

W_e weight fraction of ethylene in the liquid sample
 X_e mole fraction of ethylene in the liquid sample
 Z compressibility factor
 ρ water density, g cm⁻³

Registry No. Ethylene, 74-85-1; benzene, 71-43-2.

Literature Cited

(1) Ellis, S. R. M.; Valteris, R. L.; Harris, G. J. *Chem. Eng. Prog. Symp. Ser.* 1968, 64, 16.

- (2) Hiraoka, H. Solubility of ethylene in benzene at high pressures. *Rev. Phys. Chem. Jpn.* 1958, 28, 64.
 (3) Lyubetskii, S. G. *Zh. Prikl. Khim.* 1962, 35, 141.
 (4) Miller, S. A., Ed. *Ethylene and Its Industrial Derivatives*; Benn: London, 1969.
 (5) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1977.
 (6) Zhuze, T. P.; Zurba, A. S. *Akad. Nauk. SSR Div. Chem. Sci. Bull.* 335 (translated from *Izvest. Akad. Nauk. SSR. Otdel. Khim. Nauk.* 1960, 2, 364.

Received for review May 1, 1991. Accepted August 14, 1991.

Quaternary Liquid-Liquid Equilibrium Studies on Hydrocarbon-Solvent Systems

Jyotsna Nalhani, Mohan K. Khanna, Shrikant M. Nanoti, and Bachan S. Rawat*

Indian Institute of Petroleum, Dehra Dun 248005, India

Quaternary equilibrium tie-line data have been determined at 60 °C for the model hydrocarbon mixtures of naphtha and kerosene with sulfolane and triethylene glycol solvents. The study was carried out in order to understand the mechanism of simultaneous extraction of aromatics from naphtha and kerosene feedstocks. Benzene-heptane and 1-methylnaphthalene-dodecane model mixtures were chosen as feeds representing naphtha and kerosene cuts, respectively. The liquid-liquid equilibrium data so obtained have been predicted by the UNIFAC group contribution model. Group interaction parameters for groups which best represent triethylene glycol molecule were also calculated from the data available with the authors for those not available in the literature.

Introduction

Straight-run naphtha fractions when required for naphtha crackers and fertilizer units and kerosene fractions when required for use as aviation turbine fuel (ATF) and superior kerosene (SK) should not contain more aromatics than stipulated for these applications. These streams, therefore, require dearomatization to the extent that they become suitable for such applications. Dearomatization of naphtha (1) is done by conventional solvent extraction methods, whereas dearomatization of kerosene is done either by hydrogenation or by solvent extraction of aromatics. The present solvent extraction route for kerosene feedstocks is not attractive as this uses the cumbersome and obsolete technology of liquid sulfur dioxide extraction (2). The hydrogenation route for kerosenes, on the other hand, is attractive but is capital intensive.

An attractive scheme of simultaneous extraction (simex) of aromatics from naphtha and kerosene was tried earlier (3, 4). In this scheme, extract phases from the naphtha and kerosene columns are solvents for each other. In the process, displacement of aromatics from the hydrocarbon phase to the solvent phase and vice versa results in dearomatization of these streams.

However, the simex mechanism is complex since it involves multicomponent systems. In the present study, liquid-liquid

equilibrium (LLE) data on model hydrocarbon mixtures representing naphtha and kerosene as feeds and their respective extract phases as solvents have been generated to understand the displacement mechanism. These LLE data have been correlated by the UNIFAC (5) solution model and will be useful in the simulation of the simex scheme. Solvents used in the present study were sulfolane, triethylene glycol (TEG), and sulfolane containing 3 wt % water.

Experimental Section

Feeds Used. Benzene and heptane were supplied by S-D Fine Chemicals PVT, Ltd., 1-methyl naphthalene (1-MN) was supplied by Koch Light Laboratory, Ltd., and dodecane was supplied by J. T. Baker Chemical Co., Phillipsburg, NJ. The purities were checked by gas chromatography (GC), which indicated that all hydrocarbons had a minimum purity of 99%.

Determination of LLE. The benzene-heptane model mixture, representing the naphtha feed, was mixed with solvent containing 10 wt % 1-MN, representing the kerosene extract phase and, thus, forming a quaternary system. Similarly, the 1-MN-dodecane model mixture, representing the kerosene feed, and solvent containing 10 wt % benzene, representing the naphtha extract phase, formed the second set of the quaternary system. The concentration of 1-MN or benzene in the solvent was arbitrarily fixed at 10 wt % on the basis of previous experience with the continuous extraction runs. Thus, the former system represented the naphtha column of a simex unit, and the latter represented the kerosene column. Batch LLE data were determined at 60 °C in a jacketed mixer-settler of 200-mL capacity with a thermometer pocket and a syringe stirrer. Temperature was maintained within ± 0.05 °C of the experimental temperature by using a thermostatic bath.

