

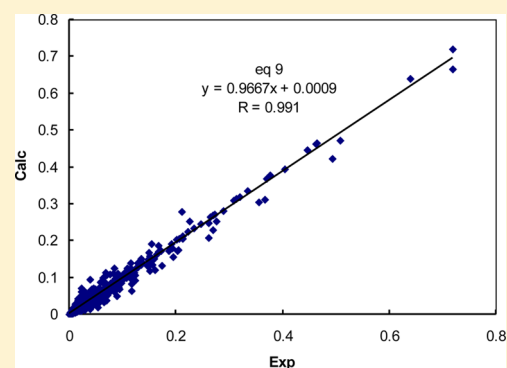
Mathematical Representation of Viscosity of Ionic Liquid + Molecular Solvent Mixtures at Various Temperatures Using the Jouyban–Acree Model

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ABSTRACT: The viscosity of room temperature ionic liquid + molecular solvents is correlated using the Jouyban–Acree model, and the accuracy of the model is evaluated using average relative deviations (ARD) of the calculated and experimental values. The overall ARD of 6.9 % was obtained for the proposed model where the overall ARD for a similar model from the literature was 22.4 %. The mean difference between ARDs of the models was statistically significant. Combined forms of the Jouyban–Acree model and the Abraham parameters were used for predicting the viscosity of the mixtures at various temperatures. The overall ARD for the investigated mixtures was 15.0 % when the experimental viscosity of the pure solvents was included. The ARD of the *in silico* version of the model was 20.7 %.



INTRODUCTION

Room temperature ionic liquids (RTILs) are a new class of solvents attracting considerable attention in the pharmaceutical/chemical industries. RTILs are used in manufacturing nanomaterials, high temperature lubricants, excipients for new drug delivery systems, novel stationary phases for gas chromatographic systems, and extraction solvents for separation of analytes. Very low vapor pressure, multiple solvation interactions with organic and inorganic compounds, very good chemical and thermal stability, high ionic conductivity, and wide melting point temperature ranges are the main advantages of RTILs over common molecular solvents. In addition to the applications of RTILs, their mixtures with molecular solvents are used in the industry providing wider physicochemical properties. Viscosity data of the mixtures are required in some related computations and a number of attempts have been made to collect the experimental values of the viscosity and density of these mixtures.^{1–23} Despite these experimental efforts, a number of mathematical models were proposed to compute the properties. The aims of this work are to propose a mathematical model to fit the viscosity data of RTILs + solvent mixtures at various temperatures and also provide global versions of the model to predict the viscosity data.

COMPUTATIONAL METHODS

Larriba et al.¹⁰ used Bringham mixing rule to estimate the viscosity of binary mixtures containing two ionic liquids. The equation is a reciprocal viscosity prediction as

$$\frac{1}{(\eta_{\text{mix}})_T} = \frac{x_1}{(\eta_1)_T} + \frac{x_2}{(\eta_2)_T} \quad (1)$$

where $(\eta_{\text{mix}})_T$ is the viscosity of the binary mixture at a given temperature (T), $(\eta_1)_T$ and $(\eta_2)_T$ denote the viscosity of RTIL and molecular solvent, x_1 and x_2 are mole fractions of RTIL and molecular solvent, respectively. One could probably generalize the equation to include other mixture compositions, such as volume fractions, mass fractions, etc. The equation is a strictly empirical equation. It is an outright prediction of viscosity in that there are no curve-fit parameters. All that one needs is the viscosity of the two pure liquids at each temperature studied.

Domanska and co-workers¹⁵ described the temperature dependence of viscosity with the Vogel–Fulcher–Tamman (VFT) equation

$$\eta = AT^{0.5} \exp\left(\frac{B}{T - T_0}\right) \quad (2)$$

and Wang et al.¹ used a slightly different variation

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \quad (3)$$

where A , T_0 , B , and η_0 are curve-fitting parameters depending on which temperature dependence was used. In each study,

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Table 1. Details of the Investigated Experimental Viscosity Data Collected from the Literature and the Average Absolute Relative Deviations (ARDs) of Equations 5 and 6

