

# Separation of Aromatics using Benign Solvents

Sarwono M., M. K.O. Hadj-Kali, and I.M. AlNashef

**Abstract**— Separation of aromatics from aliphatics is challenging because of the close range of their boiling points and the formation of several combinations of azeotropes. Until now, no feasible separation process is available for aromatic concentrations below 20 wt%. In this work, we have investigated the possibility of using selected Deep Eutectic Solvents (DESs) for the liquid-liquid extraction of aromatics. DESs have emerged as green solvents that may offer several industrial alternatives. The DESs used in this work were synthesized from ammonium salt with ethylene glycol, lactic acid and sulfolane as Hydrogen Bond Donor (HBD). Equilibrium data for the ternary system consisting of ethylbenzene and n-octane with all DESs were measured at 25°C and atmospheric pressure. The results showed comparable distribution ratio and selectivity with commercial solvents. The absence of the HBD in the hydrocarbon layer, means the reduction of the number of separation stages. In addition, the Non-Random Two Liquid (NRTL) model was successfully used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems.

**Keywords**-- Deep Eutectic Solvent; ethyl benzene/n-octane mixture; Liquid-liquid Extraction

## I. INTRODUCTION

AROMATICS are important chemicals for industry; they are used as raw materials in producing plastic and polymers and are present in the naphtha feed. The separation and production of high-purity aromatics is a difficult task because of several combinations of azeotropes and some of these hydrocarbons have close boiling points range. Commercial separation methods are liquid-liquid extractions suitable for the range of (20 to 65) wt % aromatic, for the concentration between 65 and 90 wt % using extractive and azeotropic distillation for higher aromatic content (>90 wt %). However, no feasible process for separation of aromatics that the content below 20 wt% in the feed mixture [1].

In some petroleum processes, such as naphtha steam cracking, the removal of low level aromatic contents gives many benefits like products purity, energy and lower operation costs. In this process, the cracker feed usually contains 10 – 25% of aromatic components. During the cracking process, the aromatic compounds are not converted to olefins, so the aromatics occupy a large portion of the furnaces capacity and give the burden for the separation section. The separation of aromatics from feed will give big advantages for capacity, thermal efficiency, less fouling, energy and cost [2].

Liquid extraction is the most applied process for separation with an aromatic content in the range 20 to 65 wt%. It has the advantage lower energetic demand, so it would be easy to extend the range of aromatics content in which extraction with low Aromatic content might be feasible to apply.

Typical solvents in these processes are organic compounds such as sulfolane, ethylene glycols, dimethylsulfoxide, N-methylpyrrolidone, N-formylmorpholine. Unfortunately, these solvents are generally toxic, flammable and difficult to recover. New solvents, environmental friendly, are needed for effective separation in order to replace the organic solvents.

Ionic liquids represent a potential alternative. However, it is still a challenge for the large-scale applications of ionic liquids in industry, due to complicated synthetic processes and the expensive raw material chemicals, in addition to their unknown toxicity [3].

Hence, eutectic mixtures, so-called Deep Eutectic Solvents (DESs), have emerged as a low-cost alternative of ILs. The DESs are a mixture of compounds that have a much lower melting point than individual component, because of the generation of intermolecular hydrogen bonds [4].

Deep eutectic solvents have properties comparable to ionic liquids. Their potential as tunable solvents that can be customized to a particular type of chemistry. DESs are potential candidates to be used as non-volatile ionic liquid-based. The advantages compared to traditional ionic liquids: (1) Simple to synthesize, the materials easily mixed and converted to ionic liquid without further purification. (2) Very cheap, because of the low cost of raw materials. (3) DESs are expected to have good bio-compatibility [4-5].

The research of ionic liquids as solvent for separation of aromatics reported in literature, for example ammonium type ionic [6], pyridinium and imidazolium type ionic liquids [7], octylimidazolium thiocyanate [8].

The application of DESs for separation of aromatics reported using phosphonium DESs for system toluene/heptanes [9] and for system benzene/hexane [10]. The experimental data on extraction of aromatic hydrocarbon by DESs are scarce. Therefore, it is worthwhile to study the LLE of ternary mixtures of (DESs + aromatic hydrocarbon + alkanes). To the best of our knowledge, no work was reported about the use of ammonium based of DESs for the separation of aromatics.

