J. Chem. Thermodynamics 96 (2016) 169–174

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

(Liquid + liquid) equilibria measurements for ternary systems (sulfolane + a carboxylic acid + *n*-heptane) at T = 303.15 K and at 0.1 MPa

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ARTICLE INFO

Article history:
Received 19 August 2015
Received in revised form 11 December 2015
Accepted 20 December 2015
Available online 24 December 2015

Keywords:
(Liquid + liquid) equilibrium
Sulfolane
n-Heptane
Carboxylic acid
NRTL
UNIQUAC

ABSTRACT

In the present work, new (liquid + liquid) equilibrium (LLE) values are reported for ternary systems {sulfolane(1) + acetic acid, or propanoic acid, or butanoic acid, or 2-methylpropanoic acid, or pentanoic acid, or 3-methylbutanoic acid (2) + *n*-heptane (3)} at T = 303.15 K and at p = 0.1 MPa. The mutual solubility of carboxylic acid in sulfolane is dependent on the length and structure of the alkyl chain of the carboxylic acid; it progressively increases with an increase in the alkyl chain of the carboxylic acid. The single phase homogenous region increases as the alkyl chain of the carboxylic acid increases. The *n*-heptane is most soluble in the carboxylic acid mixtures with long alkyl chain, that is, (3-methylbutanoic acid + sulfolane) and (pentanoic acid + sulfolane) systems and least soluble in the carboxylic acid with short alkyl chain (acetic acid + sulfolane) system. Carboxylic acid together with many other oxygenates and hydrocarbons are produced by SASOL Company in South Africa using the Fischer–Tropsch process. The details about this process are given in introduction section. The NRTL and UNIQUAC models were used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. It was found that the NRTL model fits the experimental values significantly better than the UNIQUAC model.

1. Introduction

In chemical industries, solvent extraction plays an important role in the separation process [1]. Solvent for extraction should have high selectivity for one of the components of the mixture that is how the solvent for extraction is selected [1,2]. Sulfolane as a solvent is a versatility due to their unique properties such as high polarity, chemically and thermally stable, recyclable, ease to handle and its low hazard characteristic [1–3]. (Liquid + liquid) data for sulfolane with other solvents have been reported by several researchers [2,4–7]. Sulfolane is highly polar hence allowing it to be highly soluble in water, while the four carbon rings provide non-polar stability. These properties allow it to be miscible with both water and hydrocarbons. The design and evaluation of industrial units for separation processes requires reliable phase equilibrium information of the different mixtures involved in the process. In this regard, the ternary (liquid + liquid) equilibrium (LLE) values are essential for a proper understanding of the solvent extraction process [1,8].

Carboxylic acid together with many other oxygenates and hydrocarbons are produced by the SASOL Company in South Africa using the Fischer–Tropsch process. The SASOL process involves production of oil from coal using the Fischer Tropsch process. Arising out of this process many oxygenates are produced together with light and heavy hydrocarbons. These oxygenates include alcohols, ethers, aldehydes, ketones and carboxylic acids. (Liquid + liquid) extraction is one of the chosen methods to separate these oxygenates, in this case carboxylic acids from hydrocarbons using polar solvents. This work is in response to collaborative work with SASOL regarding investigation of the use of sulfolane to separate acids from hydrocarbons by LLE. Carboxylic acid is an important class of compounds with a great number of industrial uses and applications. Carboxylic acids are used in coagulation of latex in the rubber industry, food industry as preservatives, cosmetic industry as perfume additives and as chemical intermediate for pharmaceutical industry. The separation of carboxylic acid from the mixtures of organic compound (different mixtures and crude oil mixtures).

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http://dx.doi.org/10.1016/j.jct.2015.12.019
0021-9614/

TABLE 1
Pure component specifications: suppliers, specified purity and GC purity.

Chemical name	Supplier	Mole fraction purity	
		Initial	GC analysis
Acetic acid	Fluka	⩾0.99	>0.99
Propanoic acid	Fluka	⩾0.99	>0.99
Butanoic acid	Fluka	⩾0.99	>0.99
2-Methylpropanoic acid	Fluka	⩾0.99	>0.99
Pentanoic acid	Fluka	⩾0.99	>0.99
3-Methylbutanoic acid	Fluka	⩾0.99	⩾0.99
Sulfolane	Fluka	⩾0.99	⩾0.99
n-Heptane	Fluka	⩾0.99	⩾0.99

Initial refer to purity reported by suppliers.

Using the Fischer–Tropsch synthesis is an important objective for physical chemists as well as chemical engineers [9,10]. The separation of carboxylic acid from hydrocarbons is commercially lucrative consideration and is an important reason of this study.

In relation to this, the present study is concerned with the LLE determination for the ternary systems{sulfolane (1) + a carboxylic acid (2) + *n*-heptane (3)} at $T = 303.15$ K at $p = 0.1$ MPa. The carboxylic acids are acetic acid, propanoic acid, butanoic acid, 2-methylpropanoic acid, pentanoic acid and 3-methylbutanoic acid. The binodal curve data have been summarized using the modified Hlavatý equation [11], beta (β) function and log γ equations will be fitted to the experimental binodal data. The Non-Random, Two Liquid (NRTL) of Renon and Prausnitz [12] and Universal Quasichemical (UNIQUAC) models of Abrams and Prausnitz [13]were used to correlate the experimental tie-lines as well as calculate the phase compositions of the ternary systems. Screened open literature shows that there are no data reported for studied systems. In continuation of our research [14–16,7] the present work focused on selection of a suitable solvent for separation of carboxylic acid from mixture of organic compounds.

