10.1071/CH12308_AC

Australian Journal of Chemistry 2013, 66(1), 50-59

Supplementary Material

The Hydrogen Bonding Interactions between 1-Ethyl-3-Methylimidazolium Lactate Ionic Liquid and Methanol

Hongyan He[A,B], Hui Chen[A], Yanzhen Zheng[C], Xiaochun Zhang[A], Xiaoqian Yao[A], Zhiwu Yu[C] and Suojiang Zhang[A,D]

[A] Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China

[B] College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

[C] Department of Chemistry, Tsinghua University, Beijing 100084, China

[D] Corresponding author . Email: sjzhang@home.ipe.ac.cn.

S1: B3LYP/6-31++g (d,p) calculated structures and absolute energies of 1-Ethyl-3-methylimidazolium cation, Lactate anion and CH_3OH as shown in Fig. 1.

1-Ethyl-3-methylimidazolium cation

E(RB3LYP)=-344.57072273 a.u.

C	0.41089900	-0.81878500	-0.20653300
C	-0.15361600	1.31301200	-0.13564700
C	1.19011800	1.22615800	0.08768000
H	0.35729600	-1.89261200	-0.30276000
H	-0.80279700	2.17320300	-0.18419300
H	1.92577100	1.99446500	0.26830200
N	1.52416600	-0.11506200	0.03999400
N	-0.62242400	0.02508900	-0.31899400
C	2.87400100	-0.67120400	0.22256300
H	3.24015700	-0.41564300	1.21834800
H	2.82718000	-1.75505700	0.11992400
H	3.54086300	-0.26290500	-0.53870200
C	-2.88998300	-0.25732800	0.70024700

H	-2.52049200	-0.91918800	1.48860400
H	-2.91935100	0.76556500	1.08603700
C	-2.03507400	-0.36075300	-0.56081100
H	-2.01743100	-1.38112200	-0.95024000
H	-2.40693700	0.29004600	-1.35617000
H	-3.91453500	-0.55353600	0.45886000

Lactate anion

E(RB3LYP)= -343.10286694 a.u.

O	-1.48321700	-1.14931900	-0.22088900
C	-0.87994600	-0.06616600	-0.03907800
C	0.64227400	-0.03010700	-0.41084100
C	1.44938900	-1.05770300	0.38486300
O	-1.32608200	1.03607900	0.40559400
O	1.15008100	1.28677700	-0.18931300
H	0.33620400	1.73297500	0.14970900
H	0.72285500	-0.26876000	-1.48381800
H	2.50963900	-1.02165400	0.10194900
H	1.05826300	-2.06334500	0.20122500
H	1.37647600	-0.84365800	1.45812000

CH_3OH

E(RB3LYP)= -115.73497066 a.u.

C	0.66793300	-0.02071700	0.00003300
H	1.08346200	0.98939800	0.00003500
H	1.03036100	-0.54580600	0.89461700
H	1.03043200	-0.54582800	-0.89451000
O	-0.74955100	0.12245000	-0.00002100
H	-1.15544500	-0.75306400	-0.00017300

S2: B3LYP/6-31++g (d, p) calculated structures and absolute energies of [EMIM][LAC] (A–B), $[Emim]^+$ and methanol(C–F), $[LAC]^-$ and methanol (G–H) as shown in Fig. 6.

[EMIM][LAC](Fig. 6(A))

E(RB3LYP)= -687.81942112 a.u.

C	1.38832400	-0.44900400	-0.00323600
C	3.41892800	0.33772500	-0.43465800
C	3.53491400	-1.00133700	-0.20086000
H	0.28127800	-0.56689500	0.15524100

