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Isothermal Vapor−Liquid Equilibrium Data at $T = 333.15$ K and Excess Molar Volumes and Refractive Indices at $T = 298.15$ K for the Dimethyl Carbonate + Methanol and Isopropanol + Water with Ionic Liquids

Hyeon-Deok Kim, In-Chan Hwang, and So-Jin Park*

Department of Chemical Engineering, Chungnam National University, 220 Gung-Dong, Yuseong-Gu,
Daejeon, 305-764, Republic of Korea

Isothermal vapor−liquid equilibrium (VLE) data at $T = 333.15$ K are reported for the four ternary systems dimethyl carbonate (DMC) + methanol + 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE), DMC + methanol + 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), isopropanol + water + EMISE, and isopropanol + water + [Bmim][BF_4] by using headspace gas chromatography. The mole fraction of ionic liquids was varied from 0.05 to 0.2. The experimental binary VLE data were correlated using the Wilson, NRTL, and UNIQUAC equations. In addition, the excess volumes and deviations in molar refractivity data are reported at $T = 298.15$ K for the sub-binary pairs of the above-mentioned ternary systems. These properties are correlated with the Redlich−Kister equation. Finally, the ternary excess volumes and deviations in molar refractivity data were calculated from the Radojkovič equation using correlated binary Redlich−Kister parameters.

Introduction

Distillation is by far the most extensively used and common industrial separation process in the petroleum, natural gas, and petrochemical industries. It is also common in many other industries including air fractionation, solvent recovery, and recycling processes.

However, distillation is a relatively energy-consuming process and is highly restricted for high boiling components and azeotropes. Azeotropes can be separated using a pressure swing method or by distillation with a liquid additive or solid salt that modifies the relative volatility of the distilled components. The use of salts has problems associated with their causticity and their limited solubility in organic compounds, whereas volatile organic solvents may contaminate the environment and the product streams.[1]

Ionic liquids (ILs) are usually liquids at room temperature and have a highly polar character caused by coulomb forces acting between the ions in the liquid state, and ILs are outstandingly good solvents for a wide range of materials.[2,3] Many applications of ILs as a “green solvent” replacing volatile organic compounds have been reported.[3] This means that they can be used as solvents or additives for azeotropic distillation in cases where the ILs interact more strongly with a certain component in the azeotropic mixture, thus causing a shift in the azeotropic point.

Despite recent research investigating the suitability of ILs as selective solvents in separation technology, the number of published vapor−liquid equilibria (VLE) data sets is still very limited.

Dimethylcarbonate (DMC) is used as a benign solvent and recently has been considered as an environmentally friendly octane booster. Isopropanol is one of the most widely used solvents, antifreeze compounds, and chemical derivatives in various industries. DMC is prepared from the catalytic oxidative carbonylation of methanol and forms an azeotrope with methanol. Isopropanol forms an azeotrope with water. Development of convenient and economical separation technology for these azeotropes still interests many scientists and engineers in industries utilizing these compounds.

In this work, 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) were used because EMISE and [Bmim][BF4] are the most promising ILs to be applied in industrial process as a solvent for extraction and azeotrope breaker in extractive distillation.[4,5] They are also not harmful to biota, easily synthesized with reasonable cost, and commercially available.[6]

In this work, we report the influence of ILs on the shift of the azeotrope for the system DMC + methanol and isoparopanol + water using 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]-[BF_4]). The isothermal vapor−liquid equilibrium (VLE) data at $T = 333.15$ K for the systems DMC + methanol and isopropanol + water with different concentrations of EMISE and [Bmim][BF_4] were measured by using headspace gas chromatography (HSGC). The experimental VLE data (ILs-free base) were correlated with the Wilson, NRTL, and UNIQUAC models. In addition, we report mixture properties, the excess molar volumes (V^E), and deviations in molar refractivity (ΔR) at $T = 298.15$ K for the binary systems DMC + methanol, DMC + EMISE, DMC + [Bmim][BF_4], methanol + EMISE, and methanol + [Bmim][BF_4]. These binary data were correlated with the Redlich−Kister polynomial.[7] Finally, the ternary V^E and ΔR data for the systems DMC + methanol + EMISE and DMC + methanol + [Bmim][BF_4] at $T = 298.15$ K are calculated from correlated Redlich−Kister parameters. This calculation was carried out using the Radojkovič equation[8] and is illustrated in isoclines.

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* Corresponding author. Tel.: +82-42-821-5684. Fax: +82-42-823-6414. E-mail address: sjpark@cnu.ac.kr.

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Table 1. Densities, Refractive Indices, and Antoine Constants of Pure Components

	ρ at 298.15 K		n_D at 298.15 K		Antoine constants[a]		
chemicals	present study	literature value	present study	literature value	A	B	C
DMC	1.06328	1.06304[b]	1.36647	1.36654[b]	7.03395	1253.59	211.600
methanol	0.78672	0.78654[c]	1.32668	1.32670[c]	8.08097	1582.27	239.726
2-propanol	0.78139	0.78110[d]	1.37497	1.37501[d]	8.00308	1505.52	211.600
water	0.99711	0.99703[c]	1.33249	1.33252[c]	8.07131	1730.63	233.426
EMISE	1.23633	1.23763[e]	1.47836	1.47940[e]	-	-	-
[Bmim][BF$_4$]	1.19278	1.20[f]	1.41831	1.4227[f]	-	-	-

[a] Ref 6. [b] Ref 19. [c] Ref 20. [d] Ref 21. [e] Ref 22. [f] Ref 23.

