Liquid–liquid equilibria for the ternary system (phosphonium based deep eutectic solvent–benzene–hexane) at different temperatures: A new solvent introduced

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ABSTRACT

In this work we studied the applicability of one ionic liquid analogues namely phosphonium based deep eutectic solvent (DES) in the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures. Experimental data for liquid–liquid equilibria (LLE) were obtained for various mixtures of (benzene + hexane + DES) at 27, 35 and 45 °C. Some of the mixtures showed excellent results in terms of aromatic selectivity and distribution ratio compared to what is currently used in industry. Chromatography analysis showed that the ethylene glycol used in forming the deep eutectic solvent was not present in the raffinate layer. This eliminates the step needed for the separation of the solvent. A comparative study of the separation effectiveness of the DES in this work with other reported ionic liquids as well as sulfolane was performed for choosing the best solvent for the intended separation.

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1. Introduction

Some petroleum processes, such as naphtha steam cracking, need the removal of low level aromatic hydrocarbons for many benefits like products' purity, lower operation costs, etc. In this process, the cracker feed usually contains 10–25% of aromatic components, but it may contain higher concentrations as well. During the cracking process, the aromatic compounds are not converted to olefins. In addition, small amounts of aromatic hydrocarbons are formed during the cracking process in the cracker furnaces [1,2]. Thus, they occupy a large portion of the furnaces' capacity.

From industrial point of view and according to the previous argument, it is beneficiary to totally remove the aromatic hydrocarbons from the feed stream to the crackers or lessen their concentration. The removal of aromatic hydrocarbons is a challenging process since these hydrocarbons have boiling points in a close range, and several combinations form azeotropes. Commercial separation methods used for this specific task are liquid–liquid extraction found to be suitable for the range of 20–65% (wt/wt) aromatic, extractive distillation suitable for the range of 65–90%

(wt/wt) aromatics and azeotropic distillation for high aromatic content (>90%, wt/wt) [3,4]. This implies that there is no suitable separation technology available for process streams with an aromatic content below 20% (wt/wt) [5].

The liquid–liquid extraction (LLE) was widely used in industry for the aromatic hydrocarbon separation and purification because of mild operation conditions and due to its simplicity [1]. Industrially used chemicals as extractants are mostly conventional polar organic solvents, like ethylene glycol, tetraethylene glycol, sulfolane, and N-methylpyrrolidone [6]. These organic solvents are generally volatile, toxic and/or flammable. Al-Sahhaf and Kapetanovic [7] had reported the use of tetraethylene glycol as LLE solvent for aromatics separation from naphtha reformate. Although different operation conditions were tested there (different temperatures and feed:solvent ratios), however, a maximum selectivity of 10.64 at 45 °C were achieved. Wang et al. [8] also applied tetraethylene glycol as LLE solvent in aromatics extraction. Five ternary and two multicomponent mixtures were studied. That work focused on preparing data for applying UNIFAC model for LLE correlation. In addition to this, Yorulmaz and Karpuzcu [9] compared between sulfolane and diethylene glycol as solvents for this process. It was concluded there that sulfolane is better than diethylene glycol in terms of selectivity and yield.

Researchers realized that it is crucial to develop new extractants with a high distribution coefficient of aromatic hydrocarbons, high selectivity of aromatics to alkanes, and with little solvent loss [1].

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Table 1
A summary of previous related research results reported in the literature. D and S are distribution coefficient of aromatic hydrocarbons and selectivity respectively.

IL	LLE system	Temp. (°C)	Best D	Best S	Ref.
[EMpy][ESO$_4$][a]	B + Hex + [EMpy][ESO$_4$]	10, 20, 25, 30	1	37.96 @ 10 °C	[38]
[EMpy][ESO$_4$][a]	B + Hep + [EMpy][ESO$_4$]	10, 25	0.87	103.17 @ 10 °C	[38]
[3-Mebupy][DCA][b]	B + Hex + [3-Mebupy][DCA]	30, 50	1.45	54.1 @ 30 °C	[39]
[3-Mebupy][DCA][b]	Xy + Hex + [3-Mebupy][DCA]	30, 55	0.53	22.6 @ 30 °C	[39]
[hmim][BF$_4$][c]	B + Hep or Dodec or Hexadec + [hmim][BF$_4$]	25	0.76	17.59 for Hep	[40]
			0.66	14.15 for Dodec	
			0.57	21.93 for Hexadec	
[hmim][PF$_6$][d]	B + Hep or Dodec or Hexadec + [hmim][PF$_6$]	25	0.87	14.2 for Hep	[40]
			0.75	18.78 for Dodec	
			0.67	39.94 for Hexadec	

[a] 1-Ethyl-3-methylpyridinium ethylsulphate.
[b] 3-Methyl-N-butylpyridinium dicyanamide.
[c] 1-Hexyl-3-methylimidazolium tetrafluoroborate.
[d] 1-Hexyl-3-methylimidazolium hexafluorophosphate.

Ionic liquids (ILs) are compounds that typically contain organic cations and inorganic anions with unique properties, such as low melting temperature (<100 °C), wide liquid phase range, high thermal stability, non-flammability, and very low vapor pressure [10–12]. The growing interest in ILs as green solvents has largely been a result of the fact that they have no measurable vapor pressure, thus they do not emit volatile organic compounds (VOCs) [13,14]. The interest for using ionic liquids to replace volatile solvents in industrial applications increased significantly in recent years. Development of new ionic liquids that are stable when contacted with air and water increased the potential for their industrial application [15–21]. Ionic liquids have also a diversity of potential applications which include and not limited to their utilization as solvents for LLE of aromatic hydrocarbons from naphtha [22–31].

