Extraction of Aromatics from Petroleum Naphtha Reformate by a 1-Cyclohexyl-2-pyrrolidone/Ethylene Carbonate Mixed Solvent

4 AUTHORS, INCLUDING:

Shaheen Abdulhafez Al-Muhtaseb
Qatar University
60 PUBLICATIONS **770** CITATIONS

SEE PROFILE

Mohamed Fahim
Pharos University
60 PUBLICATIONS **617** CITATIONS

SEE PROFILE

Extraction of Aromatics from Petroleum Naphtha Reformate by a 1-Cyclohexyl-2-pyrrolidone/Ethylene Carbonate Mixed Solvent

Gamil M. Radwan, Shaheen A. Al-Muhtaseb, Ali M. Dowaidar, and Mohamed A. Fahim*

Chemical & Petroleum Engineering Department, U.A.E. University, P.O. Box 17555, Al-Ain, United Arab Emirates

The phase equilibria for the extraction of aromatics from petroleum naphtha reformate (with a boiling range of 338–403 K) using a mixed solvent of 1-cyclohexyl-2-pyrrolidone (CHP) and ethylene carbonate (EC) have been correlated using the universal function-group activity coefficients model (UNIFAC). The interaction parameters of CHP and EC with different hydrocarbon groups present in the reformate such as CH_2 (paraffinic CH_2), ACH (aromatic CH), $ACCH_2$ (aromatic CCH_2), and each of the two solvents have been fitted to experimental concentrations of three ternary systems that contain these groups. The extraction runs have been carried out at different temperatures, solvent compositions, and solvent-to-feed ratios. Experimental results compared favorably with those predicted from the UNIFAC method. The optimum extraction conditions were determined by calculation of the minimum energy of separation. In this study these conditions were found to be at a mixed solvent composition of 65% EC (by weight) and 35% CHP. The solvent-to-feed ratio was 1.8 on a volume basis, and the extraction temperature was 329 K.

Introduction

The extraction of aromatics (benzene, toluene, and xylene (BTX)) from naphtha reformates has been commercially available for the last few decades, and several commercial processes are available. The first efficient method of BTX extraction was the "Volex" process, using a glycol-based solvent. It was superior because, for the first time, a wide-boiling feedstock could be treated directly to yield BTX aromatics of high purity without expensive prefractionation. Another BTX extraction process is the shell process which is based on sulfolane; several other solvents are also available to the industry. Union carbide selected tetraethylene glycol as the best glycol for its "Tetra" process. The "Arosolvan" process uses the *N*-methylpyrrolidone (NMP).

However, the study of the phase equilibria of these aromatics and other hydrocarbons present in the naphtha reformate with the used solvents is not available in the literature. This work takes advantage of the development of the universal function-group contribution model (UNIFAC) (Fredenslund *et al.*, 1975) for the prediction of phase equilibria in order to find the optimum conditions for the extraction of aromatics from petroleum naphtha reformate using a mixed solvent of CHP and EC.

Mixed solvents are usually used to compromise between the desired properties of the two, or more, solvents. Some mixed solvents are essential for the practical extraction processes (Fahim and El-Kilani, 1990; Mukhopadhyay and Malleswararao, 1991). 1-Cyclohexyl-2-pyrrolidone has a high capacity and a low selectivity for aromatics extraction. Ethylene carbonate has been previously studied for the extraction of aromatics (Annesini *et al.*, 1985), and it was found to be a highly selective but poorly capacitive solvent. It has been a common and good practice to have a solvent combination of two such solvents.

A mixture of EC and CHP is used in this work to extract the aromatics from the naphtha reformate. The interaction parameters between the UNIFAC groups present in the reformate and each of the used solvents were determined by correlating experimental compositions of three ternary systems according to the UNIFAC model. The UNIFAC predictions for the multicomponent system of the reformate with the mixed solvent were compared with experimental data at different temperatures, different solvent compositions, and different solvent-to-feed ratios.