The Hydrogen Bond Donor (HBD) used in this research were commercially solvent ethylene glycol, sulfolane and also lactic acid. The ethylene glycol showed high selectivity to extract aromatics at low temperatures [11]. The selectivity of sulfolane for separation benzene and hexane reported between 7-20 and distribution coefficient (D), which is defined as the ratio of the mass fraction of aromatics in the solvent rich phase to that in aliphatics rich phase between 0.4-0.7 [12]. Both solvents are commercially used as solvent for extraction

Sarwono M., M. K.O. Hadj-Kali, and I.M. AlNashef are with Chemical Engineering Department, King Saud University, Riyadh, Saudi Arabia. Email: alnashef@ksu.edu.sa

aromatics from naphta. In this experiments we also try lactic acid as hydrogen bond donor to observe the potential of this chemical as solvents, because the lactic acid is one of the most widely organic acids used in food and pharmaceutical industry [13].

## II. EXPERIMENTALS

### A. Chemicals

Pure grade compounds ethyl benzene, n-Octane were purchased from Winlab, ethylene glycol was purchased from from Panreac, sulfolane, Benzyltributylammonium chloride, Tetraethylammonium bromide and Tetraethyl-ammonium p-toluenesulfonate were purchased from Acros Organics. All chemicals were of high purity (>99%) and used without any further purification. The DESs were prepared by mixing salts with ethylene glycol, lactic acid, sulfolane as Hydrogen Bond Donor. The ammonium salts:HBD molar ratio for all the solvents were 1:4. Table I shows the DESs synthesized in this work and the abbreviations used in the following sections.

First, each mixture was heated up to 100°C and mixed until the formation of a clear liquid [6]. Mixtures of ethyl benzene and n-octane were prepared for nine concentration (10, 15, 20, 30, 40, 50, 60, 70, 80 and 90 wt%) by mixing weighed amounts of pure ethyl benzene and pure n-octane. The feed sample was then mixed with the DES with mass ratio 1:1. Each set of experiment was conducted at 25°C. The vials were placed at incubator shaker. The shaking time was six hours and followed by settling time of about 12 hours to guarantee that the equilibrium state was completely attained [8]. Samples were taken from the top and bottom layers and then analyzed using HPLC.

TABLE I  
COMPOSITION OF THE SOLVENT FOR THE EXPERIMENTS

Salt	HBD	Abv.
Tetraethylammonium p-toluenesulfonate	Ethylene glycol	DES 1
Benzyltributylammonium chloride	Lactic Acid	DES 2
Tetraethylammonium bromide	Sulfolane	DES 3
Tetraethylammonium p-toluenesulfonate	Sulfolane	DES4

### B. Analysis

The samples were withdrawn using syringe and diluted using 2-propanol. These samples were analyzed using HPLC Agilent 1100 series with zorbax eclipse xdb-c8 as column. The temperature of the column oven was set at 30°C. The mobile phase was acetonitrile and distilled water with volume ratio 3:1. The flow rate in the column was 1.4 ml min<sup>-1</sup> with a pressure of 120 bars.

## III. RESULTS AND DISCUSSION

The feasibility for potential application these solvents to perform extraction of aromatic hydrocarbon from mixture with n-octane was evaluated using parameter distribution ratio (D) and selectivity (S), calculated from experimental data. These parameters are defined by the expressions:

$$D = x_{2}^{II} / x_{2}^{I} \quad (1)$$

$$S = (x_{2}^{II} x_{1}^{I}) / (x_{2}^{I} x_{1}^{II}) \quad (2)$$

Where x is the mass fraction; superscripts I and II refer to hydrocarbon rich phase and DES rich phase while subscripts 1 and 2 refer to n-octane and ethyl benzene.

The measured composition at equilibrium in both liquid phases for each DES are reported in tables II until V respectively and also plotted in the ternary diagrams given by Fig. 1- 4.