The application of some ILs as LLE solvents for naphtha purification has already been reported in the literature [5,17,32]. Selvan et al. [17] reported that there is a great potential for using ionic liquids as good extractants for the separation of aromatic hydrocarbons from naphtha due to their remarkable selectivity towards aromatics, which could reduce the complexity and high energy cost of existing aromatic/paraffin separation processes. They are also possessing negligible vapor pressure, which eases their recovery operations compared to conventional organic solvents. Therefore, the use of the ionic liquids can lead to major savings in the installation and operational costs of the processes. Also, the economical feasibility of the liquid extraction to perform the separation of aromatics and aliphatics may take place under a wider range of feed conditions than are currently used [22].

The use of the ILs 1-ethyl-3-methyl-imidazolium iodide ([EMIM][I$_3$]) and 1-butyl-3-methyl-imidazolium iodide ([BMIM][I$_3$]) as well as 1-ethyl-3-methyl-imidazolium bis{(trifluomethyl)sulfonyl}imide ([EMIM][NTf$_2$]) in this process has been reported in Selvan et al. [17] and Arce et al. [33], with satisfactory results. Nonetheless, it was reported that for industrial use the best IL will be [EMIM][NTf$_2$] because of the low viscosity and other favourable physico-chemical properties [34]. Arce et al. [34] had also studied the effects of varying the structure of ILs by using different functional groups in the cation for this aromatics separation process. Meindersma et al. [35] compared the suitability of using sulfolane with 1,3-dimethyl-imidazolium methylsulfate ([MMIM][CH$_3$SO$_4$]), 1-ethyl-3-methyl-imidazolium ethylsulfate ([EMIM][EtSO$_4$]), 1-butyl-3-methyl-imidazolium methylsulfate ([BMIM][CH$_3$SO$_4$]) and 4-methyl-N-butylpyridinium tetrafluoroborate ([MBPy][BF$_4$]) as solvents in liquid–liquid extraction at 40 and 70 °C. The results in that research showed that out of these four ILs, [MBPy][BF$_4$] was the best solvent for the aromatic/aliphatic separation and all ILs were better than sulfolane. Domanska et al. [4]

reported the use of the ammonium-based IL ethyl(2-hydroxyethyl) dimethyl ammonium bis{(trifluomethyl)sulfonyl}imide for the extraction of benzene, p-xylene, or m-xylene from hexane or octane at 25 °C. They reported a feasible separation of aromatics using this IL due to its high selectivities and distribution ratios. Pereiro and Rodríguez [36] investigated the application of the IL [BMpyr][NTf$_2$] for the extraction of benzene, toluene, or ethylbenzene from their mixtures with heptane at 25 °C. A selectivity of 19.54 is the highest obtained in that work for the ternary mixture benzene + heptane + [BMpyr][NTf$_2$]. Arce et al. [37] investigated the application of two immiscible ILs as a solvent for this process. They applied the system of benzene + hexane + {[C$_2$mim][NTf$_2$] + [P$_{66614}$][NTf$_2$]} at 25 °C. Their results showed that there was no improvement in the separation of aromatics compared to that if they used {[C$_2$mim][NTf$_2$]} alone. But, the authors argued that a superior performance might exist using three (liquid) phases of proper combinations of solutes and ionic liquids. Table 1 shows a summary of some of published works related to the use of ILs in the separation of aromatics [38–40].

The extracted aromatic hydrocarbon can be reclaimed by temperature elevation of the ionic liquid/aromatic mixture by only a few degrees [32].

Matsumoto et al. [41] reported another technique of aromatics separation using ILs. A supported liquid membrane based on the ILs [Bmim][PF$_6$] [Hmim][PF$_6$] [Omim][PF$_6$] [Et$_2$MeMeON][Tf$_2$N] was used for this separation. It was found that the selectivity of aromatic compounds was greatly improved when supporting the liquid membranes by ILs.

Recently, ionic liquid analogues, known as deep eutectic solvents (DESs), have been recognized as alternatives to traditional solvents and ILs themselves [42]. They are a combination of a salt and a hydrogen-bond donor (HBD), in which a new compound is formed, usually having much lower melting temperature than the components of the combination. DESs are advantageous because they can be easily prepared in high purity at low cost, and their components are biodegradable and possess low toxicity. Moreover, most DESs are nonreactive with water [43].

The first generation of DESs was based on mixtures of quaternary ammonium salts with hydrogen donors such as amines and carboxylic acids. The deep eutectic phenomenon was firstly described for a mixture of choline chloride and urea with a 1:2 mole ratio, respectively. Choline chloride has a melting temperature of 302 °C and that of urea is 133 °C while the eutectic mixture melts as low as 12 °C [44]. Compared to ordinary solvents, eutectic solvents have a very low vapor pressure and are non-flammable. Other deep eutectic solvents of choline chloride were formed with malonic acid at 0 °C, phenol at −40 °C, and glycerol at −35 °C [44].

Table 2
Methyltriphenylphosphonium bromide:ethylene glycol DESs studied in this work.

