

PHASE EQUILIBRIA OF ORGANIC SULFUR COMPOUNDS FOR CLEANER FUELS

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1. Introduction

Environmental concerns have led many countries worldwide to apply stricter regulations on sulfur levels in liquid fuels. These regulations place many challenges for the refining industries. Separation process design to accomplish the removal of sulfur compounds requires knowledge of vapor-liquid equilibria (VLE) of sulfur compounds with hydrocarbons, particularly their activity coefficients at low concentration. However, the investigations concerning the systems containing sulfur compounds are scarce.

The original UNIFAC and UNIFAC-Dortmund group contribution models have been widely applied in the estimation of the VLE of organic mixtures, as they include many functional groups for organic substances. However, the application of these predictive models is limited since some important group interaction parameters of sulfur and hydrocarbon groups have not been determined. An alternative approach COSMO-RS can be used for the prediction of VLE. However, its accuracy is often inadequate to practical use. Therefore, more measurements are needed to expand the database of the estimation methods and improve the thermodynamic models of sulfur/hydrocarbon systems.

2. Approach

Typical organic sulfur compounds present in the petroleum refinery streams originating from Fluid Catalytic Cracker (FCC) are thiols, sulfides, disulfides, thiophenes and alkyl thiophenes, tetrahydrothiophenes, and benzothiophenes^{1,2}. We have determined new VLE data sets of systems containing organic sulfur compounds (thiols, sulfides, disulfides, thiophenes and tetrahydrothiophene) in different alkanes, alkenes, aromatic, and ethers with a variety of apparatuses (recirculation still, comparative ebulliometer, and static total pressure).

The VLE of sulfur compounds and hydrocarbons published in the open literature have been reviewed and updated with our measurements. This review only covers binary mixtures of available organic sulfur compounds with hydrocarbons classified as alkanes, alkenes, aromatics, and miscellaneous compounds including alcohols, aldehydes, and water. The VLE of systems containing hydrogen sulfide, carbonyl sulfide, carbon disulfide were not included. The excess enthalpy and azeotropic data are also not included in the review because of the space limitation of the manuscript pages. The purpose of this review is to summarize the present status regarding measurements that are completed, in press, or are planned in the near future. This will allow researchers to determine what additional measurements on specific classes of mixtures are required.

3. Summary of results

The results of the review are given in the following tables which give binary system, condition of measurement (temperature and pressure range), information about azeotropy, measurement method, and reference. Our measurements are typed in the bold font. Table 1 deals with VLE of thiols with alkanes, alkenes, aromatics, alcohols, aldehyde, and water. There is considerable number of VLE on thiols up to C₄-thiols with different kind of hydrocarbons except for alkenes due to the reaction between thiol and alkenes. Only one VLE for ethanethiol + propene was measured²⁷. Table 2 contains references to VLE of thiophene and alkyl thiophenes with alkanes, alkenes, aromatics, ether, and water. The measurements of systems containing alkyl thiophenes are limited to 2-methylthiophene, 3-methylthiophene, and 2-ethyl thiophene. However, there is lack of VLE data for systems containing alkylated thiophenes. Table 3 contains references to VLE binary mixtures of sulfides with alkanes, alkenes, aromatics, ether, and aldehyde. The VLE measurements on systems containing sulfide in

particular cyclic sulfide, and branched sulfides are very scarce. Table 4 contains references to mixtures of disulfide with alkanes, alkenes, aromatics, and water. Only few measurements are reported for VLE containing disulfides. Experimental work with dimethyl disulfide requires appropriate occupational health measures due to the toxicity of the compound. More measurements for systems containing disulfides with different hydrocarbons would be preferable for the predictive model development as the original UNIFAC was insufficient to describe the behavior of the systems containing disulfide by using two sulfide groups.

