Fluid Phase Equilibria 451 (2017) 12–24

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Screening solvents to extract phenol from aqueous solutions by the COSMO-SAC model and extraction process simulation

Yun Chen [a, b, *], Shaoming Zhou [a], Youchang Wang [a], Libo Li [a, **]

[a] Department of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, PR China
[b] State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, PR China

ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form
27 July 2017
Accepted 8 August 2017
Available online 10 August 2017

Keywords:
COSMO-SAC
Phenol
Solvent extraction
Solvent screening
Liquid-liquid equilibrium
Process simulation

ABSTRACT

Solvent extraction is an energy-efficient process to treat phenolic effluents in the industry, and a key step in designing an industrial extraction process is to screen a proper extraction solvent with high extraction efficiency and good physical properties. In this work, COSMO-SAC model was employed to screen the most promising extractant from 40 organic solvents, including alkanes, arenes, ethers, esters and ketones. The screening was performed based on a comparison of selectivity and solvent power, which were derived from the activity coefficient at infinite dilution. Moreover, the σ-profiles of the solvents were used to analyze the interaction between solvents and phenol. Based on the results of screening, three ketones were selected for conducting LLE experiment, and all of them performed very well with high distribution coefficient and high selectivity. The NRTL and UNIQUAC models were successfully applied to correlate the experimental LLE data, with root mean square deviation less than 1.5%. The COSMO-SAC was also used to predict the tie-line data, showing quite good agreement with corresponding experimental data. Finally, the extraction process simulation was performed for the screened solvents. It showed that, the studied ketones are promising solvents for extracting phenol from wastewater. The extraction process treating an effluent with phenol concentration of 5000 ppm was simulated. High separation efficiency (the phenol concentration in the treated water < 10 ppm) can be reached with low stage number (e.g. 4) and solvent usage (e.g. extractant: wastewater $= 1{:}25$).

1. Introduction

Unreasonable utilization of the coal not only pollutes the environment, but also wastes a large amount of resources. Coal gasification, a high effective and clean technology, is playing a significant role in protecting the environment and supplying energy for the modern society [1]. However, a large amount of highly concentrated phenolic effluents were generated by the Lurgi pressurized coal gasification process [2,3], which would cause serious damage to human beings and the biosphere. Liquid-liquid extraction, a low energy cost, high throughput, versatile and commercially efficient unit operation, has been reported to treat industrial phenolic effluents in USA [4], China [4,5] and South Africa [4], etc. A key step in designing a liquid-liquid extraction process is to develop a suitable extractant. Screening the extractant for the extraction process is quite time-consuming, for which computational screening could save a lot of time. Group contribution methods such as UNIFAC [6] are successful computational screening methods to predict thermodynamics properties such as activity coefficient, distribution coefficients and phase diagram [7,8], etc. However, the accuracy of thermodynamic predictions by UNIFAC depends heavily on the UNIFAC group interaction parameters and the data that were initially used for their fitting. Unfortunately, such data, determined by regressing huge amount of liquid-liquid phase equilibrium data, are often missing. Although the predictions are often close to the experiment results, the accuracy is also determined by the similarity of the environments and interactions between these functional groups to the database used in its parameterization [9]. UNIFAC also shows low accuracies for isomers and compounds with nonalkyl functional groups [10]. Molecular simulation methods such as molecular dynamics (MD) and Monte Carlo (MC) also have been reported to calculate thermodynamic properties [11,12]. The calculated results were affected by the selection of simulation

---

* Corresponding author. Department of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, PR China.
** Corresponding author. Department of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, PR China.
E-mail addresses: yunchen@scut.edu.cn (Y. Chen), celbli@scut.edu.cn (L. Li).

http://dx.doi.org/10.1016/j.fluid.2017.08.007
0378-3812/© 2017 Published by Elsevier B.V.

ensemble and the used empirical force fields describing interactions between atoms. Moreover, molecular simulations are usually quite expensive and time-consuming when flexible or large molecules are involved.

Recently, a novel and efficient method was proposed to predict liquid-liquid phase thermodynamic properties by Klamt's group [13,14]. In contrast to UNIFAC and other excess Gibbs free energy approaches, Klamt calculated the surface charge densities by the conductor-like screening model (COSMO) to describe molecular interactions and developed a conductor-like screening model for real solvent (COSMO-RS) that can be used to calculate the chemical potential of any substance in any mixture from quantum mechanical calculations [10,11]. Based on COSMO-RS, Lin and Sandler [10] proposed a new model, known as COSMO segment activity coefficient (COSMO-SAC), to determine the activity coefficient and to overcome the limitations of COSMO-RS, e.g. does not correctly converge to certain boundary conditions and the final expression for the activity coefficient fails to satisfy thermodynamic consistency relations [10]. In the last decade, COSMO-SAC has been widely applied in liquid-liquid equilibrium prediction and solvent screening. Mateusz [15] determined the solubility curve between acetonitrile and six C8 aliphatic ethers, and then characterized the influence of sigma-profile of different ethers on their properties by using COSMO-SAC. Hsieh [16] predicted 1-octanol-water partition coefficient and infinite dilution activity coefficient in water for alcohols and amines. Mitesh [17] studied the liquid-liquid equilibrium of ionic liquid extracting biodiesel and bio-alcohols by COSMO-SAC, and results agreed with the experimental data very well. It has been proven as an excellent combination approach to screen solvents and design an extraction process with the COSMO-SAC model and then validate the calculation results by experiments.