Salt:HBD mole ratio	Abbreviation
1:4	DES1
1:6	DES2
1:8	DES3

Table 3
Operating conditions for gas chromatograph.

Parameter	Set
Oven temperature	50 °C (5 min) ramped to 200 °C at (15 °C/min)
Carrier gas	Helium at (3 mL/min)
Injector temperature	250 °C
Detector temperature	250 °C

Industrial applications of DESs are very promising. DESs were used for many applications [10]. Recently, we reported the synthesize of novel phosphonium-based DESs along with some of their important physical properties [10].

The current work represents the first study on using phosphonium-based DES in separation applications. These DESs were prepared according to the original preparation method first described by Abbott et al. [44] and was used by Kareem et al. [10] as well. The DESs prepared in this work are summarized in Table 2.

To investigate the applicability of the synthesized DESs for extracting aromatic hydrocarbons from aliphatic/aromatic mixtures, the liquid–liquid equilibria of DESs with benzene/hexane binary systems were investigated under various operating conditions.

2. Experimental

The DESs were synthesized by mixing methyltriphenylphosphonium bromide as a salt with ethylene glycol as a hydrogen bond donor (HBD) in screw-capped bottles. Three salt:HBD molar ratios were used: 1:4; 1:6; and 1:8. The bottles were then stirred in an incubating-shaker at a temperature of 60 °C and a rotational speed of 200 rpm until a clear liquid was formed.

Mixtures of benzene and hexane were prepared for 10 different concentrations (2, 5, 7, 10, 15, 20, 30, 40, 60 and 90%, wt/wt); by mixing proper weighed amounts of pure benzene and pure hexane. DES as solvent was then added to the feed samples at two different feed:solvent mass ratios, namely 1:1 and 1:2. Each individual set of experiments was conducted at 27, 35, and 45 °C. The mixtures of benzene + hexane + DES were put in a well capped scintillation vials that were tightly closed to prevent any lose of contents.

All chemicals were of Merck (Darmstadt, Germany) origin. The purity is (>99%), thus they were used without any further purification. The water mass fraction of these chemicals as per the manufacturer's guide is $<10^{-4}$.

The vials were placed inside an incubator shaker capable of controlling both shaking speed and temperature. The shaking time was 3 h, and then vials were left inside the shaker at the same temperature for 2 h to allow the settling of the two phases. The temperature uncertainty for this shaker is ±0.05 °C.

3. Analysis

Samples were taken from both top (raffinate) and bottom (extractant) layers using needled syringes and were diluted using pure acetone. These samples were analyzed using HP 6890 Gas Chromatograph (GC) equipped with Alltech Econo-Cap EC-Wax column (30 m × 0.32 mm × 0.25 μm) and FID detector.

Only the HBD of the DES could be detected by the GC. The analysis of both layers for all the samples showed that the ethylene glycol exists only at extract layer and was never found in the raffinate layer. This is an indication that there was no loss of LLE solvent to the raffinate, eliminating the need for further purification and recovery of the solvent. The details of the used GC method are given in Table 3. GC uncertainty was found to be ±0.0005 mol%.

4. Results and discussion

In this work, distribution coefficients (Ds) and selectivities (Ss) for three different DESs formed by mixing 1:4, 1:6 and 1:8 molar ratios of methyltriphenylphosphonium bromide + ethylene glycol were tested for the potential application in the separation of benzene from a mixture of benzene + hexane. The selected DESs physical properties (density, viscosity, refractive index, electrical conductivity and pH) were reported in a previous work [45].

The aromatic's (benzene) concentrations in the benzene/hexane mixtures used in this study were 2, 5, 7, 10, 15, 20, 30, 40, 60 and 90% (wt/wt). These mixtures were considered as feed samples. This is to investigate the possible effect of varying concentrations of aromatic compounds in the naphtha stream fed to ethylene cracker. These samples were tested twice with feed:solvent mass ratios of 1:1 and 1:2. Tables 4–6 show the experimental results including Ds and Ss calculated for these tests at various temperatures, were x_1, x_2 and x_3 refer to mole fraction of benzene, mole fraction of hexane and mole fraction of DES respectively.

Analysis of samples with gas chromatography showed that the ethylene glycol which is one component of the DES has not been found in the raffinate layer after the LLE experiments. This leads to the conclusion that when ethylene glycol was employed in a DES, the interaction between the salt and HBD has trapped the ethylene glycol in the extract layer and prohibited it from transferring at low concentrations to the raffinate. This achievement is very important from an industrial point of view. Currently, ethylene glycol is applied as a LLE solvent for the same process; it transfers to the raffinate layer causing what is called as "solvent loss". By trapping the ethylene glycol in the extract layer, one important objective in the process is achieved.

For the sake of comparison with commercially used solvents, distribution coefficient and selectivity of sulfolane and N-formylmorpholine towards benzene in benzene/hexane mixtures were obtained from Chen et al. [46] and Mahmoudi and Lotfollahi [47]. These data were compared to the results obtained in this investigation and are presented in Figs. 1–4.

The data reported by Chen et al. [46] for sulfolane was conducted at 25 °C. However, in this work the results were collected at a temperature of 27 °C. The two data sets were compared, due to the fact that there is no relevant data reported at the same temperature.