TABLE II  
LLE EXPERIMENTAL DATA WITH DES1

% aro.	n-octane rich phase			DES1 rich phase			$D_{aro}$	Selec.
	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$		
10	0.134	0.866	0.000	0.008	0.005	0.987	0.06	11.09
20	0.204	0.797	0.000	0.014	0.007	0.979	0.07	7.42
30	0.308	0.692	0.000	0.020	0.006	0.974	0.06	7.40
40	0.432	0.568	0.000	0.025	0.005	0.970	0.06	7.24
50	0.503	0.497	0.000	0.030	0.003	0.968	0.06	11.11
60	0.574	0.426	0.000	0.036	0.005	0.960	0.06	5.76
70	0.697	0.303	0.000	0.043	0.003	0.954	0.06	5.42
80	0.776	0.224	0.000	0.047	0.003	0.950	0.06	4.83
90	0.882	0.118	0.000	0.060	0.006	0.934	0.07	1.39

TABLE III  
LLE EXPERIMENTAL DATA WITH DES2

% aro.	n-octane rich phase			DES2 rich phase			$D_{aro}$	Selec.
	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$		
10	0.134	0.866	0.000	0.004	0.002	0.994	0.03	10.53
15	0.183	0.817	0.000	0.006	0.003	0.991	0.03	8.57
20	0.319	0.681	0.000	0.010	0.003	0.987	0.03	7.80
30	0.373	0.627	0.000	0.011	0.005	0.984	0.03	3.85
40	0.464	0.536	0.000	0.014	0.001	0.985	0.03	12.53
50	0.575	0.425	0.000	0.017	0.004	0.979	0.03	2.83
60	0.644	0.356	0.000	0.020	0.001	0.979	0.03	7.63
70	0.733	0.268	0.000	0.020	0.001	0.979	0.03	7.02
80	0.828	0.172	0.000	0.025	0.001	0.974	0.03	9.39
90	0.903	0.097	0.000	0.008	0.000	0.992	0.01	7.29

TABLE IV  
LLE EXPERIMENTAL DATA WITH DES3

% aro.	n-octane rich phase			DES3 rich phase			$D_{aro}$	Selec.
	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$		
10	0.093	0.907	0.000	0.043	0.028	0.929	0.46	15.25
15	0.143	0.857	0.000	0.064	0.021	0.915	0.45	18.69
20	0.210	0.790	0.000	0.106	0.028	0.866	0.51	14.43
30	0.284	0.716	0.000	0.127	0.018	0.855	0.45	17.69
40	0.363	0.637	0.000	0.168	0.023	0.809	0.46	12.56
50	0.444	0.557	0.000	0.202	0.018	0.780	0.46	13.84
60	0.512	0.488	0.000	0.247	0.021	0.732	0.48	11.12
70	0.630	0.370	0.000	0.313	0.021	0.667	0.50	8.80
80	0.718	0.282	0.000	0.418	0.027	0.555	0.58	6.01

TABLE V  
LLE EXPERIMENTAL DATA WITH DES4

% aro.	n-octane rich phase			DES4 rich phase			$D_{aro}$	Selec.
	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$		
10	0.088	0.912	0.000	0.037	0.027	0.936	0.42	14.34
15	0.126	0.874	0.000	0.050	0.021	0.929	0.40	16.20
20	0.171	0.829	0.000	0.068	0.023	0.910	0.40	14.59
30	0.267	0.733	0.000	0.117	0.020	0.863	0.44	15.68
40	0.350	0.650	0.000	0.140	0.022	0.838	0.40	11.65
50	0.469	0.531	0.000	0.173	0.016	0.812	0.37	12.51
60	0.546	0.454	0.000	0.218	0.018	0.764	0.40	10.26
70	0.598	0.402	0.000	0.284	0.019	0.698	0.47	10.20
80	0.683	0.317	0.000	0.345	0.013	0.642	0.50	12.03
90	0.811	0.189	0.000	0.504	0.019	0.476	0.62	6.13

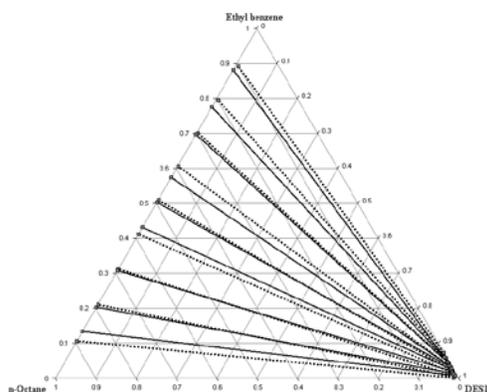


Fig. 1 Tie-lines for the ternary mixture Ethyl benzene + n-Octane + DES1 at 298.15 K. Solid lines indicate experimental tie-lines, dashed lines indicate calculated data from NRTL model

