

Liquid-liquid equilibrium data for water-ethanol-entrainer ternary system with entrainers: Cyclohexane, n-pentane, DEE (diethyl ether), DIPE (di-isopropyl ether), ETBE (ethyl tert-butyl ether)

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Abstract—The water-ethanol system was studied experimentally to find the liquid-liquid equilibrium (LLE) data at various temperature values by using five different entrainers: cyclohexane, n-pentane, DEE (diethyl ether), DIPE (di-isopropyl ether), and ETBE (ethyl tert-butyl ether). Ternary LLE data for water-ethanol-entrainer system was determined based on an experimental procedure. Exact liquid activity coefficient parameters were found by experimental data and LLE data was predicted. For this purpose, two thermodynamic models, NRTL and UNIQUAC, were compared and contrasted with experimental data to probe into the better thermodynamic model for the azeotropic processes of ethanol system. The most promising entrainer was found through root mean square and average absolute deviations.

Keywords: Liquid-liquid Equilibrium (LLE) Data, NRTL, UNIQUAC, Entrainer, Average Absolute Deviation, Root Mean Square Deviation

INTRODUCTION

High purity products are obtained from non-ideal mixtures by separation through heterogeneous azeotropic distillation. Azeotropic mixtures, having close boiling points, are normally separated by heterogeneous azeotropic distillation, homogeneous azeotropic distillation, and liquid-liquid extraction processes. Heterogeneous azeotropic distillation process is considered as the most complex due to addition of an entrainer. Ethanol, a gasoline additive, has been studied for a long time due to its utilization in chemical and petrochemical industries. Ethanol is added to gasoline to form gasohol, which is used in the production of vehicular fuel, for enhancing its octane number and making fuels more environment-friendly. Gasohol is given preference over gasoline which causes the greenhouse effect by burning of fossil fuel. Due to the aforementioned uses, separation and phase behavior of ethanol with water and entrainers is of major importance. For the process conditions and industrial equipment designing, the vapor-liquid-liquid-equilibrium (VLLE) and liquid-liquid equilibrium (LLE) data is needed [1-4]. Experimental vapor liquid equilibrium is essential for simulating the separation processes of different azeotropic mixtures [5,6]. Hence, researchers have been analyzing the experimental procedures to find LLE data for ternary systems of ethanol, water and entrainer system.

The past literature has LLE data of ethanol, pentane as entrainer, and water system by Galan, Cayero, and Aguilar [7]. Experimental LLE data and its correlation for ethanol, hexane as entrainer, and water has been studied [8,9]. VLE data for water, ethanol, and cyclohexane as entrainer has been found by Karrer and Gaube

[10], while the LLE data was studied by Connemann, Gaube, Karrer, Pfennig, Reuter [11]. Plackov, Stern also studied LLE data at 298 K [12]. Utilization of benzene as entrainer has been decreased over time due to carcinogenic effects of benzene due to which focus on other entrainers, like cyclohexane, has been increased. Currently, cyclohexane is widely used as an entrainer for separation of ternary systems all over the world. Recently, a keen interest has been found in research and development to find more entrainers to possibly increase economic and environmental benefits [13-15]. However, the experimental study on ternary systems of water-ethanol using different entrainers, like cyclohexane, n-pentane, DEE (diethyl ether), DIPE (di-isopropyl ether) and ETBE (ethyl tert-butyl ether) at different temperature conditions, is not mentioned in literature. The present work provides a wide range of liquid-liquid equilibrium data at various temperature values to make the availability of data more convenient for separation processes. Furthermore, literature lacks a thorough comparison of above-mentioned entrainers to find the best correlation of experimental and predicted data. Hence, this work analyzes the choice of entrainer for the best possible separation by comparing different entrainers, like cyclohexane, n-pentane, DEE (diethyl ether), DIPE (di-isopropyl ether), and ETBE (ethyl tert-butyl ether), for ethanol water system. Our paramount objective is to find the LLE data in ternary alcohol system for water-ethanol-entrainer and to assert the reliability of predicted data by correlating with experimental data to find the most effective entrainer.

