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Applying parachor method to the prediction of ionic liquids surface tension based on modified group contribution

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ABSTRACT

In this paper parachor method is applied to estimate surface tension of pure imidazolium based ionic liquids at the different temperatures. For this prediction a Modified Group Contribution Method is proposed to estimate the surface tension of ionic liquids covering wide ranges of temperature and chain length based on experimental data collected from literatures. The average relative error obtained from the comparison of experimental and calculated surface tension values for studied ionic liquids (less than 8.5%) shows the model has good accuracy in comparison with other predictive equations.

1. Introduction

Ionic liquids (ILs) are salts composed of an organic cation and an inorganic anion which are liquid at ambient conditions [1,2]. Because of their interesting physical and chemical properties such as negligible vapor pressure, unique permittivity, high thermal stability, good solubility for both organic and inorganic substances, and high electrical conductivity [3–5], they offer new applications in preparative chemistry and chemical engineering as new reaction media for chemical synthesis [6], biocatalysts [7], nanomaterial technologies [8], electrochemical applications [9] and separation processes [10]. Reactions have been proposed for ILs, taking advantage of phase transitions due to changes of temperature or composition, that enable elegant separation of products, educts, and catalyst. So far, most effort in ILs has been focused on the experimental and theoretical investigation of their physical and chemical properties, such as melting point, viscosity, density, thermal and electrochemical stability, solvent properties, and surface tension [11–18].

The surface tension is an important property in the study of physics and chemistry at free surfaces. It affects the transfer rates of vapor absorption where a vapor–liquid interface exists. Such data are of importance to scientists, engineers and practitioners in many fields such as chemical process and reactor engineering, flow and transport in porous media, materials selection and engineering, etc. [19,20].

Sometimes developing ionic liquids for a given purpose if experimentally measured surface tension data are not available, theoretical or empirical methods must be used to establish if the surface tensions are within acceptable limiting values defined in the design specifications. For this purpose prediction methods for surface tension of ILs are required [21].

Recently, Deetlefs et al. [11] attempted to predict surface tension by using the quantitative structure–property relationship (QSPR) correlations previously proposed by Knotts et al. [22]. Then, Gardas et al. [21] applied the QSPR correlation of Knotts et al. to predict surface tensions of assembled large database for ionic liquids. He et al. [23] presented a new method for estimating surface tensions of ionic liquids by combining the corresponding states theory with the group-contribution method, and this simple method allows the rapid and facile estimation of surface tension with acceptable deviations for a wide range of ILs. Ghatee et al. [24] correlated a linear relation between logarithm of surface tension and fluidity involving the characteristic exponent. Also the corresponding states theory has been used for the prediction of surface tension of ionic liquids [25].

In this work, we propose simple regularities for predicting the surface tension of ILs, based on parachor method using the Modified Group Contribution Method developed by Lydersen [26], and Joback and Reid [27].

Subsequent tests of this method in predicting surface tension for number of different types of ionic liquid have confirmed the validity of the presented approach. The percentage deviations in surface tension are less than 8.5% in the different temperatures and chain length.

2. Surface tension models

In order to be able to calculate the surface tension of pure ILs at various temperatures from their thermophysical and volumetric properties, the MacLeod model have been suggested [28]. It expresses the

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Table 1
Calculated physical property of studied ionic liquids using Eqs. (5)–(10).