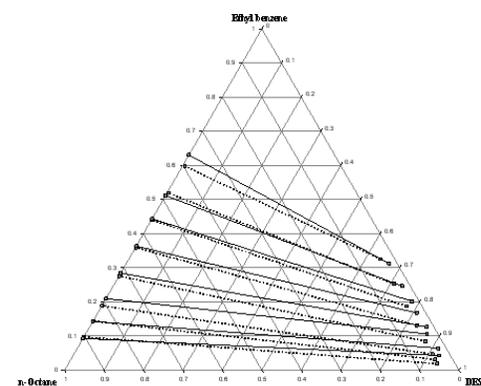


Fig. 3. Tie-lines for the ternary mixture Ethyl benzene + n-Octane + DES3 at 298.15 K. Solid lines indicate experimental tie-lines, dashed lines indicate calculated data from NRTL model

### C. Consistency of the liquid-liquid equilibrium data

The reliability of the experimental results have been ascertained by using Othmer-Tobias [14] and Hand [15] correlations given respectively by:

$$\ln\left(\frac{1-x_1^I}{x_1^I}\right) = a + b \ln\left(\frac{1-x_{DES}^{II}}{x_{DES}^{II}}\right) \quad (3)$$

$$\ln\left(\frac{x_2^I}{x_1^I}\right) = c + d \ln\left(\frac{1-x_{DES}^{II}}{x_{DES}^{II}}\right) \quad (4)$$

The linearity of each plot indicates the degree of consistency of the data. The parameters of the Othmer-Tobias correlation are given in Table VI. The regression coefficients  $R^2$  are very close to unity which indicates the degree of consistency of our experimental data.

TABLE VI  
OTHMER-TOBIAS AND HAND CORRELATION PARAMETERS

	<i>Othmer-Tobias</i>			<i>Hand</i>		
	<i>a</i>	<i>b</i>	$R^2$	<i>c</i>	<i>d</i>	$R^2$
DES1	8.306	2.457	0.984	6.732	1.881	0.979
DES2	5.003	1.197	0.951	6.053	1.379	0.973
DES3	1.907	1.390	0.993	1.753	1.190	0.997
DES4	2.044	1.374	0.990	1.896	1.177	0.996

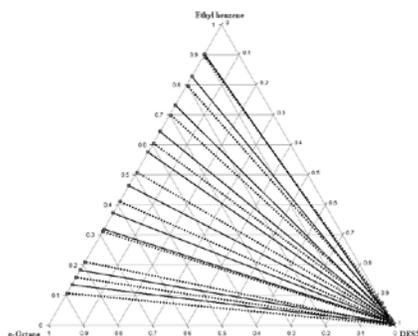


Fig. 2 Tie-lines for the ternary mixture Ethyl benzene + n-Octane + DES2 at 298.15 K. Solid lines indicate experimental tie-lines, dashed lines indicate calculated data from NRTL model

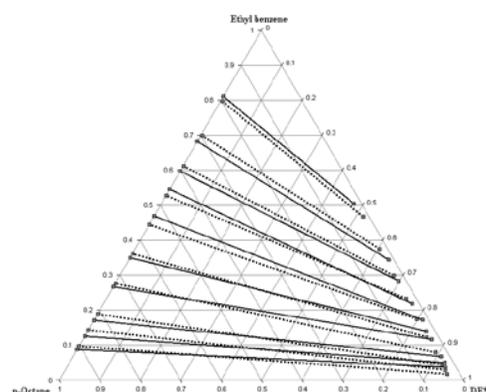


Fig. 4 Tie-lines for the ternary mixture Ethyl benzene + n-Octane + DES4 at 298.15 K. Solid lines indicate experimental tie-lines, dashed lines indicate calculated data from NRTL model

### D. Distribution coefficient

Generally, the distribution ratio increase with aromatic content, the same trend is observed for sulfolane and ethylene glycol as single solvent for aromatics separation [11-12]. The comparison between ethylene glycol and sulfolane as HBD showed that the sulfolane is more capable to absorb the aromatic. This could be attributed to the higher aromatic character [16]. The value of distribution coefficient of commercial solvent N-formylmorpholine (NFM) at same temperature, at different system (heptanes + m-xylene) showed between 0.3914-0.4861, and NFM solvent also present at raffinate phase [17] that means needed additional cost for recovery the solvent. The distribution ratio for DES3 and DES4 showed comparable with the result of separation using ionic liquids [3]. The ethylene glycol (DES1) and lactic acid (DES2) showed lower potential as HBD, but they showed no present at raffinate phase in HPLC results.