EXPERIMENTAL APPARATUS AND METHOD

Table 1 elaborates the physical data for the commercially available chemicals used in the experiment. All the chemicals used in the experimental procedure were provided by Aldrich chemicals,

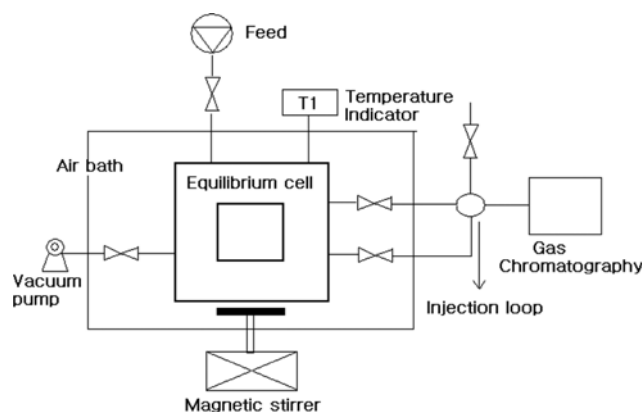
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Table 1. Physical data for chemicals used

Chemicals	Supplier	Density (at 25 °C)	Purity (%)	M.W	b.p (°C)
Ethanol	Aldrich	0.790	99.5+%	46.07	78 °C
Cyclohexane	Aldrich	0.779	99.9+%	84.16	80.7 °C
n-Pentane	Aldrich	0.626	99+%	72.15	35-36 °C
Ether	Aldrich	0.708	99.9%	74.12	34.6 °C
DIPE	Aldrich	0.724	99+%	102.18	67-69 °C
ETBE	Aldrich	0.742	99+%	102.18	72-73 °C

**Fig. 1. The experimental apparatus for liquid-liquid equilibria [16].****Table 2. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 298 K by using cyclohexane as entrainer**

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9526	0.0003	0.0471	0.0022	0.9877	0.0101
0.8489	0.0015	0.1496	0.0084	0.9340	0.0576
0.8148	0.0030	0.1821	0.0125	0.9150	0.0725
0.8118	0.0033	0.1849	0.0125	0.9142	0.0733
0.7426	0.0121	0.2453	0.0262	0.8546	0.1192
0.7212	0.0162	0.2626	0.0320	0.8360	0.1320
0.5918	0.0548	0.3539	0.0657	0.7309	0.2034
0.5218	0.0898	0.3884	0.0917	0.6631	0.2453
0.4157	0.1693	0.4150	0.1519	0.5319	0.3162
0.4031	0.1812	0.4157	0.1638	0.5115	0.3247
0.3609	0.2265	0.4126	0.2010	0.4501	0.3489

Table 3. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 303 K by using cyclohexane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9472	0.0007	0.0521	0.0000	0.9947	0.0053
0.8681	0.0010	0.1309	0.0000	0.9894	0.0106
0.7938	0.0009	0.2054	0.0045	0.9779	0.0176
0.7180	0.0057	0.2762	0.0078	0.9607	0.0314
0.4850	0.0461	0.4689	0.0128	0.8880	0.0992
0.4060	0.0731	0.5209	0.0172	0.8609	0.1219

Korea. First, all solvents were fractionally distilled by using different drying reagents followed by gas chromatography to analyze the purity of all chemicals. It is noted that all chemicals had purity over 99.5% and the chemicals were used without further purification as no noticeable impurity was found chromatographically. A vibrating-tube densimeter, Anton Paar, was used to measure the density of chemicals, and uncertainty in the measurement was noted up to $10 \text{ kg} \cdot \text{m}^{-3}$. The equipment used in the experiment is shown in Fig. 1. A vacuum pump was used to produce a vacuum state in the inlet equilibrium cell whose total volume was 300 cm^3 . Alcohol was added to the equilibrium cell and temperature was set to the desired temperature of the experiment. The liquid in the equilibrium cell was sufficiently mixed with magnetic stirrer. After stirring, the mixture was left for 3 hours in the beaker after which the mixture made two phases where the sample was taken by 1/8 inch injection tube. The sample underwent GC (gas chromatography) analysis and experimental procedure was repeated with different temperature conditions. The uncertainties were measured to

Table 4. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 308 K by using cyclohexane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9430	0.0010	0.0560	0.0040	0.9820	0.0140
0.8430	0.0030	0.1540	0.0210	0.8990	0.0800
0.7440	0.0150	0.2410	0.0390	0.8160	0.1450
0.6690	0.0330	0.2980	0.0570	0.7460	0.1970
0.5880	0.0640	0.3480	0.0960	0.6490	0.2550
0.4900	0.1240	0.3860	0.1720	0.5080	0.3200