no.	RTIL	molecular solvent/RTIL	ref no.	N	eq 5	eq 6	no.	RTIL	molecular solvent/RTIL	ref no.	N	eq 5	eq 6
1	[AP4443][ALA]	water	1	30	37.6	7.8	25	[C4MIM][PF6]	cyclopentanone	13	15	7.4	0.9
2	[AP4443][LEU]	water	1	30	50.7	8.1	26	[C4MIM][PF6]	dimethyl formamide	12	66	33.3	4.8
3	[AP4443][VAL]	water	1	30	32.3	7.2	27	[C4MIM][PF6]	ethyl acetate	13	15	15.9	1.2
4	[BHEAP]	1-propanol	2	52	16.0	21.4	28	[C4MIM][PF6]	methanol	8	15	25.3	1.7
5	[BHEAP]	ethanol	2	52	17.8	25.3	29	[C4MIM][PF6]	pentanone	13	15	2.8	0.4
6	[BHEAP]	methanol	2	52	15.9	31.9	30	[C6MIM][Br]	water	14	85	186.2	9.7
7	[BMIM][ALA]	benzyl alcohol	3	44	4.0	1.6	31	[C8IQUIN][NTf2]	1-butanol	15	55	7.7	31.9
8	[BMIM][ALA]	methanol	3	44	6.2	7.3	32	[C8IQUIN][NTf2]	2-phenylethanol	15	55	7.1	1.9
9	[BMIM][BF4]	dimethyl sulfoxide	4	77	8.6	1.2	33	[EMIM][BF4]	water	16	77	9.4	4.9
10	[BMIM][BF4]	ethylene glycol	4	55	8.1	3.5	34	[EMIM][EtSO4]	water	17	56	16.9	12.8
11	[BMIM][BF4]	water	5	88	7.1	4.0	35	[EMISE]	1-propanol	18	33	2.3	3.5
12	[BMIM][CF3SO3]	water	6	77	9.5	6.8	36	[EMISE]	2-propanol	18	33	3.1	4.8
13	[BMIM][PF6]	dimethyl sulfoxide	8	15	9.7	3.2	37	[EMISE]	ethanol	19	36	2.8	4.0
14	[BMIM][PF6]	methanol	8	15	25.6	1.7	38	[EMISE]	methanol	18	39	6.2	7.1
15	[BMIM][PF6]	methyl methacrylate	7	143	11.8	4.7	39	[EMISE]	water	19	30	4.3	5.2
16	[BMIM][PF6]	tetrahydrofuran	8	15	7.4	6.4	40	[EPY][SO4]	ethanol	20	33	6.7	3.8
17	[BMIM][SCN]	1-butanol	9	72	5.6	5.2	41	[EPY][SO4]	propan-1-ol	20	36	243.5	24.3
18	[BMIM][SCN]	1-hexanol	9	72	3.9	4.4	42	[HMIM][Tf2N]	1-octene	21	24	19.9	1.0
19	[BMIM][SCN]	1-pentanol	9	78	4.4	5.4	43	[OCPY][BF4]	water	11	140	17.8	7.2
20	[BPY][BF4]	[BPY][Tf2N]	10	72	5.9	1.1	44	[OMIM][BF4]	ethanol	22	104	32.6	4.0
21	[BUPY][BF4]	water	11	130	15.0	8.1	45	[PDMIM][BF4]	water	23	88	7.4	3.8
22	[C4MIM][PF6]	2-butanone	13	15	8.8	0.8						22.4	6.9
23	[C4MIM][PF6]	acetone	13	15	2.6	0.7							
24	[C4MIM][PF6]	acetonitrile	8	15	35.3	2.0							

the authors calculated the curve-fit coefficients for each of the binary solvent mixtures. There was no attempt to incorporate a compositional dependence into the coefficients. One might be able to reasonably put these two ideas together as

$$\frac{1}{(\eta_{\text{mix}})_T} = \frac{x_1}{\eta_{0,1} \exp\left(\frac{B_1}{T-T_{0,1}}\right)} + \frac{x_2}{\eta_{0,2} \exp\left(\frac{B_2}{T-T_{0,2}}\right)} \quad (4)$$

in which the three curve-fit parameters for each pure solvent could be computed by fitting the viscosity of each as a function of temperature. Predictions based on the above equations could be compared to eq 4 as it is a logical combination of two ideas being used in the recent literature.

The Eyring kinetic equation was used for correlating viscosity ($\eta_{m,T}$) data of binary mixtures by Gong et al.²⁴ The equation is

$$\eta_{m,T} = (A_1 + A_2 x_1) \exp\left[\frac{\left(A_3 + \frac{A_4}{T}\right) + \left(A_5 + \frac{A_6}{T}\right)x_1 + \left(A_7 + \frac{A_8}{T}\right)x_1^2}{RT}\right] \quad (5)$$

where A_1 – A_8 are the model constants calculated using a nonlinear least-squares analysis, R is the gas constant, and T is the absolute temperature.

The purpose of this work is to present the capabilities of the Jouyban–Acree model^{25–27} and its combined version with the Abraham parameters for representing the experimental data. The basic model for describing the physicochemical properties ($P_{m,T}$) of the binary mixtures with respect to solvent composition and temperature is

$$\ln P_{m,T} = x_1 \ln P_{1,T} + x_2 \ln P_{2,T} + J_0 \left[\frac{x_1 x_2}{T} \right] + J_1 \left[\frac{x_1 x_2 (x_1 - x_2)}{T} \right] + J_2 \left[\frac{x_1 x_2 (x_1 - x_2)^2}{T} \right] \quad (6)$$

where $P_{m,T}$, $P_{1,T}$, and $P_{2,T}$ are the numerical values of the property (viscosity, density, or molar volume) of the mixture and liquid 1 (RTIL in this work) and 2 (molecular solvent in this work) at temperature T , respectively, and J_i represents the model constants. The J_i terms could be calculated by regressing $(\ln P_{m,T} - x_1 \ln P_{1,T} - x_2 \ln P_{2,T})$ against $[x_1 x_2 / T]$, $[(x_1 x_2 (x_1 - x_2)) / T]$, and $[(x_1 x_2 (x_1 - x_2)^2) / T]$ by a no intercept least-squares analysis.²⁸

The correlated data was compared with the corresponding experimental data by computing the average absolute relative deviation (ARD) using

$$\text{ARD} = \frac{100}{N} \sum \left| \frac{\text{calculated}}{\text{experimental}} - 1.0 \right| \quad (7)$$

in which N is the number of data points in each set.