	T/K	T_b/K	T_c/K	V_c/	ρ/g.cm^{-3}
[C_2mim][NTf_2]	298.15	822.34	1251.48	846.94	1.51870
[C_3mim][NTf_2]	298.15	845.22	1261.66	904.05	1.49598
[C_4mim][NTf_2]	298.15	868.10	1272.40	961.16	1.45900
[C_5mim][NTf_2]	298.15	890.98	1283.70	1018.27	1.42589
[C_6mim][NTf_2]	298.15	913.86	1295.54	1075.38	1.39632
[C_7mim][NTf_2]	298.15	936.74	1298.36	1132.49	1.36974
[C_8mim][NTf_2]	298.15	959.62	1301.05	1189.60	1.34801
[C_{10}mim][NTf_2]	298.15	1005.38	1306.10	1303.82	1.31112
[C_3mpy][NTf_2]	293.15	829.10	1228.90	981.70	1.41910
[C_2C_2im][NTf_2]	293.15	845.22	1255.55	904.05	1.49649
[C_4mmim][NTf_2]	293.15	891.68	1281.00	1045.00	1.37451
[emim] [BF_4]	298.15	438.90	616.40	557.80	1.24198
[prmim] [BF_4]	298.15	530.40	706.30	786.20	1.62000
[bmim] [BF_4]	293.15	476.18	646.20	655.00	1.20862
[pmim] [BF_4]	298.15	499.06	662.77	712.11	1.18247
[hmim] [BF_4]	298.15	530.40	706.30	786.20	1.62000
[hemim] [BF_4]	298.15	544.82	707.69	826.33	1.13354
[omim][BF_4]	288.15	586.74	751.93	883.44	1.12616
[dmim] [BF_4]	293.15	613.46	781.60	997.66	1.09356
[emim][PF_6]	298.15	256.20	498.20	656.40	1.31990
[prmim][PF_6]	318.33	463.54	601.59	705.39	1.31558
[bmim][PF_6]	293.15	486.42	625.39	762.50	1.28847
[bmmim][PF_6]	293.15	486.42	625.39	762.50	1.28847
[pmim][PF_6]	298.15	577.50	742.10	819.60	1.30278
[hmim][PF_6]	293.15	532.18	672.97	876.72	1.00004
[hemim][PF_6]	298.15	623.20	787.80	933.80	1.25198
[omim][PF_6]	298.15	577.94	720.82	990.94	1.19438
[nmim][PF_6]	298.15	669.00	834.10	1048.10	1.21115
[dmim][PF_6]	301.15	623.70	769.29	1105.16	1.16070
[bmim][Br]	293.15	655.40	892.84	811.71	1.18836
[bmim][I]	293.15	613.70	871.20	607.50	1.49390
[hmim][I]	298.15	659.50	904.84	721.68	1.33979
[omim][I]	293.15	614.29	1690.10	952.87	1.14992
[bmim][Cl]	298.15	558.00	789.00	568.80	1.10488
[hmim][Cl]	298.15	603.84	829.22	682.97	1.06626
[omim][Cl]	298.15	649.60	869.48	797.19	1.03797
[emim][$MeSO_4$]	298.15	646.20	990.38	602.67	1.28380
[bmim][$MeSO_4$]	298.15	735.60	1081.60	716.90	1.21934
[hmim][$MeSO_4$]	298.15	737.72	1054.35	831.11	1.16826
[prmim][$MeSO_4$]	298.15	669.08	1006.07	659.78	1.24663
[omim][$MeSO_4$]	298.15	783.48	1087.77	945.33	1.13132
[mmim][$MeSO_4$]	298.15	666.90	1040.00	545.56	1.22000
[emim][$EtSO_4$]	298.15	669.08	1006.07	659.78	1.24799
[bmim][$EtSO_4$]	298.15	714.84	1038.04	774.00	1.63894
[prmim][$EtSO_4$]	298.15	691.96	1021.95	716.89	1.21647
[hmim][$EtSO_4$]	298.15	760.60	1070.92	888.22	1.14865
[omim][$EtSO_4$]	298.15	806.36	1104.92	1002.44	1.11586
[mmim][$EtSO_4$]	298.15	669.78	984.52	669.48	1.23778
[emim][Otf]	298.15	651.40	898.80	653.40	1.37640
[bmim][Otf]	298.45	720.00	956.30	824.80	1.27292
[omim][Otf]	298.15	799.20	1088.70	979.10	1.21471
[C_4mim][I_3]	298.35	801.42	1107.10	809.04	2.07503
[C_4mim][I_5]	298.85	989.10	1333.50	1010.62	2.76289
[C_4mim][I_7]	298.15	1176.78	1552.74	1212.20	2.91931
[C_2mim][I_7]	298.15	1131.02	1536.07	1097.98	1.91455
[C_4mim][I_9]	298.05	1364.46	1766.73	1413.78	3.02804
[C_2mim][Pro]	298.15	578.12	831.22	534.32	1.22163
[C_3mim][Pro]	298.15	601.00	839.72	591.43	1.18976
[C_4mim][Pro]	298.15	623.88	859.96	648.54	1.16220
[C_5mim][Pro]	298.15	646.76	880.27	705.65	1.13894
[C_6mim][Pro]	298.15	669.64	900.68	762.76	1.11899

Table 2
Comparison of experimental and calculated surface tensions of studied imidazolium based ionic liquids as typical.

