Equilibrium Data on Water-Ethanol-1-Dodecanol Ternary System[*]

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Abstract

The experimental liquid-liquid equilibria of a water-ethanol-1-dodecanol system were investigated at temperatures of 298.16±0.20, 303.16±0.20 and 308.16±0.20 K. The reliability of experimental tie-line data was ascertained by using Othmer-Tobias and Hand plots. Distribution coefficients (D_i) and separation factors (S) were evaluated for the immiscibility region. It was concluded that the high boiling solvent 1-dodecanol, is a possible separating agent for dilute aqueous ethyl alcohol solutions.

Key Words: ethanol, 1-dodecanol, liquid-liquid extraction

Su-Etanol-1-Dodekanol Üçlü Sisteminin Denge Verileri

Özet

Su-etanol-1-dodekanol sıvı-sıvı denge verileri deneysel olarak 298.16±0.20, 303.16±0.20 ve 308.16±0.20 K sıcaklıklarında incelenmiştir. Deneysel olarak elde edilen bağlantı doğrularının (tie-line) doğruluğu Othmer-Tobias ve Hand çizimleri ile test edilmiştir. Dağılım katsayısı (D_i) ve ayırma faktörü (S) çözünmezlik bölgesinde incelenmiştir. Yüksek kaynama noktalı 1-dodekanolün, etil alkolün sulu çözeltilerinden ayrılmasında uygun çözücü olarak kullanılabileceği sonucuna varılmıştır.

Anahtar Sözcükler: etanol, 1-dodekanol, sıvı-sıvı ekstraksiyonu

Introduction

Ethanol has been used as a fuel in motor vehicles for over 60 years in many places in the world, usually in blends with gasoline or other petroleum products. For alcoholic fermentation, the major limitation of the conventional processes comes from ethanol inhibition. When the ethanol concentration of the fermentation broth approaches 12% (V/V), both specific growth and specific production rates decrease; the cell density in the fermentor remains low, and the concentrated sugar solutions cannot be completely fermented. Conventional processes produce dilute aqueous ethanol due to end-product inhibition (Miner and Goma, 1985; Zhang and Hill, 1991). In order to concentrate the ethanol, traditional distillation processes are frequently used, but these processes are very energy intensive.

Some researchers have described the use of liquid-liquid extraction to selectively remove ethanol from water (Sola et al., 1986; Miner and Goma, 1985; Dadgar and Foutch, 1985). The availability of the relevant liquid-liquid equilibrium data (LLE) is nec-

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essary both for the design and for the simulation of the extraction processes (Arce et al., 1984; Arenson et al., 1990). The critical question in the development of a solvent extraction process is the selection of the solvent. The variables most generally considered for the process are: (i) physical properties (density difference between liquid phases and boiling point etc.), (ii) chemical properties (distribution coefficient, selectivity and flammability, etc.) and (iii) availability and cost (Kollerup and Daugulis, 1985; Kollerup and Daugulis, 1986; Jassal et al. 1994).

This study is part of a research program on the recovery of ethanol from dilute aqueous solutions using solvents with high boiling points. In this paper, to be able to evaluate 1-dodecanol as an agent for the extraction of ethanol from dilute aqueous solutions, we reported liquid-liquid equilibrium results at temperatures of 298.16±0.20, 303.16±0.20 and 308.16±0.20 K for the ternary system water-ethanol-1-dodecanol, for which no such data have previously been published.

Experimental

Materials

Ethanol and 1-dodecanol were purchased from Merck with purities of 99.5 % (W/W) and 99 % (W/W), respectively. Ethanol and 1-dodecanol were used without further purification. Water was deionised, distilled once with alkaline potassium permanganate and twice distilled by itself.

Procedure

Tie-line data were obtained by preparing ternary mixtures (water-ethanol-1-dodecanol) of known overall compositions lying within the two-phase region and after being stirred vigorously and allowed to reach equilibrium in isothermal conditions. The stirrer speed was set at 800 rpm. It was found that the suitable stirrer time was about an hour to reach equilibrium. After the stirrer was turned off, the contents were immediately allowed to enter the vertical settler also equipped with an isothermal jacket; after the complete separation of the phases, a suitable amount of each layer was removed for analysis. Temperature was controlled using a thermostat (Nuve) with a precision of 0.02 K. All mixtures were prepared by weighing with a Mettler scale accurate to within 0.00001 g.

The composition of each phase was determined by gas chromatography (HP, 6890 Series). The col-

umn was an HP-innowax (polyethylene glycol), 30 m x 320 μm x 0.5 μm film thickness. Two detectors, a thermal conductivity detector (TCD) and a flame ionization detector (FID), were installed in series for the determination of ethanol, water and 1-dodecanol concentrations. The injector and detector were set at 230 °C and the oven temperature was set isothermally at 250 °C. Nitrogen, at a flow rate of 0.8 mL/min, was used as carrier gas. Concentrations were determined by comparing 0.5 μL (split ratio: 10/1) injections with a calibration curve for each component. The errors due to gas chromatography were estimated to be less than 0.4 %.