Table 5. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 313 K by using cyclohexane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9449	0.0019	0.0533	0.0000	0.9946	0.0054
0.8692	0.0014	0.1294	0.0003	0.9890	0.0107
0.7796	0.0108	0.2096	0.0036	0.9806	0.0158
0.6950	0.0360	0.2689	0.0090	0.9592	0.0318
0.5606	0.0407	0.3986	0.0102	0.9341	0.0556
0.4549	0.0725	0.4726	0.0186	0.8809	0.1005
0.3785	0.0871	0.5344	0.0197	0.8675	0.1129

Table 6. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 323 K by using cyclohexane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9436	0.0017	0.0547	0.0000	0.9945	0.0055
0.8596	0.0079	0.1326	0.0000	0.9880	0.0120
0.7785	0.0282	0.1932	0.0069	0.9780	0.0152
0.6941	0.0427	0.2631	0.0114	0.9562	0.0325
0.5212	0.0831	0.3957	0.0160	0.9253	0.0588
0.4423	0.1015	0.4561	0.0149	0.8767	0.1084
0.3615	0.1186	0.5199	0.0223	0.8637	0.1140

Table 7. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 293 K by using n-pentane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9453	0.0095	0.0451	0.0200	0.9798	0.0001
0.8985	0.0057	0.0958	0.0215	0.9670	0.0115
0.8316	0.0058	0.1626	0.0251	0.9539	0.0210
0.8045	0.0060	0.1896	0.0263	0.9471	0.0265
0.7519	0.0115	0.2366	0.0292	0.9332	0.0376
0.6640	0.0332	0.3028	0.0492	0.8856	0.0653
0.4623	0.0692	0.4685	0.0695	0.7313	0.1991

Table 8. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 298 K by using n-pentane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.4623	0.0691	0.4585	0.0032	0.9966	0.0001
0.5234	0.0566	0.4199	0.0096	0.9789	0.0115
0.5987	0.0444	0.3568	0.0102	0.9687	0.0210
0.6640	0.0332	0.3028	0.0136	0.9598	0.0265
0.7518	0.0115	0.2366	0.0257	0.9367	0.0376
0.8045	0.0060	0.1896	0.02746	0.9072	0.0653
0.8316	0.0058	0.1625	0.0302	0.8938	0.0759
0.8985	0.0057	0.0958	0.0348	0.8528	0.1124
0.9453	0.0095	0.0451	0.0420	0.8143	0.1437

Table 9. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 303 K by using n-pentane as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9308	0.0284	0.0407	0.0181	0.9818	0.0001
0.8958	0.0136	0.0907	0.0212	0.9692	0.0096
0.8431	0.0083	0.1486	0.0275	0.9532	0.0192
0.8246	0.0066	0.1688	0.0276	0.9474	0.0250
0.7320	0.0397	0.2283	0.0324	0.9416	0.0261
0.6557	0.0352	0.3091	0.0337	0.8941	0.0722
0.5467	0.0615	0.3918	0.0710	0.7341	0.1948

Table 10. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 293 K by using di-ethyl ether as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9301	0.0362	0.0337	0.1319	0.8274	0.0407
0.8884	0.0464	0.0652	0.1234	0.7967	0.0799
0.8876	0.0411	0.0713	0.1275	0.7446	0.1280
0.8696	0.0517	0.0787	0.1698	0.6627	0.1675
0.8136	0.0974	0.0890	0.1989	0.5842	0.2169
0.7779	0.1023	0.1198	0.2106	0.5192	0.2702
0.7554	0.1133	0.1313	0.3417	0.3661	0.2922

Table 11. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 298 K by using di-ethyl ether as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9483	0.0207	0.0311	0.1595	0.7815	0.0590
0.9108	0.0390	0.0502	0.1069	0.8133	0.0799
0.8886	0.0411	0.0702	0.1317	0.7425	0.1259
0.8650	0.0482	0.0868	0.1553	0.6819	0.1628
0.7997	0.0666	0.1337	0.2177	0.6069	0.1754
0.7841	0.0775	0.1384	0.2921	0.5253	0.1826
0.7640	0.0893	0.1466	0.3009	0.4991	0.1999

Table 12. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 303 K by using di-ethyl ether as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9523	0.0231	0.0246	0.1286	0.8188	0.0526
0.9131	0.0364	0.0505	0.1045	0.8054	0.0901
0.8824	0.0397	0.0778	0.1476	0.7101	0.1423
0.8472	0.0470	0.1058	0.1672	0.6685	0.1643
0.8193	0.0719	0.1088	0.2400	0.5886	0.1714
0.7738	0.0801	0.1461	0.2679	0.5512	0.1810
0.7312	0.0839	0.1850	0.3440	0.4541	0.2019