Table 1. Phase equilibria for systems containing thiols

system	T (K)	P (kPa)	azeotropy	method	ref
• <u>thiols + alkanes</u>					
methanethiol + propane	313	304-1368	-	stat	30
methanethiol + <i>n</i> -hexane	223	0-6	-	circ	39
	233	1-11	-	circ	39
	323-373	90-467	-	stat	45
methanethiol + <i>n</i> -decane	313	1-328	-	stat	30
ethanethiol + <i>n</i> -butane	323-373	167-1526	-	stat	26
ethanethiol + 2-methylbutane	301-308	101	aze	circ	31
	333	294	aze	circ	32
	363-370	588	aze	circ	32
	361	588	aze	circ	32
ethanethiol + <i>n</i> -pentane	308-309	101	aze	circ	31
	343-344	294	aze	circ	32
	338	294	aze	circ	32
	370-371	588	aze	circ	32
	365	588	aze	circ	32
ethanethiol + isopentane	301-308	101	aze	circ	31
ethanethiol + <i>n</i> -hexane	323-373	67-292	-	stat	45
ethanethiol + <i>n</i> -dexane	323-373	12-101	-	stat	45
1-propanethiol + <i>n</i> -butane	343-383	110-1848	-	stat	24
1-propanethiol + 2-methylpentane	334-341	101	aze	circ	13
1-propanethiol + <i>n</i> -pentane	309-341	101	-	circ	13
	309-341	101	-	circ	36
1-propanethiol + <i>n</i> -hexane	341-342	101	aze	circ	13
	323-373	58-62	-	stat	45
1-propanethiol + methylcyclopentane	341-345	101	aze	circ	13
1-propanethiol + cyclohexane	341-354	101	aze	circ	13
1-propanethiol + <i>n</i> -heptane	368	90	-	ebu	17
1-propanethiol + 2,2,4- trimethylpentane	368	90	-	ebu	17
2-propanethiol + cyclopentane	323-326	101	aze	circ	13
2-methyl-2-propanethiol + propane	283-333	12-2115	-	stat	26
2-methyl-2-propanethiol + <i>n</i> -butane	347	132-880	-	stat	23
2-methyl-2-propanethiol + 2-methylpropane	347	134-1180	-	stat	23
1-butanethiol + propane	313	12-1335	-	stat	30
1-butanethiol + methylcyclopentane	343	40-96	-	circ	12
1-butanethiol + <i>n</i> -hexane	323-373	53-231	-	stat	45
1-butanethiol + 2,2,4- trimethylpentane	368	90-101	aze	circ	12
1-dodecanethiol + propane	313	137-1350	-	stat	30
1,2-ethanedithiol + propane	313	2-1345	-	stat	30
1,2-ethanedithiol + <i>n</i> -butane	345	8-882	-	stat	23
1,2-ethanedithiol + 2-methylpropane	345	8-1179	-	stat	23
benzenethiol + propane	313	1-1350	-	stat	30
• <u>thiols + alkenes</u>					
ethanethiol + propene	253-353	8-2059	-	stat	27
• <u>thiols + aromatics</u>					
methanethiol + benzene	313	25-328	-	stat	30
methanethiol + toluene	323-373	29-233	-	stat	45

Table 1. (continued)

system	T (K)	P (kPa)	azeotropy	method	ref
1-propanethiol + toluene	337-380	90	-	circ	3
	380	90	-	ebu	17
	323-373	16-101	-	stat	45
1-propanethiol + benzene	303	15-25	-	circ	46
	321	32-50	-	circ	46
	338	61-91	-	circ	46
1-butanethiol + toluene	323-373	15-83	-	stat	45
• <u>thiols + miscellaneous</u>					
methanethiol + methanol	313	35-326	-	stat	30
	263-288		aze	stat	47
methanethiol + acetone	313	57-328	-	stat	30
methanethiol + propionaldehyde	313	77-336	aze	stat	30
methanethiol + dimethyl sulfide	263	14-52	-	circ	44
	273	23-80	-	circ	44
	288	44-143	-	circ	44
methanethiol + water	323-373	77-502	-	stat	45
ethanethiol + water	323-373	39-192	-	stat	45
1-propanethiol + water	323-373	18-163	-	stat	45
ethanethiol + dimethyl sulfide	308-310	101	-	circ	31
1-propanethiol + water	288-318	101	-	dil	18
2-propanethiol + water	288-318	101	-	dil	18

