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Isobaric vapor-liquid equilibrium for methanol + methyl acetate with ionic liquids [OMMIM][Tf_2N] and [OMIM][Tf_2N] as entrainers at 101.3 kPa

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ABSTRACT

The ionic liquids 1-methyl-3-octylimidazoliumbis (trifluoromethylsulfonyl)imide ([OMIM][Tf_2N]) and 1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide ([OMMIM][Tf_2N]) were utilized as extractive distillation entrainers to make methanol as the volatile component for the separation of the azeotropic mixture of methanol and methyl acetate. Isobaric VLE data for the methanol (1) + methyl acetate (2) + [OMIM][Tf_2N] and methanol (1) + methyl acetate (2) + [OMMIM][Tf_2N] were measured at 101.3 kPa. The experimental data were correlated by NRTL model and UNIFAC model, and the NRTL model is more accurate. Both [OMIM][Tf_2N] and [OMMIM][Tf_2N] produce notable salting-out effects and make methanol as the volatile component, and the azeotropic point of methanol + methyl acetate can be eliminated if the mole fraction of [OMMIM][Tf_2N] or [OMIM][Tf_2N] is greater than 0.4. The mechanism of [OMMIM][Tf_2N] and [OMIM][Tf_2N] to improve the relative volatility of methanol to methyl acetate were investigated, and the salting-out effects of [OMMIM][Tf_2N] is a little larger.

1. Introduction

Methyl acetate is produced as a by-product in the manufacture process of poly (viny1 alcohol) [1]. In this process, methyl acetate is hydrolyzed to acetic acid and methanol and recycled, but the separation of the hydrolysis mixture is complicated, since methyl acetate and methanol can form an azeotrope. Extractive distillation is a commonly used method to separate azeotropes. The selection of solvent for the extractive distillation process is the key problem. In recent years, Ionic liquids (ILs) are often selected as solvents in the extractive distillation [2–10].

For methanol + methyl acetate system, ILs can make methyl acetate more volatile, and destroy the azeotropic point. Some ILs such as 1-butyl-1-methylpyrrolidiniumdicyanamide ([BMPYR][DCA]) [4], 1-ethyl-3-methylimidazoliumthiocyanate ([EMIM][SCN]) [11], 1-ethyl-3-methylimidazoliumacetate ([EMIM][Ac]) [12], 1-ethyl-3-methylimidazoliumtrifluoromethanesulfonate ([EMIM][triflate] [13], 1-hexyl-3-methylimidazolium chloride [HMIM][Cl] [14], 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) [15] and 1-methyl-3-octylimidazoliumtetrafluoroborate [OMIM][BF_4] [16] were selected as extractive distillation solvents for the separation of methyl acetate + methanol, and make methyl acetate as the volatile component. The vapor-liquid equilibria (VLE) of methanol + methyl acetate containing these ILs were also measured. Furthermore, some scholars compared the effects of different ILs on the separation of methanol and methyl acetate. Zhang et al. [14] [17] selected a serial of ILs with halogen anion to separate the azeotrope, and they found the separation effects were in the following order [HMIM][Cl] > [BzMIM][Cl] > [HMIM][Br] > [C4MIM][Cl] > [ClC2MIM][Cl] > [C4MIM][Br]. They stated that the hydrogen bonding interactions between ILs and methanol are stronger than that between ILs and methyl acetate, so methyl acetate is the volatile component. Yu et al. [15] utilized three phosphate ILs 1,3-dimethylimidazoliumdimethylphosphate ([MMIM][DMP]), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM][DEP]) and 1-butyl-3-methylimidazolium dibutylphosphate ([BMIM][DBP]) to separate methanol and methyl acetate mixture, and found that [MMIM][DEP]

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Table 1
Specification of chemical samples.

Chemical name	CAS	Sample source	Mass purity	Water content (mass fraction)	Analysis method
Methyl acetate	79-20-9	Chemart	99.8%	0.0005	GC[a] KF[b]
Methanol	67-56-1	Chemart	99.8%	0.0005	GC[a] KF[b]
Ethanol	64-17-5	Chemart	99.8%	0.0005	GC[a] KF[b]
[OMIM][Tf_2N][d]	178631-04-4	Aolike.China	99.8%	0.0005	LC[c] KF[b]
[OMMIM][Tf_2N][e]	350493-09-3	Aolike.China	99.8%	0.0005	LC[c] KF[b]

[a] Gas Chromatography.
[b] Karl Fischer titration.
[c] Liquid Chromatography.
[d] [OMIM][Tf_2N] = 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide.
[e] [OMMIM][Tf_2N] = 1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide.

exhibited the best separation effect. It attributes the function of ILs to the polarity, and the polarity of ILs decreases with the increasing of alkyl chain length in cation and anion. The polarity of [MMIM][DEP] is the largest, so it is the best entrainer of the three.