Table 13. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 288 K by using ETBE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9972	0.0028	0.0088	0.0156	0.9844	0
0.9779	0.00647	0.00111	0.0276	0.9368	0.0356
0.9621	0.0076	0.00821	0.0485	0.8816	0.0698
0.9398	0.00891	0.0163	0.0599	0.8545	0.0857
0.9265	0.0136	0.0156	0.0866	0.8013	0.1121
0.9066	0.0132	0.0264	0.1037	0.7368	0.1595
0.8797	0.014	0.0278	0.1578	0.6467	0.1955
0.8541	0.00932	0.0177	0.2005	0.5611	0.2384
0.8168	0.0176	0.0262	0.2865	0.4447	0.2687
0.7985	0.0191	0.0377	0.3432	0.3538	0.303

be ± 0.02 and ± 0.01 K for composition (mole fraction) and temperature, respectively. Analysis was performed using a gas chromatography equipment: Hewlett Packard, 5890 ser. II including column HP-FFAP (cross linked FFAP) (25 m * 0.32 mm * 0.52 μ m) and a detector TCD (thermal conductivity detector) was used as the GC analyzer. The injection unit, which takes the samples from equilibrium cell, was connected with GC carrier gas line having 99.999% carrier gas which was fully vaporized at 423 K. Temperature values of injection port, column, and detector were 473 K,

423 K and 523 K, respectively. Initial and final temperatures for oven were programmed as 323 K and 383 K at the rise rate of 20 K \cdot min $^{-1}$.

RESULTS AND DISCUSSION

1. LLE Data

The tie-line data obtained by experiments at different tempera-

Table 14. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 298 K by using ETBE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9947	0.0053	0	0.015	0.985	0
0.9705	0.00944	0.02	0.0312	0.9375	0.0312
0.9605	0.00695	0.0326	0.0548	0.8731	0.0721
0.9306	0.0207	0.0487	0.0602	0.8597	0.0802
0.9256	0.0174	0.057	0.0897	0.8037	0.1065
0.8978	0.0235	0.0787	0.1123	0.7378	0.1499
0.868	0.0278	0.1043	0.1599	0.6678	0.1724
0.8532	0.022	0.1248	0.2265	0.5369	0.2365
0.8012	0.0377	0.161	0.2966	0.4264	0.277
0.7902	0.0232	0.1865	0.3433	0.3666	0.2901

Table 15. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 308 K by using ETBE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9912	0.0088	0	0.0183	0.9817	0
0.9821	0.00111	0.0167	0.0402	0.9274	0.0324
0.9563	0.00821	0.0355	0.06	0.8768	0.0633
0.9325	0.0163	0.0512	0.0665	0.8569	0.0766
0.9256	0.0156	0.0587	0.0837	0.8174	0.099
0.8795	0.0264	0.0941	0.1229	0.7119	0.1652
0.8524	0.0278	0.1199	0.1657	0.6588	0.1755
0.8235	0.0177	0.1588	0.2699	0.4836	0.2465
0.8102	0.0262	0.1636	0.31	0.4086	0.2813
0.7743	0.0377	0.1879	0.3393	0.3576	0.3031

Table 16. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 298 K by using DIPE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9980	0.0020	0.0000	0.0289	0.9711	0.0000
0.9499	0.0022	0.0479	0.0351	0.9291	0.0358
0.9191	0.0020	0.0789	0.0435	0.8748	0.0817
0.8981	0.0021	0.0998	0.0538	0.8182	0.1280
0.8365	0.0045	0.1590	0.1576	0.5704	0.2720
0.8198	0.0053	0.1749	0.2020	0.4647	0.3333
0.7986	0.0061	0.1953	0.2058	0.3805	0.4137

Table 17. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 308 K by using DIPE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9984	0.0016	0.0000	0.0154	0.9846	0.0000
0.9476	0.0017	0.0507	0.0155	0.9477	0.0368
0.8958	0.0014	0.1028	0.0318	0.8161	0.1521
0.8749	0.0020	0.1231	0.0587	0.7198	0.2215
0.8517	0.0020	0.1463	0.0917	0.5980	0.3103
0.8255	0.0027	0.1718	0.1616	0.4093	0.4291
0.7901	0.0070	0.2029	0.3469	0.1996	0.4535
0.7790	0.0084	0.2126	0.2908	0.2509	0.4583

