ELSEVIER

Fluid Phase Equilibria 129 (1997) 175–186

FLUID PHASE EQUILIBRIA

Liquid–liquid equilibria for the extraction of aromatics from naphtha reformate by dimethylformamide/ethylene glycol mixed solvent

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

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

Received 29 April 1996; accepted 30 August 1996

Abstract

The phase equilibria for the extraction of aromatics from naphtha reformate (b.p. 60–135°C) in a mixed solvent of dimethylformamide (DMF) and ethylene glycol (EG) have been correlated using the UNIFAC group contribution model. The interaction parameters of DMF and EG with different hydrocarbon groups present in the reformate, such as CH_2 (paraffinic CH_2), ACH (aromatic CH) and $ACCH_2$ (aromatic CCH_2), and each of the two solvents were fitted to experimental concentrations of ternary systems containing these groups. The extraction runs were carried out at different temperatures, solvent compositions and solvent-to-feed ratios. The experimental results compared favorably with those predicted from the UNIFAC method. The minimum required energy for separation was achieved at 57°C using a 44% EG solvent with a solvent-to-feed ratio of 2.2 on a volume basis. © 1997 Elsevier Science B.V.

Keywords: Liquid–liquid equilibria; Activity coefficient; Aromatics; Naphtha reformate; Dimethyl formamide (DMF); Ethylene glycol (EG); UNIFAC

---

1. Introduction

The extraction of aromatics (benzene, toluene and xylene (BTX)) from naphtha reformates has been commercially operative for the last few decades and several commercial processes are available [1]. 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 range feed-stock could be treated directly to yield BTX aromatics of high purity without expensive pre-fractionation. Another BTX extraction method 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 process. The

---

* Corresponding author. e-mail: Fahim@ecl.uaeu.ac.ae. Fax: +(971-3) 632-382.

PII S0378-3812(96)03179-2

Arosolvan process uses *N*-methyl pyrrolidone. The REDEX process uses dimethylformamide for its high solubility of aromatic compounds.

However, studies of the phase equilibria of these aromatics with the used solvents and other hydrocarbons present in the naphtha reformate are not available in the literature. This work takes advantage of the development of the universal function-group contribution model (UNIFAC) [2] for the prediction of phase equilibria in order to study and analyze aromatic extraction from naphtha reformate using a mixed solvent of ethylene glycol (EG) and dimethyl formamide (DMF).

Mixed solvents are usually used as a compromise between the desired properties of two or more solvents. Some mixed solvents are essential for practical extraction processes [3]. Dimethyl formamide is a highly capacitive solvent (and, therefore, has a low selectivity for aromatic extraction). It is not practical to use DMF alone because of its low selectivity. Moreover, its density is very close to that of reformate, which causes problems in phase separation. Water was first mixed with DMF to enhance its selectivity; however, this did not solve the problem of its density [4]. Therefore, the addition of EG to DMF can be used to solve both problems.

A mixture of EG and DMF is used to extract the aromatics from naphtha reformate. The interaction parameters for the UNIFAC groups present in the reformate and each of the used solvents were determined by correlating the experimental compositions of four 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, solvent compositions and solvent-to-feed ratios.

2. Experimental

2.1. Chemicals

The extraction runs were carried out using naphtha reformate with a boiling range of 60–135°C and a specific gravity of 0.785. 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. EG and DMF

Table 1
The composition of the used reformate and the number of functional UNIFAC groups in each of its constituents

No.	Component	Mass %	Number of UNIFAC groups in each component						
			CH_3	CH_2	CH	C	ACH	$ACCH_3$	$ACCH_2$
1	*n*-Hexane	4.65	2	4	0	0	0	0	0
2	*n*-Heptane	9.53	2	5	0	0	0	0	0
3	Toluene	32.15	0	0	0	0	5	1	0
4	iso-Octane	4.22	5	1	1	1	0	0	0
5	Ethyl benzene	11.49	1	0	0	0	5	0	1
6	*m*-Xylene	16.73	0	0	0	0	4	2	0
7	*o*-Xylene	5.10	0	0	0	0	4	2	0
8	Cyclohexane	9.63	0	6	0	0	0	0	0
9	Benzene	6.49	0	0	0	0	6	0	0

were supplied by Fluka with a purity of greater than 98% (wt.%). The specific gravities of EG and DMF were 1.113 and 0.95, respectively.