H	4.16689300	1.07424700	-0.68142200
H	4.39867000	-1.64711600	-0.20647700
N	2.25838000	-1.46906200	0.06595800
N	2.07680100	0.65905900	-0.30844800
C	1.86623200	-2.84764300	0.37405300
H	2.34546300	-3.17127900	1.30095400
H	0.78190500	-2.86981000	0.49215300
H	2.16136200	-3.50726200	-0.44511200
C	1.83231100	2.93164300	0.68853000
H	1.46653400	2.53327600	1.63940200
H	2.91259600	3.09615700	0.76754600
C	1.46681700	1.99964000	-0.46444600
H	0.38461600	1.83000000	-0.50640600
H	1.80919100	2.39698100	-1.42499700
H	1.35349000	3.90173700	0.52566600
O	-1.29887700	-1.08798000	0.40180100
C	-1.99247900	-0.05142500	0.16430500
C	-3.52457800	-0.16321800	0.31970000
C	-4.11581500	-1.23250600	-0.60258900
O	-1.53949600	1.07756900	-0.18232100
O	-4.13205400	1.09845000	0.06993700
H	-3.37688200	1.67930700	-0.14712000
H	-3.71679700	-0.45097400	1.36499700
H	-5.20122100	-1.27840100	-0.46741400
H	-3.68389400	-2.21230800	-0.37889400
H	-3.91396900	-0.98519900	-1.65081500

[EMIM][LAC](Fig. 6(B))

E(RB3LYP)= -687.81901685 a.u.

C	-1.31929700	-0.32747900	0.10414200
C	-3.52426800	-0.17642700	0.34391700
C	-3.21474100	-1.48118100	0.09242600
H	-0.24770400	-0.01824900	0.05506900
H	-4.47510100	0.30029200	0.52141500
H	-3.84574100	-2.35208100	0.01189000
N	-1.83892600	-1.55201000	-0.05405700
N	-2.32843000	0.52279800	0.34881100
C	-1.04550500	-2.75996000	-0.33263400
H	-1.37214600	-3.19126600	-1.28175300
H	0.00690000	-2.45644100	-0.38856000
H	-1.19541900	-3.48120700	0.47416100
C	-2.55633800	2.78489700	-0.67975000
H	-1.95407700	2.50617000	-1.54886800
H	-3.61414000	2.64338300	-0.92388200
C	-2.14286200	1.97347700	0.54700600

H	-1.08297600	2.11537700	0.76909100
H	-2.72201200	2.25940000	1.43005700
H	-2.39395800	3.84836400	-0.48052100
O	1.73756400	-1.36149900	-0.38320400
C	2.07009100	-0.16445100	-0.20706100
C	3.56479400	0.20995400	-0.31247900
C	4.41496300	-0.56387200	0.69782800
O	1.27112200	0.80256800	0.05046800
O	3.73956000	1.61273600	-0.13664300
H	2.83334100	1.94158400	0.01562900
H	3.88660100	-0.06298600	-1.32916200
H	5.46726800	-0.28170700	0.59014400
H	4.31205800	-1.64067500	0.53624100
H	4.10161300	-0.32566200	1.72043600

$[Emim]^+$ and methanol(Fig. 6C)

E(RB3LYP)= -460.32342906 a.u.

C	-0.05268300	0.17751600	-0.02115100
C	-2.10809900	0.90596900	-0.39358200
C	-1.31688900	1.99004800	-0.14809600
H	0.82028700	-0.45657300	0.10950700
H	-3.16040800	0.84236400	-0.62165700
H	-1.55158300	3.04272800	-0.12363500
N	-0.03881000	1.51384500	0.08238300
N	-1.30083800	-0.21517600	-0.31114500
C	1.14891100	2.32680200	0.38482900
H	0.97915600	2.88903600	1.30495500
H	1.99950600	1.65681200	0.51159100
H	1.33816700	3.01479900	-0.44126500
C	-2.56845500	-2.11720300	0.70403500
H	-1.99257900	-2.08061900	1.63311500
H	-3.48244200	-1.53126100	0.83598100
C	-1.74372500	-1.61863100	-0.48076400
H	-0.83915700	-2.21561200	-0.61514900
H	-2.31237500	-1.66318900	-1.41337200
H	-2.86033500	-3.15551900	0.52351900
C	3.78789600	-1.22463300	-0.51725000
H	3.42783400	-0.84517300	-1.47509900
H	4.75237400	-0.75930900	-0.29049700

H	3.90787100	-2.31062200	-0.58590700
O	2.79720400	-0.87065000	0.46874000
H	3.09185300	-1.19255800	1.33118800

$[Emim]^+$ and methanol(Fig. 6D)

E(RB3LYP)= -460.32079427 a.u.