Experimental Section

Materials. Commercial grade DMC ($C_3H_6O_3$, $M = 90.08$ g·mol^{-1}, CAS-RN 616-38-6), methanol (CH_3OH, $M = 32.05$ g·mol^{-1}, CAS-RN 67-56-1), and isopropanol (C_3H_7OH, $M = 60.10$ g·mol^{-1}, CAS-RN 67-63-0) were obtained from Aldrich Chemical Co. Water (H_2O, $M = 18.02$ g·mol^{-1}, CAS-RN 7732-18-5) was supplied from J.T. Baker Chemical Company. EMISE ($C_8H_{16}N_2O_4S$, $M = 236.29$ g·mol^{-1}, CAS-RN 342573-75-5) was supplied from Fluka. The [Bmim][BF$_4$] ($C_8H_{15}N_2BF_4$, $M = 226.03$ g·mol^{-1}, CAS-RN 174501-65-6) was supplied from C-tri Chemical Company. DMC and isopropanol have no impurity by gas chromatography, and the purity of ILs, EMISE, and [Bmim][BF$_4$] was declared to have mass fraction purity greater than 0.99 by the supplier. The compounds were used without additional purification. The organic chemicals were used after water drying using molecular sieves with a pore diameter of 0.4 nm except methanol which was dried with molecular sieves of 0.3 nm. The purity of chemicals was examined by gas chromatography and by comparing the densities and refractive indices with the values reported in the literature. The water content, determined by Karl Fischer titration (Metrohm 684 KF coulometer), was less than a mole fraction of 0.0001 for all chemicals. The measured densities, refractive indices, and Antoine constants of the used chemicals are summarized in Table 1, along with the literature values.[9]

Apparatus and Procedure. Isothermal VLE measurements were carried out using headspace gas chromatography (HSGC). The HSGC consists of a gas chromatograph (HP 6890N) and a headspace sampler (HP19395A) that has an electro-pneumatic sampling system and a precision thermostat with an accuracy of ± 0.1 K. An HP-5 (−0.05 mass fraction diphenyl + 0.95 mass fraction dimethylsiloxane, 30 m × 0.32 mm × 0.25 μm) capillary column and a thermal conductivity detector were used for the analysis. The uncertainty of the measured equilibrium mole fraction was estimated as $\pm\ 1\cdot10^{-4}$. According to approximately calculated mole ratio, the heavier component was charged first in a vial and sealed with a Teflon/rubber septum and aluminum cap. Then, the volatile material was put into the glass vial with a syringe to minimize experimental error. The prepared glass vials with a sample mixture were placed in the thermostat and equilibrated more than 2 h. The equilibrium between the vapor and liquid phase will be reached very quickly because the total volume of the sample mixture is ca. 3 mL and the equilibrium cell is also very small. When equilibrium was achieved between two phases, a fixed amount of vapor phase (headspace) was automatically sampled and transported to gas chromatography for analysis by an electropneumatic sampling system. The equilibrated liquid phase mole fraction can be calculated from the measured vapor phase mole fraction and thermodynamic relation and mass balance.

Densities were measured by a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Graz, Austria). The densimeter was automatically calibrated by itself with distilled water and dry air. The uncertainty of the density meter is stated by the manufacturer as $5\cdot10^{-6}$ g·cm^{-3} in the density range of (0 to 3) g·cm^{-3}. Temperature was controlled within ± 0.01 K. The details of operating procedures have been described elsewhere.[10,11] Refractive indices (n_D) of the pure components

Table 2. Isothermal VLE Data for Ternary Systems DMC (1) + Methanol (2) + EMISE (3) and DMC (1) + Methanol (2) + [Bmim][BF$_4$] (3) at 333.15 K

DMC (1) + methanol (2) + EMISE (3)									DMC (1) + methanol (2) + [Bmim][BF$_4$] (3)		
P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1
	$x_3 = 0.05$			$x_3 = 0.10$			$x_3 = 0.20$			$x_3 = 0.20$	
84.37	0.0105	0.0070	84.19	0.0114	0.0095	84.06	0.0131	0.0076	84.08	0.0127	0.0091
84.07	0.0526	0.0479	83.30	0.0554	0.0412	82.73	0.0592	0.0330	82.84	0.0588	0.0389
83.40	0.1054	0.0895	82.29	0.1001	0.0708	81.29	0.1054	0.0573	81.50	0.1062	0.0684
82.89	0.1370	0.1032	81.21	0.1442	0.0972	79.75	0.1516	0.0803	80.14	0.1522	0.0949
82.50	0.1585	0.1227	80.03	0.1892	0.1233	78.09	0.1981	0.1033	78.74	0.1973	0.1206
81.44	0.2103	0.1495	78.79	0.2338	0.1450	76.29	0.2449	0.1256	77.26	0.2435	0.1428
80.70	0.2429	0.1646	77.47	0.2787	0.1700	74.38	0.2912	0.1487	75.65	0.2916	0.1703
80.19	0.2638	0.1727	76.11	0.3228	0.1888	72.30	0.3383	0.1726	74.06	0.3369	0.1969
78.82	0.3167	0.1967	74.65	0.3674	0.2225	70.16	0.3838	0.1961	72.37	0.3833	0.2223
77.30	0.3695	0.2218	73.13	0.4117	0.2426	67.82	0.4306	0.2218	70.55	0.4306	0.2505
75.65	0.4217	0.2457	71.44	0.4578	0.2657	65.51	0.4748	0.2498	68.69	0.4765	0.2676
73.78	0.4747	0.2720	69.84	0.4989	0.2887	63.00	0.5207	0.2848	66.70	0.5229	0.2998
71.73	0.5271	0.2940	67.87	0.5461	0.3140	60.23	0.5696	0.3263	64.57	0.5697	0.3399
69.37	0.5806	0.3256	65.82	0.5914	0.3535	57.45	0.6174	0.3601	62.33	0.6155	0.3690
66.81	0.6322	0.3609	63.71	0.6346	0.3827	54.73	0.6631	0.4087	59.90	0.6622	0.3999
63.77	0.6862	0.4041	61.26	0.6806	0.4184	51.97	0.7091	0.4552	57.34	0.7078	0.4380
60.41	0.7385	0.4538	58.71	0.7243	0.4537	49.14	0.7560	0.5118	54.54	0.7539	0.5013
56.66	0.7898	0.4921	56.12	0.7648	0.4855	46.43	0.8010	0.5934	51.54	0.7997	0.5440
52.20	0.8432	0.5867	52.83	0.8115	0.5410	43.70	0.8468	0.6752	48.02	0.8489	0.6237
47.09	0.8965	0.6724	49.19	0.8577	0.6200	40.97	0.8932	0.7654	44.79	0.8905	0.6976
41.34	0.9489	0.7996	45.59	0.8988	0.6929	38.33	0.9392	0.8433	40.64	0.9395	0.8126
-	-	-	40.94	0.9463	0.8084	35.56	0.9887	0.9873	-	-	-