Experimental Section

Chemicals. The extraction runs were carried out using a petroleum naphtha reformate with a boiling range of 338–403 K and a specific gravity of 0.787. Table 1 shows the composition of this reformate as analyzed by gas chromatography and the number of functional groups present in each of its constituents. The EC and CHP were supplied by Fluka with a purity > 99% (wt %). The specific gravity of CHP was 1.029, and its boiling point was 375 K. The melting point of EC was 308–310 K.

The specific gravity of the CHP/EC mixed solvent was measured for several samples by pycnometers and correlated as:

$$s_{\text{solvent}} = 1/[0.96996 + 0.002193(\text{EC \%})] \qquad (1)$$

where EC % is the weight percent of EC in the CHP/EC mixed solvent.

Determination of Critical Solution Temperature. In order to find the operating extraction temperatures, the miscibilities and the critical solution temperatures (CST) were measured for different solvent-to-feed ratios. The miscibilities were measured by adding a known volume of solvent to a known volume of reformate and mixing the two phases completely in a 75 mL vial. A magnetic stirrer/heater was used to raise the mixture's temperature gradually. The miscibility temperature was marked as the point where the

Table 1. Reformate Composition and the Number of Functional UNIFAC Groups in Each of Its Constituents

no.	component	mass %	CH$_3$	CH$_2$	CH	ACH	ACCH$_3$	ACCH$_2$
						no. of UNIFAC groups in each component		
1	*n*-hexane	1.89	2	4	0	0	0	0
2	cyclohexane	5.05	0	6	0	0	0	0
3	benzene	3.98	0	0	0	6	0	0
4	2,3-dimethylpentane	6.96	4	1	2	0	0	0
5	*n*-heptane	7.05	2	5	0	0	0	0
6	toluene	41.72	0	0	0	5	1	0
7	*n*-octane	3.56	2	6	0	0	0	0
8	ethylbenzene	6.59	1	0	0	5	0	1
9	*m,p*-xylene	17.68	0	0	0	4	2	0
10	*o*-xylene	5.52	0	0	0	4	2	0

turbidity of the mixture disappears and the two phases become completely miscible in each other. Heating is then cut off, and another reading is then taken when the solution cools and becomes turbid, indicating the beginning of phase separation. The two readings were within 1 K difference. The critical solution temperature is marked as the highest temperature of the miscibility curve.

Extraction Runs. Three solvent compositions were investigated for a solvent-to-feed ratio of 1:1 at a temperature of 298 K. These compositions were 55%, 60%, and 65% EC in CHP on a weight basis. The effect of temperature was also investigated by the system of 1:1 solvent-to-feed ratio and 65% EC solvent at 298, 308, 318, and 328 K, and the effect of solvent-to-feed ratios was studied by investigating the system of 65% EC solvent and 298 K at the solvent-to-feed ratios of 1:1, 1.5:1, 2:1, and 3:1. In all conditions, a stirring period of 30 min and a settling period of not less than 3 h were allowed. No sensible changes in the equilibrium compositions occurred at longer extraction or settling times.

Measurements of Phase Compositions. A Chrompack CP9001 gas chromatograph was used with a WCOT fused silica (50 m × 0.32 mm i.d.), an FID detector at 573 K, and an inlet pressure of 35 kPa. The column was coated with CB silica (5CB, DF = 1.2), and the splitter injection temperature was 573 K. The oven temperature was varied in two ranges. The first range of oven temperature was 318−393 K with a temperature rise of 8 K/min. The initial time was 5 min, and the final time was 15 min. The second range of oven temperature was 393−533 K with a temperature rise of 15 K/min. The initial time was 15 min, and the final time was 17 min.

Prediction of Phase Equilibria

The UNIFAC model (Fredenslund *et al.*, 1975) was used for the correlation of liquid−liquid equilibrium (LLE) of multicomponent systems. The correlated phase equilibrium compositions were compared with the experimental data obtained in this work.

Assume that a liquid mixture of a known overall composition and temperature has separated into two equilibrium liquid phases. Now it is required to calculate the composition of the two phases using an activity model (Henley and Seader, 1981; Mukhopadhyay, 1979).