RESULTS

The gathered viscosity data were correlated using the proposed model and the names of the components, their references, and the ARD values for eqs 5 and 6 are listed in Table 1. The proposed model, that is, eq 6, is able to represent the viscosity of binary mixtures with the overall ARD of 6.9 ± 7.8 % (number of data sets, NDS = 45). The maximum ARD of 31.9 % was observed for [BHEAP] + methanol mixtures and the minimum value (0.4 %) was observed for [C4MIM][PF6] + pentanone. Excluding these two data sets reduces the

Table 2. Abraham Solvent Parameters for RTIL/Solvents^a

RTIL/molecular solvent	<i>c</i>	<i>e</i>	<i>s</i>	<i>a</i>	<i>b</i>	<i>v</i>
[BMIM][BF4]	-0.206	0.355	2.278	-0.172	-4.415	3.635
[BMIM][CF3SO3]	-0.191	0.272	2.362	-0.060	-4.273	3.603
[BMIM][PF6]	-0.113	0.150	2.521	-1.382	-4.572	3.641
[BMIM][SCN]	-0.481	-1.152	4.939	0.749	-5.310	3.768
[BPY][BF4]	-0.423	0.168	1.860	-0.257	-4.469	4.001
[BPY][Tf2N]	-0.267	0.082	1.610	-1.467	-4.174	3.785
[BUPY][BF4]	-0.423	0.168	1.860	-0.257	-4.469	4.001
[C4MIM][PF6]	-0.113	0.150	2.521	-1.382	-4.572	3.641
[C8IQUIN][NTf2]	0.149	-0.058	2.422	-2.861	-3.920	6.099
[EMIM][BF4]	-0.061	0.425	2.353	-0.483	-3.584	4.024
[EMIM][EtSO4]	-0.124	-0.013	2.252	1.524	-4.941	3.718
[EMISE]	-0.124	-0.013	2.252	1.524	-4.941	3.718
[EPY][SO4]	-0.341	-0.200	1.834	1.439	-4.995	4.084
[OCPY][BF4]	-0.275	0.028	2.040	-0.441	-4.581	4.197
[OMIM][BF4]	0.035	0.010	2.701	-1.566	-4.684	3.837
[PDMIM][BF4]	-0.192	0.577	2.572	-0.327	-4.150	4.169
1-butanol	0.376	0.434	-0.718	-0.097	-2.350	2.682
1-hexanol	-0.006	0.460	-0.940	0.142	-3.284	3.792
1-pentanol	0.185	0.367	-0.732	0.105	-3.100	3.395
1-propanol	0.148	0.436	-1.098	0.389	-3.893	4.036
2-propanol	0.102	0.315	-1.020	0.532	-3.865	4.023
acetone	0.313	0.312	-0.121	-0.608	-4.753	3.942
acetonitrile	0.413	0.077	0.326	-1.566	-4.391	3.364
dimethyl formamide	-0.305	-0.058	0.343	0.358	-4.865	4.486
dimethyl sulfoxide	-0.194	0.327	0.791	1.260	-4.540	3.361
ethanol	0.208	0.409	-0.959	0.186	-3.645	3.928
ethyl acetate	0.441	0.591	-0.699	-0.325	-4.261	3.666
ethylene glycol	-0.243	0.695	-0.670	0.726	-2.399	2.670
methanol	0.329	0.299	-0.671	0.080	-3.389	3.512
tetrahydrofuran	0.207	0.372	-0.392	-0.236	-4.934	4.447
water	-0.994	0.577	2.549	3.813	4.841	-0.869

^aNumerical values were either taken the literature²⁹ or calculated using a group contribution method.³⁸

overall ARD to 6.4 ± 6.9 %. The overall ARDs of eq 6 for RTIL + water mixtures was 7.1 ± 2.5 (NDS = 12) and that of RTIL + organic solvents (or RTIL) was 6.8 ± 9.0 % (NDS = 33), in which there was no statistically significant difference among overall ARD values revealing good capability of the model to fit both aqueous and nonaqueous binary mixtures. Equation 5 reproduced the viscosity data of the binary mixtures with the overall ARD (\pm SD) of 22.4 ± 43.8 % which was significantly ($p < 0.017$) more than the 6.9 % of eq 6.

The main drawback of eq 6 is that it requires a number of viscosity data in the binary mixtures for computing the numerical values of the model constants, and also the viscosity of the pure solvents. To provide a global model to predict the viscosity of the mixtures, it is possible to include some physicochemical parameters representing the interactions within the binary mixtures responsible for deviation from the linear behavior. One of the best parameters to represent the interaction within the mixtures are the Abraham parameters which are developed for nonionized chemicals.^{29,30} In recent works, the parameters were also presented for ionized forms and were used in a number of applications.^{31–36}

