(Liquid + liquid) equilibria of (sulfolane + benzene + *n*-hexane), (*N*-formylmorpholine + benzene + *n*-hexane), and (sulfolane + *N*-formylmorpholine + benzene + *n*-hexane) at temperatures ranging from (298.15 to 318.15) K: Experimental results and correlation

Jafar Mahmoudi, Mohammad Nader Lotfollahi *

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan 35195-363, Iran

ABSTRACT

The experimental (liquid + liquid) equilibrium (LLE) properties for two ternary systems containing (*N*-formylmorpholine + benzene + *n*-hexane), (sulfolane + benzene + *n*-hexane) and a quaternary mixed solvent system (sulfolane + *N*-formylmorpholine + benzene + *n*-hexane) were measured at temperature ranging from (298.15 to 318.15) K and at an atmospheric pressure. The experimental distribution coefficients and selectivity factors are presented to evaluate the efficiency of the solvents for extraction of benzene from *n*-hexane. The LLE results obtained indicate that increasing temperature decreases selectivity for all solvents. The LLE results for the systems studied were used to obtain binary interaction parameters in the UNIQUAC model by minimizing the root mean square deviations (RMSD) between the experimental and calculated results. Using the interaction parameters obtained, the phase equilibria in the systems were calculated and plotted. The calculated compositions based on the UNIQUAC model were found to be in good agreement with the experimental values. The result of the RMSD obtained by comparing the calculated and experimental two-phase compositions is 0.0163 for (*N*-formylmorpholine + benzene + *n*-hexane) system and is 0.0120 for (sulfolane + benzene + *n*-hexane) system.

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1. Introduction

The separation of aromatic hydrocarbons (benzene, toluene, and xylene) from aliphatic hydrocarbons (*n*-hexane, heptanes, and octane) is an important operation in chemical and petrochemical processes. The conventional process for these separations is liquid extraction, since distillation is not suitable. The project design, operation and optimization of extraction processes require an efficient model to describe the involved (liquid + liquid) equilibria. Several thermodynamic models have been developed to meet the requirement by the concept of local composition. These models require proper binary interaction parameters which are not available for all aromatic extraction systems. To obtain the binary interaction parameters, reliable (liquid + liquid) equilibrium (LLE) data are needed. Therefore, it is usual to measure the phase equilibrium properties of the ternary or quaternary liquid systems.

Many investigators [1–7] have published the (liquid + liquid) equilibrium (LLE) of ternary and quaternary systems containing solvent, aromatic and aliphatic hydrocarbons: (sulfolane + *p*-xylene + cyclohexane), (sulfolane + *p*-xylene + *n*-hexane), and (sul-

folane + toluene + *n*-hexane) at *T* = (308.15 and 323.15) K [8]; (heptane + *N*-formylmorpholine (NFM) + aromatic hydrocarbons (benzene, toluene, and xylene)) over the temperature range of (298 to 353) K [9]; (solvent + aromatic hydrocarbon + alkane) at different temperatures (298.15 to 313.15) K, where the solvents are ethylene carbonate, dimethyl sulfoxide (DMSO), or sulfolane and the aromatic hydrocarbons are toluene or *m*-xylene and the alkanes refer to *n*-heptane, *n*-octane, or cyclohexane [10]; (tetrafluoroborate, or hexafluorophosphate, benzene, heptane, or dodecane, or hexadecane) at *T* = 298.2 K [11]; two quaternary systems (cyclohexane + 1-heptene + benzene + sulfolane) and (cyclohexane + 1-heptene + toluene + sulfolane) at *T* = 298.15 K [12]; three quaternary systems (*n*-hexane + heptane + toluene + sulfolane), (heptane + octane + *m*-xylene + sulfolane), and (heptane + benzene + toluene + sulfolane) and two quinary systems (*n*-hexane + heptane + toluene + *m*-xylene + sulfolane) and (heptane + octane + benzene + *m*-xylene + sulfolane) at *T* = 298.15 K [13]; three quaternary systems (nonane + undecane + benzene + sulfolane), (nonane + undecane + toluene + sulfolane), and (nonane + undecane + *m*-xylene + sulfolane) at *T* = (298.15 and 313.15) K [14]. However, the experimental results for the mixed solvents are still scarce: (*n*-hexane, toluene, or *m*-xylene, sulfolane, and water, or propanol) over the temperature range of (303 to 323) K; (heptane,

* Corresponding author. Tel./fax: +98 231 3354120.
  E-mail address: mnlotfollahi@semnan.ac.ir (M.N. Lotfollahi).

(benzene + toluene + p-xylene), tetraethyene glycol + water) at T = 333 K [15].

In this work, experimental LLE results for two ternary systems of (sulfolane + benzene + n-hexane) and (N-formylmorpholine + benzene + n-hexane), and a mixed solvent system of (sulfolane + N-formylmorpholine, benzene, n-hexane) were obtained over the temperature range of (298.15 to 318.15) K. The LLE values were correlated by the UNIQUAC model.

2. Experimental

Benzene, n-hexane, sulfolane, ethanol, and N-formylmorpholine (NFM) were obtained from Merck Company (Germany), all with mass fraction purity greater than 0.990. All chemicals were used without further purification.

