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Deep Eutectic Solvent (Choline Chloride / N-formyl Morpholine) Effect on Liquid-liquid Extraction of Benzene / Thiophene from n-hexane

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INTRODUCTION

Although a significant of research body exists on the aromatic/aliphatic separation techniques, there is not introduced an efficient method for extraction of aromatic mixtures with a weight fraction less than 20 % (aromatic content) at normal temperature and pressure has not been yet introduced [1-3]. Due to the azeotropic points in aromatic-aliphatic mixtures, the industrial separation of these mixtures occurs near the boiling point by increasing the third component like N-formylmorpholine (NFM) into a mixture that changes the relative volatility of the initial compounds. Moreover, NFM extraction process continues with extractive distillation to recover the NFM [4]. In general, the specification for selection of an appropriate solvent to extractive distillation are: high selectivity [4], high capacity in solving extractors [4], low volatility [5], the separation capacity [6], the solvent must be easily separable from the mixture, low price of solvent and its availability [7], no toxicity [8], chemical stability [9], without corrosive effects on the distillation tower [10,11], high boiling and low freezing point, and finally Its viscosity need to be low to increase distillation tower trays output [12,13].

At present, generally, in the petrochemical industries, sulfolan or NFM solvents are used for separation of aromatics from aliphatics. There are some problems in the use of these extractive solvents: first of all, these substances are toxic and environmentally polluted [14]. Secondly, the extraction process efficiency of the mentioned materials is not complete, and at least 1-5% of aromatic impurities remain at the end of the extraction (bottom tower of benzene distillation).

The NFM also works at non ambient pressures and temperatures; therefore, it consume a lot of energy. Then, finding an extraction solvent that works in ambient temperature and pressure is one of the research priorities [14].

In the recent decade, ionic liquids have been used as solvents for separation of aromatic – aliphatic mixtures [15-18]. The application of these neoteric solvents was growing rapidly till deep eutectic solvents (DESs) introduced as a novel generation of green solvents. Despite ionic liquids, deep eutectic solvents demonstrate easy way to prepare with high purity, they are nonreactive with water and most of them are biodegradable with lower toxicological properties. Furthermore, their lower costs in comparison with ionic liquids pave the way for growing up their applications in liquid–liquid extraction [3,19].

In this work, new type of deep eutectic solvent (DES) based on choline chloride (as hydrogen bond acceptor) in combination with hydrogen bond donor material (NFM) have been synthesized. Moreover, the experimental liquid-liquid extraction properties for several ternary systems containing (n-hexane + benzene + DES), (n-hexane + thiophene + DES) were measured at T = (298.15 to 318.15) K and atmospheric pressure. The calculated LLE results were correlated by the NRTL and UNIQUAC models.

EXPERIMENTAL PROCEDURE

MATERIALS

Choline chloride was used as hydrogen bond acceptor. The N-formyl morphloine used as hydrogen bonding donor agents. Ethanol was used for crystallization of choline chloride.

APPARATUS AND PROCEDURE

Liquid - liquid equilibrium determination were done using a gas chromatography (GC Varian-3800), equipped with column CP - Wax 52 CB (30 mx 0.25 mm x 1.25 µm) and FID detector. Internal standard method was used for calibration of gas chromatography by using of n-octane. Due to low vapor pressure of studied DESs, DES phase samples were injected to gas chromatography after 10 times dilution with ethyl alcohol. For both samples, n-octane was used as an internal standard and 0.125 g. Finally, each sample was injected three times, and the averages were reported as results. Moreover, deviation from the standard in this test is less than ± 1.

RESULTS AND DISCUSSION

SOLUBILITY RESULTS

The high solubility of aromatics and low solubility (or non-solubility) of aliphatic in DESs indicates the applicability of the deep eutectic solvent for liquid-liquid extraction. Other parameters like temperature and viscosity of DESs are effective on test results. Moreover, the prepared DESs were liquid at room temperature.

The solubility of benzene, thiophene and hexane in studied DESs were determined at T =303.15 K and atmospheric pressure via turbidity method [20, 21]. The results of turbidity test for benzene, thiophene and hexane in studied DESs in terms of DES molar fraction indicate that by increasing HBD molar ratios in synthesized DESs, the solubility of hexane gradually increases while the solubility of benzene and thiophene is reduced.

LIQUID–IIQUID EQUILIBRIA

Understanding of aromatics/aliphatic extraction process needs to measure their liquid - liquid equilibrium [22,23]. The separation efficiency is expressed by two parameters: the selectivity (S) and the distribution coefficient (β). Selectivity (S) parameter indicates the potential of solvent in solubilizing of solute without extracting other components from the primary solutions. The distribution coefficient (β) obtained from these studies is directly related to the slope of the lines, and by increasing the distribution coefficient values, the number of extraction stages decreases.

LLE DATA CORRELATION

The experimental ternary LLE data measured in this study were correlated using the non-random liquid equation (NTRL) proposed by Renon and Prausnitz [24] and the universal quasi-chemical (UNIQUAC) theory developed by Abrams and Prausnitz [25].

CONCLUSIONS

In this work, the applicability of new series of DESs based on mono- , di- and tri- ethylene glycols or ethanolamines, as novel extracting agents for the separation of the {benzene / thiophene + hexane} system were studied. Solubility test were made to find suitability of studied DESs for this separation.

The DESs indicate proper solubility for benzene and thiophene. The LLE data of the ternary systems {hexane (1) + benzene (2) + DES (3)} and {hexane (1) + thiophene (2) + DES (3)} were determined at T = 298.2 and 308.2 K and ambient pressure. The solute distribution coefficient (β) and selectivity values (S) were measured and compared with several solvents previously investigated. It was found that the solute distribution coefficient of the studied DESs is lower than that of NFM.

The temperature effect on the separation has also been studied, showing that low temperatures promote the better separation. Considering the solute distribution coefficient and selectivity values, Choline chloride: NFM (1:7) or DES 2 would be preferred over others for this separation. Finally, the NRTL and UNIQUAC models were satisfactorily applied to correlate the experimental data by treating the DESs as a single component. The obtained results show potential of studied DESs for usage in ambient conditions and below than their pure consistent melting points.

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