Results and Discussion

The experimental tie-line data of water-ethanol-1-dodecanol ternaries at 298.16±0.20, 303.16±0.20 and 308.16±0.20 K, are given in Tables 2, 3 and 4 respectively. The tie-lines at each temperature were plotted and shown in Figures 1, 2 and 3, respectively. Distribution coefficients, D_i, for ethanol ($i = 2$) and water ($i = 1$) and separation factors, S, were determined as follows:

$$D_i = W_{i3}/W_{i1} \qquad (1)$$
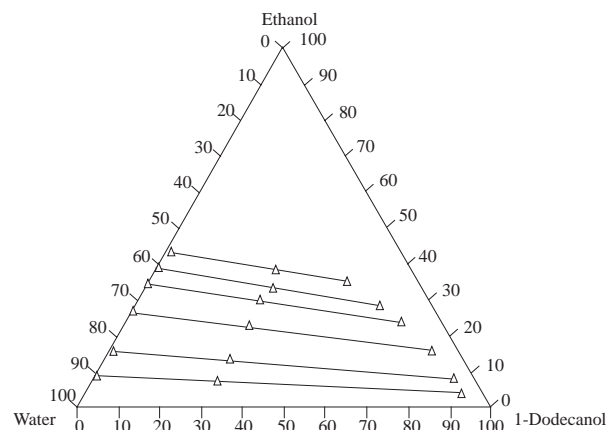
$$S = D_2/D_1 \qquad (2)$$

Figure 1. Liquid-Liquid Equilibrium Data for Water-Ethanol-1-Dodecanol Ternary at 298.16 K.

W_{i3} and W_{i1} are the weight fractions in the solvent and aqueous phases, respectively. The distribution coefficients and separation factors for each temperature are given in Tables 4, 5 and 6. The reproducibility of the tie-line data was checked by running many duplicate experiments. The maximum deviation for any data point was 1% of its absolute value.
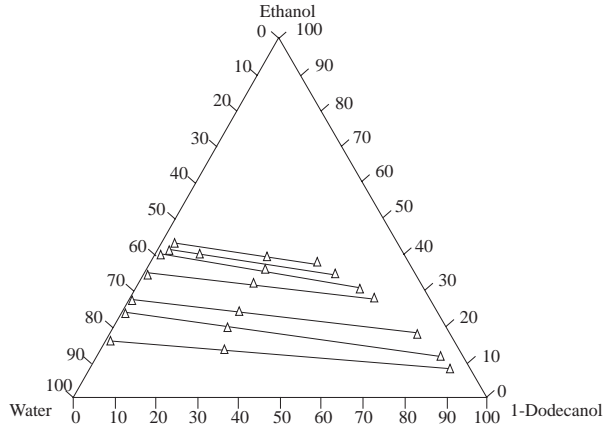
Figure 2. Liquid-Liquid Equilibrium Data for Water-Ethanol-1-Dodecanol Ternary at 303.16 K.
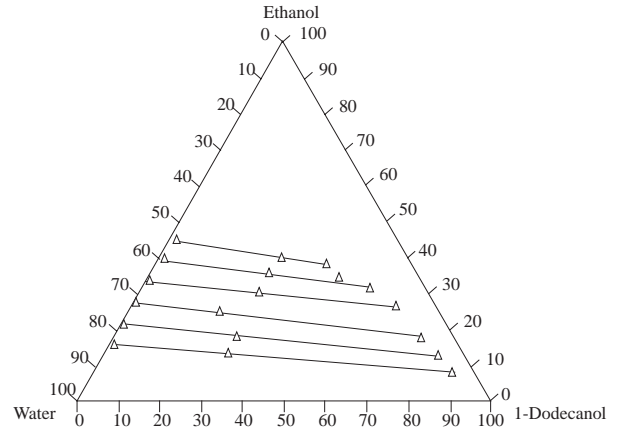

Figure 3. Liquid-Liquid Equilibrium Data for Water-Ethanol-1-Dodecanol Ternary at 308.16 K.

Table 1. Tie-Line Values of Water (1)-Ethanol (2)-1-Dodecanol (3) at 298.16 K.

water-rich phase			solvent-rich phase		
water	ethanol	1-dodecanol	water	ethanol	1-dodecanol
73.27	26.63	0.10	6.31	15.89	77.80
65.50	34.40	0.10	9.59	23.97	66.44
90.80	9.02	0.18	5.16	3.92	90.92
60.71	38.95	0.34	12.35	28.75	58.90
83.46	15.74	0.80	4.77	8.21	87.02
55.66	43.01	1.33	17.15	35.22	47.63

Table 2. Tie-Line Values for Water (1)-Ethanol (2)-1-Dodecanol (3) at 303.16 K.