From Table 4, it is found that for DES1 with DES:feed ratio of 1:1, 45 °C was the best temperature that gave the highest distribution coefficient and selectivity at low concentrations of aromatics. Even though at 27 °C relatively higher selectivity was achieved, distribution coefficients were low.

In Fig. 1 we can see that a selectivity of more than 80 was achieved at low concentrations of aromatic in the feed. In addition to this, it is also clear that some of the studied DESs were of higher selectivity towards the aromatics (benzene) than the commercially used solvent (sulfolane). However, the selectivity is decreasing at higher concentrations of aromatics in feed, a behavior similar to what is known for other solvents [4,40,48]. Moreover, it can be noted that the selectivity of feed:DES1 1:1 is higher than all the other DES curves in the range 0–0.35 wt fraction and lower than the others at the range >0.4 wt fraction (Fig. 1). This can be attributed to the amount of ethylene glycol in the used DESs. At lower aromatic

Table 4
Experimental mole fractions of the liquid–liquid extraction system of benzene (x_1) + hexane (x_2) + DES1 (x_3) at different temperatures.

Aromatic conc. in feed	Hexane-rich phase			DES-rich phase			D_{aro}	Selectivity
	x_1	x_2	x_3	x_1	x_2	x_3		
			$T = 27\,^\circ$C	Feed:DES	1:1			
0.0766	0.0532	0.9468	0	0.0143	0.0027	0.9830	0.2688	98.2662
0.1091	0.0994	0.9006	0	0.0203	0.0020	0.9777	0.2042	85.8233
0.1629	0.1298	0.8702	0	0.0291	0.0025	0.9684	0.2242	67.9864
0.2161	0.3140	0.6860	0	0.0419	0.0022	0.9558	0.1334	53.4847
0.3209	0.4293	0.5707	0	0.0751	0.0028	0.9221	0.1749	33.1421
0.4236	0.5241	0.4759	0	0.0687	0.0025	0.9288	0.1311	22.1055
0.6232	0.7048	0.2952	0	0.0864	0.0023	0.9113	0.1226	17.1902
0.9085	0.9247	0.0753	0	0.1852	0.0012	0.8136	0.2003	12.3623
			$T = 35\,^\circ$C	Feed:DES	1:1			
0.0549	0.0300	0.9700	0	0.0104	0.0035	0.9861	0.3467	87.0857
0.0766	0.0801	0.9199	0	0.0301	0.0055	0.9644	0.3758	68.5035
0.1091	0.1557	0.8443	0	0.0259	0.0043	0.9698	0.1663	46.3021
0.1629	0.2289	0.7711	0	0.1999	0.0195	0.7806	0.8733	23.0438
0.3209	0.4119	0.5881	0	0.3777	0.0174	0.6049	0.9170	32.5183
0.9085	0.9041	0.0959	0	0.5891	0.0039	0.4069	0.6516	15.8735
			$T = 45\,^\circ$C	Feed:DES	1:1			
0.2161	0.0152	0.9848	0	0.0336	0.0241	0.9423	2.2105	93.6772
0.0549	0.0432	0.9568	0	0.0962	0.0244	0.8794	2.2269	87.3624
0.0766	0.0641	0.9359	0	0.1488	0.0259	0.8252	2.3214	83.3668
0.1091	0.0847	0.9153	0	0.2120	0.0280	0.7600	2.5030	77.6854
0.1629	0.1765	0.8235	0	0.2505	0.0162	0.7333	1.4193	69.0154
0.2161	0.2360	0.7640	0	0.3785	0.0217	0.5998	1.6038	61.2915
0.3209	0.3181	0.6819	0	0.5141	0.0206	0.4652	1.6162	48.4382
0.4239	0.4805	0.5195	0	0.5639	0.0197	0.4164	1.1736	38.6384
0.6232	0.6810	0.3190	0	0.7077	0.0111	0.2812	1.0392	26.2506
0.9085	0.9300	0.0700	0	0.8130	0.0034	0.1836	0.8742	18.3909
			$T = 45\,^\circ$C	Feed:DES	1:2			
0.0549	0.0504	0.9496	0	0.0205	0.0137	0.9658	0.4065	28.1859
0.0766	0.0673	0.9327	0	0.039	0.0243	0.9357	0.5938	22.7694
0.1091	0.1148	0.8852	0	0.048	0.0208	0.9316	0.4150	17.6742
0.1629	0.1670	0.8330	0	0.081	0.0236	0.8957	0.4832	17.0581
0.2161	0.2481	0.7519	0	0.093	0.0174	0.8899	0.3737	16.1287
0.6232	0.6069	0.3931	0	0.329	0.0190	0.6516	0.5426	11.2020
0.9085	0.9143	0.0857	0	0.432	0.0138	0.5543	0.4724	2.9286

concentrations the amount of ethylene glycol present in DES1 is sufficient for the extraction of aromatics and thus the selectivity of DES1 is higher than other DESs. But at higher concentrations the amount of ethylene glycol in DES1 needed for the extraction of aromatics is not enough and thus the selectivity decreases. The same argument can be used to explain the difference between DES2 and DES3 at feed:solvent ratio of 1:2.

