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Analysis of Ternary LLE Data on Increasing Limonene Solubility in Water using Alcohol as Cosolvent

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Abstract. The quality of essential oils can be improved by increasing the concentration of oxygenated compounds. This can be achieved by extracting terpenes from the oil. As terpenes are insoluble in water, alcohols are often added to increase the solubility. It is important to find a suitable co-solvent to increase the efficiency of terpene extraction using water; this can be indicated by the miscibility (one phase) region in the water–cosolvent–terpene ternary diagram. In this work, three alcohols, i.e., methanol, ethanol and propanol, were selected as the cosolvents. The mutual solubility of water–methanol/ethanol/propanol–limonene is analysed through the phase equilibria generated from literature data and predicted by the Conductor-like Screening Model (COSMO-RS) programme. COSMO-RS was able to generate accurate LLE data at equilibrium based on the reported experimental feed compositions. The extraction efficiency of using an alcohol increased following the order methanol < ethanol < propanol according to the increment of the respective miscibility region. At equilibrium, the composition of alcohol is higher in the aqueous phase than that in the organic phase, indicating the affinity of alcohol towards water and the suitability of using alcohol as the co-solvent. As observed, in methanol, its small methyl group increased its solubility in water, but reduce the methanol solubility in limonene (terpene), thus reducing also the miscibility region. Propanol was found to be the most suitable alcohol, and this encourages us for further studies to find other green cosolvents.

INTRODUCTION

Essential oils (EOs) are also known as volatile oils because of the high concentration of volatile substances. EOs consist of huge different compounds which are soluble in alcohol, but insoluble in water. The quality of essential oils can be improved by increasing the concentration of oxygenated compounds, where one of the viable methods is by solvent extraction. Liquid–liquid extraction (LLE) is a common method used in lab scale measurement, as well as industrial application due to safe and mild operating condition. LLE is used to isolate the constituents of a mixture present in liquid phase by bringing the component in solute that is required to be separated into contact with an immiscible solvent. It is an effective alternative in industry instead of distillation especially when the components have similar boiling point. It also provides higher separation efficiency in the removal of a component that is present in small concentration, and when the recovery of heat sensitive materials is desired. However, it is critical to select a suitable solvent for an effective LLE process. Ethanol, hexane, chloroform and ether were among the solvents studied to separate terpenes from the EOs [1]. The proper extraction method of volatile compounds is based on the parameters that affect the yield and quality of EOs such as temperature, solvent, time and the types of equipment used [2].

The lack of liquid-liquid equilibrium data and thermodynamic behavior of terpenes systems encourage researchers to generate information and data to be used in larger scale applications because of the high demand of essential oils in the market. The high demand of high-quality essential oil leads researchers to apply scientific methods by using low cost, available and safe materials such as using water as solvent to extract terpenes. However, terpenes are commonly insoluble in water. Thus, cosolvents are often added to increase the solubility. Many types of cosolvents can be used in the extraction of terpenes such as hexane and chloroform. It is important to find cosolvents that are non-toxic and safe to operate. Alcohols can be used to enhance the solubility of terpenes in water.

The liquid–liquid equilibrium (LLE) studies involving EOs and solvents have been carried out over the years. Gironi et al. found that the solubility of both citral and limonene in water can be enhanced by introducing ethanol as the cosolvent [3]. Similarly, Arce et al. found that the solubility of linalool and limonene in water can be increased by adding ethanol, where the water content must be controlled and optimized [4, 5]. Meanwhile, the effect of temperature on limonene solubility in water + ethanol system was barely seen [6, 7]. In this study, the mutual solubility of water–methanol/ethanol/propanol–limonene is analysed through the phase equilibria generated from literature [8] and predicted by the Conductor-like Screening Model (COSMO-RS) programme.

METHODOLOGY

COSMO-RS was used to predict the ternary molar compositions at equilibrium based on the reported LLE tie lines in the literature. The feed composition was obtained from the assigned point on the tie lines. All compounds are imported from the C30-1201 COSMO-RS database. In the case of molecules unavailability in the database, the molecular geometry optimisation was performed using the Turbomole programme package. In Turbomole, the 3D chemical structure of the target molecule was firstly drawn. Then, the geometry optimisation was performed at the Hartree–Fock level and 6–31G* basis set. The generation of .cosmo file was then conducted through a single-point calculation by using DFT with Becke–Perdew and the Triple- ζ Valence Potential (TZVP) basis set. Finally, the .cosmo files were exported to the COSMOthermX programme with parameterisation BP_TZVP_C30_1301.ctd.

The distribution ratio of each alcohol was calculated using Eqn. 1:

$$D_{alcohol} = \frac{x_{alc,aq}}{x_{alc,org}} \quad (1)$$

where $x_{alc,aq}$ and $x_{alc,org}$ are the molar composition of alcohol in aqueous phase and organic phase, respectively.