Table 2. Phase equilibria for systems containing thiophenes

system	T (K)	P (kPa)	azeotropy	method	ref
• <u>thiophene + alkanes</u>					
thiophene + <i>n</i> -hexane	323-338	31-91	aze	circ	4
thiophene + cyclohexane	318	25-30	aze	circ	37
	318	33	aze	circ	35
	348	76-85	aze	circ	35
	348	92	aze	circ	35
	348	76	aze	circ	35
thiophene + methylcyclohexane	348	46-76	aze	circ	35
	367	90	-	ebu	17
thiophene + <i>n</i> -heptane	328	23-38	aze	circ	3
					8
thiophene + 2,2,4- trimethylpentane	343-353	40-93	aze	circ	8
	368	90	-	ebu	17
2-methylthiophene + 2,2,4- trimethylpentane	358-368	43-91	aze	circ	9
3-methylthiophene + 2-methylpentane	333	15-101	-	circ	11
3-methylthiophene + <i>n</i> -hexane	333	15-77	-	circ	11
3-methylthiophene + methylcyclopentane	343	22-96	-	circ	11
3-methylthiophene + cyclohexane	348	27-85	-	circ	10
3-methylthiophene + methylcyclohexane	373	64-99	-	circ	11
3-methylthiophene + 2,2,4- trimethylpentane	368	55-90	-	circ	10
2-ethylthiophene + 2,2,4- trimethylpentane	373-413	33-283	-	stat	25
• <u>thiophene + alkenes</u>					
thiophene + 1-hexene	323-333	31-91	-	circ	4
2-methylthiophene + 2,4,4- trimethyl-1-pentene	358	43-85	aze	circ	9
2-methylthiophene + 1-octene	373-413	53-210	aze	stat	25
3-methylthiophene + 1-hexene	333	15-91	-	circ	10
3-methylthiophene + 2,4,4- trimethyl-1-pentene	368	55-84	-	circ	10

Table 2. (continued)

system	T (K)	P (kPa)	azeotropy	method	ref
• thiophene + aromatics					
thiophene + toluene	353-380	90	-	circ	3
	380	90	-	ebu	17
	359-378	101	-	circ	42
	358-376	100	-	circ	43
		101	-	circ	47
thiophene + benzene	328	38-44	-	circ	38
	354-357	101	-	circ	41
3-methylthiophene + toluene	383	86-100	-	circ	12
3-methylthiophene + <i>o</i> -xylene	383	37-87	-	circ	12
3-methylthiophene + 1,2,4-trimethylbenzene	383	16-87	-	circ	12
• thiophene + miscellaneous					
thiophene + 2-ethoxy-2-methylpropane	333-343	45-93	-	circ	8
thiophene + water	288-308	101	-	dil	18
	312	24	aze	LLE	33
	329	53	aze	LLE	33
	339	80	aze	LLE	33
	345	101	aze	LLE	34

Table 3. Phase equilibria for systems containing sulfides

system	T (K)	P (kPa)	azeotropy	method	ref
• sulfide + alkanes					
dimethyl sulfide + propane	293-313	55-1359	-	stat	19
dimethyl sulfide + 2-methylpropane	308	91-460	-	stat	20
dimethyl sulfide + <i>n</i> -butane	317	126-426	-	stat	20
dimethyl sulfide + 2-methylbutane	300-306	101	aze	circ	40
	336-345	294	aze	circ	32
	334	294	aze	circ	32
	363-373	588	aze	circ	32
	362	588	aze	circ	32
	308-309	101	aze	circ	40
dimethyl sulfide + <i>n</i> -pentane	344-345	294	aze	circ	32
	339	294	aze	circ	32
	371-373	588	aze	circ	32
	365	588	aze	circ	32
dimethyl sulfide + isopentane	301-310	101	-	circ	31
dimethyl sulfide + <i>n</i> -hexane	288-303	101	-	dil	19
dimethyl sulfide + 2,2,4-trimethylpentane	288-303	101	-	dil	19
diethyl sulfide + 2-methylpropane	308	13-460	-	stat	21
diethyl sulfide + <i>n</i> -butane	318	18-427	-	stat	21
diethyl sulfide + <i>n</i> -hexane	323-	23-91	-	circ	6
	338				
diethyl sulfide + cyclohexane	343-353	50-100	-	circ	7
diethyl sulfide + <i>n</i> -heptane	353-363	57-97	aze	circ	5
diethyl sulfide + 2,2,4-trimethylpentane	353-363	57-97	aze	circ	5
ethyl methyl sulfide + <i>n</i> -heptane	367	90	-	ebu	17
ethyl methyl sulfide + 2,2,4-trimethylpentane	368	90	-	ebu	17
tetrahydrothiophene + propane	294-313	2-1362	-	stat	19
tetrahydrothiophene + <i>n</i> -butane	318-347	6-882	-	stat	22
tetrahydrothiophene + 2-methylpropane	318-347	7-1178	-	stat	22
tetrahydrothiophene + 2,2,4-trimethylpentane	358-368	33-91	-	circ	16