2.2. Determination of critical solution temperature

In order to find the applicable extraction temperatures, the miscibilities and critical solution temperatures (CSTs) 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 temperature of the mixture gradually. The miscibility temperature was marked as the point at which the turbidity of the mixture disappeared and the two phases became completely miscible. The heating was then stopped and another reading taken when the solution had cooled and become turbid, indicating the beginning of phase separation. The two readings were within 1°C difference. The critical solution temperature was marked as the highest temperature of a given solvent-to-feed miscibility curve.

2.3. Extraction runs

Three solvent compositions were investigated for a solvent-to-feed ratio of 1:1 at a temperature of 25°C. These compositions were 40%, 50% and 70% EG in DMF on a volume basis. The effect of temperature was also investigated by a system with a 1:1 solvent-to-feed ratio and 50% EG solvent at 25°C, 35°C and 45°C. The effect of solvent-to-feed ratios was studied by investigating a system with 70% EG solvent at 25°C and solvent-to-feed ratios of 1:1, 2:1 and 3:1. Under all conditions, a stirring period of 30 min and a settling period of not less than 2 h were allowed. No detectable changes were in the equilibrium compositions occurred at longer extraction or settling times.

2.4. Measurements of phase compositions

Two Chrompack CP9001 gas chromatographs were operated in parallel to cover the suitable operating conditions for all constituents. Both columns were made of WCOT fused silica (50

Table 2
Accuracy of different concentration measurements

Compound	Accuracy
n-Hexane	±0.824%
iso-Octane	±0.877%
n-Heptane	±0.837%
Toluene	±0.570%
Ethyl benzene	±0.691%
m-Xylene	±0.749%
o-Xylene	±0.705%
Cyclohexane	±2.286%
Benzene	±2.619%
DMF	±1.255%
EG	±0.833%
Average	±1.113%

m × 0.32 mm i.d.) with FID detectors at 300°C and an inlet absolute pressure of 136 kPa. The first column was coated with CB silica (5 CB, DF = 1.2); the injector temperature was 225°C, the oven temperature 45–120°C and the temperature rise 8°C min^{-1}. The initial time was 5 min and the final time 18 min. This column measured the concentrations of *n*-hexane, iso-octane, *n*-heptane, toluene, ethyl benzene, *m*-xylene and *o*-xylene in the samples. The second column was coated with CB wax (52 CB) connected to an injector side with a short column (10 m × 0.25 mm i.d.) coated with CB silica (5 CB, DF = 1.2). The injector temperature was 250°C, with an oven temperature of 50–200°C and a temperature rise of 15°C min^{-1}. The initial time was 10 min and the final time 13 min. This column measured the concentrations of cyclohexane, benzene, DMF and EG.

The accuracy of concentration measurements for the different compounds studied in this work range from ±0.570 to ±2.619%. Table 2 shows the estimated accuracy of the concentrations of the different compounds.

3. Prediction of phase equilibria

The UNIFAC model [2] 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.

Consider a liquid mixture of known overall composition and temperature that has separated into two equilibrium liquid phases. It is now required to calculate the composition of the two phases using the UNIFAC model [5].