RESULT AND DISCUSSION

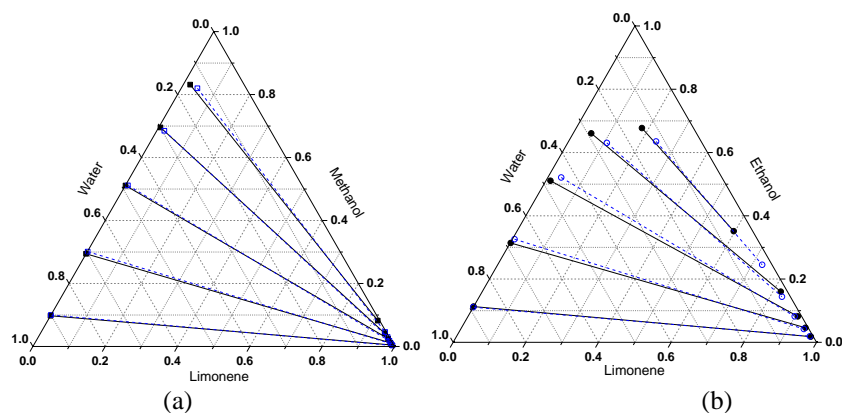
In view of ternary phase diagram, the aim of adding alcohol as cosolvent is to reduce the miscible region. The higher area of miscible region indicates the higher mutual solubility of the three components, i.e., water, terpene and alcohol, thus higher performance of co-solvency. The ternary molar compositions of water, alcohols and limonene are tabulated in Tab. 1 and depicted in Fig. 1. As seen in Fig. 1(a), methanol showed the least area in the miscible region

compared to those shown by the ethanol and propanol. Moreover, the molar fraction of methanol in the organic phase is also relatively small, indicating the unfavorable attraction between methanol and limonene. Nonetheless, the molar composition of alcohol in the organic phase increased steadily when methanol is changed with ethanol and propanol. A positive slope was exceptionally observed in the lowest tie line of water–propanol–limonene system, indicating the higher affinity of propanol with limonene than that with water. As seen in Fig. 1 (c), propanol showed the highest miscible region area with the highest molar composition of methanol in the organic phase.

COSMO-RS was able to accurately predict the tie lines for water–methanol–limonene and water–ethanol–limonene systems, where the concentration of alcohols in the aqueous phase were slightly underestimated. In contrast, for water–propanol–limonene system, COSMO-RS generated comparable tie lines with the experimental results where the concentrations of propanol in the aqueous phase were overestimated. These estimations are generally acceptable since the area of miscible regions produced by COSMO-RS in all systems were nearly as much as those in the experimental works. This finding supports the advantages of using COSMO-RS as an a priori tool to predict the thermodynamic phase equilibria without requiring experimental data.

TABLE 1. Ternary molar composition of water, alcohols and limonene at equilibrium generated by COSMO-RS

Organic phase			Aqueous phase		
<i>Water (1) + Methanol (2) + Limonene (3)</i>					
X ₁	X ₂	X ₃	X ₁	X ₂	X ₃
0.0040	0.0030	0.9930	0.9000	0.1000	0
0.0050	0.0090	0.9860	0.6980	0.3010	0.0010
0.0050	0.0180	0.9770	0.4820	0.5120	0.0070
0.0040	0.0300	0.9650	0.2940	0.6850	0.0210
0.0030	0.0460	0.9510	0.1350	0.8200	0.0450
<i>Water (1) + Ethanol (2) + Limonene (3)</i>					
0.0090	0.0190	0.9720	0.8890	0.1110	0
0.0140	0.0420	0.9440	0.6680	0.3260	0.0060
0.0190	0.0820	0.8990	0.4420	0.5210	0.0370
0.0230	0.1440	0.8330	0.2620	0.6310	0.1080
0.0270	0.2450	0.7280	0.1240	0.6350	0.2410
<i>Water (1) + Propanol (2) + Limonene (3)</i>					
0.0170	0.0500	0.9320	0.9820	0.0180	0
0.0460	0.1450	0.8090	0.6130	0.3630	0.0240
0.0520	0.1650	0.7830	0.5470	0.4120	0.0410
0.0650	0.2100	0.7250	0.4390	0.4760	0.0850
0.0820	0.2640	0.6540	0.3450	0.5070	0.1490



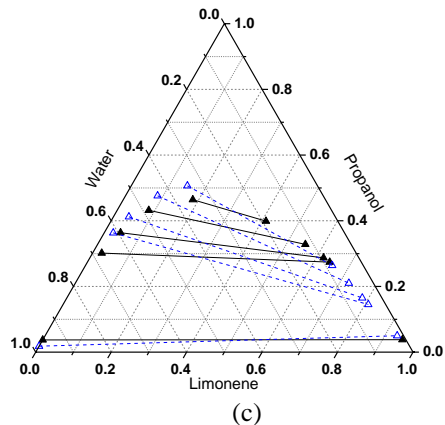


FIGURE 1: Tie lines of ternary LLE for water + methanol/ethanol/propanol + limonene. The solid symbols and continuous lines represent experimental data [8], while the hollow symbols and dashed lines are the COSMO-RS predictions.

