\infty}_{IL}$	-	$H^{E,\infty}_{IL}$	4147±140	$H^{E,\infty}_{IL}$	-2845±123	$H^{E,\infty}_{IL}$	-5310±398

Ethylene glycol	q ₁	-3930±9	q ₁	-3691±22	q ₁	-101±3	q ₁	2265±3
	q ₂	3832±45	q ₂	1796±25	q ₂	-92±5	q ₂	-2203±5
	$H^{E,\infty}_{IL}$	847±21	$H^{E,\infty}_{IL}$	1906±48	$H^{E,\infty}_{IL}$	139±6	$H^{E,\infty}_{IL}$	-584±43
Formamide	q ₁	-4023±40	q ₁	-3656±43	q ₁	-3285±21	q ₁	-2166±4
	q ₂	2410±155	q ₂	2270±63	q ₂	2175±32	q ₂	2236±9
	$H^{E,\infty}_{IL}$	1738±6	$H^{E,\infty}_{IL}$	1529±63	$H^{E,\infty}_{IL}$	1285±59	$H^{E,\infty}_{IL}$	550±36
DMF	q ₁	5068±29	q ₁	7783±107	q ₁	5567±34	q ₁	-5630±57
	q ₂	-2984±37	q ₂	-4799±147	q ₂	-3440±46	q ₂	4759±111
	$H^{E,\infty}_{IL}$	-2204±87	$H^{E,\infty}_{IL}$	-3231±135	$H^{E,\infty}_{IL}$	-2319±104	$H^{E,\infty}_{IL}$	1785±84
CHCl ₃	q ₁	-	q ₁	1656±20	q ₁	-43784±176	q ₁	-37328±216
	q ₂	-	q ₂	1331±21	q ₂	112706±897	q ₂	24860±309
	q ₃	-	q ₃	0	q ₃	0	q ₃	-1335831 ±45267
	$H^{E,\infty}_{IL}$	-	$H^{E,\infty}_{IL}$	-329±122	$H^{E,\infty}_{IL}$	4403±412	$H^{E,\infty}_{IL}$	14498±738
D ₂ O	q ₁	-	q ₁	-446±9	q ₁	-	q ₁	-
	q ₂	-	q ₂	271±14	q ₂	-	q ₂	-
	$H^{E,\infty}_{IL}$	-	$H^{E,\infty}_{IL}$	197±10	$H^{E,\infty}_{IL}$	-	$H^{E,\infty}_{IL}$	-

Table S3: The A_L values for different solvents at 298.15 K

Solvent	$A_L / (\text{J kg}^{-1} \text{mol}^{-3/2})$	Solvent	$A_L / (\text{J kg}^{-1} \text{mol}^{-3/2})$
Water	2879	Ethylene Glycol	2948
D ₂ O	2707	Formamide	1394
Methanol	4717	DMF	4186
Ethanol	5622	Chloroform	2800
1-propanol	7002	-	-