The J_i terms of eq 6 which stand for the various solvent–solvent interactions in the mixture,³⁷ may be represented by Abraham parameters and hence eq 6 may be rewritten as eq 8 for viscosity data,

$$\ln \eta_{m,T} = x_1 \ln \eta_{1,T} + x_2 \ln \eta_{2,T} + \frac{x_1 x_2}{T} \left[\begin{aligned} &W_0 + W_1(c_1 - c_2)^2 + W_2(e_1 - e_2)^2 \\ &+ W_3(s_1 - s_2)^2 + W_4(a_1 - a_2)^2 \\ &+ W_5(b_1 - b_2)^2 + W_6(v_1 - v_2)^2 \end{aligned} \right] + \frac{x_1 x_2 (x_1 - x_2)}{T} \left[\begin{aligned} &W'_0 + W'_1(c_1 - c_2)^2 + W'_2(e_1 - e_2)^2 \\ &+ W'_3(s_1 - s_2)^2 + W'_4(a_1 - a_2)^2 \\ &+ W'_5(b_1 - b_2)^2 + W'_6(v_1 - v_2)^2 \end{aligned} \right] + \frac{x_1 x_2 (x_1 - x_2)^2}{T} \left[\begin{aligned} &W''_0 + W''_1(c_1 - c_2)^2 + W''_2(e_1 - e_2)^2 \\ &+ W''_3(s_1 - s_2)^2 + W''_4(a_1 - a_2)^2 \\ &+ W''_5(b_1 - b_2)^2 + W''_6(v_1 - v_2)^2 \end{aligned} \right] \quad (8)$$

where subscripts 1 and 2 are the properties of solvents 1 and 2, and W terms are the model constants representing the two and three body interactions of the components. From a strictly mathematical point-of-view, they are adjustable curve-fit parameters determined from regressing $(\ln \eta_{m,T} - x_1 \ln \eta_{1,T} - x_2 \ln \eta_{2,T})$ against $x_1 x_2 / T$, $(x_1 x_2 (c_1 - c_2)^2) / T$, $(x_1 x_2 (e_1 - e_2)^2) / T$, $(x_1 x_2 (s_1 - s_2)^2) / T$, $(x_1 x_2 (a_1 - a_2)^2) / T$, $(x_1 x_2 (b_1 - b_2)^2) / T$, $(x_1 x_2 (v_1 - v_2)^2) / T$, $(x_1 x_2 (x_1 - x_2)) / T$, $(x_1 x_2 (x_1 - x_2) (c_1 - c_2)^2) / T$, $(x_1 x_2 (x_1 - x_2) (e_1 - e_2)^2) / T$, $(x_1 x_2 (x_1 - x_2) (s_1 - s_2)^2) / T$, $(x_1 x_2 (x_1 - x_2) (a_1 - a_2)^2) / T$, $(x_1 x_2 (x_1 - x_2) (b_1 - b_2)^2) / T$,

$(x_1x_2(x_1 - x_2)(v_1 - v_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2(c_1 - c_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2(e_1 - e_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2(s_1 - s_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2(a_1 - a_2)^2)/T$, $(x_1x_2(x_1 - x_2)^2(b_1 - b_2)^2)/T$ and $(x_1x_2(x_1 - x_2)^2(v_1 - v_2)^2)/T$, using a no intercept least-squares analysis. The collected data with available Abraham parameters (see Table 2) were fitted to eq 8 and after excluding the nonsignificant coefficients ($p > 0.05$), the obtained trained model was

$$\begin{aligned} \ln \eta_{m,T} = & x_1 \ln \eta_{1,T} + x_2 \ln \eta_{2,T} + \frac{x_1x_2}{T} [181.555 \\ & + 135.913(c_1 - c_2)^2 - 48.327(e_1 - e_2)^2 \\ & - 6.473(a_1 - a_2)^2 + 2.643(b_1 - b_2)^2] \\ & + \frac{x_1x_2(x_1 - x_2)}{T} [-132.339 + 182.404(c_1 - c_2)^2 \\ & - 124.917(e_1 - e_2)^2 + 10.572(s_1 - s_2)^2 \\ & - 7.140(b_1 - b_2)^2] + \frac{x_1x_2(x_1 - x_2)^2}{T} \\ & \times [6.893(b_1 - b_2)^2] \end{aligned} \quad (9)$$

which correlates the viscosity data with the correlation coefficient of 0.866, F value of 449 and significance level of < 0.0005 ($N = 1652$). A wide viscosity range (0.000316 to 1.036980 kPa·s) was correlated by the model. When the viscosity data were back-calculated by eq 9, the minimum ARD (4.2 %) was observed for [C4MIM][PF6] + acetone mixtures and the maximum ARD (67.1 %) for [BMIM][BF4] + ethylene glycol mixtures. The overall ARD was 15.0 ± 12.6 % (NDS = 30) (for details of ARDs see Table 3). Figure 1 shows a plot of the calculated versus experimental viscosity data along with the linear equation and correlation coefficient in which excellent correlation was observed ($R = 0.991$). Equation 9 requires the experimental viscosity data of the pure solvents at each temperature as input data to predict the viscosity of binary mixtures.