Table 18. Experimental tie-line data for water (1)-entrainer (2)-ethanol (3) system at 318 K by using DIPE as entrainer

Aqueous phase			Organic phase		
X ₁₁	X ₂₁	X ₃₁	X ₁₂	X ₂₂	X ₃₂
0.9984	0.0016	0.0000	0.0191	0.9809	0.0000
0.9489	0.0015	0.0496	0.0133	0.9560	0.0307
0.9052	0.0013	0.0935	0.0309	0.8224	0.1467
0.8853	0.0012	0.1135	0.0426	0.7380	0.2194
0.8601	0.0015	0.1384	0.0775	0.6065	0.3160
0.8431	0.0016	0.1553	0.1115	0.4955	0.3930
0.8158	0.0035	0.1807	0.2177	0.3562	0.4261

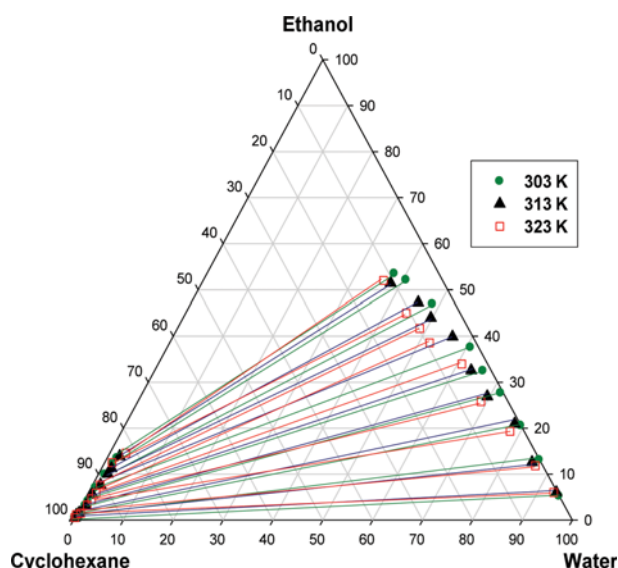


Fig. 2. Equilibrium compositions of water/cyclohexane/ethanol system.

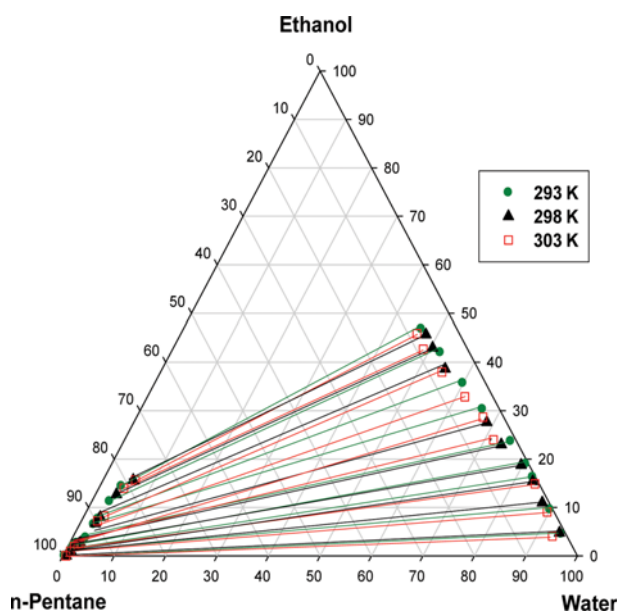


Fig. 3. Equilibrium compositions of water/n-pentane/ethanol system.

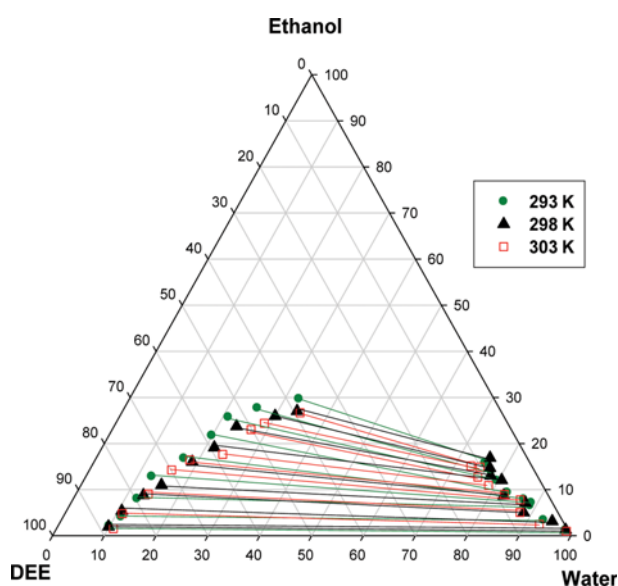


Fig. 4. Equilibrium compositions of water/DEE/ethanol system.