Table 3. Isothermal VLE Data for Ternary Systems Isopropanol (1) + Water (2) + EMISE (3) and Isopropanol (1) + Water (2) + [Bmim][BF$_4$] (3) at 333.15 K

isopropanol (1) + water (2) + EMISE (3)						isopropanol (1) + water (2) + [Bmim][BF$_4$] (3)		
P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1	P_{cal}/kPa	x_1	y_1
	$x_3 = 0.10$			$x_3 = 0.20$			$x_3 = 0.20$	
21.72	0.0110	0.0947	21.37	0.0124	0.0814	21.21	0.0115	0.0872
27.23	0.0572	0.3067	25.48	0.0599	0.2427	25.34	0.0600	0.2469
30.63	0.1043	0.4081	28.19	0.1087	0.3695	27.99	0.1066	0.3510
32.79	0.1500	0.4576	30.03	0.1541	0.4230	31.77	0.2018	0.4836
34.37	0.1975	0.4994	31.64	0.2038	0.4837	33.26	0.2493	0.5387
35.50	0.2432	0.5241	32.88	0.2491	0.5149	34.64	0.2978	0.5618
36.42	0.2903	0.5495	34.03	0.2966	0.5419	35.89	0.3456	0.5946
37.17	0.3368	0.5717	35.08	0.3452	0.5670	36.96	0.3902	0.6237
37.81	0.3847	0.5967	35.99	0.3922	0.5976	38.94	0.4851	0.6614
38.36	0.4312	0.6119	36.86	0.4417	0.6222	39.84	0.5368	0.6835
38.83	0.4778	0.6377	37.56	0.4865	0.6430	40.55	0.5848	0.7232
39.62	0.5730	0.6520	38.21	0.5333	0.6693	41.13	0.6316	0.7440
39.91	0.6176	0.6644	38.75	0.5782	0.6895	41.60	0.6787	0.7615
40.30	0.7115	0.7329	39.29	0.6305	0.7180	41.95	0.7282	0.7913
40.34	0.8023	0.8011	39.66	0.6745	0.7447	42.13	0.7680	0.8074
40.17	0.8513	0.8402	40.00	0.7268	0.7733	42.23	0.8198	0.8277
39.88	0.8955	0.8851	40.19	0.7701	0.7941	42.14	0.8712	0.8610
39.33	0.9459	0.9401	40.30	0.8247	0.8421	41.82	0.9151	0.8871
-	-	-	40.24	0.8696	0.8739	40.63	0.9676	0.9210
-	-	-	39.94	0.9197	0.9074	41.77	0.9197	0.9074
-	-	-	39.41	0.9603	0.9400	40.90	0.9603	0.9400
-	-	-	38.75	0.9897	0.9637	39.38	0.9897	0.9637

and mixtures were measured by a digital precision refractometer (KEM, model RA-520N, Kyoto, Japan). The refractometer was calibrated with distilled water, and the uncertainty of this refractometer is stated as ± $5 \cdot 10^{-5}$ within the range from 1.32 to 1.40 and ± $1 \cdot 10^{-4}$ within the range from 1.40 to 1.58. The experimental procedure is described in detail elsewhere.[12] Calibrations of the density meter and refractometer were carried out periodically by using doubly distilled water or dried air. Mixture samples were prepared simultaneously for density and refractive index measurements.

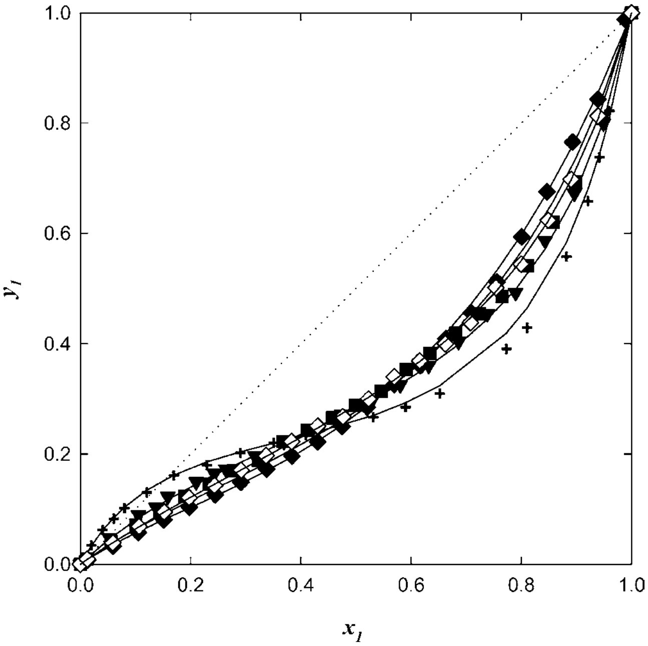

Figure 1. $x-y$ for the systems DMC (1) + methanol (2) + ILs at 333.15 K, at several mole fractions of ILs: +, calculated from literature data for the IL-free system;[24] ▼, DMC (1) + methanol (2) + EMISE (3) at $x_3 = 0.050$; ■, DMC (1) + methanol (2) + EMISE (3) at $x_3 = 0.100$; ♦, DMC (1) + methanol (2) + EMISE (3) at $x_3 = 0.200$; ◇, DMC (1) + methanol (2) + [Bmim][BF$_4$] (3) at $x_3 = 0.200$; solid lines were calculated by correlated parameters (Table 4).