C	-0.08447100	-0.96553900	-0.10070100
C	-0.11008700	1.21919800	-0.41432100
C	1.18464200	0.84353600	-0.19278600
H	-0.40333900	-1.99188700	0.00034400
H	-0.53508900	2.19008100	-0.61435700
H	2.11176500	1.40277300	-0.16394200
N	1.17739600	-0.52586000	0.00103900
N	-0.88701800	0.07630600	-0.35466900
C	2.36317600	-1.35623700	0.27841100
H	3.24077200	-0.71258600	0.21059200
H	2.28997300	-1.77832900	1.28261100
H	2.43121100	-2.15639900	-0.46065700
C	-3.09904000	0.55616400	0.70986200
H	-2.85896200	-0.01987400	1.60805000
H	-2.86058100	1.60742600	0.89412200
C	-2.35921600	0.01577200	-0.51213500
H	-2.61163300	-1.03021100	-0.70045200
H	-2.60450200	0.58203900	-1.41430700
H	-4.17598100	0.48248500	0.53493200
C	5.00383900	2.01160900	1.10288200
H	4.39994600	1.83556600	1.99483500
H	5.97886400	1.53067800	1.23325100
H	5.13883300	3.09038800	0.97247200
O	4.28413200	1.43764900	-0.00513800
H	4.79665000	1.58212400	-0.81175200

$[Emim]^+$ and methanol(Fig. 6E)

E(RB3LYP)= -460.32019489 a.u.

C	0.08740000	-0.81669200	-0.27885400
C	-0.35660900	1.25325800	0.36543600
C	0.98892100	1.04968700	0.48032300
H	-0.03012000	-1.82608000	-0.64242300
H	-0.97089400	2.12264600	0.58112000
H	1.77446800	1.71177800	0.80952600
N	1.24799500	-0.24793800	0.07429400
N	-0.89933300	0.07260900	-0.11235000
C	2.57008700	-0.88812600	0.03385700
H	2.99801100	-0.90383600	1.03778000
H	2.45918700	-1.91002900	-0.32824500
H	3.22331600	-0.33309700	-0.64180800
C	-3.16558200	-0.21570800	0.90255200
H	-2.81958400	-1.00496100	1.57623500
H	-3.13193500	0.74342800	1.42525400
C	-2.33721100	-0.17303600	-0.37871400
H	-2.39579700	-1.11658800	-0.92626700
H	-2.67668400	0.62336000	-1.04548400
H	-4.20801500	-0.42087100	0.64322600
C	-2.73363800	4.67097700	0.10690500
H	-2.43295100	4.37894900	-0.90092800
H	-3.81538300	4.84133600	0.11904200
H	-2.21156500	5.59467200	0.37834600
O	-2.36785600	3.58675600	0.97931500
H	-2.60266900	3.82665100	1.88528100

$[Emim]^+$ and methanol(Fig. 6F)

E(RB3LYP)= -460.31851602 a.u.

C	0.03795700	-0.95581300	0.05873300
C	-0.04273900	1.18899300	-0.46130900
C	1.25156300	0.87756200	-0.16346100
H	-0.25138200	-1.97859600	0.24611800
H	-0.46320900	2.13502800	-0.76297300
H	2.12605900	1.50862900	-0.16827700
N	1.28227900	-0.46751100	0.15961600

N	-0.78591000	0.03081800	-0.31837000
C	2.47846900	-1.23288000	0.53771100
H	2.92073000	-0.79667300	1.43502700
H	2.19135200	-2.26456300	0.74007500
H	3.19901700	-1.21071700	-0.28174000
C	-3.04799800	0.54535900	0.61658100
H	-2.82800600	0.07050400	1.57697600
H	-2.84250500	1.61619700	0.69996300
C	-2.24910200	-0.09389000	-0.51715300
H	-2.46445800	-1.16133400	-0.60411100
H	-2.47743000	0.36892100	-1.48063400
H	-4.11537300	0.42341100	0.41239300
C	1.48741300	5.01085400	-0.01848000
H	1.19198800	4.65823400	0.97151900
H	2.50913300	5.40253700	0.03647200
H	0.80521200	5.81068300	-0.32718500
O	1.40496300	3.87993900	-0.90256600
H	1.66981800	4.16499400	-1.78693400

$[LAC]^-$ and methanol (Fig. 6G)

E(RB3LYP)= -458.86387456 a.u.