Further reduction could be achieved by using another version of the model which is

$$\begin{aligned} \ln \eta_{m,T} = & \alpha_0 x_1 + \frac{x_1}{T} \left\{ \alpha_1 + \alpha_2 c_1 + \alpha_3 e_1 + \alpha_4 s_1 + \alpha_5 a_1 + \alpha_6 b_1 + \alpha_7 v_1 \right. \\ & \left. + \alpha_8 a_1 \cdot b_1 + \alpha_9 \frac{a_1}{v_1} + \alpha_{10} \frac{b_1}{v_1} + \alpha_{11} \frac{a_1 \cdot b_1}{v_1} \right\} + \beta_0 x_2 \\ & + \frac{x_2}{T} \left\{ \beta_1 + \beta_2 c_2 + \beta_3 e_2 + \beta_4 s_2 + \beta_5 a_2 + \beta_6 b_2 + \beta_7 v_2 \right. \\ & \left. + \beta_8 a_2 \cdot b_2 + \beta_9 \frac{a_2}{v_2} + \beta_{10} \frac{b_2}{v_2} + \beta_{11} \frac{a_2 \cdot b_2}{v_2} \right\} + \frac{x_1x_2}{T} \left[\begin{aligned} & W_0 + W_1(c_1 - c_2)^2 + W_2(e_1 - e_2)^2 \\ & + W_3(s_1 - s_2)^2 + W_4(a_1 - a_2)^2 \\ & + W_5(b_1 - b_2)^2 + W_6(v_1 - v_2)^2 \end{aligned} \right] \\ & + \frac{x_1x_2(x_1 - x_2)}{T} \left[\begin{aligned} & W'_0 + W'_1(c_1 - c_2)^2 + W'_2(e_1 - e_2)^2 \\ & + W'_3(s_1 - s_2)^2 + W'_4(a_1 - a_2)^2 \\ & + W'_5(b_1 - b_2)^2 + W'_6(v_1 - v_2)^2 \end{aligned} \right] + \frac{x_1x_2(x_1 - x_2)^2}{T} \left[\begin{aligned} & W''_0 + W''_1(c_1 - c_2)^2 + W''_2(e_1 - e_2)^2 \\ & + W''_3(s_1 - s_2)^2 + W''_4(a_1 - a_2)^2 \\ & + W''_5(b_1 - b_2)^2 + W''_6(v_1 - v_2)^2 \end{aligned} \right] \end{aligned} \quad (10)$$

This version does not require any experimental viscosity data. When available data were fitted to eq 10, the trained model after excluding nonsignificant variables was

Table 3. Average Relative Deviation of eqs 9 and 11

RTIL	molecular solvent/RTIL	N	eq 9	eq 11
[BMIM][BF4]	dimethyl sulfoxide	77	5.6	4.4
[BMIM][BF4]	ethylene glycol	55	67.1	40.9
[BMIM][BF4]	water	88	17.0	18.4
[BMIM][CF3SO3]	water	77	15.0	22.0
[BMIM][PF6]	dimethyl sulfoxide	15	13.1	22.2
[BMIM][PF6]	methanol	15	15.8	16.5
[BMIM][PF6]	tetrahydrofuran	15	17.2	37.4
[BMIM][SCN]	1-butanol	72	6.5	13.3
[BMIM][SCN]	1-hexanol	72	4.6	14.8
[BMIM][SCN]	1-pentanol	78	5.9	17.3
[BPY][BF4]	[BPY][Tf2N]	72	22.5	15.7
[BUPY][BF4]	water	130	30.5	26.7
[C4MIM][PF6]	acetone	15	4.2	25.4
[C4MIM][PF6]	acetonitrile	15	7.2	13.9
[C4MIM][PF6]	dimethyl formamide	66	7.1	23.9
[C4MIM][PF6]	ethyl acetate	15	8.0	24.3
[C4MIM][PF6]	methanol	15	15.7	16.4
[C8IQUIN][NTf2]	1-butanol	55	33.5	10.8
[EMIM][BF4]	water	77	23.0	18.9
[EMIM][EtSO4]	water	56	13.0	14.9
[EMISE]	1-propanol	33	4.3	26.8
[EMISE]	2-propanol	33	7.7	35.6
[EMISE]	ethanol	36	9.4	15.1
[EMISE]	methanol	39	21.6	18.3
[EMISE]	water	30	8.4	12.5
[EPY][SO4]	ethanol	33	6.8	34.4
[EPY][SO4]	propan-1-ol	36	6.9	25.3
[OCPY][BF4]	water	140	25.7	23.8
[OMIM][BF4]	ethanol	104	13.1	15.3
[PDMIM][BF4]	water	88	13.4	15.6
	overall		15.0	20.7

For the other data sets, the Abraham parameters were not available.

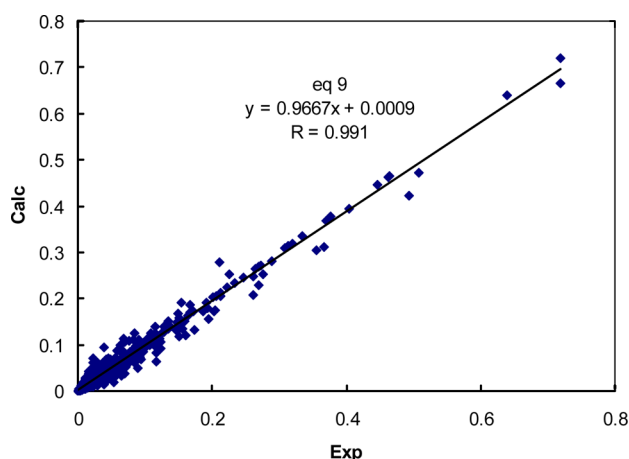


Figure 1. Plot of the calculated viscosities using eq 9 versus experimental values.