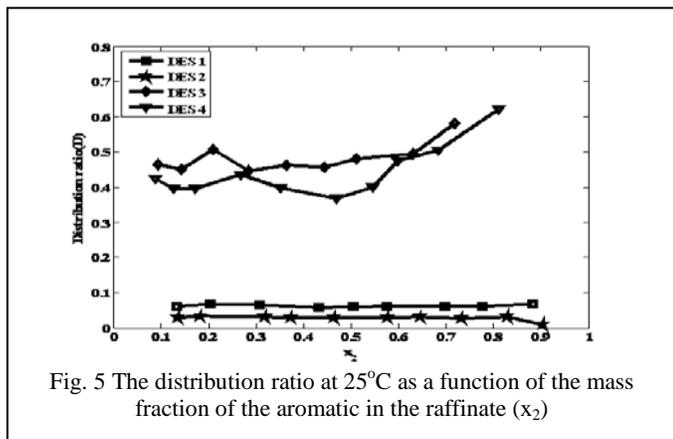


Fig. 5 The distribution ratio at 25°C as a function of the mass fraction of the aromatic in the raffinate ( $x_2$ )

### E. Selectivity

Figure 6 shows the Ethyl benzene selectivity as a function of its concentration in the raffinate. It is clear that the selectivity decreases with increasing the aromatic content in the raffinate. The same trend was also reported in for other traditional solvents [3,11, 12, 18]. Sulfolane as HBD showed better results compared to ethylene glycol and lactic acid. The higher selectivity at lower concentrations of aromatics in the feed is an important factor for the solvent selection for low content of aromatics. The reported selectivity for commercial solvent sulfolane at 30°C for the system of benzene and n-hexane was 9.89 – 18.36. However, the selectivity for N-formylmorpholine for the same system was 4.67 – 18.81[12]. Therefore DES3 and DES4 showed comparable selectivity with those for commercial solvents.

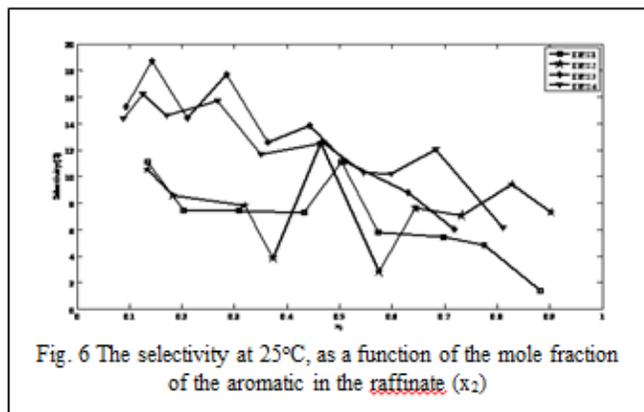


Fig. 6 The selectivity at 25°C, as a function of the mole fraction of the aromatic in the raffinate ( $x_2$ )

### F. Liquid-Liquid Equilibrium modeling

When performing a liquid-liquid equilibrium calculation, phase compositions are obtained by solving an isothermal liquid- liquid flash at given temperature and pressure. This flash consists on the following system of equations:

Material Balance:

$$x_i - (1-\dot{E}) x_i^{L1} - \dot{E} x_i^{L2} = 0 \quad i = 1, \text{NC} \quad (5)$$

Equilibrium Equation:

$$x_i^{L1} \gamma_i^{L1} - x_i^{L2} \gamma_i^{L2} = 0 \quad i = 1, \text{NC} \quad (6)$$

Equation of summation:

$$\sum_i x_i^{L1} - \sum_i x_i^{L2} = 0 \quad i = 1, \text{NC} \quad (7)$$

With,  $\dot{E}$  the liquid-liquid splitting ratio,  $x_i$  the composition of component  $i$  in the mixture,  $x_i^{L1}$  the composition of component  $i$  in the liquid phase L1,  $x_i^{L2}$  the composition of component  $i$  in the liquid phase L2,  $\gamma_i^{L1}$  and  $\gamma_i^{L2}$  are the activity coefficients of component  $i$  in the liquid phase L1 and L2 respectively. NC is the number of constituents.

Many equations were developed to correlate activity coefficients, but the equations which are in common use are those based on the concept of local composition introduced by Wilson in 1964 [19] such as the NRTL (Non-Random Two Liquid) equation of Renon and Prausnitz [20], the UNIQUAC (UNIversal QUAsi-Chemical) equation of Abrams and Prausnitz [21] and the UNIFAC (UNIversal Functional Activity Coefficient) method in which activity coefficients are calculated from group contributions [22].