Table 3. (continued)

system	T (K)	P (kPa)	azeotropy	method	ref
• sulfide + alkenes					
dimethyl sulfide + 1-butene	313	107-455	-	stat	20
dimethyl sulfide + <i>cis</i> -2-butene	313	106-332	-	stat	20
dimethyl sulfide + <i>trans</i> -2-butene	317	126-414	-	stat	20
dimethyl sulfide + 2-methylpropene	313	107-465	-	stat	20
dimethyl sulfide + 1-hexene	288-303	101	-	dil	19
dimethyl sulfide + 2,4,4- trimethyl-1-pentene	288-303	101	-	dil	19
diethyl sulfide + 1-butene	313	15-452	-	stat	21
diethyl sulfide + <i>cis</i> -2-butene	313	15-333	-	stat	21
diethyl sulfide + <i>trans</i> -2-butene	317	18-418	-	stat	21
diethyl sulfide + 2-methylpropene	313	15-466	-	stat	21
diethyl sulfide + 1-hexene	323-333	23-91	-	circ	6
tetrahydrothiophene + <i>trans</i> -2-butene	318-347	6-869	-	stat	22
tetrahydrothiophene + 2-methylpropene	318-346	6-1055	-	stat	22
tetrahydrothiophene + 2,4,4- trimethyl-1-pentene	358-368	33-85	-	circ	16
• sulfide + aromatics					
diethyl sulfide + toluene	361-380	90	-	circ	3
tetrahydrothiophene + toluene	368-383	46-100	-	circ	15
tetrahydrothiophene + <i>o</i> -xylene	368-383	22-75	-	circ	15
• sulfide + miscellaneous					
dimethyl sulfide + water	278-323	101	-	LLE	28
	371-372	101	-	circ	29
dimethyl sulfide + methanethiol	263-288		-	stat	44
dimethyl sulfide + methanol	263-288		-	stat	44
diethyl sulfide + 2-ethoxy-2-methylpropane	333-343	34-93	-	circ	7

Table 4. Phase equilibria for systems containing disulfides

system	T (K)	P (kPa)	azeotrop y	metho d	r ef
• disulfide + alkanes					
dimethyl disulfide + 2,2,4-trimethylpentane	368	65-96	aze	circ	14
diethyl disulfide + 2,2,4-trimethylpentane	368	16-91	-	circ	14
• disulfide + alkenes					
dimethyl disulfide + 2,4,4- trimethyl-1-pentene	368	65-89	aze	circ	14
• disulfide + aromatics					
dimethyl disulfide + toluene	368	63-67	aze	circ	14
• disulfide + miscellaneous					
dimethyl disulfide + water	278-323	101	-	LLE	28

stat – static total apparatus, **circ** – recirculation still, **ebu** – ebulliometry, **dil** – dilutor, **LLE** – liquid-liquid equilibrium, **aze** – azeotropic

4. Conclusions

The recent VLE measurements of different organic sulfur compounds in hydrocarbons provide a database to get more information about the behavior of sulfur compounds, which is needed for thermodynamic model development and also for predictive model development. Measurements for determining phase equilibria of organic sulfur compounds containing disulfides and benzothiophenes with different kind of hydrocarbons in our laboratory are still continued and more data will be published in the near future. New measurements are focused on filling in gaps on systems that needed for thermodynamic model and predictive model developments.

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