$$\begin{aligned} \ln \eta_{m,T} = & -7.085x_1 + \frac{x_1}{T} \left\{ -1381.472 + 317.451c_1 \right. \\ & + 128.713e_1 + 29.338s_1 + 427.664a_1 + 576.548v_1 \\ & \left. + 3430.864\frac{a_1}{v_1} - 883.984\frac{b_1}{v_1} + 1083.890\frac{a_1 \cdot b_1}{v_1} \right\} \\ & - 5.137x_2 + \frac{x_2}{T} \{ 649.173 - 230.029c_2 + 517.417e_2 \\ & + 187.305s_2 - 256.863a_2 + 215.281b_2 + 218.199v_2 \\ & - 49.271a_2 \cdot b_2 \} + \frac{x_1 x_2}{T} [274.842 + 130.361(e_1 - e_2)^2 \\ & - 14.032(s_1 - s_2)^2 - 7.967(a_1 - a_2)^2 \\ & + 9.154(v_1 - v_2)^2] + \frac{x_1 x_2 (x_1 - x_2)}{T} [-176.488 \\ & + 259.610(c_1 - c_2)^2 - 309.306(e_1 - e_2)^2 \\ & + 22.617(s_1 - s_2)^2 - 22.911(b_1 - b_2)^2] \\ & + \frac{x_1 x_2 (x_1 - x_2)^2}{T} [154.378 - 52.663(a_1 - a_2)^2 \\ & + 52.629(v_1 - v_2)^2] \end{aligned} \quad (11)$$

Equation 11 correlates the viscosity data of RTIL + molecular solvents/RTIL with the correlation coefficient of 0.998, F value of 14874 and significance level of < 0.0005 ($N = 1652$). When the viscosity data are back-calculated by eq 11, the minimum ARD (4.4 %) was observed for [BMIM][BF₄] + dimethyl sulfoxide mixtures and the maximum ARD (40.9 %) for [BMIM][BF₄] + ethylene glycol mixtures where the overall ARD was 20.7 ± 8.4 % (NDS = 30) (for details of ARDs see Table 3). Figure 2 illustrates the linear plot of the predicted viscosity data by eq 11 against the corresponding experimental values along with the equation and the correlation coefficient. In comparison with eq 9, lower correlation and more scattered plot is obtained; however, eq 11 is an *in silico* model and requires the Abraham parameters of the pure solvents which usually are available from the literature or could be calculated using group contribution methods.

In conclusion, the proposed models provided reasonable accurate results to calculate the viscosity of RTILs + solvent mixtures with respect to their composition and temperature.

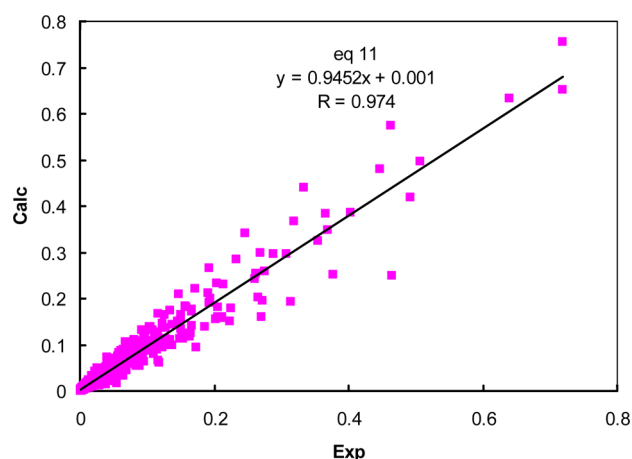


Figure 2. Plot of the calculated viscosities using eq 11 versus experimental values.

The overall ARD of 6.4 % was obtained for correlated data, 15.0 % for predicted data employing experimental data of $\eta_{1,T}$ and $\eta_{2,T}$ and 20.7 % for *in silico* prediction of the data revealing that the Jouyban-Acree model is able to accurately represent the viscosity data of the mixtures and Abraham parameters are good predictors of the interactions occurring in the mixtures. The overall ARD of a similar model from the literature, that is, eq 5, was 22.4 which is significantly higher than the corresponding value for the proposed model.

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Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Wang, Z.; Fu, L.; Xu, H.; Shang, Y.; Zhang, L.; Zhang, J. Density, Viscosity, and Conductivity for the Binary Systems of Water+Dual Amino-Functionalized Ionic Liquids. *J. Chem. Eng. Data* **2012**, *57*, 1057–1063.
- (2) Kurnia, K. A.; Mutalib, A. M. Densities and Viscosities of Binary Mixture of the Ionic Liquid Bis(2-hydroxyethyl)ammonium Propionate with Methanol, Ethanol, and 1-Propanol at $T = (293.15, 303.15, 313.15, \text{ and } 323.15)$ K and at $P = 0.1$ MPa. *J. Chem. Eng. Data* **2011**, *56*, 79–83.
- (3) Yu, Z.; Gao, H.; Wang, H.; Chen, L. Densities, Viscosities, and Refractive Properties of the Binary Mixtures of the Amino Acid Ionic Liquid [bmim][Ala] with Methanol or Benzylalcohol at $T = (298.15 \text{ to } 313.15)$ K. *J. Chem. Eng. Data* **2011**, *56*, 2877–2883.
- (4) Ciocirlan, O.; Croitoru, O.; Lulian, O. Densities and Viscosities for Binary Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid with Molecular Solvents. *J. Chem. Eng. Data* **2011**, *56*, 1526–1534.
- (5) Zhou, Q.; Wang, L. S.; Chen, H. P. Densities and Viscosities of 1-Butyl-3-Methylimidazolium Tetrafluoroborate+H₂O Binary Mixtures from 303.15 to 353.15 K. *J. Chem. Eng. Data* **2006**, *51*, 905–908.
- (6) Ge, M. L.; Zhao, R. S.; Yi, Y. F.; Zhang, Q.; Wang, L. S. Densities and Viscosities of 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate + H₂O Binary Mixtures at $T = (303.15 \text{ to } 343.15)$ K. *J. Chem. Eng. Data* **2008**, *53*, 2408–2411.
- (7) Fan, W.; Zhou, Q.; Sun, J.; Zhang, S. Density, Excess Molar Volume, and Viscosity for the Methyl Methacrylate+1-Butyl-3-methylimidazolium Hexafluorophosphate Ionic Liquid Binary System at Atmospheric Pressure. *J. Chem. Eng. Data* **2009**, *54*, 2307–2311.