O	0.37525500	-0.89925900	0.37780900
C	-0.35854500	0.09588700	0.12199100
C	-1.88381400	-0.07970800	0.38553000
C	-2.47810700	-1.22349200	-0.43898100
O	-0.01741900	1.22903400	-0.31696200
O	-2.55543900	1.14629300	0.09883800
H	-1.80538700	1.71106000	-0.19753300
H	-2.00453600	-0.31177500	1.45553300
H	-3.55044000	-1.32643200	-0.23169600
H	-1.96998900	-2.16268200	-0.20021800
H	-2.35584700	-1.01975100	-1.50928400
C	3.41951100	0.54126700	-0.04007200
H	4.27152500	0.70523800	-0.71626800
H	2.59191600	1.19616100	-0.34230700

H	3.73952500	0.84202500	0.97477500
O	3.04981700	-0.82177400	-0.09472700
H	2.07125500	-0.87191800	0.07653200

$[LAC]^-$ and methanol (Fig. 6H)

E(RB3LYP)= -458.85753754 a.u.

O	-2.58609000	-0.75204400	0.89272100
C	-1.63893200	-0.67819600	0.08155600
C	-0.67601200	0.55127000	0.21007200
C	-1.40411500	1.88324200	0.04314000
O	-1.31719900	-1.46804000	-0.86200500
O	0.34719700	0.40619400	-0.78854500
H	0.03392300	-0.44132400	-1.21492100
H	-0.20978500	0.51352800	1.20585900
H	-0.70630700	2.72417500	0.14025900
H	-2.18749000	1.97261500	0.80192300
H	-1.86951700	1.93620100	-0.94804200
C	3.27193200	-0.71939900	0.51061700
H	4.32405600	-0.71498500	0.82009500
H	2.65422000	-0.91025200	1.40250100
H	3.12424300	-1.56058100	-0.18544200
O	2.99084900	0.53002600	-0.08405000
H	2.04135700	0.53002800	-0.35950100

S3: B3LYP/6-31++g (d, p) calculated structures and absolute energies of a methanol molecule interacting with [EMIM][LAC] as shown in Fig. 7.

[EMIM][LAC] and methanol (Fig. 7A)

E(RB3LYP)= -803.57436550 a.u.

C	-1.64502900	0.21748100	-0.17942200
C	-3.74072900	-0.47763000	-0.40579900
C	-3.73623800	0.88082500	-0.52387000
H	-0.53993100	0.21543300	-0.04452200
H	-4.55200400	-1.18612700	-0.45646500

H	-4.54030400	1.57751000	-0.70008000
N	-2.42293400	1.29443500	-0.37744900
N	-2.43072300	-0.87006200	-0.19431400
C	-1.94898000	2.68320500	-0.46312400
H	-2.55052300	3.30307700	0.20544700
H	-0.89790100	2.73623400	-0.16302200
H	-2.05563100	3.03999600	-1.49049900
C	-2.32609200	-2.78714200	1.39673100
H	-1.86281000	-2.18243600	2.18185300
H	-3.40928700	-2.80561100	1.55963100
C	-1.95366400	-2.25666600	0.01379200
H	-0.86482100	-2.23439500	-0.11711200
H	-2.39596600	-2.86550700	-0.78057600
H	-1.94981300	-3.80952700	1.49657300
O	1.20807400	0.26438900	0.11086700
C	1.77756700	-0.87125600	-0.00235700
C	3.31986700	-0.90133700	-0.00268900
C	3.89989800	-0.14309500	-1.20164900
O	1.18401800	-1.97322800	-0.11344100
O	3.77912300	-2.24605400	0.00008100
H	2.96224200	-2.77711900	-0.06410900
H	3.65286200	-0.41202100	0.92511600
H	4.99258500	-0.19885700	-1.17632300
H	3.59629500	0.90802400	-1.18590800
H	3.55790400	-0.59640100	-2.13841600
C	2.01015800	3.54537000	1.23369100
H	1.74229500	4.60539400	1.28306400
H	1.87073700	3.10565000	2.23237200
H	3.07489700	3.47407900	0.96892100
O	1.18100100	2.93297000	0.26023200
H	1.38650100	1.96884400	0.21266600

[EMIM][LAC] and methanol (Fig. 7B)

E(RB3LYP)= -803.57236950 a.u.