A material balance on the system gives the following equation:

$$z_i = x_i^E \theta + x_i^R (1 - \theta) \qquad (2)$$

where

$$\theta = n^E / n^F \qquad (3)$$

Table 2. *R* and *Q* Values for the Used UNIFAC Groups (Hansen *et al.*, 1992)

group	R	Q	group	R	Q
CH$_3$	0.9011	0.848	ACCH$_2$	1.0396	0.660
CH$_2$	0.6744	0.540	ACCH$_3$	1.2663	0.968
CH	0.4469	0.228	EC	2.9727	2.520
ACH	0.5313	0.400	CHP	6.8987	2.580

Rearranging eq 2 gives

$$x_i^E = K_i z_i / [1 + \theta(K_i - 1)] \qquad (4)$$

or

$$1 = \sum_i \{ K_i z_i / [1 + \theta(K_i - 1)] \} \qquad (5)$$

where

$$K_i = x_i^E / x_i^R = \gamma_i^R / \gamma_i^E \qquad (6)$$

The values z_i, x_i^E, and x_i^R are the mole fractions of component i in the initial charge (the feed), the extract, and the raffinate phases, respectively. The total number of moles of the initial charge to the cell is n^F, and n^E and n^R are the number of moles of the extract phase and the raffinate phase, respectively. γ_i^E and γ_i^R are the activity coefficients of component i in the extract and the raffinate phases, respectively. The activity coefficients can be calculated from the UNIFAC model using an appropriate set of interaction parameters. The R and Q values for the UNIFAC groups included in the systems studied are shown in Table 2.

Solving eq 5 for θ with K_i values initially guessed from the ratios of the measured equilibrium compositions, new values of equilibrium compositions can be calculated using eqs 4 and 6. The corresponding activity coefficients in each phase are then calculated using the UNIFAC model, and the equilibrium is tested according to eq 7.

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R \qquad (7)$$

When the equality in eq 7 is achieved with an acceptable tolerance (an absolute relative error of 10^{-11} between all successive predictions was reached in this work), the last calculated mole fractions are taken as the predicted equilibrium compositions. Otherwise, the K_i values are corrected by the activity coefficients according to eq 7 and the iterative procedure is repeated again starting from solving eq 6 for θ.

Determination of Interaction Parameters

To estimate the interaction parameters, three ternary LLE systems were studied at different temperatures.

Table 3. Ternary Systems Studied[a]

ternary no.	component 1	component 2	component 3	UNIFAC groups
1	EC	CHP	dodecane	EC, CHP (CH$_3$, CH$_2$)
2	EC	ethylbenzene	heptane	EC, ACH, ACCH$_2$, (CH$_3$, CH$_2$)
3	benzyl alcohol	CHP	1-hexadecene	CHP, ACH, ACCH$_2$, (CH$_3$, CH$_2$)

[a] The listed groups are only the studied ones.

Table 4. Liquid−Liquid Equilibria of the Ternary System EC + CHP + Dodecane

EC		CHP		dodecane	
phase 1	phase 2	phase 1	phase 2	phase 1	phase 2
		298 K			
0.1241	0.0232	0.6482	0.2367	0.2277	0.7401
0.2960	0.0152	0.6072	0.1514	0.0968	0.8334
0.4336	0.0186	0.5189	0.1067	0.0475	0.8748
0.5513	0.0138	0.4239	0.0798	0.0248	0.9064
		308 K			
0.2960	0.0283	0.5907	0.1765	0.1133	0.7952
0.4437	0.0180	0.4987	0.1228	0.0576	0.8591
0.5621	0.0142	0.4094	0.0924	0.0285	0.8935
0.6657	0.0113	0.3192	0.0732	0.0151	0.9156
		313 K			
0.2966	0.0349	0.5781	0.2001	0.1253	0.7649
0.4353	0.0265	0.5024	0.1388	0.0623	0.8348
0.5633	0.0177	0.4053	0.1046	0.0313	0.8777
0.6629	0.0172	0.3189	0.0801	0.0181	0.9028
0.9983	0.0013	0.0000	0.0000	0.0017	0.9987
		318 K			
0.2882	0.0482	0.5632	0.2458	0.1486	0.7060
0.4383	0.0339	0.4916	0.1587	0.0701	0.8074
0.5310	0.0255	0.4249	0.1232	0.0441	0.8513
0.6637	0.0243	0.3180	0.0869	0.0183	0.8888
0.9996	0.0014	0.0000	0.0000	0.0004	0.9986
		323 K			
0.2810	0.0641	0.5522	0.3234	0.1668	0.6125
0.4265	0.0493	0.4986	0.1643	0.0749	0.7863
0.6762	0.0230	0.3038	0.0958	0.0200	0.8812
0.9998	0.0033	0.0000	0.0000	0.0002	0.9967