- (8) Zafarani-Moattar, M. T.; Majdan-Cegincara, R. Viscosity, Density, Speed of Sound, and Refractive Index of Binary Mixtures of Organic Solvent+Ionic Liquid, 1-Butyl-3-Methylimidazolium Hexafluorophosphate at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2359–2365.
- (9) Domanska, U.; Laskowska, M. Effect of Temperature and Composition on the Density and Viscosity of Binary Mixtures of Ionic Liquid with Alcohols. *J. Solution Chem.* **2009**, *38*, 779–799.
- (10) Larriba, M.; García, S.; Navarro, P.; García, J.; Rodríguez, F. Physical Properties of *N*-Butylpyridinium Tetrafluoroborate and *N*-Butylpyridinium Bis(trifluoromethylsulfonyl)imide Binary Ionic Liquid Mixtures. *J. Chem. Eng. Data* **2012**, *57*, 1318–1325.
- (11) Mokhtarani, B.; Sharifi, A.; Mortaheb, H. R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and Viscosity of Pyridinium-Based Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 323–329.
- (12) Yanfang, G.; Tengfang, W.; Dahong, Y.; Changjun, P.; Honglai, L.; Ying, H. Densities and Viscosities of the Ionic Liquid [C4mim]-[PF6]+*N,N*-Dimethylformamide Binary Mixtures at 293.15 to 318.15 K. *Chin. J. Chem. Eng.* **2008**, *16*, 256–262.
- (13) Wang, J.; Zhu, A.; Zhao, T.; Zhuo, K. Excess Molar Volumes and Excess Logarithm Viscosities for Binary Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Hexafluorophosphate with Some Organic Compounds. *J. Solution Chem.* **2005**, *34*, 585–569.
- (14) Li, J. G.; Hu, Y. F.; Sun, S. F.; Liu, Y. S.; Liu, Z. C. Densities and Dynamic Viscosities of the Binary System (Water + 1-Hexyl-3-methylimidazolium bromide) at Different Temperatures. *J. Chem. Thermodyn.* **2010**, *42*, 904–908.
- (15) Domanska, U.; Zawadzki, M.; Lewandowska, A. Effect of Temperature and Composition on the Density, Viscosity, Surface Tension, and Thermodynamic Properties of Binary Mixtures of *N*-Octylisoquinolinium Bis{(trifluoromethyl)sulfonyl}imide with Alcohols. *J. Chem. Thermodyn.* **2012**, *48*, 101–111.
- (16) Zhang, S.; Li, X.; Chen, H.; Wang, J.; Zhang, J.; Zhang, M. Determination of Physical Properties for the Binary System of 1-Ethyl-3-Methylimidazolium Tetrafluoroborate + H₂O. *J. Chem. Eng. Data* **2004**, *49*, 760–764.
- (17) Rodriguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.
- (18) Gonzalez, E. J.; Gonzalez, B.; Calvar, N.; Dominguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate with Several Alcohols at *T* = (298.15, 313.15, and 328.15) K and Atmospheric Pressure. *J. Chem. Eng. Data* **2007**, *52*, 1641–1648.
- (19) Gonzalez, E. J.; Gonzalez, B.; Calvar, N.; Tojo, E.; Dominguez, A. Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethyl Sulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.
- (20) Gonzalez, B.; Calvar, N.; Gomez, E.; Dominguez, I.; Dominguez, A. Synthesis and Physical Properties of 1-Ethylpyridinium Ethyl Sulfate and its Binary Mixtures with Ethanol and 1-Propanol at Several Temperatures. *J. Chem. Eng. Data* **2009**, *54*, 1353–1358.
- (21) Ahosseini, A.; Weatherley, L. R.; Scurto, A. M. Viscosity and Diffusivity for the Ionic Liquid 1-Hexyl-3-methylimidazolium Bis-(trifluoromethylsulfonyl)amide with 1-Octene. *J. Chem. Eng. Data* **2011**, *56*, 3715–3721.
- (22) Mokhtarani, B.; Mojtahedi, M. M.; Mortaheb, H. R.; Mafi, M.; Yazdani, F.; Sadeghian, F. Densities, Refractive Indices, and Viscosities of the Ionic Liquids 1-Methyl-3-Octylimidazolium Tetrafluoroborate and 1-Methyl-3-Butylimidazolium Perchlorate and Their Binary Mixtures with Ethanol at Several Temperatures. *J. Chem. Eng. Data* **2008**, *53*, 677–682.
- (23) Ge, M. L.; Ren, X. G.; Song, Y. J.; Wang, L. S. Densities and Viscosities of 1-Propyl-2,3-Dimethylimidazolium Tetrafluoroborate + H₂O at *T* = (298.15 to 343.15 K). *J. Chem. Eng. Data* **2009**, *54*, 1400–1402.