water-rich phase			solvent-rich phase		
water	ethanol	1-dodecanol	water	ethanol	1-dodecanol
55.30	42.30	2.40	22.28	37.35	40.37
56.37	41.47	2.16	19.82	34.67	45.51
58.75	40.13	1.12	15.01	30.72	54.27
64.66	34.46	0.88	14.16	27.62	58.22
72.03	26.97	1.00	7.63	17.85	74.52
83.00	16.00	1.00	4.88	7.90	87.22

Table 3. Tie-Line Values for Water (1)-Ethanol (2)-1-Dodecanol (3) at 308.16 K.

water-rich phase			solvent-rich phase		
water	ethanol	1-dodecanol	water	ethanol	1-dodecanol
66.76	32.59	0.65	9.98	26.38	63.64
72.87	26.36	0.77	6.81	17.43	75.76
60.16	38.33	1.51	13.85	31.17	54.98
83.62	14.58	1.80	5.32	8.58	86.10
77.42	20.58	2.00	6.26	12.33	81.41
54.04	43.72	2.24	21.03	37.29	41.68

Table 4. Distribution Coefficients Di of Water (1)-Ethanol (2) and Separation Factors, S=D2/D1 at 298.16 K.

D_2	D_1	S
0.5967	0.0861	6.93
0.6968	0.1464	4.76
0.4346	0.0568	7.65
0.7381	0.2034	3.63
0.5216	0.0571	9.13
0.8189	0.3081	2.66

Table 5. Distribution Coefficients, D_i, of Water (1), Ethanol (2) and Separation Factors, S= D_2/D_1, with 1-Dodecanol as Solvent, at 303.16±0.20 K.

D_2	D_1	S
0.8658	0.3964	2.1841
0.8360	0.3515	2.3784
0.7651	0.2554	2.9957
0.8015	0.2190	3.6598
0.6618	0.1058	6.2552
0.4937	0.0588	8.3963

Othmer-Tobias Correlation Method and Hand Correlation Method: The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer-Tobias and Hand equations (Solimo et al, 1997). The Othmer-Tobias correlation and Hand correlation equations are given as Equation (3) and Equation (4), respectively.

$$ln(\frac{1-W_{33}}{W_{33}}) = a_1 + b_1 ln(\frac{1-W_{11}}{W_{11}}) \qquad (3)$$

$$ln(\frac{W_{23}}{W_{33}}) = a_2 + b_2 ln(\frac{W_{21}}{W_{11}}) \qquad (4)$$

The plot of Othmer-Tobias correlation was made of the ln((1-W_{33})/W_{33}) vs. ln((1-W_{11})/W_{11}) to determine a and b coefficients. Similarly, the plot of the Hand Correlation was made of the ln ((W_{23}/W_{33}) vs. ln (W_{21}/W_{11}) to determine a and b coefficients. Firstly, we applied Othmer-Tobias and Hand methods to the ternary system. The values of the parameters a and b, and correlation coefficient (R^2) are given in Table 7. The proximity of the correlation coefficient (R^2) to 1 indicates the degree of consistency of the related data. The two-phase region was slightly affected by increasing temperature.

Table 6. Distribution Coefficients D_i of Water (1)-Ethanol (2) and Separation Factors, S=D_2/D_1 at 308.16 K.

D_2	D_1	S
0.8094	0.1495	5.41
0.6612	0.0934	7.08
0.8132	0.2302	3.53
0.5885	0.0636	9.25
0.5991	0.0808	7.41
0.8529	0.3891	2.19

Table 7. The Coefficients of Othmer-Tobias and Hand Equations Obtained Using Least Square Method

T/K	298.16			303.16			308.16		
Coefficients	a	b	R^2	a	b	R^2	a	b	R^2
Othmer-Tobias	-0.1472	0.8327	0.9587	0.5945	1.6284	0.9745	-0.3216	0.6564	0.9809
Hand	0.0646	0.7362	0.9922	0.2104	1.6058	0.9856	-0.0923	0.6804	0.9883

It was concluded that the solvent with a high boiling point (1-dodecanol) is a possible separating agent for dilute aqueous ethanol solutions.

Acknowledgement

Nomenclature

a_1	:	Othmer-Tobias equation constant
a_2	:	Hand equation constant
b_1	:	Othmer-Tobias equation slope constant
b_2	:	Hand equation slope constant
D_i	:	distribution coefficient of the ith component.

i	:	Component number of water(1), ethanol(2) and solvent (1-dodecanol)(3)
S	:	separation factor.
W_i	:	mass fraction of the i th component
W_{11}	:	mass fraction of water (1) in the aqueous phase
W_{21}	:	mass fraction of ethanol (2) in the aqueous phase

W_{31}	:	mass fraction of solvent (3) in the aqueous phase
W_{13}	:	mass fraction of water (1) in the solvent-rich phase
W_{23}	:	mass fraction of ethanol (2) in the solvent-rich phase
W_{33}	:	mass fraction of solvent (3) in the solvent-rich phase

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