Table 5. Liquid−Liquid Equilibria of the Ternary System EC + Ethylbenzene + Heptane

EC		ethylbenzene		heptane	
phase 1	phase 2	phase 1	phase 2	phase 1	phase 2
		313 K			
0.9908	0.0018	0.0083	0.0786	0.0009	0.9197
0.9907	0.0039	0.0088	0.1673	0.0005	0.8288
0.9663	0.0091	0.0328	0.3426	0.0009	0.6482
0.9633	0.0013	0.0356	0.3611	0.0010	0.6376
		318 K			
0.9905	0.0043	0.0082	0.1013	0.0012	0.8945
0.9838	0.0041	0.0148	0.1482	0.0014	0.8477
0.9739	0.0068	0.0250	0.2941	0.0011	0.6991
0.9643	0.0090	0.0347	0.3669	0.0010	0.6241
		323 K			
0.9987	0.0010	0.0000	0.0000	0.0013	0.9990
0.9836	0.0039	0.0145	0.1389	0.0019	0.8572
0.9708	0.0075	0.0276	0.2551	0.0016	0.7374
0.9647	0.0112	0.0341	0.3258	0.0012	0.6630
0.9592	0.0140	0.0390	0.3456	0.0018	0.6404
		328 K			
0.9990	0.0017	0.0000	0.0000	0.0010	0.9983
0.9988	0.0068	0.0010	0.2447	0.0002	0.7485
0.9592	0.0114	0.0401	0.3943	0.0007	0.5942
0.9654	0.0089	0.0339	0.3236	0.0007	0.6676
0.9627	0.0132	0.0365	0.3612	0.0008	0.6256
		333 K			
0.9994	0.0038	0.0000	0.0000	0.0006	0.9962
0.9592	0.0091	0.0402	0.4058	0.0006	0.5852
0.9743	0.0093	0.0249	0.3348	0.0007	0.6560
0.9673	0.0091	0.0310	0.3580	0.0017	0.6330

The ternaries were chosen to cover all the UNIFAC groups included in the reformate−mixed solvent system

Table 6. Liquid−Liquid Equilibria of the Ternary System Benzyl Alcohol + CHP + 1-Hexadecene

benzyl alcohol		CHP		1-hexadecene	
phase 1	phase 2	phase 1	phase 2	phase 1	phase 2
		298 K			
0.9622	0.1704	0.0000	0.0000	0.0378	0.8296
0.7456	0.1431	0.1884	0.0507	0.0659	0.8062
0.7157	0.1464	0.2159	0.0596	0.0685	0.7940
0.6625	0.1729	0.2503	0.0373	0.0872	0.7899
0.5677	0.1671	0.3193	0.1150	0.1130	0.7178
		303 K			
0.9588	0.2128	0.0000	0.0000	0.0412	0.7872
0.7859	0.1800	0.1630	0.0667	0.0511	0.7533
0.7201	0.1820	0.2033	0.0783	0.0766	0.7397
0.6613	0.2079	0.2416	0.0435	0.0971	0.7485
0.5641	0.1983	0.3077	0.1387	0.1282	0.6631
		308 K			
0.9540	0.2212	0.0000	0.0000	0.0460	0.7788
0.7272	0.2032	0.1869	0.0682	0.0859	0.7286
0.6926	0.2025	0.2161	0.0867	0.0913	0.7109
0.6370	0.2197	0.2469	0.1135	0.1161	0.6667
0.5656	0.2229	0.2953	0.1543	0.1392	0.6228
		313 K			
0.9483	0.2349	0.0000	0.0000	0.0517	0.7651
0.7435	0.2388	0.1622	0.0691	0.0943	0.6921
0.7301	0.2267	0.1774	0.0752	0.0926	0.6981
0.6921	0.2321	0.2069	0.0865	0.1010	0.6814
0.6218	0.2222	0.2347	0.1112	0.1435	0.6666
		318 K			
0.9389	0.3081	0.0000	0.0000	0.0611	0.6919
0.7169	0.3030	0.1666	0.0866	0.1165	0.6104
0.7618	0.1700	0.1687	0.0499	0.0696	0.7801
0.6971	0.3045	0.1785	0.0939	0.1243	0.6016
0.6623	0.2602	0.2030	0.0965	0.1347	0.6433