- (24) Gong, Y. H.; Shen, C.; Lu, Y. Z.; Meng, H.; Li, C. X. Viscosity and Density Measurements for Six Binary Mixtures of Water (Methanol or Ethanol) with an Ionic Liquid ([BMIM][DMP] or [EMIM][DMP]) at Atmospheric Pressure in the Temperature Range of (293.15 to 333.15) K. *J. Chem. Eng. Data* **2012**, *57*, 33–39.
- (25) Jouyban, A.; Khoubnasabjafari, M.; Vaez-Gharamaleki, Z.; Fekahari, Z.; Acree, W. E., Jr. Calculation of the Viscosity of Binary Liquids at Various Temperatures Using Jouyban–Acree Model. *Chem. Pharm. Bull.* **2005**, *53*, 519–523.
- (26) Jouyban, A.; Soltani, S.; Chan, H.-K.; Acree, W. E., Jr. Modeling Acid Dissociation Constant of Analytes in Binary Solvents at Various Temperatures Using Jouyban–Acree Model. *Thermochim. Acta* **2005**, *428*, 119–123.
- (27) Jouyban, A.; Fathi-Azarbayjani, A.; Khoubnasabjafari, M.; Acree, W. E., Jr. Mathematical Representation of the Density of Liquid Mixtures at Various Temperatures using Jouyban–Acree Model. *Indian J. Chem.* **2005**, *44A*, 1553–1560.
- (28) Jouyban, A. Review of the Cosolvency Models for Predicting Solubility of Drugs in Water-Cosolvent Mixtures. *J. Pharm. Pharm. Sci.* **2008**, *11*, 32–58.
- (29) Abraham, M. H.; Smith, R. E.; Luchtefeld, R.; Boorem, A. J.; Luo, R.; Acree, W. E., Jr. Prediction of Solubility of Drugs and Other Compounds in Organic Solvents. *J. Pharm. Sci.* **2010**, *99*, 1500–1515.
- (30) Jouyban, A.; Soltanpour, Sh.; Soltani, S.; Tamizi, E.; Fakhree, M. A. A.; Acree, W. E., Jr. Prediction of Drug Solubility in Mixed Solvents Using Computed Abraham Parameters. *J. Mol. Liq.* **2009**, *146*, 82–88.
- (31) Grubbs, L. M.; Ye, S.; Saifullah, M.; McMillan-Wiggins, M. C.; Acree, W. E., Jr.; Abraham, M. H.; Twu, P.; Anderson, J. L. Correlations for Describing Gas-to-Ionic Liquid Partitioning at 323 K Based on Ion-Specific Equation Coefficient and Group Contribution Versions of the Abraham Model. *Fluid Phase Equilib.* **2011**, *301*, 257–266.
- (32) Acree, W. E., Jr.; Sprunger, L. M.; Achi, S. S.; Abraham, M. H. Linear Free Energy Relationship Correlations for Enthalpies of Solvation of Organic Solutes into Room-Temperature Ionic Liquids Based on the Abraham Model With Ion-Specific Equation Coefficients. *Ind. Eng. Chem. Res.* **2009**, *48*, 8704–8709.
- (33) Zhang, K.; Chen, M.; Scriba, G. K. E.; Abraham, M. H.; Fahr, A.; Liu, X. Human Skin Permeation of Neutral Species and Ionic species: Extended Linear Free-Energy Relationship Analyses. *J. Pharm. Sci.* **2012**, *101*, 2034–2044.
- (34) Zhang, K.; Chen, M.; Scriba, G. K. E.; Abraham, M. H.; Fahr, A.; Liu, X. Linear Free-Energy Relationship Analysis of Retention Factors in Cerasome Electrokinetic Chromatography Intended for Predicting Drug Skin Permeation. *J. Pharm. Sci.* **2011**, *100*, 3105–3113.
- (35) Abraham, M. H. The Permeation of Neutral Molecules, Ions, and Ionic Species through Membranes: Brain Permeation as an Example. *J. Pharm. Sci.* **2011**, *100*, 1690–1701.
- (36) Abraham, M. H.; Austin, R. P. The Effect of Ionized Species on Microsomal Binding. *Eur. J. Med. Chem.* **2012**, *47*, 202–205.
- (37) Acree, W. E., Jr. Mathematical Representation of Thermodynamic Properties. Part II. Derivation of the Combined Nearly Ideal Binary Solvent (NIBS)/Redlich-Kister Mathematical Representation from a Two-Body and Three-Body Interactional Mixing Model. *Thermochim. Acta* **1992**, *198*, 71–79.
- (38) Revelli, A. L.; Mutelet, F.; Jaubert, J. N. Prediction of Partition Coefficients of Organic Compounds in Ionic Liquids: Use of a Linear Solvation Energy Relationship with Parameters Calculated through a Group Contribution Method. *Ind. Eng. Chem. Res.* **2010**, *49*, 3883–3892.