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Measurement, correlation, and prediction of vapor pressure for binary and ternary systems containing an ionic liquid 1,3-dimethylimidazolium methylsulfate

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ABSTRACT

Vapor pressure data for water, ethanol, 1-propanol, and 2-propanol, as well as the mixtures of {water + 1-propanol} and {water + 2-propanol}, were experimentally measured in the presence of an ionic liquid (IL) 1,3-dimethylimidazolium methylsulfate ([MMIM][MS]) at varying IL-contents and temperatures using a quasi-static ebulliometric method. The experimental vapor pressure data for binary systems containing IL were correlated using NRTL model with an overall relative root mean square deviation (rRMSD) of 0.0055, and the obtained binary NRTL parameters were employed to predict the vapor pressure for two ternary systems with an overall rRMSD less than 0.0234. Moreover, the inter-molecular interaction between [MMIM][MS] and volatile solvent was assessed theoretically in terms of the predicted activity coefficients of solvents for binary systems and quantum chemical calculations with polarizable continuum model. Finally, isobaric VLE data were predicted for three ternary systems containing [MMIM][MS] with IL mole fraction of 0.05, 0.15, and 0.25 at 101.325 kPa, respectively. The results indicate that [MMIM][MS] might be applied as a promising entrainer to separate the azeotropic mixtures of {water + ethanol}, {water + 1-propanol}, and {water + 2-propanol} by extractive distillation.

1. Introduction

As a novel class of chemical compounds, ionic liquids (ILs) have attracted substantial attention among many applications, especially in separation process, such as separating azeotropic mixtures [1], extracting aromatic hydrocarbons from aliphatic hydrocarbons [2], removing sulfur or nitrogen in fuel oil [3], absorbing acid or alkaline gases selectively [4], and capturing CO_2 [5]. Owning to their specific properties (e.g., almost null volatility at room temperature, easy recyclability, high thermal stability, nonflammability, and structural tenability), ILs show great potential to avoid some environmental and operational problems caused by conventional organic solvents [6].

Knowledge of the phase equilibria for systems containing ILs is crucially important to understand the thermodynamic behavior of ILs, as well as to develop thermodynamic models for process design or optimization. The experimental determination of vapor–liquid equilibria (VLE) is fundamental to apply ILs as entrainers in extractive distillation effectively [1,7]. Presently, numerous studies have been conducted to select ILs for the separation of azeotropic mixtures of {water + ethanol} [8], {water + propanol} [9,10], {water + acetonitrile} [11,12], {ethanol + ethyl acetate} [13,14], {methanol + acetone} [15,16], {methanol + dimethyl carbonate} [17,18], and so forth. Among those various systems reported, the VLE for aqueous systems have been investigated the most extensively. Li and co-workers [19–23] reported a series of VLE data for {water + methanol/ethanol} systems containing an imidazolium- or alkanolammonium-based IL, and discussed the effect of ILs on the volatility of varying solvents. Domínguez et al. [24–26] evaluated the effect of 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][ES], 1-butyl-3-methylimidazolium methylsulfate [BMIM][MS], and 1-ethyl-3-methylpyridinium ethylsulfate [EMPY][ES] on the isobaric VLE for {water + ethanol} system, and correlated the experimental data with e-NRTL and NRTL equations. Banerjee et al. [27] found that the model based on conductor-like screening model for real solvents (COSMO-RS) could provide fairly close predictions of the VLE behavior of systems containing ILs as compared to the results of common activity coefficient models. They also applied this method as a prior screening to evaluate the relative volatility of ILs that contain various cations and anions for {water + alcohols} and {water + tetrahydrofuran} systems [28]. Recently, Lei et al. [29] proposed using the mixture

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Table 1
Antonie constans A_i,B_i, and C_i for compounds involved in this work [34].

Compound	Antonie constant		
	A_i	B_i	C_i
Water	7.074056	1657.459	−46.13
Ethanol	7.30243	1630.868	−43.569
1-Propanol	6.97878	1497.734	−69.056
2-Propanol	6.86634	1360.183	−75.557

of IL and solid inorganic salt in place of the single IL as entrainers for separation of {water + ethanol} mixture, and this method provide a new direction to ease operation and increase separation efficiency in extractive distillation.

Relative to the tremendous combination of azeotropic mixtures and ILs, studies on the VLE behavior for systems containing ILs, nevertheless, appear quite limited, let along the interaction mechanism between ILs and volatile solvents. In past decades, most research attention has been paid to the ILs with halogen-containing anions, such as hexafluorophosphate $[PF_6]^-$ and tetrafluoroborate $[BF_4]^-$; however, these water-unstable fluorinated ILs tend to arise problems like toxicity or corrosion [30]. Therefore, it is fairly necessary to carry out investigation on halogen-free ILs. To this end, the low-cost halogen-free IL [31], 1,3-dimethylimidazolium methylsulfate ([MMIM][MS]), was studied here to evaluate the effect on the VLE behavior of {water + alcohol} systems.