as shown in Table 3. The temperature was maintained constant using a constant-temperature jacket around the used cell. The used thermostat for this jacket (Julabu PC-F18) has a ±0.2 K controller with a temperature range of 253−373 K. The studied ternaries and their equilibrium compositions are shown in Tables 4−6, and these data were used to estimate the interaction parameters.

Discussion of Results

From the critical solution temperatures shown in Figure 1, it can be seen that increasing EC in the solvent increases the critical solution temperature. This will result in easier separation between the two liquid phases. The reason for this phenomenon is that EC has less capacity than CHP to dissolve the aromatic reformate constituents.

Increasing the solvent-to-feed ratio decreases the critical solution temperature. Therefore, the separation between the two liquid phases will be difficult at high temperatures when high solvent-to-feed ratios are used. Thus, longer settling times were needed for high solvent-to-feed ratios. All extraction runs were operated at temperatures at least 25 K less than the critical solution temperature to ensure achieving two clear liquid phases.

The critical miscibility temperature (CST) was correlated as a function of the solvent-to-feed ratio (S:F) and the solvent composition (EC %) using the experi-

Table 7. Optimized UNIFAC Interaction Parameters According to the Equation $a_{ij} = a^0_{ij} + a^1_{ij}(T/K - 273.15)$

i	j	a^0_{ij}/K	a^1_{ij}	a^0_{ji}/K	a^1_{ji}
EC	CHP	−234.891	4.314	−244.837	−1.738
EC	CH$_3$, CH$_2$, CH	−318.935	10.072	449.929	1.869
EC	ACH	507.630	−9.684	2870.330	−27.379
EC	ACCH$_2$, ACCH	2324.100	−49.610	2529.380	−26.943
CHP	CH$_3$, CH$_2$, CH	−95.834	−2.763	−1142.260	24.753
CHP	ACH	−191.253	4.920	−1451.600	31.520
CHP	ACCH$_2$, ACCH	−659.900	14.985	−249.215	5.358
CH$_3$, CH$_2$, CH	ACH	578.072	−9.884	132.730	24.247
CH$_3$, CH$_2$, CH	ACCH$_2$, ACCH	−3179.890	115.206	−186.327	5.068
ACH	ACCH$_2$, ACCH	−900.355	16.865	−271.934	9.562
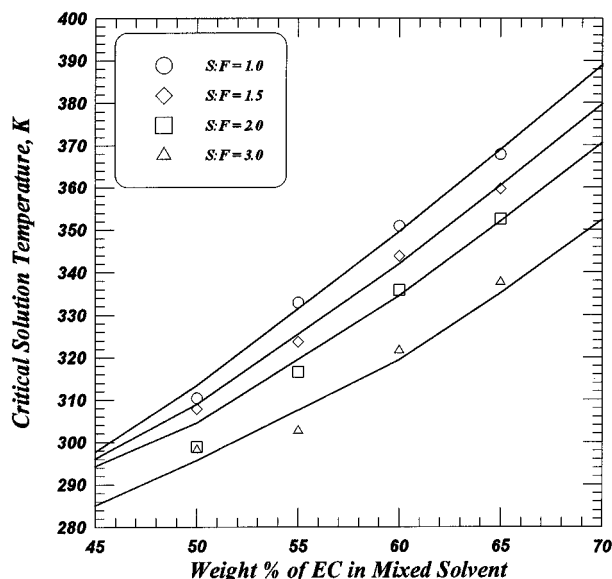
Figure 1. Critical solution temperatures for the naphtha reformate with a EC/CHP mixed solvent.