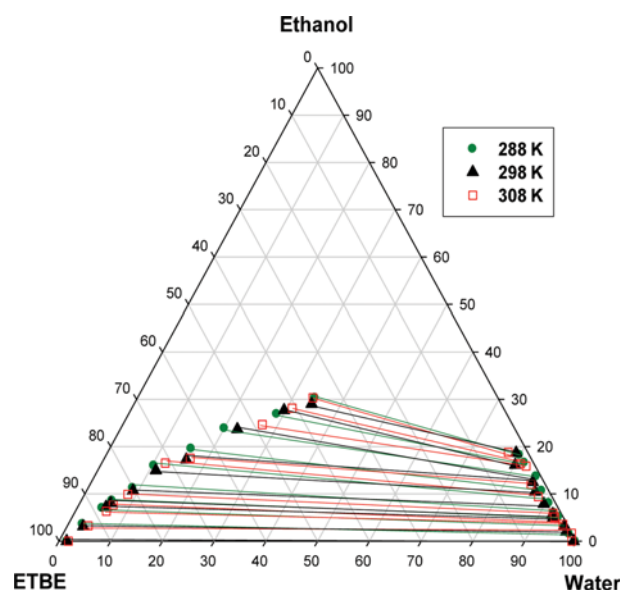


Fig. 5. Equilibrium compositions of water/ETBE/ethanol system.

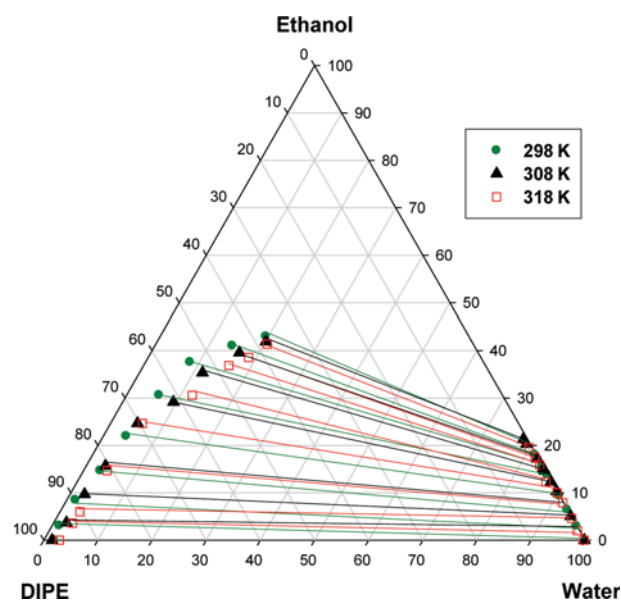


Fig. 6. Equilibrium compositions of water/DIPE/ethanol system.

ture conditions are shown in Tables 2-18 which give compositions for both aqueous and organic phases. The experimental data were used to draw the tie lines for five different entrainers which were used. Figs. 2-6 depict tie-line plots for water-entrainer-ethanol system while using cyclohexane, n-pentane, DEE (di-ethyl ether), DIPE (di-isopropyl ether), and ETBE (ethyl tert-butyl ether). Tie lines were drawn at various temperature values in concurrence with the experimental data. It is clear from the figures that the two phase region in tie line graphs has an inverse relationship with the temperature and same trend is followed by all entrainers.

2. NRTL Model

In this study, NRTL (non-random two liquid) [17-19] and UNIQUAC (UNIversal QUAsi Chemical) [20-23] models were used

for the calculation of liquid activity coefficients to find the most reliable model. The experimental data was used to find the binary interaction parameters and regression was done to predict the LLE data with NRTL and UNIQUAC models. Renon and Prausnitz proposed NRTL model in 1968 [18]. NRTL model is widely used for correlating LLE data. Equation for NRTL model is given below:

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left[\tau_{ij} - \frac{\sum_l x_l G_{il}}{\sum_k G_{kl} x_k} \right] \quad (1)$$

$$G_{ij} = \exp[-(\alpha_{ij} + \beta_{ij} T) \tau_{ij}], \quad \tau_{ij} = \frac{g_{ij} - g_{ii}}{RT}$$

$$\tau_{ij} = \tau_{ji} = 0, \quad G_{ii} = G_{jj} = 1$$

In Eq. (1), τ_{ij} , α_{ij} and G_{ij} are the parameters of NRTL model, while “i” and “j” are the component numbers. Table 19 shows the binary interaction parameters found by calculation in NRTL model. As cited in reference [18], the values of α_{ij} had fixed values of 0.2 or 0.3 as shown in the table while the other parameters remain unfixed and were calculated by NRTL model.