A material balance on the system gives the following equations.

$$Z_i = X_i^{\mathrm{E}}\theta + X_i^{\mathrm{R}}(1-\theta) \tag{1}$$

where

$$\theta = E/F \tag{2}$$

Rearranging Eq. (1) gives

$$X_i^{\mathrm{E}} = K_i Z_i / [1 + \theta(K_i - 1)] \tag{3}$$

or

$$1 = \sum_i \{K_i Z_i / [1 + \theta(K_i - 1)]\} \tag{4}$$

where

$$K_i = X_i^{\mathrm{E}} / X_i^{\mathrm{R}} = \gamma_i^{\mathrm{R}} / \gamma_i^{\mathrm{E}} \tag{5}$$

where Z_i, X_i^{E} and X_i^{R} are the mole fractions of component i in the initial charge (the feed), extract and raffinate phases, respectively. F is the total number of moles of the initial charge to the cell, and E and 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 raffinate phases, respectively. The activity coefficients can be calculated from the UNIFAC model using an appropriate set of interaction parameters.

Solving Eq. (4) for θ with K_i values initially estimated from the ratios of the measured equilibrium compositions, new values of the equilibrium compositions can be calculated using Eqs. (3) and (5). The corresponding activity coefficients in each phase are then calculated using the UNIFAC model and the equilibrium is tested according to

$$\gamma_i^{\mathrm{E}} X_i^{\mathrm{E}} = \gamma_i^{\mathrm{R}} X_i^{\mathrm{R}} \tag{6}$$

When the equality in Eq. (6) 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. (6) and the iterative procedure is repeated again starting from the solvation of Eq. (5) for θ.

Table 3
LLE data of the ternary system EG/DMF/heptane [a]

EG		DMF		Heptane	
Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
20°C					
0.0000	0.0000	0.9189	0.0162	0.0811	0.9838
0.9956	0.010	0.0000	0.0000	0.0044	0.9899
0.3975	0.0175	0.5920	0.0342	0.0104	0.9483
0.2586	0.0032	0.7316	0.0309	0.0098	0.9659
0.5813	0.0054	0.4148	0.0097	0.0038	0.9849
30°C					
0.0000	0.0000	0.9044	0.0241	0.0956	0.9759
0.9963	0.0303	0.0000	0.0000	0.0037	0.9697
0.3906	0.0090	0.6015	0.0614	0.0079	0.9377
0.2615	0.0037	0.7265	0.0397	0.0120	0.9566
0.5783	0.0105	0.4192	0.0248	0.0025	0.9646
40°C					
0.0000	0.0000	0.8942	0.0377	0.1058	0.9623
0.9954	0.0513	0.0000	0.0000	0.0046	0.9487
0.4225	0.0079	0.5709	0.0361	0.0066	0.9559
0.0009	0.0026	0.9985	0.0429	0.0006	0.9545
0.5811	0.0053	0.4139	0.0182	0.0051	0.9765
50°C					
0.0000	0.0000	0.9416	0.4027	0.0584	0.5973
0.9955	0.0821	0.0000	0.0000	0.0045	0.9179
0.4081	0.0192	0.5833	0.0620	0.0086	0.9189
0.2694	0.0024	0.7160	0.0580	0.0146	0.9396
0.5912	0.0021	0.4083	0.0173	0.0005	0.9807

[a] Concentrations are in mole fractions.

Table 4
LLE data of the ternary system dodecane/ethyl benzene/DMF [a]

Dodecane		Ethyl benzene		DMF	
Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
20°C					
0.0000	0.0000	0.9189	0.0162	0.0811	0.9838
0.9405	0.0145	0.0000	0.0000	0.0550	0.9855
0.5764	0.0618	0.2744	0.2193	0.1492	0.7186
0.4994	0.0462	0.3918	0.2352	0.1088	0.7186
30°C					
0.9095	0.0147	0.0000	0.0000	0.0091	0.9853
0.6386	0.0336	0.2942	0.1568	0.0672	0.8108
0.5016	0.0462	0.3273	0.2023	0.1711	0.7515
0.4817	0.0517	0.3304	0.2150	0.1879	0.7333
40°C					
0.9063	0.0165	0.0000	0.0000	0.0937	0.9835
0.6556	0.0243	0.2575	0.1227	0.0869	0.8529
0.4732	0.0480	0.3676	0.1905	0.1592	0.7615
0.4724	0.0010	0.3708	0.1502	0.1568	0.8399
50°C					
0.8956	0.0162	0.0000	0.0000	0.1044	0.9839
0.6481	0.0332	0.2139	0.1126	0.1380	0.8542
0.5376	0.0458	0.3130	0.1814	0.1494	0.7728
0.5677	0.0493	0.2767	0.2086	0.1556	0.7421

[a] Concentrations are in mole fractions.