Results and Discussion

Isothermal VLE. VLE data for the systems DMC + methanol and isopropanol + water with different contents of EMISE or [Bmim][BF$_4$] were measured and are listed in Tables 2 and 3. The measured data were correlated with common g^E models: Wilson,[13] NRTL,[14] and UNIQUAC.[15] The mole fractions in the tables are recalculated on an IL-free basis. The correlated and experimental VLE data ($x-y$, $P-x-y$) of the systems DMC + methanol with EMISE or with [Bmim][BF$_4$] are plotted in Figures 1 and 2 as an IL-free basis with the IL-free VLE data[16] at the same system and conditions. The mole fractions of EMISE

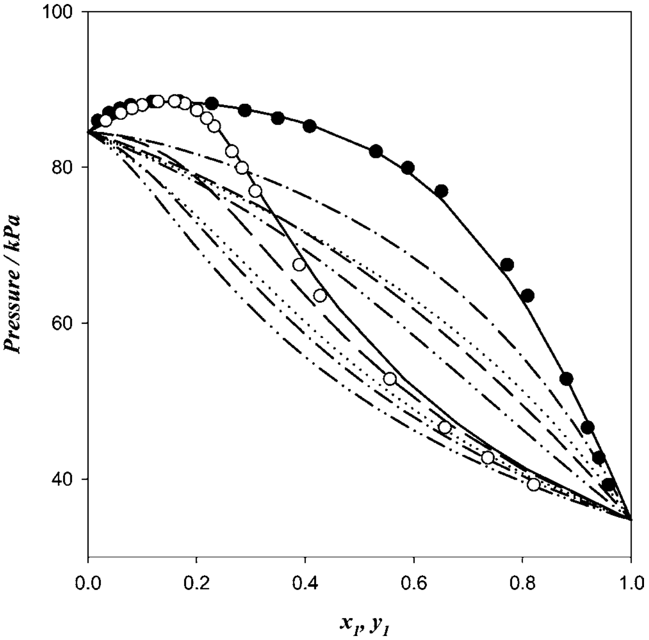

Figure 2. $P-x-y$ for the systems DMC (1) + methanol (2) + ILs at 333.15 K, at several mole fractions of ILs. Prediction from parameters calculated with the model equation, at EMISE mole fractions of −, $x_3 = 0.050$; −•−, $x_3 = 0.100$; −••−, $x_3 = 0.200$; at [Bmim][BF$_4$] mole fractions of •••, $x_3 = 0.200$; ●, solid line, calculated from literature data for the IL-free system.[24]

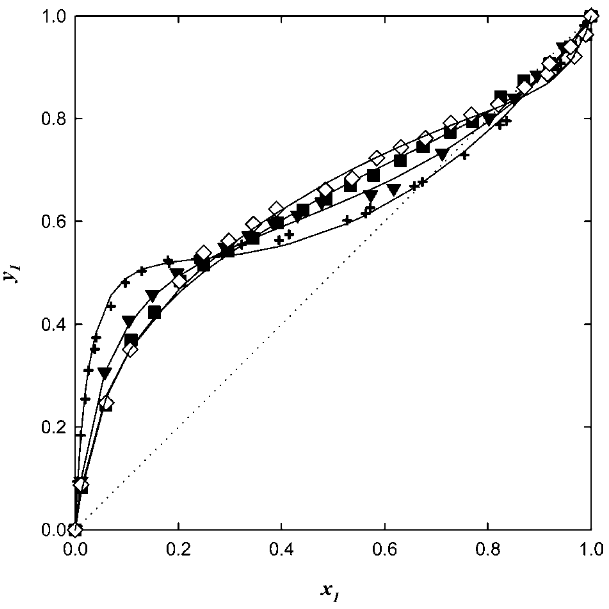

Figure 3. $x-y$ for the systems isopropanol (1) + water (2) + ILs at 333.15 K, at several mole fractions of ILs: +, calculated from literature data for the IL-free system;[19] ▼, isopropanol (1) + water (2) + EMISE (3) at $x_3 = 0.100$; ■, isopropanol (1) + water (2) + EMISE (3) at $x_3 = 0.200$; ◇, isopropanol (1) + water (2) + [Bmim][BF$_4$] (3) at $x_3 = 0.200$; solid lines were calculated by correlated parameters (Table 4).

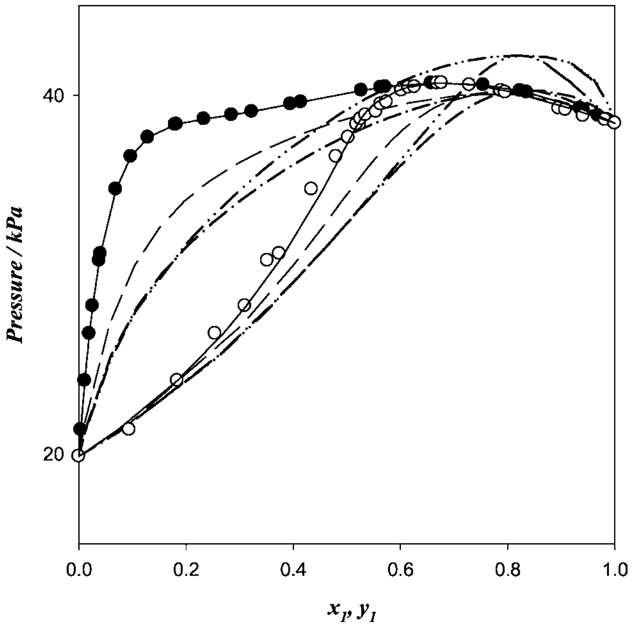

Figure 4. $P-x-y$ for the systems isopropanol (1) + water (2) + ILs at 333.15 K, at several mole fractions of ILs. Prediction from parameters calculated with the model equation, at EMISE mole fractions of -·-, $x_3 = 0.100$; -··-, $x_3 = 0.200$; at [Bmim][BF$_4$] mole fractions of --, $x_3 = 0.200$; ●, solid line, calculated from literature data for the IL-free system.[17]

(x_3) are 0.05, 0.1, and 0.2, while that of [Bmim][BF$_4$] was fixed as 0.2. For the case of the isopropanol + water system, the mole fraction of EMISE (x_3) was fixed as 0.1 and 0.2. Figures 3 and 4 show the $x-y$ and $p-x-y$ diagram for the isopropanol + water system on an IL-free basis, respectively.

The addition of EMISE or [Bmim][BF$_4$] to the systems DMC + methanol or isopropanol + water gave an increase in the mole fraction of methanol and isopropanol in the vapor phase. In the case of the DMC + methanol system, the azeotrope disappeared completely at IL concentrations of $x_3 = 0.1$. There is no significant difference between the two ILs, but EMISE showed a slightly better salting-out effect. In the case of the isopropanol + water system, the azeotrope was not eliminated completely but rather shifted to $x_1 = 0.7965$ from $x_1 = 0.6832$ (IL free base) at the concentration of the EMISE, $x_3 = 0.1$, and shifted to $x_1 = 0.8842$ at $x_3 = 0.2$. EMISE also showed a slightly better salting-out effect than [Bmim][BF4]. The azeotrope was moved to $x_1 = 0.8424$ at the concentration of [Bmim][BF4], $x_3 = 0.2$.