In this work, we first experimentally investigated the effects of [MMIM][MS] on the vapor pressure of water, ethanol, 1-propanol, 2-propanol, {water + 1-propanol}, and {water + 2-propanol} mixtures at different temperatures and IL-contents. The vapor pressure data for binary systems were correlated using NRTL model, and the obtained binary model parameters were used to predict the vapor pressure of two ternary systems of {water + 1-propanol + [MMIM][MS]} and {water + 2-propanol + [MMIM][MS]}. Then the intermolecular interaction between [MMIM][MS] and the volatile solvents was estimated in terms of predicted activity coefficients of solvents in binary systems and quantum chemical calculations. Finally, the isobaric VLE data for three ternary systems containing [MMIM][MS] with IL mole fraction of 0.05, 0.15, and 0.25 at 101.325 kPa were used to assess the separation ability of [MMIM][MS] for the azeotropic systems of {water + ethanol}, {water + 1-propanol}, and {water + 2-propanol} by extractive distillation.

2. Experimental

2.1. Materials

The chemical reagents used here were deionized water, ethanol, 1-propanol, 2-propanol, 1-methylimidazole, dimethyl sulfate. Analytical reagent grade ethanol, 1-propanol, and 2-propanol with a purity of $w \geq 99.7\%$ were purchased from

Table 2
Experimental and calculated vapor pressure data for the binary system {water[1] + [MMIM][MS][2]}.[a]

T (K)	P^{exp} (kPa)	P^{cal} (kPa)	γ_1^{exp}	γ_1^{cal}
$x_1 = 0.9905$				
325.33	13.43	13.56	0.9879	0.9972
331.95	18.43	18.61	0.9879	0.9975
340.11	26.70	26.97	0.9878	0.9977
346.26	34.87	35.20	0.9884	0.9979
353.75	47.62	47.99	0.9905	0.9981
361.49	64.56	65.06	0.9905	0.9982
368.44	83.85	84.49	0.9908	0.9984
373.85	102.08	102.74	0.9921	0.9985
$x_1 = 0.9788$				
323.95	12.29	12.40	0.9790	0.9876
334.22	20.07	20.27	0.9795	0.9891
340.02	26.11	26.34	0.9814	0.9899
348.63	37.81	38.15	0.9820	0.9908
354.91	48.87	49.34	0.9819	0.9915
362.40	65.52	66.17	0.9825	0.9921
369.00	83.94	84.73	0.9835	0.9927
374.64	102.84	103.82	0.9836	0.9931
$x_1 = 0.9643$				
326.30	13.43	13.46	0.9676	0.9703
334.54	19.87	19.93	0.9700	0.9730
340.82	26.28	26.47	0.9679	0.9748
349.80	38.64	38.92	0.9701	0.9772
356.19	50.09	50.50	0.9706	0.9787
363.85	67.39	68.05	0.9707	0.9803
370.05	84.99	85.75	0.9727	0.9815
375.42	102.96	104.02	0.9724	0.9824
$x_1 = 0.9204$				
329.08	13.94	13.67	0.9207	0.9027
338.00	21.13	20.83	0.9237	0.9106
344.09	27.56	27.36	0.9223	0.9155
352.14	38.60	38.56	0.9225	0.9214
359.25	51.34	51.44	0.9244	0.9261
366.50	67.65	68.12	0.9242	0.9306
373.22	86.82	87.35	0.9287	0.9344
377.84	102.37	103.03	0.9308	0.9368

[a] Standard uncertainties u are $u(T) = 0.02$ K, $u(x) = 0.0001$, and $u(P) = 0.04$ kPa.

Table 3
Experimental and calculated vapor pressure data for the binary system {ethanol[1] + [MMIM][MS][2]}.[a]

T (K)	P^{exp} (kPa)	P^{cal} (kPa)	γ_1^{exp}	γ_1^{cal}
$x_1 = 0.9760$				
308.92	14.03	14.08	1.3174	1.3212
317.47	21.82	21.89	1.2758	1.2787
322.45	27.88	27.97	1.2550	1.2578
329.73	39.32	39.39	1.2308	1.2317
335.72	51.53	51.53	1.2150	1.2136
341.95	67.49	67.40	1.2003	1.1976
348.02	86.77	86.61	1.1878	1.1843
352.23	102.76	102.46	1.1810	1.1764
$x_1 = 0.9476$				
309.15	13.92	14.03	1.3285	1.3373
317.82	21.77	21.93	1.2862	1.2935
322.67	27.66	27.82	1.2679	1.2729
329.55	38.28	38.43	1.2454	1.2478
335.82	50.84	50.94	1.2285	1.2283
342.31	67.30	67.32	1.2136	1.2113
348.41	86.56	86.55	1.2004	1.1977
352.50	102.13	101.87	1.1955	1.1898
$x_1 = 0.9194$				
308.57	13.26	13.40	1.3490	1.3615
317.37	20.90	21.12	1.3041	1.3157
321.98	26.27	26.51	1.2864	1.2955
330.71	39.69	39.93	1.2581	1.2631
336.29	51.06	51.22	1.2447	1.2458
342.81	67.61	67.74	1.2293	1.2285
348.39	85.17	85.21	1.2186	1.2158
352.82	101.98	101.63	1.2145	1.2070
$x_1 = 0.8189$				
309.50	13.17	13.26	1.4264	1.4401
317.29	19.70	19.84	1.3858	1.3983
324.16	27.72	27.78	1.3630	1.3676
331.99	40.18	39.96	1.3452	1.3385
337.66	51.67	51.38	1.3283	1.3207
344.20	68.31	67.86	1.3124	1.3031
349.76	85.65	85.15	1.2992	1.2902
354.24	102.45	101.63	1.2933	1.2812

[a] Standard uncertainties u are $u(T) = 0.02$ K, $u(x) = 0.0001$, and $u(P) = 0.04$ kPa.