Focus will be directed to low aromatics concentrations as they represent a practical separation problem as discussed above. Table 4 shows that at 45 °C and feed:DES1 ratio of 1:2, the distribution coefficient as well as the selectivity were quite low compared to the corresponding feed:DES1 ratio of 1:1 at same temperature. It can be concluded that for DES1, the best operation conditions were at feed:DES mass ratio of 1:1 and temperature of 45 °C whereby a
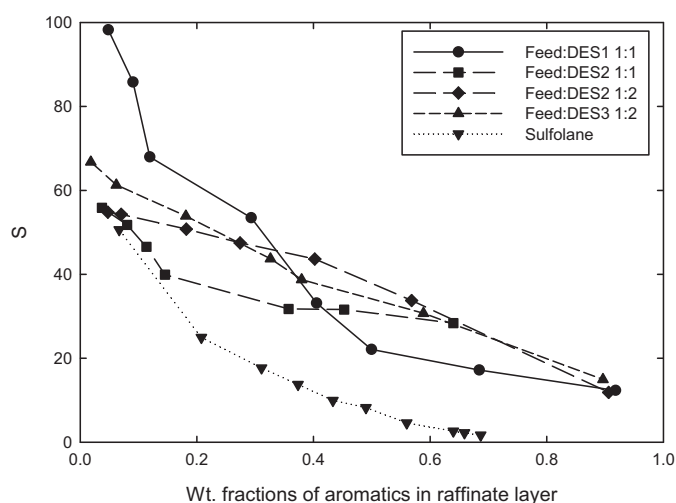

Fig. 1. Selectivities (Ss) of selected studied systems at 27 °C compared to sulfolane at 25 °C as in Chen et al. [46].
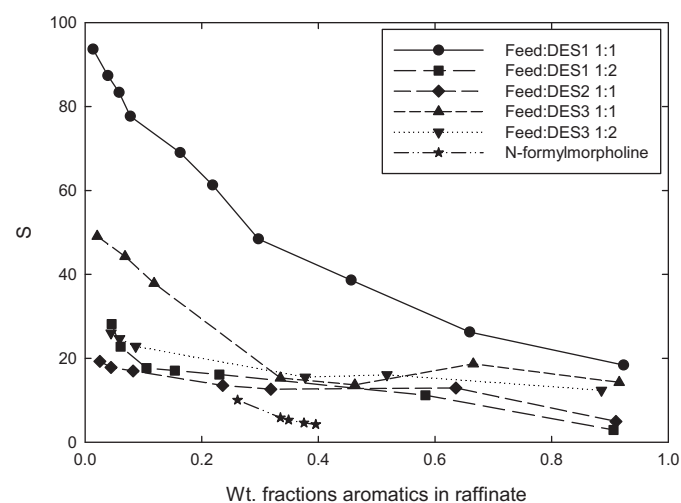

Fig. 2. Selectivities (Ss) of selected studied systems at 45 °C compared to N-formylmorpholine at 45 °C as in Mahmoudi and Lotfollahi [47].

Table 5
Experimental mole fractions of the liquid–liquid extraction system of benzene (x_1) + hexane (x_2) + DES2 (x_3) at different temperatures.

Aromatic conc. in feed	Hexane-rich phase			DES-rich phase			D_{aro}	Selectivity
	x_1	x_2	x_3	x_1	x_2	x_3		
			$T = 27\,°C$	Feed:DES	1:1			
0.0549	0.0405	0.9595	0	0.0320	0.0140	0.9540	0.7901	55.8284
0.0766	0.0880	0.9120	0	0.1598	0.0319	0.8084	1.8159	51.7673
0.1091	0.1236	0.8764	0	0.2778	0.0389	0.6834	2.2476	46.5461
0.1629	0.1575	0.8425	0	0.3120	0.0450	0.6430	1.9810	39.9321
0.3209	0.3800	0.6200	0	0.4527	0.0232	0.5241	1.1913	31.7304
0.4239	0.4772	0.5228	0	0.5461	0.0188	0.4351	1.1444	31.5927
0.6232	0.6619	0.3381	0	0.5600	0.0101	0.4299	0.8460	28.3772
			$T = 35\,°C$	Feed:DES	1:1			
0.0220	0.0217	0.9783	0	0.0084	0.0042	0.9875	0.3855	83.6372
0.0549	0.0553	0.9457	0	0.0245	0.0062	0.9693	0.4430	75.9853
0.1091	0.1120	0.8880	0	0.0558	0.0068	0.9374	0.4982	65.6097
0.1629	0.1380	0.8620	0	0.0494	0.0052	0.9454	0.3580	57.8295
0.3209	0.3616	0.6384	0	0.1165	0.0041	0.8794	0.3222	45.7220
0.4239	0.4726	0.5274	0	0.1583	0.0045	0.8372	0.3350	42.6704
0.6232	0.6512	0.3488	0	0.2790	0.0045	0.7166	0.4284	32.9897
			$T = 45\,°C$	Feed:DES	1:1			
0.0220	0.0280	0.9720	0	0.0292	0.0493	0.9215	1.0429	19.2720
0.0549	0.0486	0.9514	0	0.0566	0.0593	0.8840	1.1646	17.8298
0.0766	0.0900	0.9100	0	0.0966	0.0692	0.8341	1.0733	16.9890
0.2161	0.2543	0.7457	0	0.2187	0.0466	0.7347	0.8600	13.5238
0.3209	0.3399	0.6601	0	0.2377	0.0344	0.7279	0.6993	12.6410
0.6232	0.6576	0.3424	0	0.3110	0.0129	0.6761	0.4729	12.9165
0.9085	0.9182	0.0818	0	0.3945	0.0070	0.5985	0.4296	4.9432
			$T = 27\,°C$ 0	Feed:DES	1:2			
0.0549	0.0517	0.9483	0	0.0812	0.0263	0.8926	1.5706	54.7872
0.0766	0.0770	0.9230	0	0.1060	0.0243	0.8697	1.3767	54.2974
0.2161	0.1973	0.8027	0	0.1964	0.0160	0.7877	0.9954	50.7522
0.3209	0.2937	0.7063	0	0.3311	0.0161	0.6528	1.1273	47.4936
0.4239	0.4258	0.5742	0	0.3760	0.0119	0.6122	0.8830	43.6521
0.6232	0.5923	0.4077	0	0.4963	0.0101	0.4936	0.8379	33.7821
0.9085	0.9143	0.0857	0	0.5666	0.0045	0.4290	0.6197	11.8640
			$T = 35\,°C$ 0	Feed:DES	1:2			
0.0549	0.0382	0.9618	0	0.0890	0.0271	0.8839	2.3298	70.8133
0.0766	0.0697	0.9303	0	0.0992	0.0260	0.8748	1.4232	60.0704
0.1091	0.1104	0.8896	0	0.1234	0.0244	0.8522	1.1178	46.5789
0.1629	0.1607	0.8393	0	0.1498	0.0265	0.8236	0.9322	30.4954
0.3209	0.3169	0.6831	0	0.3435	0.0253	0.6312	1.0839	20.0500
0.4239	0.4685	0.5315	0	0.3630	0.0146	0.6224	0.7748	33.4902
0.9085	0.9184	0.0816	0	0.5514	0.0039	0.4447	0.6004	12.5264