Table 4. Wilson, NRTL, and UNIQUAC Model Parameters and Mean Deviations between the Calculated and Experimental Vapor-Phase Mole Fraction (Δy_1) for Each Binary System at 333.15 K

model equation	A_{12} / J·mol^{-1}	A_{21} / J·mol^{-1}	α	Δy_1
DMC (1) + methanol (2) + EMISE (3)				
$x_3 = 0.05$				
Wilson	−31.4039	625.8839	-	0.0035
NRTL	50.2092	515.5739	0.3000	0.0035
UNIQUAC	483.6547	−64.7643	-	0.0035
$x_3 = 0.10$				
Wilson	−218.0590	668.1532	-	0.0030
NRTL	160.2678	273.2243	0.3007	0.0031
UNIQUAC	516.2400	−130.3669	-	0.0033
$x_3 = 0.20$				
Wilson	453.1190	49.4798	-	0.0081
NRTL	−670.6889	1249.2448	0.2996	0.0060
UNIQUAC	−105.5969	303.4284	-	0.0080
DMC (1) + methanol (2) + [Bmim][BF$_4$] (3)				
$x_3 = 0.20$				
Wilson	−223.7446	578.5295	-	0.0029
NRTL	52.4103	294.7295	0.3004	0.0028
UNIQUAC	452.8618	−129.7399	-	0.0028
isopropanol (1) + water (2) + EMISE (3)				
$x_3 = 0.10$				
Wilson	−52.5096	1176.7859	-	0.0067
NRTL	−75.6121	1166.5556	0.3023	0.0078
UNIQUAC	820.0103	−333.2036	-	0.0095
$x_3 = 0.20$				
Wilson	−228.7142	1145.4052	-	0.0105
NRTL	73.8392	766.4007	0.2985	0.0101
UNIQUAC	1131.3812	−481.3179	-	0.0084
isopropanol (1) + water (2) + [Bmim][BF$_4$] (3)				
$x_3 = 0.20$				
Wilson	−585.1138	1485.4530	-	0.0130
NRTL	538.9631	438.3708	0.7176	0.0124
UNIQUAC	1633.8194	−556.0345	-	0.0115

The adjustable g^E model parameters are listed in Table 4, along with the mean deviation of equilibrium vapor phase mole fraction (Δy_1) between experimental and calculated values. Equation 1 is the objective function (OF), used for optimization of g^E models. The input parameters for this optimization were x_1,y_1 and P

$$\mathrm{OF} = \sum (P_{\mathrm{exp}} - P_{\mathrm{cal}})^2 \tag{1}$$

The term Δy_1 was calculated from eq 2, and in most cases, Δy_1 was less than 0.003.

$$\Delta y_1 = \frac{|\Delta y_{1,\mathrm{exp}} - \Delta y_{1,\mathrm{cal}}|}{N} \tag{2}$$

where N is the number of experimental data points. The binary parameters (A_{ij}) for the activity coefficient (γ) models of Wilson, NRTL, and UNIQUAC are

$$A_{ij} = (\lambda_{ij} - \lambda_{ii})/\mathrm{J \cdot mol^{-1}}\ \text{(Wilson)}$$

$$A_{ij} = (g_{ij} - g_{ii})/\mathrm{J \cdot mol^{-1}}\ \text{(NRTL)}$$

$$A_{ij} = (u_{ij} - u_{ii})/\text{J} \cdot \text{mol}^{-1} \text{ (UNIQUAC)}$$

where λ_{ij}, g_{ij}, and u_{ij} are interaction energy for each equation between molecules i and j.

Table 5. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for Binary Systems DMC (1) + Methanol (2), DMC (1) + EMISE (2), DMC (1) + [Bmim][BF$_4$] (2), Methanol (1) + EMISE (2), and Methanol (1) + [Bmim][BF$_4$] (2) at 298.15 K

x_1	ρ / $\text{g}\cdot\text{cm}^{-3}$	V^E / $\text{cm}^3\cdot\text{mol}^{-1}$	n_D	ΔR / $\text{cm}^3\cdot\text{mol}^{-1}$
		DMC (1) + methanol (2)		
0.0000	0.78672	−0.0062	1.32668	0.0000
0.0501	0.81435	−0.0212	1.33071	−0.7028
0.0997	0.83896	−0.0308	1.33427	−1.2605
0.2008	0.88251	−0.0535	1.34139	−2.0243
0.3003	0.91819	−0.0641	1.34700	−2.4219
0.4002	0.94852	−0.0679	1.35162	−2.5472
0.5005	0.97463	−0.0684	1.35583	−2.4410
0.6004	0.99716	−0.0637	1.35891	−2.1818
0.7015	1.01704	−0.0524	1.36093	−1.8047
0.8012	1.03429	−0.0364	1.36336	−1.2776
0.8999	1.04944	−0.0155	1.36501	−0.6830
0.9483	1.05631	−0.0068	1.36566	−0.3660
1.0000	1.06328	0.0000	1.36647	0.0000
		DMC (1) + EMISE (2)		
0.0000	1.23633	0.0000	1.47908	0.0000
0.0502	1.23317	−0.1197	1.47687	−1.2299
0.0999	1.22981	−0.2332	1.47443	−2.3986
0.1987	1.22327	−0.5662	1.46971	−4.4984
0.2999	1.21547	−0.8850	1.46385	−6.3609
0.3994	1.20615	−1.1356	1.45729	−7.7740
0.5006	1.19457	−1.3242	1.44906	−8.7443
0.5999	1.18067	−1.4473	1.43953	−9.0878
0.7001	1.16311	−1.4827	1.42848	−8.6197
1.0000	1.06328	0.0000	1.36647	0.0000
		DMC (1) + [Bmim][BF$_4$] (2)		
0.0000	1.19278	0.0000	1.41831	0.0000
0.0510	1.19117	−0.2210	1.41760	−1.0594
0.1014	1.18924	−0.4031	1.41675	−2.0520
0.1987	1.18498	−0.7298	1.41501	−3.7912
0.2999	1.17976	−1.0447	1.41282	−5.3347
0.4012	1.17339	−1.3145	1.41049	−6.5148
0.5000	1.16572	−1.5229	1.40796	−7.2437
0.6005	1.15589	−1.6601	1.40459	−7.4891
0.7007	1.14306	−1.6759	1.39931	−7.1521
0.8003	1.12552	−1.4878	1.39196	−6.0041
0.9000	1.10022	−0.9657	1.38162	−3.7523
1.0000	1.06328	0.0000	1.36647	0.0000
		Methanol (1) + EMISE (2)		
0.0000	1.23633	0.0000	1.47908	0.0000
0.0487	1.23201	−0.0784	1.47873	−2.1462
0.0977	1.22732	−0.1620	1.47637	−4.4600
0.1978	1.21677	−0.3825	1.47035	−9.0516
0.2989	1.20348	−0.5582	1.46618	−13.0598
0.3991	1.18670	−0.6771	1.46462	−16.2836
0.4991	1.16538	−0.7797	1.46284	−18.8497
0.5993	1.13734	−0.8630	1.45585	−20.7747
0.7002	1.09894	−0.9417	1.43992	−21.6284
0.7999	1.04362	−0.9639	1.41722	−20.1902
0.9002	0.95354	−0.7606	1.39225	−14.1911
0.9502	0.88435	−0.4860	1.37316	−8.4158
1.0000	0.78672	0.0000	1.32668	0.0000
		Methanol (1) + [Bmim][BF$_4$] (2)		
0.0000	1.19278	0.0000	1.41831	0.0000
0.0517	1.18858	−0.0772	1.41844	−1.9891
0.1040	1.18387	−0.1444	1.41726	−4.0849
0.1995	1.17409	−0.2662	1.41454	−7.7710
0.2975	1.16214	−0.4055	1.41296	−11.1162
0.3993	1.14682	−0.5439	1.41485	−13.8624
0.5002	1.12734	−0.6560	1.41652	−16.0621
0.5990	1.10237	−0.7531	1.41435	−17.6909
0.6994	1.06786	−0.8367	1.40537	−18.4418
0.7997	1.01659	−0.7849	1.39145	−17.2024
0.9000	0.93460	−0.5637	1.37496	−12.1309
0.9501	0.87282	−0.3487	1.36221	−7.1944
1.0000	0.78672	0.0000	1.32668	0.0000