C	-1.35685300	-0.79361900	0.27093500

C	-3.32977300	-0.04211400	0.94113700
C	-3.54940200	-1.09921600	0.10818200
H	-0.27010000	-0.94015200	0.11061600
H	-4.02611600	0.59265200	1.46406000
H	-4.46720100	-1.55605600	-0.22605900
N	-2.30441200	-1.55459000	-0.29371900
N	-1.95820400	0.12881400	1.03037200
C	-2.02300200	-2.64940600	-1.22465700
H	-2.44383100	-2.41646100	-2.20549000
H	-0.94052000	-2.75214700	-1.30815800
H	-2.45422400	-3.57884000	-0.84583200
C	-1.70972200	2.57908400	1.42301200
H	-1.56178100	2.74839900	0.35321300
H	-2.76129400	2.74679500	1.67977700
C	-1.24088300	1.17451000	1.79434700
H	-0.18340200	1.04928800	1.54812900
H	-1.38780400	0.96442600	2.85900600
H	-1.11234200	3.30692600	1.98037700
O	1.39566600	-1.43696800	-0.23786000
C	2.07020300	-0.38391300	-0.08979600
C	3.60407100	-0.50492600	0.01858600
C	4.02382200	-1.40789600	1.18122100
O	1.59395900	0.79861900	-0.01784700
O	4.19524000	0.78160000	0.15365400
H	3.43758600	1.39616500	0.13082400
H	3.94830400	-0.95930100	-0.92358000
H	5.11563400	-1.47177600	1.22256400
H	3.60877100	-2.41179300	1.05487500
H	3.67178000	-0.99312100	2.13240200
C	-0.11951600	2.00228300	-2.82267900
H	-1.02006100	2.25598400	-3.39115500
H	0.50301200	2.90522400	-2.74198700
H	0.44356700	1.24501700	-3.38751100
O	-0.52866600	1.52304200	-1.55195000
H	0.27507300	1.27014000	-1.03234900

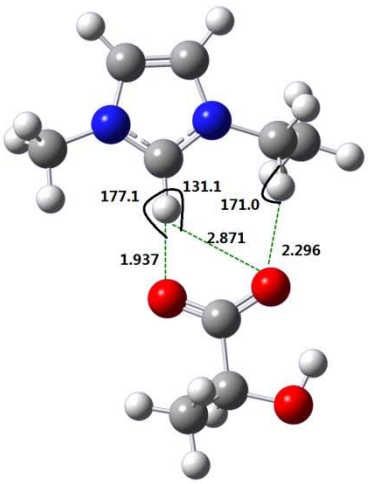
[EMIM][LAC] and methanol (Fig. 7C)

E(RB3LYP)= -803.56033166 a.u.