Table 6
Experimental mole fractions of the liquid–liquid extraction system of benzene (x_1) + hexane (x_2) + DES3 (x_3) at different temperatures.

| Aromatic conc. in feed	Hexane-rich phase			DES-rich phase			D_{aro}	Selectivity
	x_1	x_2	x_3	x_1	x_2	x_3		
			$T = 45\,°C$	Feed:DES	1:1			
0.0549	0.0229	0.9771	0	0.0126	0.0097	0.9776	0.5502	49.0895
0.0766	0.0753	0.9247	0	0.0236	0.0064	0.9700	0.3134	44.2756
0.1091	0.1292	0.8708	0	0.0652	0.0159	0.9189	0.5046	37.8525
0.3209	0.3573	0.6427	0	0.1706	0.0180	0.8114	0.4775	15.3110
0.4239	0.4868	0.5132	0	0.1915	0.0119	0.7966	0.3934	13.6618
0.6232	0.6867	0.3133	0	0.2701	0.0077	0.7222	0.3933	18.6847
0.9085	0.9229	0.0771	0	0.3802	0.0022	0.6177	0.4120	14.2579
			$T = 27\,°C$	Feed:DES	1:2			
0.2161	0.0203	0.9797	0	0.0135	0.0102	0.9763	0.6650	66.7727
0.0766	0.0680	0.9320	0	0.0433	0.0095	0.9472	0.6368	61.2956
0.1629	0.1964	0.8036	0	0.1203	0.0083	0.8714	0.6125	53.9058
0.3209	0.3484	0.6515	0	0.2537	0.0121	0.7343	0.7282	43.6918
0.4239	0.4029	0.5971	0	0.2935	0.0115	0.6950	0.7285	38.7396
0.6232	0.6119	0.3881	0	0.3901	0.0075	0.6023	0.6375	30.7340
0.9085	0.9051	0.0949	0	0.5344	0.0038	0.4618	0.5904	14.9444
			$T = 45\,°C$	Feed:DES	1:2			
0.0549	0.0492	0.9508	0	0.0639	0.0446	0.8915	1.2988	26.0379
0.0766	0.0650	0.9350	0	0.0091	0.0055	0.9854	0.1392	24.6750
0.1091	0.0949	0.9051	0	0.0076	0.0032	0.9892	0.0801	22.8512
0.4239	0.4005	0.5995	0	0.0332	0.0031	0.9637	0.0829	15.5226
0.6232	0.5422	0.4578	0	0.1889	0.0102	0.8009	0.3484	16.0670
0.9085	0.8951	0.1049	0	0.5184	0.0049	0.4767	0.5792	12.3742
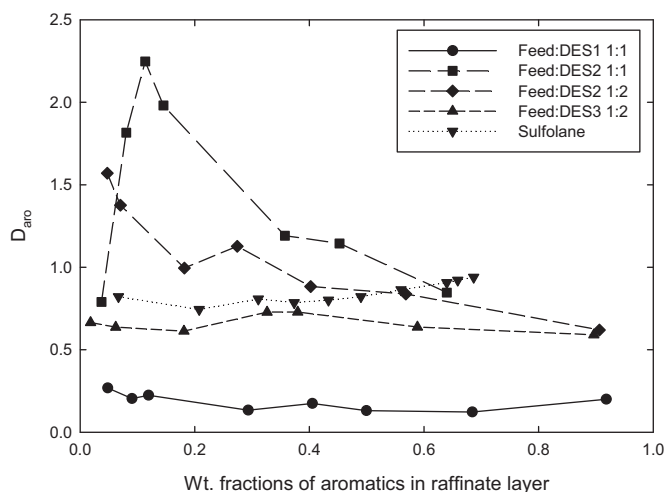
Fig. 3. Distribution coefficients for aromatic hydrocarbon (D_{aro}) of selected studied systems at 27 °C compared to sulfolane at 25 °C as in Chen et al. [46].