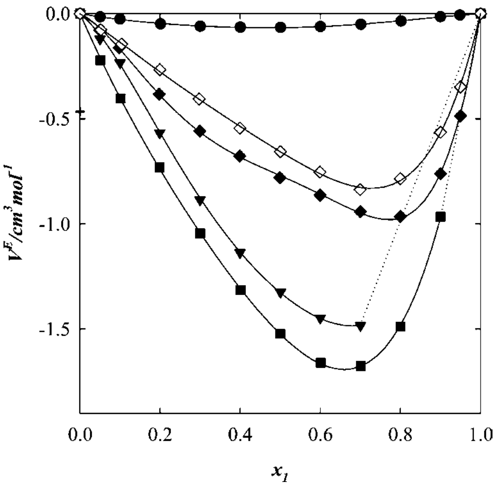

Figure 5. V^E ($\text{cm}^3\cdot\text{mol}^{-1}$) for five binary systems at 298.15 K: ●, DMC (1) + methanol (2); ▼, DMC (1) + EMISE (2); ■, DMC (1) + [Bmim][BF$_4$] (2); ♦, methanol (1) + EMISE (2); ◇, methanol (1) + [Bmim][BF$_4$] (2). Solid curves were calculated from Redlich−Kister parameters.

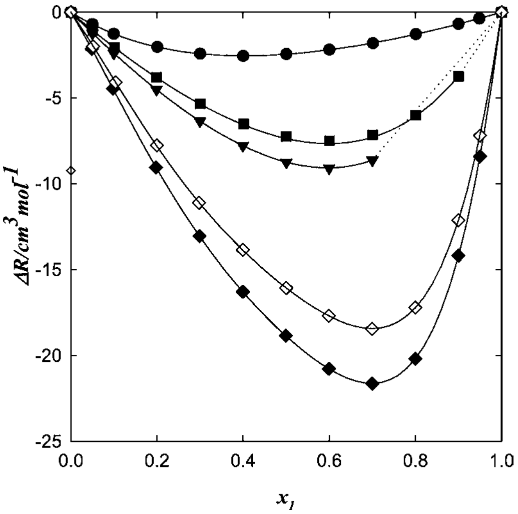

Figure 6. ΔR ($\text{cm}^3\cdot\text{mol}^{-1}$) for five binary systems at 298.15 K: ●, DMC (1) + methanol (2); ▼, DMC (1) + EMISE (2); ■, DMC (1) + [Bmim][BF$_4$] (2); ♦, methanol (1) + EMISE (2); ◇, methanol (1) + [Bmim][BF$_4$] (2). Solid curves were calculated from Redlich−Kister parameters.

Excess Molar Volumes. Density and refractive indices at 298.15 K for the same mixtures without ILs were measured and are in Table 5, along with the calculated values of V^E and ΔR. The term V^E for multicomponent mixtures was calculated from the measured densities from eq 3.

$$V^E/\text{cm}^3 \cdot \text{mol}^{-1} = \frac{\sum_i x_i M_i}{\rho_m} - \sum_i \left(\frac{x_i M_i}{\rho_i}\right) \tag{3}$$

where x_i, M_i, ρ_i, and ρ_m are the mole fraction, molar mass, pure component density, and mixture density, respectively.

Values for ΔR were calculated from molar refractivity (R_m) data for the pure components and the mixtures, which are derived from measured densities and refractive indices using eqs 4 through 7.[17,18]

$$\Delta R/\text{cm}^3 \cdot \text{mol}^{-1} = R_m - \sum_i \phi_i R_i \tag{4}$$

$$R_m = \left(\frac{n_D{}^2 - 1}{n_D{}^2 + 1}\right)\left(\frac{\sum_i x_i M_i}{\rho_m}\right) \tag{5}$$

$$R_i = \left(\frac{n_{D,i}^{\ 2} - 1}{n_{D,i}^{\ 2} + 1}\right)\left(\frac{M_i}{\rho_i}\right) \tag{6}$$

and

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j} \tag{7}$$

where ϕ_i, n_D, $n_{D,i}$, and V_i are the volume fraction of the pure components in the mixture, the refractive index of the mixture, and the refractive index and molar volume of a pure component, respectively.