Table 5
LLE data of the ternary system dodecane/benzene/DMF [a]

Dodecane		Benzene		DMF	
Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
20°C					
0.8907	0.0143	0.0619	0.046	0.0475	0.9397
0.9104	0.0149	0.0534	0.0470	0.0362	0.9381
0.9000	0.0142	0.0472	0.0336	0.0529	0.9522
30°C					
0.8240	0.0219	0.1117	0.0865	0.0640	0.8916
0.8900	0.0163	0.0560	0.0362	0.0541	0.9475
0.8792	0.0147	0.0555	0.0396	0.0652	0.9457
40°C					
0.9014	0.0151	0.0262	0.0192	0.0724	0.9657
0.7431	0.0192	0.0922	0.0371	0.1647	0.9437
0.9055	0.0183	0.0397	0.0273	0.0548	0.9543

[a] Concentrations are in mole fractions.

Table 6
LLE data of the ternary system EG/heptane/ethyl benzene [a]

EG		Heptane		Ethyl benzene	
Phase I	Phase II	Phase I	Phase II	Phase I	Phase II
20°C					
0.9956	0.0101	0.0044	0.9899	0.0000	0.0000
0.9811	0.0012	0.0000	0.0000	0.0189	0.9988
0.9856	0.0279	0.0036	0.4260	0.0109	0.5461
0.9706	0.0183	0.0175	0.3033	0.0119	0.6785
0.9818	0.0025	0.0032	0.2188	0.0150	0.7787
30°C					
0.9963	0.0303	0.0037	0.9697	0.0000	0.0000
0.9793	0.0056	0.0000	0.0000	0.0207	0.9944
0.9858	0.0117	0.0026	0.4414	0.0116	0.5469
0.9782	0.0082	0.0025	0.3198	0.0193	0.6720
0.9806	0.0350	0.0024	0.2017	0.0170	0.7632
40°C					
0.9954	0.0513	0.0046	0.9487	0.0000	0.0000
0.9819	0.0064	0.0000	0.0000	0.0181	0.9936
0.9750	0.0182	0.0154	0.4350	0.0095	0.5468
0.9808	0.0067	0.0032	0.2426	0.0160	0.7508
0.9796	0.0066	0.0027	0.1960	0.0177	0.7974
50°C					
0.9955	0.0821	0.0045	0.9179	0.0000	0.0000
0.9784	0.0003	0.0000	0.0000	0.0216	0.9997
0.9685	0.0097	0.0617	0.4087	0.0149	0.5816
0.9824	0.0113	0.0029	0.2896	0.0147	0.6991
0.9616	0.0163	0.0024	0.1803	0.0360	0.8035

[a] Concentrations are in mole fractions.

Table 7
The optimized UNIFAC interaction parameters according to the equation: $a_{ij} = a^{\circ}_{ij} + a^{1}_{ij}(T/\mathrm{K} - 273.15)$

i	j	a°_{ij} (K)	a^{1}_{ij}	a°_{ji} (K)	a^{1}_{ji}
EG	DMF	143.012	−11.847	2832.530	−50.194
EG	CH_3, CH_2, CH	123.010	3.031	−24.468	14.468
EG	ACH	354.285	−9.992	2384.890	−28.818
EG	$ACCH_2$, ACCH	1220.840	−27.985	180.468	21.227
DMF	CH_3, CH_2, CH	−49.436	1.782	463.264	−3.511
DMF	ACH	−1437.450	32.333	1072.310	−24.781
DMF	$ACCH_2$, ACCH	1072.270	−30.262	830.385	−21.148
CH_3, CH_2, CH	ACH	1274.860	−30.054	−707.591	24.061
CH_3, CH_2, CH	$ACCH_2$, ACCH	−311.725	7.206	−738.353	22.249
ACH	$ACCH_2$, ACCH	−657.130	17.963	−265.015	8.753