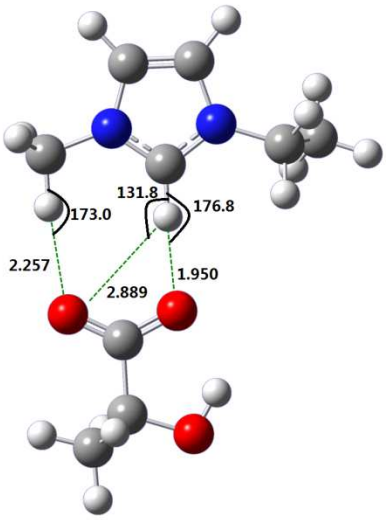
C	-0.36620000	-0.46312500	-0.22475800
C	-2.44103900	0.30576000	-0.03457700
C	-2.51639100	-1.03293300	-0.28249900
H	0.74682900	-0.56890900	-0.25498400
H	-3.23514100	1.01812100	0.11888000
H	-3.37872500	-1.67239500	-0.37801000
N	-1.21283800	-1.49029200	-0.39795200
N	-1.09538600	0.63849700	-0.00113700
C	-0.77419100	-2.86348100	-0.65892800
H	-1.15474000	-3.19672800	-1.62739700
H	0.31679700	-2.87265900	-0.66820400
H	-1.14150500	-3.52532200	0.12890800
C	-0.75707400	2.91473000	-0.95926900
H	-0.28078000	2.52211000	-1.86239400
H	-1.82301600	3.06775800	-1.16056500
C	-0.51744200	1.98151400	0.22567800
H	0.55446100	1.82189400	0.38801800
H	-0.96937700	2.37505800	1.14151900
H	-0.30953100	3.88896700	-0.74089500
O	2.37355800	-1.10688500	-0.33761600
C	3.02347500	-0.05542100	-0.05370400
C	4.56584200	-0.14392800	-0.05335700
C	5.07672100	-1.18077000	0.95045800
O	2.52309600	1.07328900	0.22461400
O	5.12644500	1.13396500	0.22442600
H	4.34314700	1.70409600	0.35401600
H	4.86678300	-0.45266800	-1.06643700
H	6.17091400	-1.21142100	0.92729000
H	4.68363000	-2.17264100	0.70893000
H	4.76529100	-0.91220500	1.96613600
C	-6.46807000	-0.01899500	1.14699300
H	-5.81963800	-0.23835900	1.99756300
H	-6.99236800	0.92529600	1.33964300

H	-7.20279900	-0.82783200	1.04810300
O	-5.61992700	0.06984700	-0.00223500
H	-6.16181300	0.26857400	-0.77624000

S4: The optimized structures and parameters of [EMIM][LAC] in condensed phase. The methanol solvent was used: methanol (ε=32.6).



-28.4 kJ/mol



-28.3 kJ/mol

S5: The Second-order interaction energies of selected anti-bonding orbital based on the NBO analysis of possible structures formed by a methanol molecule and [EMIM]$^+$ or [LAC]$^-$ as shown in Fig. 6: [Emim]$^+$ and methanol (C–F); [LAC]$^-$ and methanol (G–H).

Conformer	Proton Acceptor→Donor	E(2), kJ/mol
Fig. 6 (C)	$LP_{(1)O}–\sigma^*_{(1)C2–H15}$	12.38
	$LP_{(2)O}–\sigma^*_{(1)C2–H15}$	31.74
	$LP_{(1)O}–\sigma^*_{(1)C6–H18}$	3.85
Fig. 6 (D)	$LP_{(1)O}–\sigma^*_{(1)C4–H16}$	4.31
	$LP_{(2)O}–\sigma^*_{(1)C4–H16}$	32.45
	$LP_{(1)O}–\sigma^*_{(1)C6–H19}$	9.66
	$LP_{(2)O}–\sigma^*_{(1)C6–H19}$	0.46
Fig. 6 (E)	$LP_{(1)O}–\sigma^*_{(1)C5–H17}$	13.38
	$LP_{(2)O}–\sigma^*_{(1)C5–H17}$	29.44
	$LP_{(1)O}–\sigma^*_{(1)C8–H23}$	0.62
Fig. 6 (F)	$LP_{(1)O}–\sigma^*_{(1)C4–H16}$	1.13
	$LP_{(2)O}–\sigma^*_{(1)C4–H16}$	9.79
	$LP_{(1)O}–\sigma^*_{(1)C5–H17}$	1.46
	$LP_{(2)O}–\sigma^*_{(1)C5–H17}$	3.19
Fig. 6 (G)	$LP_{(1)O}–\sigma^*_{(1)O–H}$	32.20

	$LP_{(2)O}–\sigma^*_{(1)O–H}$	87.86
Fig. 6 (H)	$LP_{(1)O}–\sigma^*_{(1)O–H}$	11.67
	$LP_{(2)O}–\sigma^*_{(1)O–H}$	92.42