In this work, COSMO-SAC model was used to screen solvents to extract phenol (from aqueous solution) from common organic solvents, including: alkanes, arenes, alcohols, ethers, esters and ketones. The selectivity and distribution coefficients of these solvents were calculated from the activity coefficient at infinite dilution by analyzing the sigma-profiles. Then, liquid-liquid equilibrium experiments and extraction process simulation were performed to further study the most promising solvents predicted by the COSMO-SAC calculation.

2. Approach

2.1. The COSMO-SAC model

COSMO-SAC was first proposed by Lin in 2002, and then an improvement on the definition of hydrogen bonding was developed by Wang [18] in 2007. Later Hsieh [19] proposed a refinement COSMO-SAC (2010) which consider the electrostatic interaction parameter as a temperature-dependent parameter. In 2013, Xiong [9] made a refinement on calculating activity coefficients by including the dispersive interaction contribution. There are two steps to determine the thermodynamic activity coefficients by COSMO-SAC method using quantum chemical calculations. The first step is to calculate the sigma-profile for each involved compounds, and then the activity coefficient was determined by those sigma-profiles, the details can be found elsewhere [9,20]. The activity coefficients at infinite dilution (γ^{∞}) of phenol and water in solvents were determined by using COSMO-SAC to describe the volatility of the solute and the intermolecular energy between a solute and solvent. A series of separation parameters (selectivity (S^{∞}), solvent power (SP^{∞})) were calculated by γ^{∞} to analyze the removal efficiency of each extractant for phenol. Selectivity at infinite dilution can be expressed in terms of activity coefficient as shown in the following expression.

$$S^{\infty} = \frac{\gamma^{\infty}_{B,S}}{\gamma^{\infty}_{A,S}} \tag{1}$$

where $\gamma^{\infty}_{B,S}$ and $\gamma^{\infty}_{A,S}$ denote the activity coefficient of water and phenol in solvent S at infinite dilution, respectively. The high selectivity indicates that solvent S interacts favorably with phenol (low $\gamma^{\infty}_{A,S}$ value, usually showing high mutual solubility between S and phenol) but unfavorably with water (high $\gamma^{\infty}_{B,S}$ value, usually showing low mutual solubility between S and water). Moreover, the selectivity value directly relate to the stage number of the extraction column.

The amount of a solvent required for the extraction process was related to the solvent power (SP^{∞}), which indicates the maximum amount of phenol that can be dissolved in solvent S and is expressed as follows:

$$SP^{\infty} = \frac{1}{\gamma^{\infty}_{A,S}} \tag{2}$$

Table 1
The activity coefficient at infinite dilution calculated by COSMO-SAC at 298.15 K and 333.15 K.

Number	Solvent(i)	298.15 K		333.15 K	
		$\gamma_{phenol,i}$	$\gamma_{water,i}$	$\gamma_{phenol,i}$	$\gamma_{water,i}$
	Alkanes				
1	cyclohexane	152.70	589190	69.35	105380
2	hexane	123.83	399150	58.32	74716
3	heptane	121.15	370530	56.99	69173
4	octane	119.68	341820	56.07	63611
5	benzene	22.98	45008	14.15	12131
6	toluene	24.36	47966	14.95	12688
7	ethylbenzene	27.23	54300	16.45	13983
	Alcohols				
1	1-pentanol	0.109	3.069	0.149	3.132
2	1-hexanol	0.100	3.277	0.138	3.347
3	2-ethyl-1-butanol	0.163	4.810	0.211	4.720
4	2-hexanol	0.128	4.354	0.171	4.332
5	2-methyl-1-pentanol	0.150	4.595	0.197	4.526
6	1-butanol	0.094	2.451	0.131	2.548
7	2-butanol	0.121	3.400	0.162	3.434
8	2-methyl-2-propanol	0.068	1.794	0.098	1.942
9	1-heptanol	0.125	4.021	0.167	4.015
10	1-octanol	0.130	4.445	0.172	4.399
	Ethers				
1	1-propoxypropane	0.080	15.938	0.120	15.351
2	ethyl propyl ether	0.072	14.882	0.109	14.307
3	n-butyl ethyl ether	0.087	17.865	0.130	16.990
4	diisopropyl ether	0.050	6.852	0.080	7.381
5	2-methoxy-2-methypropane	0.059	8.556	0.090	8.664
6	methyl n-butyl ether	0.086	19.360	0.127	17.853
7	methyl n-pentyl ether	0.097	20.636	0.141	19.011
	Esters				
1	propyl acetate	0.140	28.149	0.186	22.481
2	n-butyl acetate	0.178	40.652	0.232	31.743
3	isobutyl acetate	0.158	31.639	0.208	25.281
4	ethyl acetate	0.123	22.719	0.166	18.350
5	n-pentyl acetate	0.163	35.330	0.214	27.934
6	isopentyl acetate	0.161	32.566	0.211	25.932
7	dimethyl carbonate	0.287	49.037	0.347	34.812
	Ketones				
1	2-butanone	0.066	9.985	0.096	9.066
2	2-pentanone	0.070	10.940	0.102	10.000
3	3-methyl-2-butanone	0.079	13.343	0.114	11.914
4	methyl isobutyl ketone	0.092	15.067	0.130	13.499
5	2-hexanone	0.077	12.383	0.111	11.272
6	3,3-dimethyl-2-butanone	0.094	13.836	0.133	12.399
7	mesityl oxide	0.073	10.428	0.108	9.888
8	cyclohexanone	0.043	7.714	0.068	7.634
9	1-phenylethanone	0.144	21.730	0.190	18.328