In Fig. 2, the effect of alcohol alkyl length can be clearly observed, where the immiscibility region has steadily reduced in the order of methanol (highest immiscibility), ethanol and propanol (lowest immiscibility). The distribution coefficients of each alcohol cosolvents is depicted in Fig. 3, where all data points in the corresponding ternary systems showed the distribution coefficient of propanol (D_{propanol}) higher than unity, except the first tie line of water–propanol–limonene ($D_{\text{propanol}} = 0.36$). Moreover, the values of D_{methanol} were persistent in propanol system, indicating the nearly independent relation between methanol composition in feed and its corresponding cosolvency. In contrast, both ethanol and methanol systems showed the increased distribution ratio with respect to the increased concentration of alcohol in the feed.

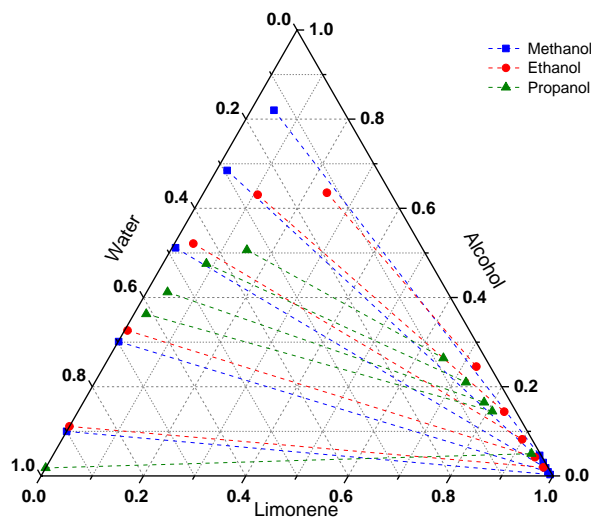


FIGURE 2: Ternary tie lines predicted by COSMO-RS for water + methanol/ethanol/propanol + limonene systems.

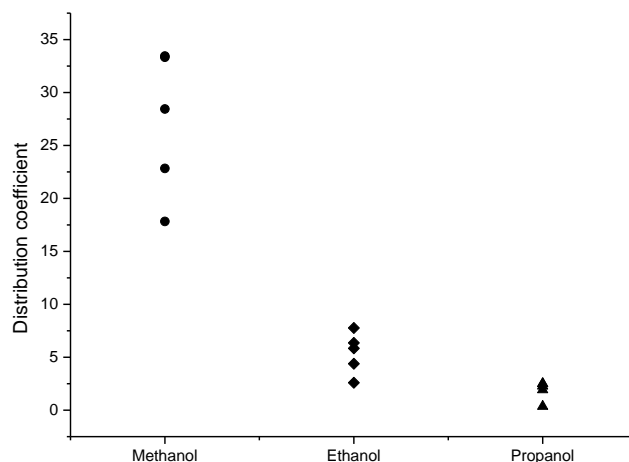


FIGURE 3: Distribution coefficients of methanol/ethanol/propanol in the corresponding ternary systems as calculated from the COSMO-RS data points.

It can be expected that at higher distribution coefficient of alcohol, the mutual miscibility of alcohol with terpene will be lower, thus will reduce terpene extraction efficiency. This can be seen in the water–methanol–limonene system. Furthermore, methanol is not applicable in high temperature applications due to its low boiling point (64.7 °C). Methanol vaporizes more easily compared to ethanol and 1-propanol and is unsuitable for extraction process at high temperatures.

CONCLUSION

Alcohols are among the suitable cosolvents to extract terpenes from EOs using water. In this study, the mutual solubility of three alcohols (methanol, ethanol and propanol) was analysed through the phase equilibria generated from literature and predicted by the COSMO-RS. The LLE data predicted by COSMO-RS were in good agreement with those reported experimentally. The feasibility of using alcohol increased from methanol < ethanol < propanol due to the increment of the respective miscibility region. The suitability of using alcohol as cosolvent with water was proved since the composition of alcohol is higher in the aqueous phase at equilibrium. As observed in methanol, it can be expected that the reduced alkyl chain of alcohol increased its solubility in water, but this will reduce alcohol solubility with terpene, thus reduce the miscibility region. Propanol demonstrated the most suitable alcohol in this work, and this finding provides recommendation of finding other potential green solvents with better cosolvency effects.

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