Ionic liquid	T/K	σ_{exp}/mN.m^{-1}	σ_{cal}/mN.m^{-1}	Ref.
[C_2mim][NTf_2]	298.15	37.01	36.17	[32]
[C_3mim][NTf_2]	298.15	35.86	35.81	[32]
[C_4mim][NTf_2]	298.15	33.74	35.46	[32]
[C_5mim][NTf_2]	298.15	32.87	35.18	[32]
[C_6mim][NTf_2]	298.15	30.88	34.93	[32]
[C_7mim][NTf_2]	298.15	31.33	34.51	[32]
[C_8mim][NTf_2]	298.15	31.79	33.28	[32]
[C_{10}mim][NTf_2]	298.15	31.32	26.54	[32]
[C_3mpy][NTf_2]	293.15	36.00	39.15	[33]
[C_2C_2im][NTf_2]	293.15	35.76	40.08	[33]
[C_4mmim][NTf_2]	293.15	37.40	33.96	[33]
[emim] [BF_4]	298.15	54.40	55.73	[34]
[prmim] [BF_4]	298.15	59.00	53.59	[35]
[bmim] [BF_4]	293.15	44.81	46.39	[24]
[pmim] [BF_4]	298.15	39.60	40.86	[36]
[hmim] [BF_4]	298.15	36.80	39.47	[37]
[hemim] [BF_4]	298.15	34.40	36.07	[38]
[omim][BF_4]	298.15	30.70	33.91	[24]
[dmim] [BF_4]	293.15	23.65	24.39	[39]
[prmim][PF_6]	318.33	46.41	46.18	[40]
[bmim][PF_6]	293.15	44.10	38.83	[24]
[bmmim][PF_6]	303.15	44.80	32.58	[41]
[pmim][PF_6]	298.15	44.51	39.80	[4]
[hmim][PF_6]	293.15	39.02	33.31	[24]
[hemim][PF_6]	298.15	30.86	34.34	[4]
[omim][PF_6]	298.15	33.95	35.25	[40]
[nmim][PF_6]	298.15	27.55	30.17	[4]
[dmim][PF_6]	301.15	30.70	29.90	[42]
[omim][Br]	293.15	32.00	38.75	[43]
[bmim][I]	293.15	53.30	54.14	[24]
[hmim][I]	298.45	40.23	42.95	[11]
[omim][I]	293.15	32.70	31.55	[43]
[bmim][Cl]	298.15	47.80	47.59	[24]
[hmim][Cl]	298.15	42.50	45.68	[24]
[omim][Cl]	298.15	33.80	38.77	[24]
[emim][$MeSO_4$]	298.15	62.90	57.11	[44]
[bmim][$MeSO_4$]	298.15	45.90	48.02	[45]
[hmim][$MeSO_4$]	298.15	33.59	32.23	[46]
[prmim][$MeSO_4$]	298.15	52.30	55.07	[44]
[omim][$MeSO_4$]	298.15	30.41	29.43	[46]
[mmim][$MeSO_4$]	298.15	55.46	60.76	[46]
[emim][$EtSO_4$]	298.15	46.96	50.20	[47]
[bmim][$EtSO_4$]	298.15	41.70	42.61	[44]
[prmim][$EtSO_4$]	298.15	48.60	53.42	[44]
[hmim][$EtSO_4$]	298.15	31.77	31.03	[46]
[omim][$EtSO_4$]	298.15	28.67	28.06	[46]
[mmim][$EtSO_4$]	298.15	58.30	55.82	[46]
[emim][Otf]	298.15	39.20	40.00	[48]
[bmim][Otf]	298.45	33.97	29.87	[11]
[omim][Otf]	298.15	28.50	36.27	[43]
[C_4mim][I_3]	298.35	51.84	41.75	[11]
[C_4mim][I_5]	298.85	55.26	39.01	[11]
[C_4mim][I_7]	298.15	58.19	40.00	[11]
[C_2mim][I_7]	298.15	63.41	52.44	[11]
[C_4mim][I_9]	298.05	64.18	46.15	[11]
[C_2mim][Pro]	298.15	39.60	45.74	[49]
[C_3mim][Pro]	298.15	38.40	43.55	[49]
[C_4mim][Pro]	298.15	37.00	41.67	[49]
[C_5mim][Pro]	298.15	35.70	40.09	[49]
[C_6mim][Pro]	298.15	34.80	38.55	[49]

temperature-independent relationship between density, ρ, and surface tension, σ, Eq. (1).

$$\sigma^{1/4} = K.\rho \tag{1}$$

where K is a constant which is independent of temperature. It is a characteristic of the compound under consideration. Shortly afterwards, Sugden [29] slightly modified MacLeod's original expression by multiplying each side of the expression with molecular weight, M_w, to give a constant $K \times M_w$, Eq. (2), which he called the parachor, P_{ch}, Eq. (3).

$$M_W.\sigma^{1/4} = K.M_W.\rho \tag{2}$$

$$P_{ch} = \frac{M_W.\sigma^{1/4}}{\rho} = K.M_W \tag{3}$$