To find the experimental points that define the tie line in the phase diagram, experiments were carried out in equilibrium 250 cm^3 glass cells. The cell temperature was regulated by a thermostatic bath (Grant instruments (Cambridge) Ltd. (type SE 15, England)), accurate to ±0.2 °C. The mixture was prepared directly inside the cell, and the components were weighted on an analytical balance (A&D Company, GF-600, Japan) accurate to 0.001 g. For

sulfolane, the mixture was agitated with a magnetic stirrer (Stuart Scientific SM 27, UK) for 3 h and then left for 20 h. For N-formylmorpholine, the mixture was agitated with a magnetic stirrer for 1 h and then left for 5 h. Preliminary tests showed that these times were enough to achieve the equilibrium. Subsequently, the system divided into two liquid phases that became clear and transparent at equilibrium, with a well defined interface. After decanting, samples from the two liquid phases were taken for analysis. The samples were diluted in pure ethanol and analyzed by gas chromatography equipped with a helium ionisation detector (HID). The analysis was repeated at least three times. The average of these readings was taken for the component compositions. A good separation of the components was attained using a TRB-WAX capillary column (60 m × 0.32 mm) with a poly ethylene glycol of 0.5 μm film. The temperatures of the injector and the detector were maintained at 513.15 K. The column temperature was controlled by programming temperature, after 10 min of holding at 373.15 K; the column temperature was raised to the final temperature of 493.15 K at the rate of 15 K · min^{-1}. Helium was used as the carrier gas at the rate of 1 cm^3 · min^{-1}. Software supplied by Chrompack (detailed hydrocarbon analyzer) was used to handle the data generated by GC. The gas chromatograph was calibrated

TABLE 1
Experimental results for the ternary system {sulfolane (1) + benzene (2) + n-hexane(3)} at different temperatures.

T/K	Hexane rich phase (II)			Sulfolane rich phase (I)			S	K
	w_1	w_2	w_3	w_1	w_2	w_3		
308.15	0.0981	0.4351	0.4668	0.6923	0.2776	0.0301	9.8944	0.6380
	0.0693	0.4203	0.5104	0.7192	0.2532	0.0276	11.1401	0.6024
	0.0391	0.3807	0.5802	0.7626	0.2142	0.0232	14.0722	0.5626
	0.0277	0.3029	0.6694	0.8194	0.1612	0.0194	18.3631	0.5322
313.15	0.0901	0.4232	0.4867	0.6477	0.3085	0.0438	8.1005	0.7290
	0.0761	0.4086	0.5153	0.7209	0.2449	0.0342	9.0311	0.5994
	0.0715	0.3842	0.5443	0.7503	0.2256	0.0241	13.2611	0.5872
	0.0574	0.2844	0.6582	0.8059	0.1705	0.0236	16.7197	0.5995
	0.0499	0.2392	0.7109	0.8398	0.1396	0.0206	20.1388	0.5836
318.15	0.0798	0.4434	0.4768	0.6696	0.2875	0.0429	7.2068	0.6484
	0.0704	0.4250	0.5046	0.7247	0.2396	0.0384	7.4087	0.5637
	0.0598	0.3854	0.5548	0.7819	0.1923	0.0258	10.7290	0.4990
	0.0485	0.3001	0.6514	0.8335	0.1456	0.0209	15.1200	0.4852

$S = (w_1/w_3)^I/(w_2/w_3)^{II}$.
$K = w_2^I/w_2^{II}$.

TABLE 2
Experimental results for the ternary system {NFM (1) + benzene (2) + n-hexane(3)} at different temperatures.

T/K	Hexane rich phase (II)			N-formylmorpholine rich phase (I)			S	K
	w_1	w_2	w_3	w_1	w_2	w_3		
303.15	0.1661	0.3526	0.4813	0.6445	0.2749	0.0806	4.6721	0.7796
	0.1206	0.3327	0.5467	0.6725	0.2547	0.0728	5.7486	0.7655
	0.1072	0.3207	0.5721	0.6916	0.2396	0.0688	6.2123	0.7471
	0.0844	0.3085	0.6071	0.7350	0.2091	0.0559	7.3619	0.6778
	0.0414	0.2545	0.7041	0.7820	0.1716	0.0464	10.2332	0.6743
	0.0537	0.1264	0.8199	0.8896	0.0821	0.0283	18.8132	0.6495
308.15	0.1531	0.3612	0.4857	0.6391	0.2778	0.0831	4.4951	0.7691
	0.1328	0.3441	0.5231	0.6596	0.2599	0.0805	4.9082	0.7553
	0.1174	0.3281	0.5545	0.6894	0.2375	0.0731	5.4909	0.7239
	0.0877	0.2976	0.6147	0.7474	0.1932	0.0594	6.7182	0.6492
	0.0519	0.2605	0.6876	0.8147	0.1464	0.0389	9.9353	0.5620
	0.0599	0.1305	0.8096	0.8904	0.0815	0.0218	17.9901	0.6224
313.15	0.1003	0.3956	0.5041	0.6358	0.2796	0.0846	4.2102	0.7068
	0.0895	0.3754	0.5351	0.6655	0.2570	0.0775	4.7272	0.6846
	0.0798	0.3490	0.5712	0.6985	0.2283	0.0732	5.1044	0.6541
	0.0627	0.3349	0.6024	0.7229	0.2185	0.0586	6.7074	0.6524
	0.0391	0.2615	0.6994	0.7936	0.1627	0.0437	9.9575	0.6222

$S = (w_2/w_3)^I/(w_2/w_3)^{II}$.
$K = w_2^I/w_2^{II}$.