2. Experimental

2.1. Materials

The purities (mole fraction) of the materials are as follows: sulfolane (>0.99), *n*-heptane (>0.99), acetic acid (>0.99), propanoic acid (>0.99), butanoic acid (>0.99), 2-methylpropanoic acid

TABLE 2
Physical properties of the pure components at $T = 303.15$ K at $p = 0.1$ MPa, molar volumes, V_m, refractive index, n_D, volume and surface parameters, R and Q.

Component	n_D		$V_{mi}/(\mathrm{cm^3/mol^{-1}})^a$	R	Q
	Exp.	Lit.			
Acetic acid	1.3716 [14,7]	1.3716 [17]	57.73 [17]	2.202 [1]	2.072 [1]
Propanoic acid	1.3829 [14,7]	1.38255 [19]	75.48 [17]	2.877 [1]	2.612 [1]
Butanoic acid	1.3947 [14,7]	1.39398 [19]	93.21 [17]	3.551 [1]	3.152 [1]
2-Methylpropanoic acid	1.3913	1.38892 [19]	93.64 [17]	3.550 [1]	3.148 [1]
Pentanoic acid	1.4047 [14,7]	1.40438 [20]	109.76 [17]	4.226 [1]	3.692 [1]
3-Methylbutanoic acid	1.3997 [14,7]	1.3997 [17]	111.87 [17]	4.225 [1]	3.688 [1]
n-Heptane	1.3844	1.38248 [21]	147.40 [17]	5.174 [18]	4.396 [18]
Sulfolane	1.4815	1.4815 [17]	95.30 [17]	4.036 [18]	3.200 [18]

Standard uncertainty u are: $u(n_D) = \pm 0.0092$, $u(T) = \pm 0.03$ K and $u(p) = \pm 0.04$ MPa.

TABLE 3
Composition of points on the binodal curve at $T = 303.15$ K at $p = 0.1$ MPa for the systems: {sulfolane (1) + a carboxylic acid (2) + *n*-heptane (3)}, equilibrium mole fraction, x_1, x_2.

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
	Acetic acid				*Propanoic acid*		
0.0060	0.0000	0.1164	0.8170	0.0060	0.0000	0.2135	0.6293
0.0085	0.1050	0.1941	0.7664	0.0079	0.0090	0.3112	0.6033
0.0110	0.1950	0.2713	0.6986	0.0109	0.1090	0.5110	0.4351
0.0120	0.2834	0.4730	0.5046	0.0123	0.1890	0.6186	0.3442
0.0130	0.3859	0.5647	0.4220	0.0169	0.2862	0.7280	0.2421
0.0150	0.4964	0.6782	0.3079	0.0179	0.3821	0.8519	0.1234
0.0180	0.5863	0.8326	0.1554	0.0217	0.4309	0.9143	0.0687
0.0215	0.7320	0.9060	0.0803	0.0410	0.4946	0.9528	0.0278
0.0262	0.7825	0.9360	0.0471	0.1260	0.6123	0.9850	0.0000
0.0525	0.8202	0.9850	0.0000				
	Butanoic acid				*2-Methylpropanoic acid*		
0.0060	0.0000	0.3259	0.5237	0.0060	0.0000	0.3399	0.5462
0.0065	0.0235	0.5577	0.3827	0.0085	0.1991	0.5517	0.3943
0.0074	0.0635	0.6372	0.3094	0.0094	0.2959	0.6559	0.3097
0.0085	0.1072	0.7428	0.2051	0.0256	0.3744	0.7588	0.2054
0.0254	0.2110	0.8668	0.1031	0.0300	0.4065	0.8541	0.1048
0.0388	0.3179	0.9296	0.0541	0.0585	0.5060	0.9143	0.0531
0.0450	0.4644	0.9743	0.0249	0.1392	0.5727	0.9497	0.0253
0.1287	0.5617	0.9850	0.0000	0.2029	0.5836	0.9850	0.0000
0.2139	0.5652						
	Pentanoic acid				*3-Methylbutanoic acid*		
0.0060	0.0000	0.3582	0.4983	0.0060	0.0000	0.3600	0.5018
0.0089	0.2340	0.5736	0.3619	0.0069	0.1323	0.5783	0.3522
0.0250	0.2961	0.6726	0.2716	0.0090	0.1961	0.6910	0.2687
0.0345	0.3366	0.7901	0.1810	0.0319	0.2681	0.7938	0.1808
0.0432	0.3467	0.8806	0.0919	0.0522	0.3917	0.8971	0.0849
0.0572	0.4850	0.9315	0.0405	0.0690	0.5190	0.9326	0.0497
0.1529	0.5659	0.9521	0.0258	0.1526	0.5752	0.9559	0.0243
0.2494	0.5394	0.9850	0.0000	0.2643	0.5451	0.9850	0.0000

Standard uncertainty u are: $u(T) = \pm 0.03$ K $u(x) = \pm 0.005$ and $u(p) = \pm 0.04$ MPa.