The experimental values of V^E and ΔR at $T = 298.15$ K are plotted in Figures 5 and 6, respectively. The DMC + IL systems have an immiscible region, and they are illustrated as a dotted line in the figures.

The V^E for all the measured systems showed negative deviation from ideal behavior over the whole composition range. The excess volume is strongly related to the liquid's structure and molecular interactions. Therefore, excess volumes are a function of molecular interactions between the components of the mixture. Negative deviations from ideality could be caused from the hydrogen bonding of alcohols and strong polarity of the ILs. Maximum negativity was shifted to the right of the equimolar amounts, except for the DMC + methanol system, in which V^E was close to zero for the whole composition ranges.

The ΔR of all the measured binary systems showed negative values as well, likely because refractive indices are also related to molecular interactions. However, the maximum negative ΔR was shown in the methanol + EMISE system, while the DMC + [Bmim][BF$_4$] system showed a maximum negative V^E among measured systems. It is believed that the reflective index deviation depends not only on the strength of specific interactions but also on the molecular size and shape of the components. The magnitude of negativity of the system follows the order: methanol + EMISE > methanol + [Bmim][BF$_4$] > DMC + EMISE > DMC + Bmim][BF$_4$] > DMC + methanol.

The binary V^E and ΔR data were correlated with a four-parameter Redlich−Kister polynomial.

$$V^E \text{ or } \Delta R/\text{cm}^3 \cdot \text{mol}^{-1} = x_1 x_2 \sum_{i=1}^{4} A_i (x_1 - x_2)^{i-1} \tag{8}$$

The standard deviation of the fits, σ_{st}, is defined as

$$\sigma_{st}/\text{cm}^3 \cdot \text{mol}^{-1} = \left[\frac{\sum_i ((V^E \text{ or } \Delta R)_{cal} - (V^E \text{ or } \Delta R)_{exp})_i^2}{(N - n)}\right]^{1/2} \tag{9}$$

where N is the number of experimental data points and n is the number of fitted parameters.

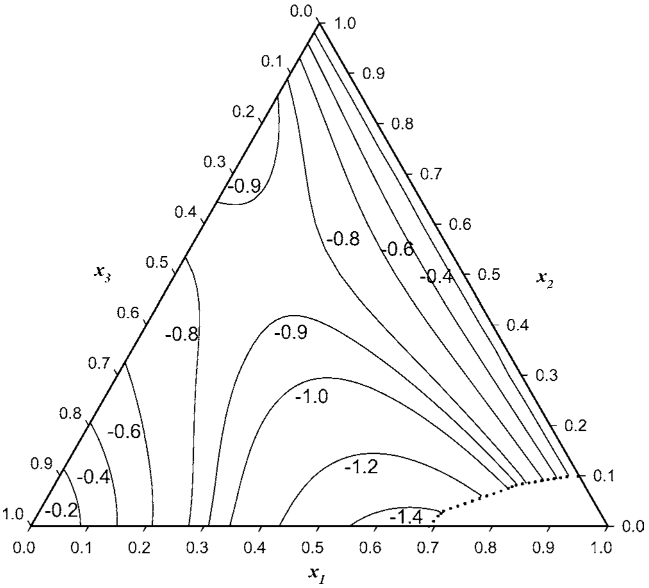

Figure 7. Isoclines of V^E (cm^3·mol^{-1}) for the ternary system DMC (1) + methanol (2) + EMISE at 298.15 K.

The correlated parameters are listed in Table 6, and the solid lines in Figures 5 and 6 were calculated with correlated parameters. The mean deviations of V^E between experimental and calculated data were (0.0015, 0.0098, 0.0062, 0.0093, and 0.0097) g·cm^{-3} for DMC + methanol, DMC + EMISE, DMC + Bmim][BF$_4$], methanol + EMISE, and ethanol + [Bmim][BF$_4$], respectively. The mean deviations of ΔR were (0.0078, 0.0091, 0.0159, 0.0052, and 0.0196) cm^3·mol^{-1} for the systems DMC + methanol, DMC + EMISE, DMC + Bmim][BF$_4$], methanol + EMISE, and ethanol + [Bmim][BF$_4$], respectively.

In addition, the V^E and ΔR for the ternary systems DMC + methanol + EMISE and DMC + methanol + [Bmim][BF$_4$] were estimated from the correlated sub-binary Redlich−Kister parameters in Table 6 using the Radojkovič equation. As shown in Figures 5 and 6, when DMC or methanol mixed with ILs, the negativity of V^E and ΔR was increased compared to the mixture of DMC + methanol. This might be due to clustering of DMC or methanol molecules, which causes the excess properties of these liquids to be more negative. Therefore, the ternary V^E and ΔR of the systems DMC + methanol + ILs showed large negative values in the whole concentration ranges that can be foreseen from the negative binary V^E and ΔR data. The solid lines in Figures 7 to 10 represent the isoclines of ternary V^E and ΔR. The dotted line in the figures illustrates the immiscible region, which was roughly determined experimentally.

Conclusions

The VLE behavior for the systems DMC + methanol + EMISE, DMC + methanol + [Bmim][BF$_4$], isopropanol +

Table 6. Fitted Parameters for the Redlich−Kister Equation and Standard Deviations for V^E and ΔR for Binary Systems DMC (1) + Methanol (2), DMC (1) + EMISE (2), DMC (1) + [Bmim][BF$_4$] (2), Methanol (1) + EMISE (2), and Methanol (1) + [Bmim][BF$_4$] (2) at 298.15 K

	systems	A_1	A_2	A_3	A_4	σ_{st}
V^E	DMC (1) + methanol (2)	−0.2651	0.0399	0.0364	0.0663	0.0015
	DMC (1) + EMISE (2)	−5.3008	−3.1435	−2.0480	−2.6779	0.0090
	DMC (1) + [Bmim][BF$_4$] (2)	−6.0952	−3.7193	−2.3687	−0.3811	0.0062
	methanol (1) + EMISE (2)	−3.0807	−1.6806	−3.2514	−3.7754	0.0093
	methanol (1) + [Bmim][BF$_4$] (2)	−2.6240	−2.3073	−2.0014	−1.0677	0.0097
ΔR	DMC (1) + methanol (2)	−9.7898	3.6037	−1.5814	0.6042	0.0078
	DMC (1) + EMISE (2)	−34.9758	−13.4306	−4.2531	−0.6173	0.0082
	DMC (1) + [Bmim][BF$_4$] (2)	−28.9500	−10.3538	−5.0150	−2.7791	0.0116
	methanol (1) + EMISE (2)	−75.4797	−45.3179	−45.0598	−33.8560	0.0045
	methanol (1) + [Bmim][BF$_4$] (2)	−64.2524	−38.6254	−38.8418	−28.6837	0.0196