Most of the ILs solvent in literature make methyl acetate as the volatile component, however, in some process such as transesterification of methyl acetate and butanol or ethanol by reactive and extractive distillation (RED) [18], the azeotropic mixture of methanol and methyl acetate exists in the reaction solution, and methanol is required to be the volatile component. The selection of effective entrainer making methanol as the volatile component is much more difficult than that making methyl acetate as the volatile component. In our previous works [19,20], we used 1-octyl-3-methylimidazoliumexafluorophosphate [OMIM][PF_6] and 1-butyl-3-methylimidazoliumbis [(trifluoromethyl) sulfonyl]imide [BMIM][Tf_2N] as entrainer to make methanol as the volatile component. However, the VLE data to make methanol as the volatile component are modest. To investigate the different interactions of IL - methanol and IL - methyl acetate, More VLE data for methanol + methyl acetate + IL are required.

Table 2
The experimental VLE data for the ternary system of methanol (1) + methyl acetate (2) + [OMIM][Tf_2N] (3) at 101.3 kPa.

x_3	T/K	x_1	x_1'	y_1	α_{12}
0.200	339.70	0.000	0.000	0.000	
0.199	338.60	0.070	0.088	0.133	1.592
0.199	337.50	0.151	0.188	0.243	1.384
0.200	336.95	0.240	0.300	0.349	1.252
0.206	336.75	0.308	0.388	0.421	1.147
0.200	337.10	0.395	0.493	0.496	1.012
0.200	337.95	0.489	0.611	0.582	0.886
0.198	338.80	0.564	0.703	0.641	0.755
0.200	340.45	0.647	0.808	0.749	0.707
0.201	342.65	0.736	0.920	0.870	0.581
0.199	344.80	0.801	1.000	1.000	
0.400	358.30	0.000	0.000	0.000	
0.399	356.80	0.053	0.088	0.137	1.656
0.400	355.25	0.113	0.189	0.261	1.511
0.400	354.35	0.170	0.283	0.367	1.471
0.399	353.70	0.234	0.390	0.457	1.320
0.398	353.40	0.302	0.502	0.562	1.274
0.400	353.55	0.359	0.599	0.639	1.184
0.399	353.85	0.420	0.699	0.721	1.114
0.400	354.45	0.476	0.793	0.808	1.094
0.399	355.40	0.542	0.902	0.909	1.087
0.400	356.60	0.600	1.000	1.000	
0.499	370.25	0.000	0.000	0.000	
0.500	368.35	0.045	0.091	0.143	1.678
0.497	366.60	0.095	0.188	0.276	1.647
0.499	365.35	0.146	0.291	0.385	1.524
0.499	364.35	0.197	0.393	0.479	1.420
0.497	363.70	0.250	0.497	0.586	1.433
0.499	363.50	0.299	0.596	0.655	1.285
0.500	363.35	0.354	0.707	0.750	1.244
0.499	363.65	0.411	0.821	0.842	1.162
0.497	364.05	0.454	0.903	0.915	1.154
0.500	364.50	0.500	1.000	1.000	

[a] Standard uncertainties: $u(x) = 0.002$, $u(y) = 0.002$, $u(T) = 0.05$ K, $u(P) = 0.1$ kPa.

In this work, we utilized 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [OMIM][Tf_2N] and 1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [OMMIM][Tf_2N] as entrainers to separate the azeotrope of methanol and methyl acetate by making methanol as the volatile component, and compared the effects of the two ILs on methanol and methyl acetate. The VLE data of methanol (1) + methyl acetate (2) + ILs (3) were measured at 101.3 kPa, and the VLE data of the ternary mixture were correlated by the nonrandom two liquids (NRTL) model [21] and UNIFAC-Lei model [22].

2. Experiment

2.1. Materials

Methanol and methyl acetate were purchased from Chemart (Tianjin) Chemical Reagents Co., Ltd China. The purities were higher than 99.8% (mass fraction). The ILs [OMIM][Tf_2N] and [OMMIM][Tf_2N] were purchased from Aolike Chemical Reagents Co., Ltd, Lanzhou, China, with a purity higher than 98.0% (mass fraction). The structures of the ILs are illustrated in the electronic supporting information (ESI), Fig. A. 1. The ILs were dried by vacuum evaporation at 343.15 K for 24 h to remove the volatile trace impurities. The final mass fraction of water content in ILs was less than 0.0005, determined by Karl Fischer titration. All the other chemicals were used directly without further purification. The overall information of the chemicals used in this study were summarized in Table 1.

2.2. Apparatus and procedure

The VLE experiments were conducted by an all glass dynamics recirculating still, and the detail of the apparatus was described in our previous work [12]. The isobaric VLE data of the methanol (1) + methyl acetate (2) + ILs (3) ternary system were measured at 101.3 kPa, and the pressure of the system was maintained constant by a vacuum pump and a gas buffer system. The pressure was measured by a manometer with the standard uncertainty of 0.1 kPa. The temperature was measured by a thermometer with the standard uncertainty of 0.05 K. For each data point of our experiments, the ternary mixtures with a certain mole fraction were accurately prepared by a digital balance (Mettler-Toledo AL204) with the standard uncertainty of 0.0001 g. After the temperature of the still was maintained constant over 30 min, the liquid and vapor phase samples were taken every 20 min and analyzed, until the standard deviation of the last five samples was less than 0.002.