3. UNIQUAC Model

Abrams and Prausnitz [23] developed the UNIQUAC (universal quasi-chemical) model. UNIQUAC equation is also widely used like NRTL equation for correlating vast variety of systems. The expression for UNIQUAC model is given as follows:

$$\ln \gamma_i = (\ln \gamma_i)^C + (\ln \gamma_i)^R \quad (2)$$

$$(\ln \gamma_i)^C = \ln \left[\frac{\phi_i}{x_i} \right] + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + L_i - \left[\frac{\phi_i}{x_i} \right] \sum_{j=1}^n l_j x_j \quad (3)$$

$$(\ln \gamma_i)^R = \left(1 - \ln \sum_{j=1}^n \theta_j \tau_{ji} \right) - q_i \sum_{j=1}^n \left[\frac{\phi_j \tau_{ij}}{\sum_{k=1}^n \theta_k \tau_{kj}} \right] \quad (4)$$

$$l_j = \frac{Z}{2} (r_i - q_i) - (r_i - 1), \quad Z = 10, \quad \tau_{ii} = \tau_{jj} = 1$$

$$\theta_i = \frac{q_i x_i}{\sum_{j=1}^n q_j x_j}, \quad \phi_i = \frac{r_i x_i}{\sum_{j=1}^n r_j x_j}, \quad \tau_{ji} = \exp \left(- \frac{U_{ji} - U_{ii}}{RT} \right)$$

$$r_i = \frac{V w_i}{15.17}, \quad q_i = \frac{A w_i}{2.5 \times 10^8}$$

In the above mentioned UNIQUAC expressions, q_i is area parameter of component “i”, r_i is volume parameter of component “i”, u_{ij} is parameter for interaction between components “i” and “j” ($u_{ij} = u_{ji}$), Z is coordinate number, is combinatorial part of activity coefficient of component i, is residual part of activity coefficient of component i, is area fraction of component i, and taken as volume fraction of component “i”. Table 19 lists the parameters calculated by UNIQUAC model.

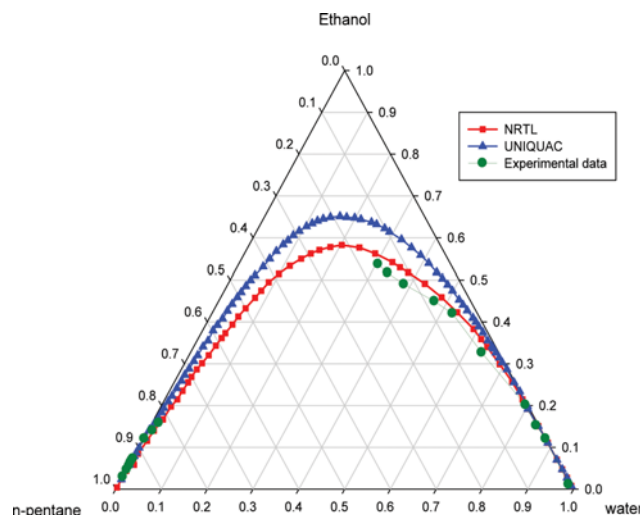


Fig. 7. Comparison of experimental LLE data to the data calculated by NRTL and UNIQUAC models.

4. Regression of Parameters

By utilizing experimental data, the binary interaction parameters of NRTL and UNIQUAC models were regressed and the calculated data was compared with experimental data. The system water, ethanol with entrainer n-pentane was regressed to find the reliability of experimental data. Fig. 7 shows a comparison of experimental data for n-pentane with NRTL and UNIQUAC models. It can be seen from the comparison that the experimental data for n-pentane correlates well with the liquid activity coefficient models. The expressions for objective function (OF) and root mean square deviation (RMSD) for parameter regression of LACT models are as follows:

$$OF = \min \sum_{k=1}^2 \sum_{j=1}^3 \sum_{i=1}^N [x_{j,k}^{exp}(i) - x_{j,k}^{cal}(i)]^2 \quad (5)$$

