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Measurement, correlation, and prediction of vapor pressure for binary and ternary systems containing an alkylsulfate-based ionic liquid

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ABSTRACT

Vapor pressure data for water, 1-propanol, 2-propanol, as well as the mixtures of {water + 1-propanol} and {water + 2-propanol}, were measured by a quasi-static ebulliometric method, in the presence of an alkylsulfate-based IL, namely, 1-ethyl-3-methylimidazolium methylsulfate ([EMIM][MS]) or 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][ES]). The experimental vapor pressure data for binary systems containing IL were correlated by NRTL model with an overall relative root mean square deviation (rRMSD) of 0.0053, and the obtained binary NRTL parameters were employed to predict the vapor pressure for two ternary systems with an overall rRMSD of 0.0196. In addition, isobaric vapor–liquid equilibria were predicted for the ternary systems containing [EMIM][MS], [EMIM][ES], 1,3-dimethylimidazolium methylsulfate ([MMIM][MS]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [EMIM][OTf], respectively, with IL mole fraction of 0.05, 0.15, and 0.25 at 101.325 kPa. It was found that the addition of IL can enhance the relative volatility of propanol to water, and the separation ability follows the order of [MMIM][MS] > [EMIM][MS] > [EMIM][ES] > [EMIM][BF_4] > [EMIM][OTf], which was further explained at electronic level with quantum chemical calculation. Therefore, the azeotropic mixtures of {water + 1-propanol}, and {water + 2-propanol} might be separated effectively by the addition of the alkylsulfate-based ILs in extractive distillation.

1. Introduction

In chemical industry, the separation of azeotropic or close boiling mixtures is usually realized with special distillation, such as extractive distillation and salt distillation, in which an entrainer is added into the mixtures for increasing relative volatility. However, the volatile organic solvents used in extractive distillation are likely to harm workers, pollute environment, and consume excessive energy in solvent recycle process, while the inorganic salts used in salt distillation may cause the problems of pipeline blockage and equipment corrosion. Ionic liquids (ILs) are prospective alternatives to conventional solvents in special distillation [1], since several ILs can combine the advantages of both organic solvents and inorganic salts, showing the favorable properties of negligible volatility, good stability, easy recyclability, non-flammability, and structural tenability [2].

Vapor–liquid equilibria (VLE) data are the foundation of process design and equipment selection in distillation. Up to now, many researchers have studied the VLE behavior for systems containing ILs, aiming to screen suitable ILs as entrainers in extractive distillation to enhance separation efficiency [3]. Among those ILs, imidazolium-based ILs are widely investigated, including the ILs with water-unstable fluorinated anions like tetrafluoroborate ($[BF_4]^-$) and hexafluorophosphate ($[PF_6]^-$), which can release toxic hydrogen fluoride under aqueous environment [4], and some expensive ILs with the anion of bis(trifluromethanesulfonyl)imide ($[NTf_2]^-$) or trifluoromethanesulfonate ($[OTf]^-$), which seriously limited their technical application in large scale. Compared with those flawed ILs as entrainers, the hydrophilic ILs with alkylsulfate and dialkylphosphate anions have shown great potential in extractive distillation, owing to their low-viscosity, non-toxicity, and reasonable price [5,6]. Several works have been done to determine the VLE data for systems containing alkylsulfate- and dialkylphosphate-based ILs. Li et al. measured the vapor pressure for binary and ternary systems containing dialkylphosphate-based ILs, including 1-methyl-3-methylimidazolium dimethylphosphate ([MMIM][DMP]),

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Table 1
Specifications of chemical samples.

Chemicals	Source	Purity	Purification method	Analysis method
Water	Distilled in the laboratory	Electrical conductivity < 5 μS cm^{-1} (298.15 K)	None	Electrical conductivity measurement[a]
1-Propanol	Guangfu Chemical Regent Co., Tianjin, China	Mass fraction > 0.997	4A molecular sieves	GC[b]
2-Propanol	Guangfu Chemical Regent Co., Tianjin, China	Mass fraction > 0.997	4A molecular sieves	GC[b][EMIM][MS]
[EMIM][MS]	Synthesized in the laboratory	Mole fraction > 0.990	Distillation	^{1}H NMR, ^{13}C NMR[c]
[EMIM][ES]	Synthesized in the laboratory	Mole fraction > 0.990	Distillation	^{1}H NMR, ^{13}C NMR[c]

[a] Measured at 298.15 K with a conductivity meter (type EC-215, Hanna Co., Italy).
[b] Checked with a gas chromatography (type GC2010, SHIMADZU Co., Japan) equipped with a FID detector and FFAP capillary column.
[c] Recorded on a 400.0 MHz NMR spectrometer (Bruker Co., Germany) at T = 300 K using deuterated water (D_2O) as the external reference solvent.

1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP]), 1-ethyl-3-ethylimidazolium diethylphosphate ([EEIM][DEP]), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]), and 1-butyl-3-emthylimidazolium dibutylphosphate ([BMIM][DBP]). Their results indicated that the addition of ILs can change the relative volatility of a solvent, and that ILs can exhibit "ionic" or "molecule" character in different solvents [7–9]. On the other hand, 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][ES]), one of the first commercial "bulk" ionic liquids (available on a ton-scale), was reported to have the ability to break the azeotrope of water–ethanol mixture with sufficient IL-content [10,11].