mental data shown in Figure 1. The resulting regression is

$$\text{CST (K)} = 110.1254 + 4.2418\,(\text{EC \%}) - 23.6408\,(\text{S:F}) + 1850142\,(\text{S:F})/(\text{EC \%})^3 \quad (8)$$

The UNIFAC equilibrium model was fitted to the experimental compositions of those ternaries by optimizing its interaction parameters. The interaction parameters were optimized to the experimental data using the multiple system regression program "ESTLLE" provided by Sørensen (1980) according to the UNIFAC groups shown in Table 1. The resulting values

for the interaction parameters between each pair of the UNIFAC main groups were fitted linearly with the temperature according to eq 9. An R^2 value above 0.90 was obtained in all formulas.

$$a_{ij} = a^0_{ij} + a^1_{ij}(T - 273.15) \quad (9)$$

The values of a^0_{ij} and a^1_{ij} for each pair resulting from the regression are shown in Table 7.

The predictions of the phase equilibria have shown some deviation from experimental results when treating small concentrations such as those of the aromatics in the extract phase and EC and CHP in the raffinate phase. The percent root mean square deviation (RMSD) was used to assess this deviation. An average RMSD value of 7.67% was achieved and considered satisfactory. The RMSD values and the experimental compositions are shown in Tables 8 and 9.

A wide data base was generated by using the optimized interaction parameters to generate activity coefficients and compositions of the two liquid phases at equilibrium. This information, in turn, was used to calculate the minimum work required for separation using the following equation (Henley and Seader, 1981):

$$-W_{min} = 8.314\,T\{n^E\sum_i[x_i^E\ln(x_i^E\gamma_i^E)] + n^R\sum_i[x_i^R\ln(x_i^R\gamma_i^R)] - n^F\sum_i[z_i\ln(z_i\gamma_i^F)]\}/n^{Ref} \quad (10)$$

where $-W_{min}$ is the minimum work required for separation (J/mol of reformate feed) and n^{Ref} is the number of moles of naphtha reformate fed to the extraction cell.

This data base was generated at different solvent-to-feed ratios, solvent compositions, and extraction temperatures. The minimum work was considered to be the dependent variable of the other independent operating variables. Multiple regression was performed and

Table 8. Experimental Liquid−Liquid Equilibria of the Petroleum Naphtha Reformate + (EC−CHP) Mixed Solvent

	S:F = 1 at 298 K						65% EC at 298 K						S:F = 1, 65% EC					
	55% EC		60% EC		65% EC		S:F = 1.5		S:F = 2		S:F = 3		308 K		318 K		328 K	
component	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}
n-hexane	0.021	0.003	0.010	0.002	0.015	0.001	0.025	0.000	0.021	0.001	0.031	0.002	0.022	0.001	0.020	0.002	0.020	0.002
cyclohexane	0.058	0.008	0.041	0.007	0.053	0.004	0.073	0.003	0.083	0.005	0.106	0.005	0.062	0.004	0.058	0.006	0.058	0.006
benzene	0.025	0.020	0.021	0.018	0.025	0.017	0.029	0.013	0.024	0.012	0.019	0.010	0.034	0.016	0.032	0.018	0.032	0.017
2,3-dimethyl-pentane	0.066	0.008	0.049	0.007	0.063	0.005	0.084	0.003	0.097	0.005	0.123	0.005	0.066	0.004	0.062	0.006	0.063	0.006
n-heptane	0.069	0.011	0.059	0.010	0.068	0.006	0.088	0.003	0.108	0.006	0.130	0.005	0.071	0.004	0.069	0.007	0.069	0.006
toluene	0.262	0.137	0.272	0.152	0.288	0.113	0.262	0.095	0.251	0.087	0.226	0.066	0.293	0.106	0.280	0.116	0.283	0.112
n-octane	0.029	0.005	0.036	0.006	0.033	0.002	0.042	0.002	0.059	0.003	0.069	0.002	0.035	0.002	0.034	0.003	0.033	0.003
ethylbenzene	0.036	0.018	0.041	0.021	0.041	0.014	0.038	0.013	0.036	0.012	0.031	0.009	0.040	0.014	0.039	0.015	0.039	0.014
m,p-xylene	0.096	0.047	0.111	0.058	0.111	0.038	0.102	0.033	0.102	0.030	0.085	0.023	0.111	0.035	0.107	0.038	0.109	0.038
o-xylene	0.029	0.015	0.033	0.018	0.033	0.012	0.030	0.011	0.029	0.010	0.024	0.007	0.032	0.012	0.031	0.012	0.032	0.012
EC	0.139	0.542	0.155	0.522	0.121	0.640	0.091	0.657	0.065	0.650	0.050	0.679	0.107	0.653	0.176	0.629	0.133	0.632
CHP	0.170	0.187	0.171	0.179	0.148	0.147	0.137	0.168	0.126	0.179	0.106	0.188	0.126	0.149	0.093	0.146	0.129	0.150
$-W_{min}$/J·mol^{-1}	−4038.2		−4347.9		−4688.5		−5798.0		−7185.4		−10195.7		−4163.3		−2421.9		−2455.5	
θ	0.59		0.61		0.64		0.67		0.69		0.71		0.70		0.73		0.91	