Table 19. Parameters calculated by NRTL, UNIQUAC (water (1)-ethanol (2)-entrainer (3))

Model			NRTL			UNIQUAC	
Entrainer	i	j	$B_{i,j}$	$B_{j,i}$	$\alpha_{i,j}$	$A_{i,j}$	$A_{j,i}$
Cyclohexane	Water	Ethanol	721.10	437.83	0.3	-48.54	-15.91
	Water	Cyclohexane	-60.00	660.00	0.2	540.36	1247.30
	Ethanol	Cyclohexane	1225.89	2807.80	0.3	-43.12	465.56
n-Pentane	Water	Ethanol	536.26	-456.02	0.3	-48.55	-15.92
	Water	n-Pentane	-613.31	4578.79	0.2	-345.58	3371.30
	Ethanol	n-Pentane	207.71	595.49	0.3	-56.72	472.06
Ether	Water	Ethanol	536.26	-456.02	0.3	-48.55	-15.19
	Water	Ether	-2457.34	1243.67	0.2	-666.72	1278.33
	Ethanol	Ether	35.83	384.29	0.3	-86.46	323.41
DIPE	Water	Ethanol	759.36	-76.24	0.3	-48.55	-15.92
	Water	DIPE	1542.40	461.95	0.2	86.67	602.34
	Ethanol	DIPE	149.63	351.29	0.3	-52.69	312.87
ETBE	Water	Ethanol	759.36	-76.24	0.3	-900.48	-15.91
	Water	ETBE	536.26	-456.02	0.2	3746.95	-8084.08
	Ethanol	ETBE	196.55	585.27	0.3	-183.54	515.01

Table 20. AAD (average absolute deviation) and RMSD (root mean square deviation) values for entrainers used

Entrainer		NRTL	UNIQUAC
Cyclohexane	AAD	0.0066	0.01
	RMSD	0.0050	0.009
n-Pentane	AAD	0.00071	0.0052
	RMSD	0.00038	0.0098
Ether	AAD	0.0023	0.044
	RMSD	0.0067	0.076
DIPE	AAD	0.0036	0.0084
	RMSD	0.0014	0.0041
ETBE	AAD	0.00045	0.17
	RMSD	0.00099	0.18

$$\text{RMSD} = 100 \times \sqrt{\frac{\sum_{k=1}^2 \sum_{j=1}^3 \sum_{i=1}^N [x_{j,k}^{\text{exp}}(i) - x_{j,k}^{\text{cal}}(i)]^2}{6N}} \quad (6)$$

Where x^{exp} =experimental mole fractions; x^{cal} =calculated mole fractions; and N=number of tie lines in data, while j and k are no. of components and phases, respectively. The binary interaction parameters for water-ethanol-entrainer system are given in Table 19.

The predicted LLE data was compared and contrasted with experimental data and the results show that the predicted values correlate well with the experimental LLE data. Water ethanol system, having n-pentane as an entrainer, was used as an example to compare the results. Fig. 7 shows phase equilibrium of experimental LLE data and predicted LLE data for using NRTL and UNIQUAC models, which depicts that the predicted data does not show significant deviations from the data found experimentally. The point to ponder is that the NRTL model comes out as the best model in correlation as it has less deviation than the UNIQUAC model. The results for average absolute deviation and root mean square deviation are shown in Table 20. Hence, NRTL model is recommended for the prediction of LLE data for water-ethanol-entrainer systems and n-pentane comes out as the most promising entrainer by comparing the results with other used entrainers.

CONCLUSION

Ternary LLE data of ethanol system was developed with the help of experimental procedure. The experimental data was correlated with the liquid activity coefficient models and the results show its perfect correlation with NRTL and UNIQUAC models. The comparison between NRTL and UNIQUAC models shows that NRTL is better than UNIQUAC for the prediction of LLE data. In this water ethanol system, it has been concluded that n-pentane is an effective entrainer for separation of ethanol from water, as it shows root mean square deviation of 0.00038 with NRTL model.

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NOMENCLATURE

$(x_{1j}, x_{2j}, x_{3j}, x_{12}, x_{22}, x_{32})=x_{ij}$: composition of component i in j phase while j being water in aqueous phase and entrainer in organic phase

i, j : component numbers

$\alpha_{i,j}, A_{i,j}, B_{i,j}, B_{i,j}$: binary interaction parameters

RMSD : root mean square deviation

AAD : average absolute deviation

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