The NRTL thermodynamic model was found to be useful for correlating the experimental data of LLE as it was reported in many publications. This model was initially described by Renon and Prausnitz in 1968 [23]. LLE data are correlated by minimizing an objective function based on the squared differences between calculated and experimental compositions. Then binary parameters would be fitted to the ternary data resulting in a good representation of the data. It was used also for systems containing ILs [24, 25].

In this model, within a liquid solution, local compositions are presumed to account for the short range order and non-random molecular orientations that result from differences in molecular sizes and intermolecular forces. For a multi-component system, NRTL equation is:

$$\frac{G^{ex}}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j G_{ji} x_j}$$

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j G_{ji} x_j} + \sum_j \frac{G_{ij} x_j}{\sum_k G_{kj} x_k} \left( \tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k} \right)$$

$$\text{With: } \ln G_{ij} = -\alpha_{ij} \tau_{ij} \quad \alpha_{ij} = \alpha_{ji} \quad \tau_{ii} =$$

(8)

Whereby  $\tilde{A}_{ij}$ ,  $\tilde{A}_{ji}$  are binary interaction parameters and  $\pm_{ij}$  is the non-randomness parameter. In our work, the model development was achieved within Simulis® environment, a thermo physical properties calculation server provided by ProSim [26] and available as an MS-Excel add-in.

The value of the third non-randomness parameter,  $\pm_{ij}$ , in the NRTL model was fixed to 0.20 while the interaction parameters  $\tilde{A}_{ij}$  and  $\tilde{A}_{ji}$  were estimated from “6M” experimental data points (where M represents the number of tie lines) by minimizing the quadratic criterion between calculated and experimental solubilities of each constituent in each phase:

$$\text{Criterion} = \frac{1}{6M} \sum_i \sum_j \sum_k (s_{ijk}^{exp} - s_{ijk}^{cal})^2 \quad (9)$$

Where  $s$  is the solubility expressed in mole fraction and the subscripts  $i$ ,  $j$ , and  $k$  designate the component, phase, and the tie lines, respectively.

Table V show the values of the binary interaction parameters obtained using the NRTL model with each ternary

system. As can be seen, the temperature dependence was neglected for the fitting parameters in this temperature window and the interaction between ethylbenzene and n-octane was considered independent of the solvent.

VII  
NRTL BINARY INTERACTION PARAMETERS

<i>i</i>	<i>j</i>	$\bar{A}_{ij}$	$\bar{A}_{ji}$
<b>EB</b>	<b>nC6</b>	<b>-189.22</b>	<b>-379.30</b>
EB	DES1	1096.46	299.94
nC6	DES1	2841.47	911.93
EB	DES2	1096.46	299.94
nC6	DES2	2841.47	911.93
EB	DES3	2026.28	5842.25
nC6	DES3	2860.73	734.36
EB	DES4	2580.52	-182.12
nC6	DES4	5236.50	979.77

In table V, EB stands for ethylbenzene and nC6 for n-octane. The previous figures 1 until 4 show the ternary diagrams including the calculated compositions by NRTL correlation. It can be seen from these figures that the calculated compositions have good agreement with the experimental ones, and the tie-lines of both compositions coincide in most of the cases. The slight difference is within the experimental uncertainty.

#### IV. CONCLUSION

Separation of aromatic from aliphatic hydrocarbons is a challenging process. In this work, Deep Eutectic Solvents synthesized from ammonium salt with ethylene glycol, lactic acid and sulfolane as hydrogen bond donor were used for the liquid-liquid extraction of ethylbenzene from n-octane.

The ability of these solvents to selectively extract aromatics from mixture aromatic and aliphatics was proven. The solvent formed from Tetrabutylammonium bromide and Tetraethylammonium p-toluenesulfonate and Sulfolane as HBD showed the better performance, i.e. distribution ratio and selectivity, which is comparable with the results obtained by commercial solvents used in industry. The HBD, i.e. ethylene glycol, lactic acid and sulfolane, were not found in the raffinate phase. This remarkable fact will facilitate the separation process protocol and hence reduce the cost of the process. Finally, the experimental data was satisfactorily correlated using the NRTL model, showing that this classical model can easily be adopted with systems including Deep Eutectic Solvents.

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