3.1. Determination of interaction parameters

To estimate the interaction parameters, four ternary LLE systems were studied at different temperatures. A constant temperature was maintained using a temperature jacket around the cell. The thermostat used for this jacket (Julabu PC-F18) has a ±0.2°C controller with a temperature range of −20 to 100°C. The studied ternaries and their equilibrium compositions are shown in Tables 3–6.

The UNIFAC equilibrium model was fitted to the experimental compositions of the ternaries by optimizing its interaction parameters. The used objective function was similar to that employed by Sørensen [6] using the UNIFAC groups shown in Table 1. The resulting values for the interaction parameters between each pair of UNIFAC main groups were fitted linearly with temperature according to

$$a_{ij} = a^{\circ}_{ij} + a^{1}_{ij}(T - 273.15) \tag{8}$$

The values of a°_{ij} and a^{1}_{ij} for each pair are shown in Table 7.

4. Discussion of results

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

Increasing the solvent-to-feed ratio decreases the critical solution temperature. Therefore, separation of 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

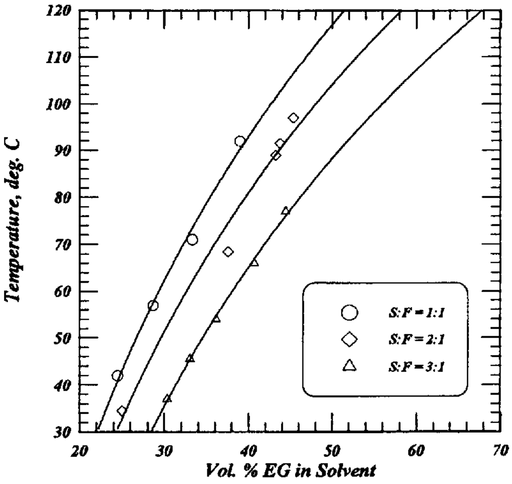

Fig. 1. Critical solubility temperatures for the used solvent-to-feed ratios.

Table 8
The results of the multicomponent system with a DMF–EG mixed solvent

Component	S:F = 1 at 25°C						S:F = 1 at 35°C		S:F = 1 at 45°C		S:F = 2 at 25°C		S:F = 3 at 25°C	
	40% [a]		50% [a]		70% [a]		50% [a]		50% [a]		70% [a]		70% [a]	
	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	0.050	0.004	0.039	0.002	0.044	0.000	0.002	0.000	0.023	0.002	0.026	0.000	0.044	0.001
iso-Octane	0.042	0.002	0.038	0.001	0.036	0.000	0.018	0.001	0.027	0.001	0.037	0.000	0.045	0.006
n-Heptane	0.107	0.007	0.097	0.003	0.093	0.000	0.053	0.003	0.070	0.004	0.098	0.001	0.117	0.015
Toluene	0.256	0.081	0.276	0.065	0.308	0.028	0.292	0.067	0.273	0.066	0.302	0.029	0.277	0.008
Ethyl benzene	0.088	0.022	0.098	0.017	0.104	0.006	0.131	0.023	0.116	0.021	0.116	0.007	0.106	0.009
m-Xylene	0.131	0.031	0.145	0.023	0.153	0.008	0.197	0.045	0.173	0.030	0.172	0.010	0.157	0.001
o-Xylene	0.039	0.010	0.043	0.008	0.046	0.003	0.060	0.011	0.053	0.010	0.051	0.003	0.046	0.000
Cyclo-hexane	0.110	0.010	0.106	0.005	0.113	0.001	0.042	0.039	0.066	0.035	0.096	0.001	0.113	0.018
Benzene	0.047	0.022	0.050	0.018	0.053	0.007	0.028	0.029	0.034	0.028	0.044	0.006	0.041	0.006
DMF	0.119	0.408	0.084	0.362	0.039	0.222	0.137	0.314	0.126	0.324	0.048	0.209	0.039	0.211
EG	0.010	0.402	0.024	0.495	0.010	0.724	0.040	0.469	0.038	0.478	0.009	0.731	0.016	0.718
θ	0.37		0.43		0.54		0.52		0.84		0.69			0.77
% RMSD [b]	12.11		10.90		7.34		7.32		5.90		7.48		8.09	

[a] Volume% EG.