The known weights of the feed and solvent of known composition were taken in the mixer-settler and stirred well for 25 min to establish equilibrium between the phases. The phases were allowed to settle for about the same time at the same temperature and then withdrawn separately, weighed, and analyzed. Solvent was removed from the raffinate phase by a water washing and from the extract phase by azeotropic distillation with water (6).

The aromatics in the solvent-free extract and raffinate were determined by gas chromatography.

The benzene content in the system benzene-heptane-(solvent + 1-MN) and the 1-MN content in the system 1-MN-do-

* To whom correspondence should be addressed.

Table I. Experimental and Predicted LLE Data at 60 °C for the Benzene-Heptane-Solvent Systems^a

wt % benzene in feed	wt % 1-MN in solvent	extract phase, wt %								raffinate phase, wt %								
		solvent mixture				aromatics benzene		saturates heptane		solvent mixture				aromatics benzene		saturates heptane		
		solvent		1-MN		expt	pred	expt	pred	expt	pred	solvent		1-MN		expt	pred	expt
Solvent = Sulfolane ($S/F = 1$ by Weight)																		
12.2	10.0	89.8	90.2	5.2	4.1	3.3	4.2	1.7	1.5	1.3	0.8	6.9	6.2	7.0	7.8	84.8	85.2	
25.9	9.7	84.6	84.5	4.2	4.1	9.1	9.5	2.1	1.9	2.1	1.5	5.5	5.9	15.3	16.4	76.5	76.2	
50.6	10.1	70.9	69.9	4.2	4.5	21.3	21.9	3.6	3.7	4.8	3.7	4.6	5.6	30.9	31.5	59.7	59.2	
64.7	9.5	60.8	61.5	4.0	4.7	29.4	28.6	5.8	5.2	9.4	6.1	4.8	5.6	40.1	38.0	45.7	50.3	
RMSD = 0.7																		
Solvent = TEG ($S/F = 1$ by Weight)																		
10.1	10.1	94.0	96.0	3.5	1.2	1.4	1.9	1.1	0.8	0.4	0.8	7.7	8.2	6.9	7.8	85.0	83.3	
25.0	10.2	90.5	92.8	2.7	1.3	5.4	5.1	1.3	0.8	0.7	1.1	7.3	8.5	20.7	19.4	71.2	71.1	
50.6	9.8	84.3	86.1	2.8	1.4	11.6	11.6	1.4	0.9	1.8	1.7	7.8	8.6	42.5	39.7	47.9	49.9	
75.2	10.8	73.7	76.6	3.0	1.9	21.4	20.6	1.9	0.9	5.7	2.8	7.9	10.0	62.6	59.7	23.8	27.5	
RMSD = 1.3																		
Solvent = Sulfolane + 3 wt % Water ($S/F = 1$ by Weight)																		
10.3	10.2	91.9	92.2	3.8	3.2	3.0	3.2	1.4	1.4	0.7	0.7	7.0	6.8	6.0	7.0	86.3	85.5	
24.9	10.0	86.4	86.6	3.8	3.4	8.1	8.3	1.6	1.7	3.1	1.3	6.4	6.7	14.0	16.8	76.5	75.2	
48.0	10.0	75.9	75.1	3.7	3.9	17.9	18.3	2.5	2.7	4.9	3.3	7.1	6.6	31.5	31.7	56.5	58.4	
69.9	10.0	61.2	59.4	4.5	4.6	29.3	30.8	4.9	5.2	10.9	7.2	6.6	6.4	44.7	43.8	37.8	42.6	
RMSD = 1.0																		

^a S/F = solvent to feed ratio.Table II. Experimental and Predicted LLE Data at 60 °C for the 1-MN-Dodecane-Solvent Systems^a