Fig. 5. Phase diagram with the LLE data for (DES + hexane + benzene) systems at 27 °C.

selectivity of greater than 93 was achieved at low aromatic concentrations.

Fig. 2 shows a comparison between the selectivity achieved by some of the studied systems in this work to those of N-formylmorpholine reported by Mahmoudi and Lotfollahi [47]. Similarly, these selected systems were of much higher selectivity compared to the conventional solvent (N-formylmorpholine). These experimental findings support the argument which this paper is based on, that it is still possible to find solvents able to compete with the industrially used solvents and other studied solvents in the literature.

On the other hand, Figs. 3 and 4 show a comparison among the distribution coefficient of DESs and sulfolane at 25 °C and N-formylmorpholine at 45 °C respectively. These figures show that the distribution coefficients of sulfolane and N-formylmorpholine are not the lowest. However, the DES combination of 1:6 molar ratio of salt:HBD was superior to sulfolane in both selectivity and distribution coefficients at feed:solvent ratio of 1:1 and 1:2 at 27 °C. Moreover, the DES combination of 1:4 molar ratio of salt:HBD was higher than that of N-formylmorpholine at 45 °C.

Interestingly, Table 5 shows different findings. For DES2, the mass ratio 1:2 feed:DES2 was better in terms of distribution
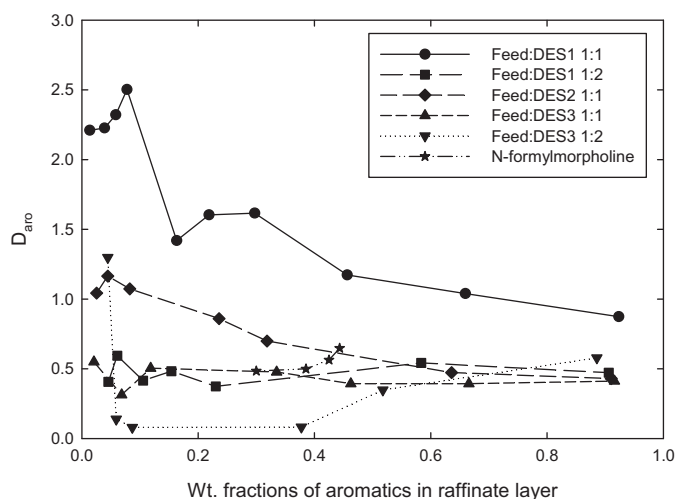
coefficient and selectivity. At 35 °C and feed:DES2 ratio of 1:2, $S > 70$ with high distribution coefficient were achieved. While at 35 °C and feed:DES2 ratio of 1:1 the selectivity was 83.6 at aromatic concentration of 0.0549 wt% in the feed, the distribution coefficient was not as high as it is in mass ratio 1:2 feed:DES2. Other temperatures of application were not able to improve the distribution coefficient and selectivity.

Table 6 gives the separation results using DES3. In this case it is clear that at Feed:DES3 mass ratio of 1:2 and 27 °C, the highest distribution coefficient and selectivity were achieved. At a DES:feed mass ratio of 1:1 and 45 °C, it was possible to achieve a selectivity of almost 50% but the distribution coefficient was low compared to that at 27 °C.

As a conclusion from all the data presented in Tables 4–6, it is clear that DES1 achieved the best separation efficiency at a feed:DES ratio of 1:1 and a temperature of 45 °C. Thus, DES1 can be considered as the optimum composition that can be adopted for further process investigation and analysis.

It is worth mentioning here that sometimes the distribution coefficient does not show a monotonic trend in its values. This is also noticed for the selectivity profile for certain cases. This behavior is typical as similar findings were reported for hydrocarbons separation [4,40,48]. The fluctuation could be due to the interaction between the DES and the benzene which is polar in nature and temperature-independent.

The experimental results presented above show that generally, at low concentrations of aromatics in the feed, the distribution coefficient is relatively higher than usual. Again, it's a good indication that the separation of aromatics at low concentrations is promising with DESs. Also it can be seen that for DESs 2 and 3, a Feed:DES mass ratio of 1:2 was the best in terms of its distribution coefficient and selectivity. Finally, DES1 which is made of methyl triphenylphosphonium bromide + ethylene glycol at molar ratio of 1:1 salt:HBD was the best solvent with more than 98% selectivity at low concentrations of aromatics.

The fluctuations in selectivity and distribution coefficients seen in Figs. 2–4 are common in the literature when ILs were used, see for example Meindersma et al. [24], whereby similar fluctuations were noticed.

Figs. 5–7 are the ternary diagrams of the selected systems at 27, 35 and 45 °C respectively. They show clearly how a good separation was achieved which further support the argument of this work.

