

LIQUID-LIQUID EXTRACTION OF ALKYLATED (C₄-, C₆- AND C₈-) BENZENE WITH CETANE USING INDUSTRIAL SOLVENTS

R.K. Joshi

Department of Chemistry

VSKC Rajkiya Snatkottar Mahavidyalaya,

Dakpathar (Vikasnagar), Dehradun, Uttarakhand, India

ABSTRACT

Liquid liquid equilibrium data have been determined with sulfolane and model hydrocarbon mixtures consisting of butylbenzene-n-cetane, hexylbenzene-n-cetane, octylbenzene-n-cetane using industrial solvents e.g. N-methyl pyrrolidone (NMP) and tri and tetraethylene glycol and their mixtures (as cosolvent) with sulfolane. The data so obtained have been predicted for effect of solvent and temperature on selectivity and solubility.

Key Words: Liquid liquid equilibrium, selectivity, solubility.

INTRODUCTION

Hydrocarbons in the C₁₀-C₂₀ range represent the kerosene fraction (150-300°C) of petroleum and are highly complex because of the presence of constituents like normal- and iso paraffins, naphthenes and alkylated benzenes, naphthalenes, tetralins and indans. Each of these classes of hydrocarbons, in turn, consists of a large number of isomers. It is, therefore, difficult to represent such petroleum fractions by a single binary model hydrocarbon mixture.

Moreover, such typical model compounds are not readily available. Basic liquid-liquid equilibrium (LLE) data for hydrocarbons in this carbon number range are required to be generated for each of these types of hydrocarbon classes. The data thus generated would be used subsequently to represent a particular fraction for design and simulation of the solvent-extraction process for removal/recovery of aromatics in these fractions.

Rational design of the extraction processes requires characterization of the complex petroleum fraction and models for the prediction of their liquid-liquid equilibria. It has been suggested that particular petroleum fraction e.g. aviation turbine fuel (ATF), by model hydrocarbons, together with equilibrium predictions by UNIFAC forms sufficiently accurate data-base for the simulation model (1). On similar lines, higher

petroleum fractions like kerosene and gas oil can be represented by models consisting of key components of representative hydrocarbon types of average carbon number (2).

Hence design of extraction column for systems containing these higher fractions makes it essential to generate equilibrium data on synthetic mixtures of known hydrocarbons in the C₁₀-C₂₀ range with industrial as well as new solvents.

Estimation of binary NRTL or UNIQUAC parameters also requires the availability of experimental LLE or infinite dilution activity coefficient data. Such equilibrium data for hydrocarbons in this carbon number range are limited (3) due to the non-availability of model compounds which represent these fractions.

Present studies report LLE data generated only on alkylated (C₄-, C₆- and C₈-) benzene with cetane using industrial solvents e.g. NMP and tri- and tetraethylene glycol and tri and tetraethylene glycol and their mixtures (as cosolvent) with sulpholane. Such a combination of solvents is reported to give the advantages of lower consumption of energy, lower solvent to feed ratio, with a consequent reduction in the dimension of the column. The studies reveal effect of temperature, carbon number and structure of aromatic moiety, structure of solvent and effect of anti solvent and co-solvent on extraction of the aromatics.

MATERIALS AND METHODS

The C₄-, C₆- and C₈- alkylated benzenes used in the present studies were prepared in the laboratory by Friedel-Craft's alkylation of the respective aromatics with C₄-, C₆- and C₈- olefins respectively (4). The olefins, in turn, were prepared by dehydration of alcohols (butanol, hexanol and octanol) resulting in various olefinic isomers (5). The alkylated product was, therefore, subjected to distillation to collect different heart cuts representing C₄-, C₆- and C₈-alkylated aromatic products respectively. Table 1 shows the literature (6-8) and experimental values of the physico-chemical properties of the respective alkylated aromatics.

Liquid-liquid equilibria on the C₄-, C₆- and C₈-alkylated benzene- n-cetane-solvent systems were determined. Experiments were made in glass jacketed mixer-settled' controlled at 40, 60 and 100°C by circulation of water through the external jacket from a thermostatic bath. Specific amounts of the feed and the combination solvent were taken into the cell and stirred for 10 min, which is sufficient length of time as determined in trial experiments for establishment of equilibrium between phases. The equilibrium phases were then allowed to settle for 10 min, and were separately withdrawn and analysed. Solvent was removed from the raffinate phase by water-washing and from the extract phase by azeotropic distillation with water. Overall experimental LLE data collected on these systems at various temperatures are presented in Table 2-5.