wt % 1-MN in feed	wt % benzene in solvent	extract phase, wt %								raffinate phase, wt %								
		solvent mixture				aromatics 1-MN		saturates dodecane		solvent mixture				aromatics 1-MN		saturates dodecane		
		solvent		benzene		expt	pred	expt	pred	expt	pred	solvent		benzene		expt	pred	expt
Solvent = Sulfolane ($S/F = 1$ by Weight)																		
15.0	10.0	89.2	88.8	4.0	3.9	6.1	7.0	0.7	0.3	0.9	0.6	6.4	6.1	8.9	8.0	83.8	85.3	
23.8	11.2	84.6	83.6	3.9	4.6	10.5	11.4	1.0	0.4	1.5	0.9	6.3	6.8	13.1	12.4	79.1	80.0	
49.4	10.1	70.1	69.9	3.8	4.5	24.1	24.8	2.0	0.9	3.3	1.6	5.4	6.0	26.7	24.9	64.6	67.5	
74.5	10.0	54.8	58.2	5.0	5.0	36.4	35.1	3.8	1.7	6.0	4.8	5.7	6.6	41.2	39.4	47.1	49.2	
85.8	10.0	49.7	54.3	3.8	4.7	41.5	39.0	5.0	1.9	6.1	6.2	5.3	6.2	45.7	44.1	42.9	43.5	
RMSD = 1.3																		
Solvent = TEG ($S/F = 1$ by Weight)																		
10.9	9.7	94.7	96.0	1.7	2.1	3.1	1.8	0.5	0.9	0.5	0.5	6.0	6.9	6.3	8.8	87.3	83.8	
24.6	10.2	91.3	93.6	2.2	2.3	6.0	4.0	0.5	0.1	0.6	0.7	7.4	7.5	19.9	19.9	72.1	71.9	
51.2	9.9	84.2	89.1	2.6	2.5	12.6	8.2	0.6	0.1	0.7	1.0	7.5	7.6	43.5	42.7	48.3	48.7	
74.8	9.8	77.7	85.0	2.6	2.7	19.0	12.3	0.7	0.1	2.1	1.4	6.6	7.4	65.4	64.9	25.9	26.3	
RMSD = 1.8																		
Solvent = Sulfolane + 3 wt % Water ($S/F = 1$ by Weight)																		
9.8	9.4	92.4	92.8	3.0	3.3	4.2	3.8	0.4	0.2	1.4	0.5	5.8	6.1	4.3	6.0	88.5	87.5	
24.6	10.0	85.7	86.2	2.9	3.8	10.7	9.7	0.7	0.3	1.5	0.8	5.6	6.7	15.0	14.6	77.8	78.0	
52.4	9.2	71.6	71.6	2.5	3.9	24.6	23.7	1.3	0.8	2.6	1.7	5.7	5.8	33.1	30.3	58.7	62.1	
79.9	9.9	52.0	55.9	3.8	4.6	40.6	37.8	3.6	1.7	6.2	6.1	5.5	6.2	51.3	47.9	37.1	39.9	
RMSD = 1.2																		

decane-(solvent + benzene) were varied in order to get the tie lines in the entire region of the binodal curve.

Results and Discussion

The phase equilibrium data (LLE) generated to understand the displacement mechanism in simex are presented in Tables I and II. These quaternary systems treated as pseudoternary, consisting of benzene (1)-heptane (2)-(sulfolane + 1-MN) (3) and 1-MN (1)-dodecane (2)-(sulfolane + benzene) (3), represent naphtha and kerosene extraction columns in simex, respectively. Figures 1 and 2 are typical representation of these systems with sulfolane.

Results show that benzene from the benzene-heptane feed mixture got extracted into the solvent phase originally containing 1-MN (representing the extract phase coming from the kero-

sene column) while 1-MN took the opposite route (Table I). Whereas, in the system 1-MN-dodecane-solvent vice versa was true (Table II), where 1-MN got extracted into the solvent phase coming from the naphtha column with extracted benzene which was displaced from the solvent phase. Thus, the movement of the components was from the region of higher concentration to the region of lower concentration due to the available concentration gradient.

This explains why in simex the kerosene aromatics get replaced in the naphtha column by naphtha aromatics from the kerosene extract phase, while naphtha aromatics get replaced in the kerosene column by kerosene aromatics from the naphtha extract phase. Thus, each of the two columns of simex, represented by the two sets of quaternary systems studied, act both as extraction and recovery columns. These data generated on the quaternary systems not only explain the

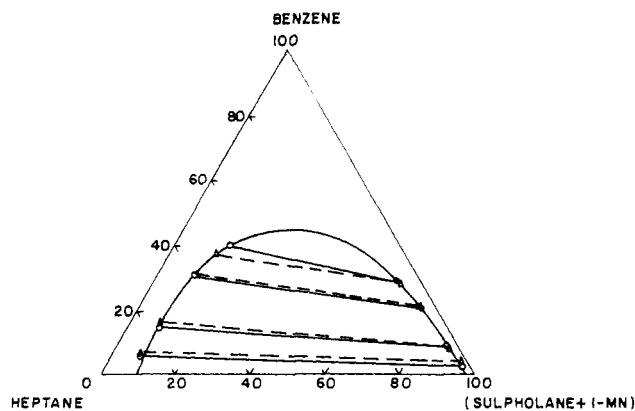


Figure 1. Phase equilibrium diagram for the pseudoternary benzene-heptane-(sulfolane + 1-MN) system at 60 °C: (-O-) experimental values; (-Δ-) predicted values.

