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Short Communication

Experiments and thermodynamic models for ternary liquid-liquid equilibrium systems of diethoxymethane + ethanol + water system at different temperatures

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ABSTRACT

Liquid-liquid equilibrium (LLE) data for the diethoxymethane + ethanol + water ternary system has been studied at 298.2, 308.2 and 318.2 K at 101.3 kPa. The efficiency of water to extract ethanol from diethoxymethane was assessed by the distribution coefficients and separation factors. The reliability of the experimental LLE data was verified with the Othmer-Tobias and Hand equations. The thermodynamic NRTL and UNIQUAC models were successfully applied to correlate the experimental LLE data of the studied systems with all the RMSD% values were less 0.6 and the values for binary interaction parameters were obtained. Water was proven to be very promising in extracting ethanol from diethoxymethane solution.

1. Introduction

Diethoxymethane (DEM) has been used extensively in various industrial applications which can be broadly classified into two major categories: DEM as a solvent in organic processes and DEM as a reagent for organic chemistry [1]. Due to its low boiling point (88 °C), high stability in basic conditions, water-immiscible and nonhygroscopic properties, DEM can potentially replace the commonly used solvents such as tetrahydrofuran, ethyl acetate, dichloromethane, dimethoxyethane, methylal, et al. Also it can act as a high performance solvent for watersensitive and phase-transfer catalyzed reactions [2] without need for drying. Besides, DEM is widely used in organic chemistry [1], using as a chemical intermediate of ethoxymethylating agent, a source of formaldehyde, as well as a carbonylation substrate. Recently, DEM can be found new application as useful fuel additives to reduce soot and carbon monoxide emissions as well as to increase octane ratings [3,4]. At present, the acetalization reaction of formaldehyde with ethanol in the presence of an acidic catalyst is the most economical way to prepare DEM [5], as shown in Fig. 1.

After completion of the reaction, the reaction solution contains DEM, ethanol, water, etc. DEM forms a binary azeotrope with both water and ethanol [1], bringing a great difficulty to obtain highly purified DEM in distillation operation. Azeotropic distillation with cyclohexane or dichloromethane as entrainers is applied for the production and purification of DEM [6,7]. By comparison, liquid-liquid extraction is also an alternative to the conventional techniques for DEM upgrading. Thus the reliable liquid-liquid equilibrium (LLE) data are needed to design and optimize industrial units for solvent extraction processes [8–11]. Ethylene glycol, 1,3-propanediol, 1,4-butanediol and formamide were introduced as extracting solvents [12]. Although these solvents provide reasonable liquid-liquid separations, the search for new and more suitable solvents that can facilitate further increases in separation efficiency is important. Water is the by-product in the acetalization reaction. Given the immiscibility nature of DEM and water, the use of water as extracting solvent, allowing the drying of DEM to very low water content without introducing a new compound, affords good economics.

The purpose of this work is to explore the multicomponent phase behaviors of ethanol in DEM and water mixture, the LLE data of the ternary system DEM + ethanol + water was determined at 298.2, 308.2 and 318.2 K at 101.3 kPa. As far as the authors are aware, these data have never been reported in any previous references. Distribution coefficients (D) and separation factors (S) were calculated. The reliability of these data was assessed by Othmer-Tobias and Hand equations. Additionally, all experimental LLE data were correlated using the Non-Random Two-Liquid (NRTL) [13] and Universal Quasi-Chemical

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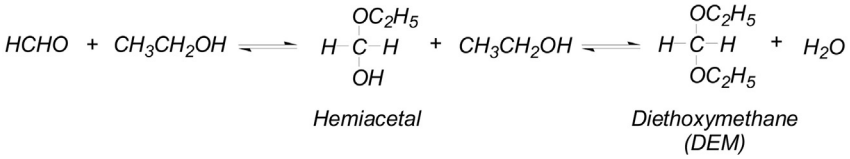

Fig. 1. The acetalization reaction of ethanol with formaldehyde.

Table 1
Details of the chemical reagents used in this work.

Chemical	Supplier	Mass fraction purity	Purification method	Purity analysis method	CAS
Diethoxymethane	Aladdin reagent company	>0.99	None	GC[a]	462-95-3
Ethanol	Aladdin reagent company	>0.995	None	GC	64-17-5
Distilled water	Self-made	–	None	GC	7732-18-5

[a] Gas chromatography.

(UNIQUAC) [14] models, and the binary interaction parameters were obtained.

2. Experimental

2.1. Materials

The detailed information of chemical reagents used in this work is listed in Table 1. Diethoxymethane and ethanol were purchased from Aladdin reagent company (Shanghai, China). Distilled water was prepared in our laboratory. The purity of the chemical reagents was analyzed by gas chromatography (GC) and no peak of impurity was detected out. All these chemicals were used without further purification as typical LLE studies did [15–17].

2.2. Apparatus and procedures

The equilibrium experiments for the ternary system DEM + ethanol + water was carried out at 298.2, 308.2, 318.2 K and 101.3 kPa. The details about experimental equipment have been presented in our previous work and the reliability of the experimental system has been evaluated [18–20]. The mixture was vigorously stirred for >2 h and then was left for at least 12 h to reach the phase equilibrium. The temperature of the ternary mixture was kept constant by using a thermostatic bath with a fluctuation of 0.1 K. The evaporated compounds were completely condensed by the condenser to ensure the mass balance.