[b] $\%\mathrm{RMSD} = (100\%)\{[\Sigma(X^E_{exp} - X^E_{calc})^2 + \Sigma(X^R_{exp} - X^R_{calc})^2]/(2N_c)\}^{1/2}$.

operated at temperatures at least 25°C lower than the critical solution temperature to ensure separation into two clear liquid phases.

The CST can be correlated as a function of solvent-to-feed ratio (S:F) and solvent composition (EG%) according to the following equation:

$$\mathrm{CST\,(K)} = 273.15 - 13.310(\mathrm{S{:}F}) + 2.051(\mathrm{EG\%}) + 0.0146(\mathrm{EG\%})^2 \qquad (9)$$

The phase equilibria predictions showed some deviation from the experimental results when treating small concentrations such as those of the aromatics in the extract phase, and EG and DMF in the raffinate phase. The percentage root mean square deviation (RMSD) was used to assess this deviation. An average RMSD value of 8.4% was achieved and considered satisfactory. The RMSD value decreases when increasing the temperature and/or the EG content. This means that the UNIFAC predictions improved at high temperatures and high EG contents. In all cases, the RMSD values are small, and good agreement with experimental compositions was achieved. The experimental compositions and corresponding RMSD values are presented in Table 8.

The optimized interaction parameters were used to mathematically predict the equilibrium compositions of the reformate/EG–DMF system using the UNIFAC model. The equilibrium compositions were predicted for the two-phase region under conditions where a temperature difference of at least 25°C was maintained below the critical solution temperatures as calculated from Eq. (9). The solvent compositions ranged from 1 to 99% EG by volume, with solvent-to-feed ratios ranging from 0.5 to 4

Table 9
Multiple regression results

i	c_i	V_i
1	2.859×10^{-4}	$(\mathrm{EG\%})^3$
2	-17.2525	$(\mathrm{S{:}F})^{-2}$
3	96.1576	SF^2
4	-9.5300	SF^3
5	12171336929	T^{-3}
6	-30752.6	$(\mathrm{EG\%})T^{-1}$
7	9778434.4	$(\mathrm{EG\%})T^{-2}$
8	-1229851	$(\mathrm{EG\%})^{-1}T^{-1}$
9	0.0801	$(\mathrm{S{:}F})T(\mathrm{EG\%})$
10	0.0041	$(\mathrm{EG\%})T(\mathrm{S{:}F})^{-1}$
11	1.0643	$(\mathrm{S{:}F})T$
12	-25.767	$(\mathrm{S{:}F})(\mathrm{EG\%})$
13	1960.12	$(\mathrm{S{:}F})(\mathrm{EG\%})^{-1}$
14	3.678×10^{-143}	$\exp T$

on volume basis and temperatures from 5 to 60°C. The minimum work for phase separation (J/mol of feed) is calculated according to the following formula [7]:

$$W_{\min} = -8.314T\left\{\theta\sum_i\left[X_i^{\mathrm{E}}\ln\left(X_i^{\mathrm{E}}\gamma_i^{\mathrm{E}}\right)\right] + (1-\theta)\Sigma_i\left[X_i^{\mathrm{R}}\ln\left(X_i^{\mathrm{R}}\gamma_i^{\mathrm{R}}\right)\right] - \Sigma_i\left[Z_i\ln\left(Z_i\gamma_i^{\mathrm{F}}\right)\right]\right\} \tag{10}$$