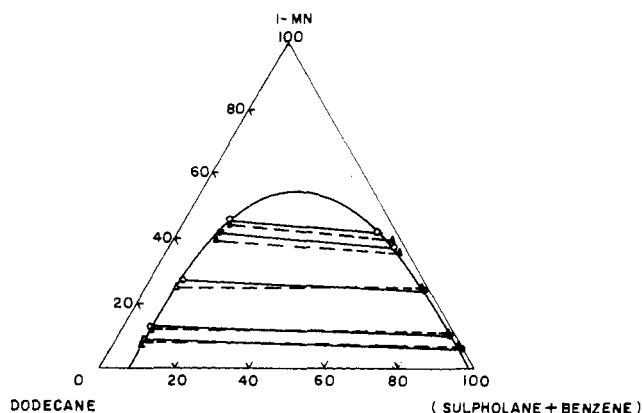


Figure 2. Phase equilibrium diagram for the pseudoternary 1-MN-dodecane-(sulfolane + benzene) system at 60 °C: (-O-) experimental values; (-Δ-) predicted values.

displacement mechanism of simex process but can also assist in the design and simulation of the two columns.

The LLE data obtained for the above quaternary systems were predicted by UNIFAC. For computation, the hydrocarbons were represented by standard UNIFAC groups, and their interaction parameters were taken from Rahman (7). Sulfolane was considered as one independent group while TEG was represented as the combination of one DEG, one CH₂, and one CH₂O groups (β) as the group interaction parameters for DEG (diethylene glycol) and not for TEG as a whole are available in the literature. The group interaction parameters for DEG-CH₂O and CH₂O-DEG (otherwise not available) were calculated from the LLE data on 1-MN-dodecane-(TEG + benzene) at 60 °C. The estimated interaction parameters are 121.809 K for DEG-CH₂O and 10.205 K for CH₂O-DEG groups. Hydrocarbon-

solvent and solvent-hydrocarbon group interaction parameters were taken from Magnussen et al. (9).

The root mean square deviation (RMSD) between the experimental and calculated extract and raffinate-phase compositions were calculated as follows:

$$\text{RMSD} = 100 \left[\sum_k \sum_i \sum_j (x_{ijk} - \hat{x}_{ijk})^2 / 6M \right]^{1/2}$$

The predicted and experimental values are given in the tables and plotted in Figures 1 and 2. Low RMSD values show that the data are well predicted by UNIFAC model.

Conclusion

In the quaternary systems studied, benzene from a benzene-heptane mixture, representing the naphtha feed, moved from the feed to the solvent phase, while 1-MN moved out from the extract phase. In the case of the 1-MN-dodecane mixture, representing the kerosene feed, vice versa takes place, wherein 1-MN moved from the feed to the extract phase and benzene takes the opposite route. Thus, the displacement of benzene (naphtha-range aromatics) by 1-MN (kerosene-range aromatics) and vice versa were attributed to the available concentration gradient. This LLE data when predicted by the UNIFAC group contribution method compared fairly well with the experimental values.

List of Symbols

x = composition

M = number of experimental tie lines

Superscript

$\hat{}$ = estimated values

Subscripts

$i = 1, 2, 3, \dots, n$ (components)

$j = I, II$ (phases)

$k = 1, 2, 3, \dots, M$ (tie lines)

Registry No. TEG, 112-27-6; 1-MN, 90-12-0; C₆H₆, 71-43-2; C₇H₁₆, 142-82-5; C₁₂H₂₆, 112-40-3; sulfolane, 126-33-0.

Literature Cited

- (1) *Studies on Process Development for Aromatic Extraction with Sulfolane*; IIP Report No. 8222; 1972; Vol. 1, Part 1.
- (2) Edeleanu, L. U.S. Patent 911533; 1907.
- (3) Plummer, M. A.; Pouska, G. A. *Hydrocarbon Process.* **1973**, *52* (6), 91.
- (4) Khanna, M. K. Ph.D. Thesis; Garhwal University, India, 1984.
- (5) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria using UNIFAC-s group-contribution method*; Elsevier Scientific Publishing Co.: Amsterdam-Oxford-New York, 1977.
- (6) Rawat, B. S.; Gulati, I. B. *J. Appl. Chem. Biotechnol.* **1976**, *26*, 425.
- (7) Rahman, M. *Chem. Eng. Sci.* **1984**, *39* (11), 1543-1558.
- (8) Dobhal, J. Ph.D. Thesis; Garhwal University, India, 1991.
- (9) Magnussen, T.; Rasmussen, P.; Fredenslund, A. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331-339.

Received for review May 2, 1991. Accepted August 14, 1991.