Fig. 4. Distribution coefficients for aromatic hydrocarbon (D_{aro}) of selected studied systems at 45 °C compared to N-formylmorpholine at 45 °C as in Mahmoudi and Lotfollahi [47].
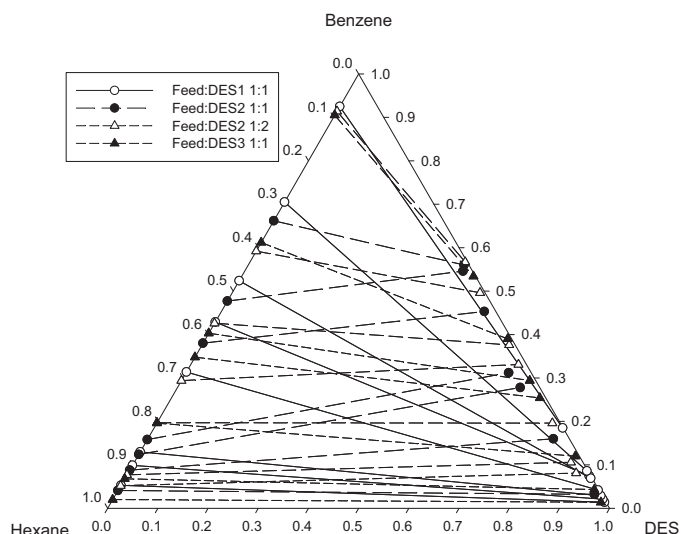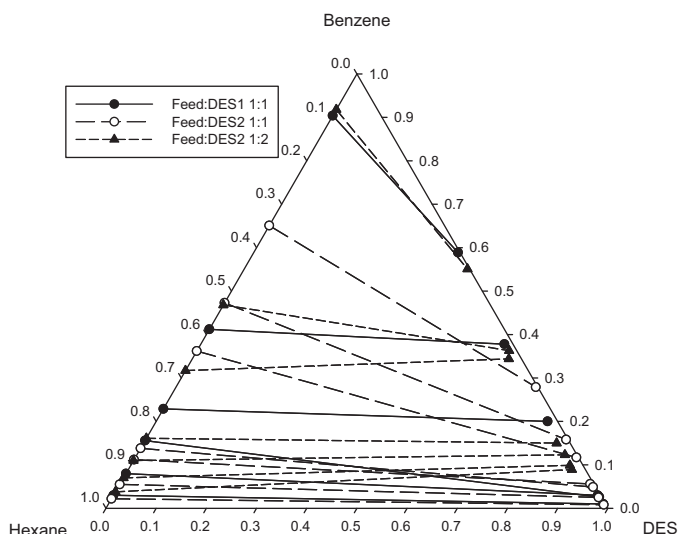
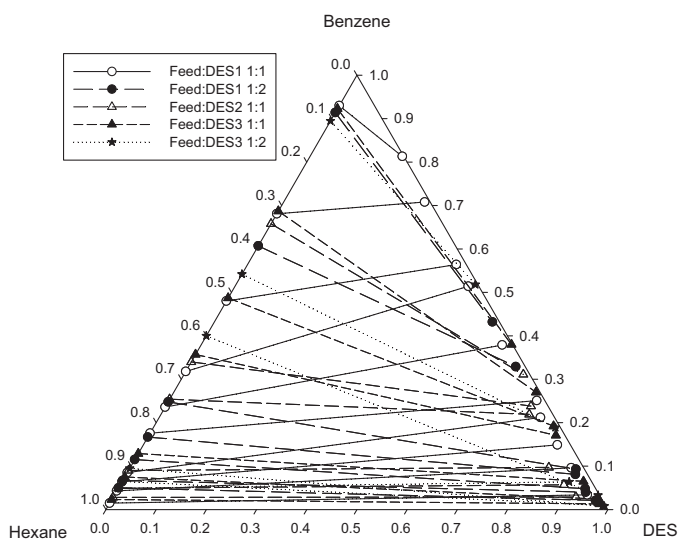**Fig. 6.** Phase diagram with the LLE data for (DES + hexane + benzene) systems at 35 °C.

Fig. 7. Phase diagram with the LLE data for (DES + hexane + benzene) systems at 45 °C.

5. Conclusions

A novel class of ionic liquids' analogues namely deep eutectic solvents formed by the mixing of methyltriphenylphosphonium bromide as a salt and ethylene glycol as a hydrogen bond donor was synthesized. Three different molar ratios were chosen for this work. Liquid–liquid equilibria experiments were carried out to investigate the ability of these DESs to selectively extract aromatic hydrocarbons from aromatic/aliphatic mixtures such as naphtha. All prepared DESs showed superior results compared to that of sulfolane and N-formylmorpholine. Particularly, the DES of molar ratio of 1:6 salt:HBD gave best separation performance compared to sulfolane while the 1:4 DES gave the best performance as compared to N-formylmorpholine. These new solvents are ionic liquid's analogues with melting points below room temperature. Their viscosity is lower than sulfolane and do not show problems of decomposition over time (stable).

Effect of temperature on the extraction was clear. Extraction efficiency at 45 °C was the best compared to lower temperatures

and hence further investigation is recommended on the selected systems at this temperature.

Ethylene glycol, which is one constituent of the studied DES, has not been found in the raffinate layer after the LLE experiments. This leads to the conclusion that when ethylene glycol is employed in a DES form, it interacts with the salt and get trapped in the extract layer. This prohibits it from transferring at low aromatics concentrations to the raffinate. This achievement is very important from an industrial point of view. Currently, ethylene glycol is applied as a solvent for the same process. During mixing some of it transfers to the raffinate causing what is called "solvent loss". By trapping the ethylene glycol in the extract layer as a DES component, one important objective of the process operation economy is achieved.

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