After phase equilibrium was reached, the mixture was split into the DEM rich phase and the water rich phase. The sample's

Table 2
Experimental LLE data in mass fraction for DEM (1) + ethanol (2) + water (3) system at 298.2, 308.2, 318.2 K at 101.3 kPa, together with the distribution coefficient D and separation factor S.[a,b]

Solvent	DEM rich phase			Water rich phase			Feed composition			D	S
	w^{I}_1	w^{I}_2	w^{I}_3	w^{II}_1	w^{II}_2	w^{II}_3	w_1	w_2	w_3		
298.2 K	0.9883	–	0.0117	0.0663	–	0.9337	0.5003	–	0.4997	–	–
	0.9741	0.0111	0.0148	0.0717	0.0414	0.8869	0.4848	0.0309	0.4843	3.722	50.57
	0.9585	0.0228	0.0187	0.0836	0.0779	0.8384	0.4717	0.0571	0.4712	3.420	39.20
	0.9362	0.0387	0.0251	0.0917	0.1122	0.7961	0.4589	0.0826	0.4584	2.897	29.57
	0.8793	0.0790	0.0417	0.1025	0.1653	0.7322	0.4358	0.1289	0.4353	2.094	17.97
	0.8451	0.1023	0.0526	0.1173	0.1857	0.6970	0.4252	0.1501	0.4247	1.815	13.08
	0.7869	0.1355	0.0776	0.1252	0.2074	0.6674	0.4091	0.1818	0.4091	1.530	9.613
	0.7400	0.1603	0.0998	0.1396	0.2247	0.6357	0.4005	0.1989	0.4005	1.402	7.428
	0.6886	0.1856	0.1258	0.1636	0.2394	0.5970	0.3914	0.2172	0.3914	1.290	5.429
308.2 K	0.9873	–	0.0127	0.0546	–	0.9454	0.5003	–	0.4997	–	–
	0.9693	0.0126	0.0181	0.0612	0.0396	0.8992	0.4848	0.0309	0.4843	3.152	49.92
	0.9496	0.0269	0.0235	0.0685	0.0767	0.8548	0.4717	0.0571	0.4712	2.850	39.50
	0.9244	0.0452	0.0305	0.0776	0.1077	0.8147	0.4589	0.0826	0.4584	2.384	28.38
	0.8976	0.0649	0.0375	0.0820	0.1350	0.7830	0.4474	0.1058	0.4469	2.080	22.76
	0.8638	0.0882	0.0481	0.0980	0.1592	0.7428	0.4358	0.1289	0.4353	1.806	15.92
	0.8062	0.1248	0.0690	0.1108	0.1874	0.7018	0.4160	0.1670	0.4170	1.501	10.93
	0.7574	0.1522	0.0904	0.1244	0.2066	0.6690	0.4063	0.1863	0.4074	1.358	8.268
	0.7068	0.1758	0.1174	0.1454	0.2211	0.6336	0.3975	0.2041	0.3985	1.258	6.115
	0.6619	0.2005	0.1376	0.1658	0.2366	0.5976	0.3885	0.2221	0.3895	1.180	4.713
318.2 K	0.9880	–	0.0120	0.0408	–	0.9592	0.5004	–	0.4996	–	–
	0.9725	0.0111	0.0164	0.0464	0.0268	0.9268	0.4884	0.0240	0.4877	2.415	50.58
	0.9546	0.0242	0.0213	0.0563	0.0574	0.8863	0.4758	0.0491	0.4751	2.375	40.30
	0.9305	0.0397	0.0299	0.0610	0.0888	0.8502	0.4638	0.0731	0.4631	2.239	34.14
	0.9077	0.0598	0.0325	0.0705	0.1157	0.8138	0.4519	0.0969	0.4512	1.934	24.91
	0.8666	0.0865	0.0470	0.0820	0.1409	0.7771	0.4391	0.1224	0.4385	1.629	17.21
	0.8265	0.1119	0.0616	0.0995	0.1550	0.7456	0.4289	0.1428	0.4283	1.385	11.51
	0.7833	0.1383	0.0783	0.1087	0.1791	0.7123	0.4185	0.1637	0.4179	1.295	9.333
	0.7346	0.1661	0.0993	0.1331	0.1986	0.6684	0.4074	0.1858	0.4068	1.195	6.600
	0.6807	0.1907	0.1286	0.1649	0.2152	0.6199	0.3971	0.2063	0.3966	1.129	4.659
	0.6235	0.2163	0.1601	0.1934	0.2350	0.5715	0.3881	0.2243	0.3876	1.086	3.502

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u(p) = 1$ kPa, $u(w_1) = 0.0035$, $u(w_2) = 0.0035$, $u(w_3) = 0.0049$.
[b] w_1: mass fraction of DEM; w_2: mass fraction of ethanol; w_3: mass fraction of water.