Table 9. Predicted Liquid−Liquid Equilibria of the Petroleum Naphtha Reformate + (EC−CHP) Mixed Solvent

| | S:F = 1 at 298 K | | | | | | 65% EC at 298 K | | | | | | S:F = 1, 65% EC | | | | | |
| | 55% EC | | 60% EC | | 65% EC | | S:F = 1.5 | | S:F = 2 | | S:F = 3 | | 308 K | | 318 K | | 328 K | |
component	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}	x^R_{exp}	x^E_{exp}
n-hexane	0.002	0.014	0.001	0.013	0.001	0.013	0.002	0.009	0.002	0.007	0.002	0.005	0.000	0.012	0.000	0.011	0.084	0.001
cyclohexane	0.007	0.036	0.006	0.035	0.005	0.034	0.006	0.023	0.008	0.018	0.008	0.011	0.001	0.032	0.002	0.031	0.194	0.007
benzene	0.046	0.002	0.049	0.002	0.051	0.001	0.043	0.001	0.037	0.001	0.030	0.001	0.057	0.004	0.058	0.006	0.009	0.021
2,3-dimethyl-pentane	0.004	0.044	0.003	0.042	0.003	0.041	0.004	0.029	0.005	0.022	0.006	0.015	0.000	0.038	0.001	0.036	0.283	0.003
n-heptane	0.004	0.045	0.003	0.043	0.003	0.041	0.004	0.029	0.005	0.022	0.006	0.015	0.000	0.038	0.001	0.037	0.287	0.003
toluene	0.420	0.007	0.446	0.006	0.471	0.005	0.398	0.003	0.343	0.002	0.274	0.002	0.567	0.008	0.575	0.029	0.001	0.191
n-octane	0.001	0.020	0.001	0.019	0.001	0.018	0.001	0.013	0.002	0.010	0.002	0.007	0.000	0.017	0.000	0.016	0.132	0.001
ethylbenzene	0.056	0.002	0.059	0.002	0.062	0.002	0.053	0.001	0.046	0.001	0.037	0.000	0.070	0.005	0.064	0.009	0.001	0.026
m,p-xylene	0.157	0.001	0.166	0.001	0.175	0.001	0.148	0.000	0.127	0.000	0.102	0.000	0.214	0.001	0.225	0.006	0.000	0.070
o-xylene	0.049	0.000	0.052	0.000	0.055	0.000	0.046	0.000	0.040	0.000	0.032	0.000	0.067	0.000	0.070	0.002	0.000	0.022
EC	0.025	0.688	0.017	0.709	0.011	0.729	0.034	0.791	0.059	0.824	0.099	0.852	0.000	0.666	0.000	0.637	0.004	0.511
CHP	0.230	0.141	0.197	0.128	0.162	0.116	0.261	0.100	0.327	0.092	0.403	0.092	0.022	0.179	0.004	0.179	0.005	0.145
% RMSD[a]	6.63		7.31		6.10		6.28		7.23		8.69		7.65		8.38		10.74	

[a] % RMSD = $(100\%)\{[\sum(x^E_{exp} - x^E_{calc})^2 + \sum(x^R_{exp} - x^R_{calc})^2]/(2N)\}^{1/2}$.

