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Liquid–liquid equilibria for the binary systems of sulfolane with branched cycloalkanes

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Abstract

Liquid–liquid equilibrium (LLE) data were measured for three binary systems containing sulfolane and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) over the temperature range around 300–460 K using a circulation type equipment with an equilibrium view cell. The compositions of both branched cycloalkane-rich and sulfolane-rich phases were analyzed by on-line gas chromatography. The binary liquid–liquid equilibrium data were correlated with the NRTL model and UNIQUAC model using temperature-dependent parameters. The both models correlated with a good accuracy.

Keywords: Liquid–liquid equilibria; Sulfolane; Methylcyclopentane; Methylcyclohexane; Ethylcyclohexane

1. Introduction

The low molecular-weight aromatic hydrocarbons are benzene, toluene, and xylenes. They serve as important building blocks for main product in petrochemical industry. Traditionally, these fundamental compounds have been produced via catalytic reformation of naphtha or through steam cracking of naphtha or gas oils, producing streams such as reformate and pyrolysis gasoline [1]. BTX (benzene, toluene and xylene) derived from such traditional methods typically include substantial amounts of non-aromatic compounds having similar boiling points. Conventional distillation process cannot effectively separate the aromatic compounds from the reformate or the pyrolysis gasoline (crude BTX products). As an effective method, extraction and extractive distillation with a separating agent, especially a polar solvent, have been used to separate the slightly polar aromatics from the non-polar non-aromatics. The employed solvents for these processes are *N*-methyl-2-pyrrolidinone (NMP) [2], *N*-formylmorpholine (NFM) [3,4], glycol [5,6], and sulfolane [7–11]. Recently, sulfolane have mainly been used as solvent. Sulfolane used in UOP, Shell and GT-BTXsm processes offers good thermal and hydrolytic stability, high density, high boiling point, and a good selectivity and meets the requirements as a solvent.

Binary LLE data containing sulfolane for wide temperature ranges have become necessary to simulate the extraction and the extractive distillation process for the separation of aromatics from hydrocarbon mixtures. However, LLE data for these mixtures are not available in the literature and the databank of simulators. Therefore, the liquid–liquid equilibrium data for the sulfolane and branched cycloalkanes (methylcyclopentane, methylcyclohexane, and ethylcyclohexane) binary systems were measured in the temperature range from about 300–460 K. Experimental data were correlated with NRTL model [12] and UNIQUAC model [13] with the temperature-dependent parameters.

2. Experimental

2.1. Materials

The suppliers and purities of the chemicals are listed in Table 1 together with the purities determined using a HP 5890 gas chromatograph with a thermal conductivity detector. The chemicals were used without further purification.

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Table 1
Suppliers and purity of the used chemicals

Chemical	Supplier	Spec.[a] (%)	Purity[b] (%)
Sulfolane	Fluka chemical Co.	>99.50	>99.96
Methylcyclopentane	ACROS	>95.00	>99.15
Methylcyclohexane	Junsei Chemical Co., Ltd.	>99.00	>99.89
Ethylcyclohexane	ACROS	>99.00	>99.94

[a] The purity reported by the supplier.
[b] The purity determined as area ratio by the gas chromatography with a thermal conductivity detector.

2.2. Experimental apparatus

Details of this apparatus were given in our previous studies [14]. The volume of the equilibrium cell was 240 cm^3. The cell was made of stainless steel (SUS. 316) and placed inside the air bath, controlled by a PID temperature controller to the desired temperature within ±0.1 K (maximum temperature 573.2 K). The cell and the quartz window were sealed with PTFE (Teflon) gaskets. The mixing was promoted by the magnetic stirrer. The temperature was measured using a platinum resistance thermometer (1502A by Hart Scientific, Inc.). Its uncertainty was estimated to be within ±0.006 K. The thermometer was calibrated at the ice point and by comparison to standard platinum thermometers (SPRTs) calibrated on the basis of the international temperature scale of 1990 (ITS-90). The sampling system was connected to a gas chromatograph (Hewlett Packard 5890 Series II) with a thermal conductivity detector (TCD) and a 1.828 m × 0.003 175 m column packed with Chromosorb WHP 100/120 coated with OV-101.

2.3. Experimental procedure

The mixture was fed into the equilibrium cell that was initially evacuated. The mixture was stirred for at least 1 h with the magnetic stirrer and then left to settle for at least 2 h. Each phase was circulated with recirculation pumps for 1 h. The samples were analyzed by gas chromatography. The temperatures of the injector and the detector were maintained at 593.15 K. After

Table 2
Experimental and calculated LLE data for the methylcyclopentane (1) + sulfolane (2) system

T (K)	Methylcyclopentane rich phase, x_{11}			Sulfolane rich phase, x_{12}		
	Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC
304.32	0.9859	0.9853	0.9853	0.0267	0.0261	0.0261
323.81	0.9791	0.9792	0.9792	0.0374	0.0383	0.0383
343.98	0.9704	0.9712	0.9712	0.0532	0.0549	0.0550
352.45	0.9648	0.9672	0.9671	0.0608	0.0634	0.0634
364.35	0.9582	0.9608	0.9607	0.0786	0.0768	0.0768
372.69	0.9555	0.9559	0.9558	0.0878	0.0871	0.0871
382.30	0.9507	0.9496	0.9496	0.1019	0.1005	0.1004
393.37	0.9444	0.9414	0.9414	0.1234	0.1176	0.1175
402.64	0.9382	0.9338	0.9338	0.1395	0.1335	0.1334
409.75	0.9310	0.9274	0.9274	0.1487	0.1468	0.1467
422.23	0.9189	0.9149	0.9150	0.1685	0.1723	0.1723
433.67	0.8996	0.9016	0.9017	0.1943	0.1989	0.1990
444.67	0.8757	0.8870	0.8870	0.2201	0.2273	0.2278

Table 3
Experimental and calculated LLE data for the methylcyclohexane (1) + sulfolane (2) system

T (K)	Methylcyclohexane rich phase, x_{11}			Sulfolane rich phase, x_{12}		
	Experimental	NRTL	UNIQUAC	Experimental	NRTL	UNIQUAC
303.96	0.9994	0.9984	0.9984	0.0193	0.0210	0.0208
318.48	0.9898	0.9955	0.9956	0.0278	0.0315	0.0315
333.69	0.9869	0.9922	0.9921	0.0417	0.0403	0.0403
348.76	0.9861	0.9872	0.9871	0.0586	0.0510	0.0511
364.49	0.9830	0.9800	0.9798	0.0736	0.0664	0.0665
373.89	0.9752	0.9739	0.9736	0.0859	0.0783	0.0785
383.87	0.9707	0.9669	0.9665	0.0937	0.0922	0.0924
394.20	0.9606	0.9579	0.9576	0.1076	0.1089	0.1091
403.74	0.9580	0.9493	0.9491	0.1228	0.1257	0.1259
414.02	0.9459	0.9380	0.9379	0.1374	0.1459	0.1460
423.84	0.9329	0.9261	0.9262	0.1522	0.1666	0.1668
433.86	0.9202	0.9133	0.9137	0.1760	0.1899	0.1903
444.73	0.8946	0.8984	0.8992	0.2122	0.2179	0.2187
453.97	0.8749	0.8865	0.8878	0.2375	0.2417	0.2433
464.91	0.8526	0.8737	0.8754	0.2805	0.2700	0.2732