In our previous work, the effects of 1-methyl-3-methylimidazolium methylsulfate [MMIM][MS] on the vapor pressure of water, 1-propanol, 2-propanol, {water + 1-propanol}, and {water + 2-propanol} were studied [12]. In order to discuss the influence of alkylsulfate-based ILs with various anion structures on the VLE behavior of {water + propanol} mixtures, herein, we shifted the study object to 1-ethyl-3-methylimidazolium methylsulfate ([EMIM][MS]) and 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][ES]). Thus, the vapor pressure data for water, 1-propanol, and 2-propanol, as well as the mixtures of {water + 1-propanol} and {water + 2-propanol}, were measured in the presence of [EMIM][MS] or [EMIM][ES] at varying IL-content and temperature. The experimental data for binary systems were correlated by NRTL model, and the obtained binary model parameters were used to predict the vapor pressure of the ternary systems of {water + 1-

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

T/K	P^{exp}/kPa	P^{cal}/kPa	γ_1^{exp}	γ_1^{cal}
x_1 = 0.9911				
325.47	13.58	13.68	0.9910	0.9987
332.85	19.31	19.45	0.9915	0.9988
339.46	26.10	26.25	0.9929	0.9989
347.77	37.35	37.57	0.9932	0.9990
353.71	47.73	47.97	0.9940	0.9990
360.69	62.89	63.18	0.9946	0.9991
367.95	82.80	83.09	0.9957	0.9991
373.32	100.79	100.94	0.9977	0.9992
x_1 = 0.9801				
324.84	12.91	13.06	0.9831	0.9939
332.78	18.88	19.09	0.9837	0.9944
341.06	27.44	27.75	0.9837	0.9948
347.98	36.97	37.35	0.9853	0.9952
355.55	50.42	50.91	0.9861	0.9955
362.67	66.52	67.20	0.9857	0.9957
368.80	83.60	84.49	0.9854	0.9960
373.91	100.75	101.65	0.9873	0.9961
x_1 = 0.9659				
324.90	12.61	12.77	0.9713	0.9834
334.35	19.81	20.03	0.9739	0.9849
341.79	27.62	27.98	0.9732	0.9859
350.10	39.34	39.87	0.9739	0.9869
355.56	49.12	49.78	0.9744	0.9875
363.58	67.17	68.05	0.9756	0.9883
369.47	83.67	84.75	0.9762	0.9888
374.66	100.80	102.14	0.9763	0.9893
x_1 = 0.9182				
332.13	16.38	16.21	0.9390	0.9291
339.27	22.75	22.53	0.9421	0.9332
344.26	28.31	28.10	0.9428	0.9358
349.55	35.37	35.22	0.9425	0.9384
357.67	49.22	49.08	0.9449	0.9421
364.82	64.72	64.82	0.9437	0.9451
371.71	83.58	83.73	0.9461	0.9478
376.98	100.94	101.12	0.9480	0.9497

[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 {water (1) + [EMIM][ES] (2)}.[a]

T/K	P^{exp}/kPa	P^{cal}/kPa	γ_1^{exp}	γ_1^{cal}
x_1 = 0.9916				
323.87	12.56	12.66	0.9918	0.9991
331.50	18.16	18.28	0.9929	0.9992
338.66	25.20	25.35	0.9934	0.9992
347.39	36.83	37.01	0.9942	0.9993
353.98	48.34	48.54	0.9952	0.9993
361.95	66.15	66.38	0.9958	0.9994
368.29	83.99	84.21	0.9968	0.9994
372.77	99.02	99.04	0.9992	0.9994
x_1 = 0.9813				
323.35	12.07	12.17	0.9872	0.9959
333.94	20.07	20.20	0.9885	0.9962
339.07	25.31	25.48	0.9880	0.9964
347.50	36.48	36.70	0.9884	0.9967
354.15	47.98	48.25	0.9881	0.9968
362.54	66.72	67.03	0.9894	0.9970
368.78	84.30	84.65	0.9913	0.9972
373.25	99.07	99.49	0.9913	0.9973
x_1 = 0.9684				
325.26	12.97	13.10	0.9789	0.9889
334.56	20.22	20.37	0.9822	0.9898
340.04	25.84	26.10	0.9805	0.9903
349.33	38.53	38.87	0.9824	0.9910
355.44	49.40	49.87	0.9821	0.9914
362.84	66.02	66.57	0.9837	0.9919
369.46	84.53	85.21	0.9836	0.9923
373.88	99.14	99.93	0.9843	0.9926
x_1 = 0.9292				
327.81	13.63	13.72	0.9438	0.9537
335.28	19.37	19.52	0.9420	0.9564
341.78	25.91	26.16	0.9433	0.9585
349.88	36.66	37.01	0.9441	0.9610
356.81	48.60	49.07	0.9447	0.9629
363.92	64.01	64.72	0.9470	0.9648
371.26	84.05	85.01	0.9511	0.9665
375.70	98.70	99.70	0.9550	0.9675

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