RESULTS AND DISCUSSION

Effect of temperature on solubility and selectivity of solvents for the aromatic component, using tetraethylene glycol (tetraEG) as solvent, was studied at 60 and 100°C. Solubility for the respective alkyl benzene increased with temperature while at the same temperature it decreased with increase in the carbon number of the alkyl substituent i.e. highest for butyl benzene followed by hexyl- and octyl benzene respectively (Table 3-4). The selectivity for alkylated benzene decreased with increases in temperature and in wt% aromatics in feed (Table 3-4). However, order for selectivity for the aromatic component at each temperature remained same i.e. C₄->C₆->C₈- alkylated benzenes.

LLE studies were done on the C₄-, C₆- and C₈-alkylated benzene with cetane using NMP+5% water as the solvent system to study the effect of structure of aromatic component on its extraction. It was observed that selectivity decreased with increasing paraffinicity (Table-2).

Experiments were conducted to study the effect of different solvents on extraction of butyl benzene from its mixture with cetane. The solvents studied were NMP+5% water, tetraethylene Glycol and tri and tetraethylene glycol and their mixtures (as cosolvent) with sulpholane. NMP+5% water had highest solvent capacity (Table 2-5) while triethylene glycol (30%) + sulpholane (70%) was found to be most selective as well as and solubility of tetraethylene glycol was lowest.

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Table-1

Physico-chemical properties of pure C₄-, C₆- and C₈- alkylated benzene, C₁₂, C₁₆ alkanes and sulpholane

Product	Density		Refractive Index at 20°C	
	Experimental Value	Literature Value	Experimental Value	Literature Value
Sec-Butylbenzene	0.8621	0.8621 (1)	1.4892	1.4902 (1)
3-Phenylhexane	0.8598	0.8557(2)	1.4868	1.4859 (2)
1-Phenylloctane	0.8572	0.8582 (3)	1.4845	1.4851 (3)
Dodecane	0.7486	0.7490 (4)	1.4218	1.4221 (4)
Cetane	0.7730	0.7734 (5)	1.4340	1.4344 (5)
Sulpholane ^a	1.2605	1.2610 (6)	1.4807	1.4810 (6)

^a Density and refractive index values at 30°C

Table-2

Liquid-liquid extraction data on n-cetane-C₄-, C₆- and C₈-alkylated benzene system

Butylbenzene-n-cetane-NMP(+5%water), Temperature: 40°C

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	10.2	2	2.31	0.65	97.04	5.34	89.97	4.69	2.96	59.76
2	29.8	2.06	8.42	1.37	90.21	13.57	78.13	8.3	9.79	35.36
3	49	2.05	13.54	2.33	84.13	23.52	66.25	10.23	15.87	16.35
4	79.2	1.97	24.87	5.35	69.78	41.35	41.69	16.96	30.21	4.68

Hexyl benzene-n-cetane-NMP(+5%water), Temperature: 40°C

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	5.6	2.11	1.3	1.29	97.41	2.79	90.19	7.02	2.59	32.59
2	28.2	2.03	6.36	1.57	92.07	16.21	75.88	7.91	7.93	18.96
3	50.8	2.05	12.22	1.96	85.82	31.6	56.66	11.74	14.18	11.2
4	68.2	1.96	18.6	2.88	78.72	40.38	41.03	18.59	21.48	6.57

Octyl benzene-n-cetane-NMP(+5%water), Temperature: 40°C

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	10.6	2.02	1.44	1.18	97.38	6.52	87.98	5.5	2.62	16.42
2	28	2	4.43	1.43	94.14	18.97	73.13	7.9	5.86	11.94
3	49.1	2.02	9.59	1.71	88.7	33.13	54.99	11.88	11.31	9.26
4	69	2.06	13.8	1.85	84.35	47.19	35.31	17.5	15.65	5.59

Table-3

Liquid-liquid extraction data on n-cetane-C4-, C6- and C8-alkylated benzenes-Tetraethyleneglycol (TetraEG) systems at 60°C

Butylbenzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	14	1.98	1.27	0.15	98.58	11.71	87.52	0.77	1.42	62.38
2	36.6	2.06	3.63	0.42	95.95	31.08	67.59	1.33	4.05	18.94
3	61.2	2.08	7.39	0.55	92.06	53.34	45.07	1.59	7.94	11.23
4	77.2	1.97	8.69	0.36	90.95	72.02	25.57	2.41	9.05	8.52

Hexylbenzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	11	2.09	0.83	0.21	98.96	8.74	90.6	0.66	1.04	41.45
2	22.2	2.25	1.35	0.29	98.36	18.69	80.72	0.59	1.64	19.81
3	47.2	1.98	3.21	0.28	96.51	43.27	54.62	2.11	3.49	14.52
4	67.4	1.99	4.17	0.22	95.61	63.92	34.72	1.36	4.39	10.11

Octylbenzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	16.9	2.04	0.93	0.4	98.67	15.05	84.59	0.36	1.33	13.12
2	28.4	2.03	1.12	0.25	98.63	26.81	72.48	0.71	1.37	12.15
3	49.2	1.98	1.84	0.2	97.96	45.46	53.37	1.17	2.04	10.81
4	71.6	2.07	2.59	0.18	97.22	68.48	30.19	1.33	2.78	6.63

Table-4

Liquid-liquid extraction data on n-cetane-C4-, C6- and C8-alkylated benzenes-Tetra ethylene glycol (TetraEG) systems at 100°C

Butyl benzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	10	2.07	1.29	0.88	97.83	6.29	91.95	1.76	2.17	21.49
2	27	2.07	3.36	0.59	96.04	21.63	76.68	1.7	3.96	20.09
3	49.5	2.06	6.3	0.7	93	41.24	55.8	2.96	7	12.18
4	82.5	2.03	13.65	0.57	85.78	67.55	26.27	6.18	14.22	9.33

Hexyl benzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	10.8	2.17	1.01	0.74	98.26	7.28	91.08	1.64	1.74	17.14
2	27.9	2.1	2.12	0.51	97.37	23.03	74.98	1.99	2.63	13.52
3	57.8	2.05	5.25	0.55	94.2	46.71	47.94	3.35	5.8	9.38
4	81.4	2.16	7.81	0.41	91.78	74.34	21.21	4.44	8.22	5.29

Octyl benzene-n-cetane-TetraEG

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	13	2.04	0.87	0.61	98.52	11.61	86.8	1.59	1.48	10.76
2	40.2	2.1	2.33	0.47	97.2	37.44	60.06	2.51	2.8	7.94

3	60.4	1.88	3.39	0.35	96.26	56.12	41.31	2.57	3.75	7.1
4	70.1	1.88	3.87	0.31	95.83	65.44	31.51	3.06	4.17	6.03

Table-5

Liquid-liquid extraction data on n-cetane-C4-, C6- and C8-alkylated benzenes -Sulfolane+ Triethylene glycol monomethyl ether systems at 60°C

Butyl benzene-n-cetane-sulfolane(70%)+Triethylene glycol monomethyl ether (30%)

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	9.8	2.02	1.56	0.39	98.05	6.52	92.2	1.28	1.95	55.56
2	22.8	1.99	3.89	0.48	95.63	15.48	82.47	2.05	4.38	43.12
3	52.4	2.12	10.43	0.62	88.95	36.29	60.24	3.47	11.05	27.98
4	68.9	2.12	15.23	0.68	84.09	47.8	46.67	5.53	15.91	21.73

Hexyl benzene-n-cetane- sulfolane(70%)+Triethylene glycol monomethyl ether (30%)

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	10.6	2	1.87	0.63	97.5	6.6	90.46	2.94	2.5	40.25
2	30	2.01	5.75	0.77	93.48	19.06	77.69	3.25	6.52	30.47
3	54.7	1.98	12.39	0.95	86.66	35.87	58.77	5.36	13.34	21.44
4	71.8	1.99	18.56	1.39	80.05	47.25	43.96	8.79	19.95	12.36

Octyl benzene-n-cetane- sulfolane(70%)+Triethylene glycol monomethyl ether (30%)

S. No.	Aromatics in feed, Wt%	S/F	Extract phase composition, wt%			Raffinate phase composition, wt%			Solubility	Selectivity
			Aromatics	Saturates	Solvent	Aromatics	Saturates	Solvent		
1	11	2.09	0.84	0.35	98.81	8.84	89.4	1.76	1.21	23.37
2	23	2.07	2.13	0.34	97.53	22.41	75.01	2.58	2.47	21.09
3	45	2.02	3.54	0.29	96.17	43.69	53.39	2.92	3.84	14.65
4	74.2	2.05	6.16	0.2	93.64	67.1	27.94	4.96	6.36	12.59