The minimum work values generated by Eq. (10) at different combinations of temperatures, solvent compositions, and solvent-to-feed ratios were correlated by multiple regression analysis (stepwise

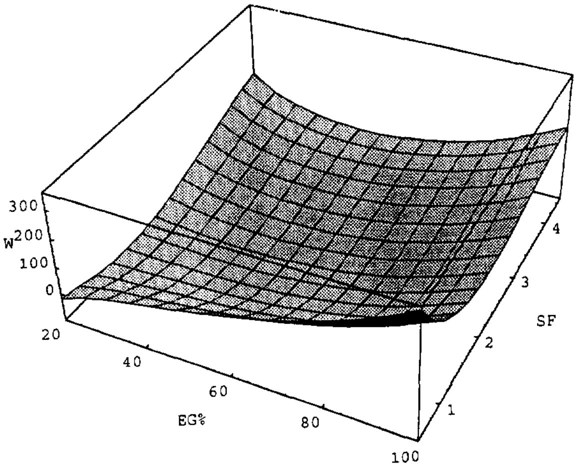

Fig. 2. Minimum work for phase separation at a temperature of 330 K.

method), resulting in Eq. (11) where the values of the coefficients c_i and the terms V_i are listed in Table 9.

$$W_{\min} = \sum_{i=1}^{14} c_i V_i \tag{11}$$

The least value of the minimum work was optimized using EXCEL 5.0 optimizer with quadratic estimates, central derivatives and the Newton search method. The optimum conditions generated by this method at the minimum value of $W_{\min}$ were found to be a solvent-to-feed ratio of 2.2, a solvent composition of 44% EG and 56% DMF on volume basis, and a temperature of 57°C. The graphical presentation of $W_{\min}$ in the range used is plotted as a function of the operating conditions, as shown in Fig. 2.

5. Conclusions

The UNIFAC model was successfully used to predict the phase equilibria of reformate components with a mixed solvent of DMF and EG. The average RMSD between the experimental and predicted values was 8.4%.

The minimum work for phase separation was used to find the optimum operating conditions. These conditions are a solvent-to-feed ratio of 2.2, a 44 EG% solvent on volume basis, and a temperature of 57°C.

6. List of symbols

a	interaction parameter
c	minimum work correlation constant in Table 9
CST	critical solubility temperature
E	amount of the extract phase (moles)
(EG%)	volume percentage of EG in the mixed solvent
F	amount of the initial charge (moles)
N_c	number of components in the system
R	amount of the raffinate phase (moles)
(S:F)	volumetric solvent-to-feed ratio
T	temperature (K)
V	minimum work correlation variable in Table 9
$W_{\min}$	minimum work done on the system by its surroundings (J mol^{-1})
X_i	concentration of component i (mole fraction)
Z_i	concentration of component i in the initial charge (mole fraction)

6.1. Greek symbols

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

6.2. Subscripts

i	components (or groups) counter
j	groups counter

6.3. Superscripts

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

References

[1] M. Rahman, P. Mikitenko and L. Asselinenu, Chem. Eng. Sci., 39 (1984) 1543.

[2] A. Fredenslund, J. Gmehling, M.L. Michelsen, P. Rasmussen and J.M. Prausnitz, Ind. Eng. Chem., Process Des. Dev., 16 (1977) 450.

[3] A. Fahim and A.S. El-Kilani, J. Sep. Sci. Technol., 25 (1990) 1803.

[4] K. Ethirajulu and A. Roy, Chem. Age India, 38 (1987) 45.

[5] M. Mukhopadhyay and K. Dongaonkar, Ind. Eng. Chem., Process Des. Dev., 22 (1983) 521.

[6] J.M. SØrensen, Phase Equilibria and Separation Processes, MAN 8106: ESTM, Institute for Kemiteknik, Lyngby, Denmark, 1980.

[7] E.J. Henley and J.D. Seader, Equilibrium-Stage Separations in Chemical Engineering, Wiley, New York, 1981.