Table 10. Multiple Regression Results

i	c_i	V_i
1	−0.780	$(S:F)^{-1}$
2	−0.00718	$(S:F)^{-2}$
3	−0.0182	$T/(EC\ \%)$
4	1600.382	$[(EC\ \%)\ T]^{-1}$
5	−59.918	$(S:F)/[T(EC\ \%)]$
6	0.00238	$T/(S:F)$
7	2.283×10^{-5}	$\exp(S:F)$
8	1.500	$[(EC\ \%) + (S:F)]^{-1}$

resulted in the following equation:

$$-W_{min} = ((S:F)\ T)^2 [\sum_i c_i V_i] \qquad (11)$$

where the fitted values of the c's and the forms of the Vs are presented in Table 10.

The least value of the minimum work was optimized using a EXCEL-5.0 optimizer with quadratic estimates, central derivatives, and the Newton search method. The optimum conditions at which the minimum value of $-W_{min}$ was achieved were found to be at a solvent-to-feed ratio of 1.8, a solvent composition of 65% EC and 35% CHP on a weight basis, and an extraction temperature of 329 K.

Conclusions

The UNIFAC model was successfully used to predict phase equilibria of reformate components with a mixed solvent of CHP and EC. The average RMSD between experimental and predicted values was 7.67%. The minimum work for phase separation was used to find the optimum operating conditions. These conditions were found to be a solvent-to-feed ratio of 1.8, a 65% EC solvent, and a temperature of 329 K.

Nomenclature

a_{ij} = interaction parameter
c_i = constants for minimum work correlation in Table 10
CST = critical solubility temperature (K)
EC % = weight percent of EC in the mixed solvent (%)
n = number of moles
N = total number of components in the system
Q = area parameter of UNIFAC groups
R = volume parameter of UNIFAC groups
s = specific gravity
(S:F) = volumetric solvent-to-feed ratio
T = temperature (K)

V_i = variables for minimum work correlation in Table 10
$-W_{min}$ = minimum work done on the system by its surroundings (J/mol)
x_i = concentration of component i (mole fraction)
z_i = concentration of component i in the initial charge (mole fraction)

Greek Symbols

θ = molar ratio of the extract phase to the original feed
γ = activity coefficient

Superscripts

E = extract phase
F = feed (initial cell charge)
R = raffinate phase
Ref = reformate feed

Subscripts

i = components (or groups) counter
j = groups counter

Literature Cited

Annesini, M.; Capparucci, C.; Marrelli, L.; Vergara, A. Phase Equilibria of Binary Systems Containing Ethylene Carbonate and an Aromatic Compound. *Fluid Phase Equilib.* **1985**, *23*, 293.

Fahim, M. A.; El-Kilani, A. S. Prediction of Optimum Composition of Mixed Solvent in the Extraction of Aromatics using UNIFAC *J. Sep. Sci. Technol.* **1990**, *25*, 1803.

Fredenslund, A.; Jones, R.; Prausnitz, J. Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* **1975**, *21*, 1086.

Hansen, K. H.; Coto, B.; Kahlmany, B. *SEP 9212, IVC-SEP*; Institute of Kemiteknik: Lyngby, Denmark, 1992.

Henley, E. J.; Seader, J. D. *Equilibrium-Stage Separations in Chemical Engineering*; John Wiley & Sons: New York, 1981.

Mukhopadhyay, M. A Thermodynamic method Based upon the Theory of Regular Solutions for Selection of Solvents and Process Conditions for Aromatics Extraction. *J. Chem. Technol. Biotechnol.* **1979**, *29*, 634.

Mukhopadhyay, M.; Malleswararao, Y. Solvency−Selectivity Behaviour of a mixed (NMP+TEG) Solvent for Aromatics Extraction. *Indian Chem. Eng.* **1991**, *33* (4), 80.

Sørensen, J. M. *Phase Equilibria and Separation Processes. MAN 8106: ESTM*; Institute for Kemiteknik: Lyngby, Denmark, 1980.