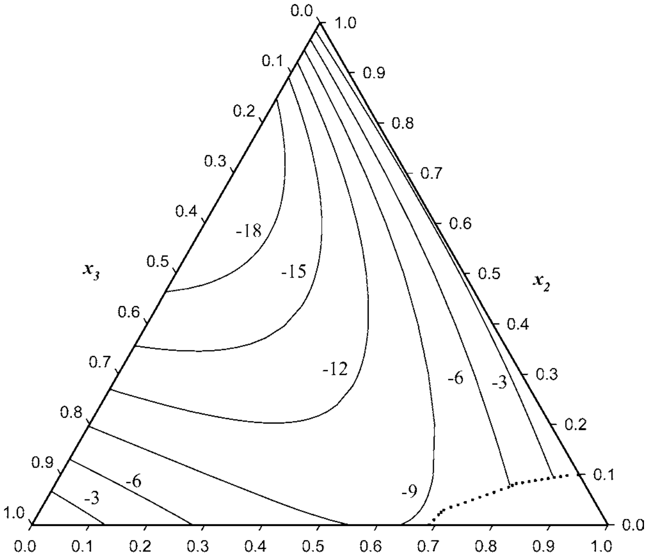

Figure 8. Isoclines of ΔR ($cm^3 \cdot mol^{-1}$) for the ternary system DMC (1) + methanol (2) + EMISE at 298.15 K.

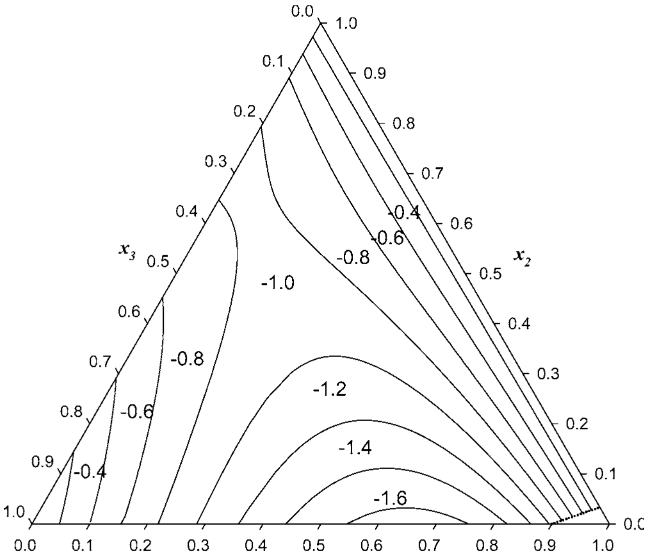

Figure 9. Isoclines of V^E ($cm^3 \cdot mol^{-1}$) for the ternary system DMC (1) + methanol (2) + [Bmim][BF$_4$] at 298.15 K.

water + EMISE, and isopropanol + water + [Bmim][BF$_4$] has been investigated at $T = 333.15$ K with the help of HSGC. Ionic liquids, EMISE, and [Bmim][BF$_4$] were effective to break or to move the azeotropic point. An azeotrope of the system DMC + methanol disappeared at the concentration of ionic liquids, $x_3 = 0.1$, while the azeotrope of the system isopropanol + water did not disappear but rather shifted significantly from the original azeotropic concentration of the IL free base. The VLE data correlated well with the common g^E models of Wilson, NRTL, and UNIQUAC.

The experimental V^E and ΔR data for the binary systems DMC + methanol, DMC + EMISE, DMC + [Bmim][BF$_4$], methanol + EMISE, and ethanol + [Bmim][BF$_4$] showed negative deviations from ideal behavior, and they correlated well with the Redlich−Kister equation. Negative deviations from ideality could be caused from the hydrogen bonding of alcohols and strong polarity of the ILs.

The binary systems DMC + EMISE or + [Bmim][BF$_4$] have an immiscible region in the DMC-rich phase. In addition, the negative ternary V^E and ΔR were estimated from the correlated binary Redlich−Kister parameters for the systems DMC + methanol + EMISE and DMC + methanol + [Bmim][BF$_4$]. When the system DMC + methanol mixed with ILs, the negativity of V^E and ΔR was increased compared to the binary mixture of DMC + methanol. This might be due to clustering of DMC or methanol molecules.

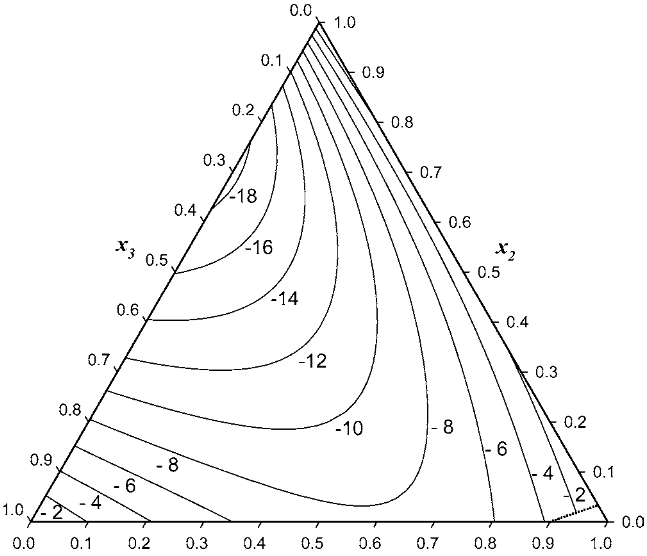

Figure 10. Isoclines of constant ΔR ($cm^3 \cdot mol^{-1}$) for the ternary system DMC (1) + methanol (2) + [Bmim][BF$_4$] at 298.15 K.

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