Liquid-liquid extraction of Methanol from aqueous solutions using n-Hexane and Toluene as solvents.

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Abstract

The present work deals with the use of toluene and n-hexane as solvents for the liquid-liquid extraction of methanol at ambient temperature and atmospheric pressure. Data for the binodal curves have been determined by cloud-point titration method and conjugate points on tie-line were obtained by correlating the refractive index of the binodal curves as a function of composition. The distribution coefficient and the selectivity factor of the solvents used were calculated and plotted for the extraction effectiveness of these last. The results obtained show that toluene solvent has a higher selectivity factor than the n-hexane solvent for the extraction of methanol from aqueous solutions.

Keywords: *n-Hexane, liquid-liquid extraction, methanol, selectivity factor, toluene.*

I.   Introduction

A fundamental operation in chemical engineering, liquid-liquid extraction is today the separation process most used in the industrial field [1]. This method of separation has two main fields of application: the large organic chemical industry on the one hand, hydrometallurgy and the nuclear industry on the other. Liquid-liquid extraction is also widely used to separate compounds with close boiling point and azeotropes [2].   Currently a number of researches have reported the application of liquid-liquid extraction in the recovery and removal of alcohols [3, 4]. Liquid–liquid extraction, sometimes also called solvent extraction, is an important alternative to distillation for the separation and the recovery of alcohols from aqueous solutions. The choice of solvent is important in liquid –liquid extraction. The following factors need to be considered when selecting a suitable solvent for a given extraction:

i- a high affinity for solute: alcohol, over water, which is a measure of selectivity factor, *ii-* a high partition ratio or coefficient for solute , This determines the quantity of solvent needed, *iii-* ideally solvent should be immiscible,   low solubility with water.

The focus of the present work is to study   the experimental data on the phase equilibria of water + methanol with one of two solvents: n-hexane and toluene. Partition coefficients, n-hexane and toluene selectivity's were calculated from the experimental tie-lines data.

II.   Material and Methods

A. Chemicals

Methanol, n-Hexane and toluene were of analytical grades (Biochem, Panreac). With a purity of 99.5%, 95% and 99.8%, respectively. The refractive indices (n_D) of pure components available in the literature

in [5,6,7]and measured at T = 293.15K, were shown in Table 1.

Table 1. Refractive indices (n_D) of the used components.

Component	Measured refractive index	Literature refractive index
Methanol	1.3331	1.3290
n-hexane	1.3331	1.3290
Toluene	1.4970	1.4960

B. Liquid–liquid extraction experiments

The solubility isotherm (binodal curve) was determined, at 298.15 K and atmospheric pressure, by the cloud point method [5, 6]. A known volume, homogeneous and transparent binary mixtures (methanol + water), was prepared in glass beakers and at room temperature. The mixtures are stirred by a Selecta type magnetic stirrer with medium speed. Solvent was then gradually added to the mixture using a pipette until the appearance of a cloudiness indicated by the turbidity of the mixture, the poured volume of the solvent is noted. The refractive index (n_D) of the new mixtures is measured using a refractometer type *HI 96801 ± 0.2 Bix*.

The compositions of the binodal curves were plotted against the refractive index (n_D) and were used as calibration curves to determine the compositions of the tie lines (conodals).

The determination of the tie-line data was obtained by preparing a series of ternary mixtures (diluent + solute + solvent) for the two systems studied at room temperature. Each mixture is vigorously stirred with a magnetic stirrer for 2 hours to allow intimate contact between the phases, and then introduced into a separator funnel for 24 hours [5]. After complete separation of the phases, by decantation, an appropriate amount of each phase (extract and raffinate) was taken for analysis by refractometry. The compositions of each component were determined from the calibration curves.
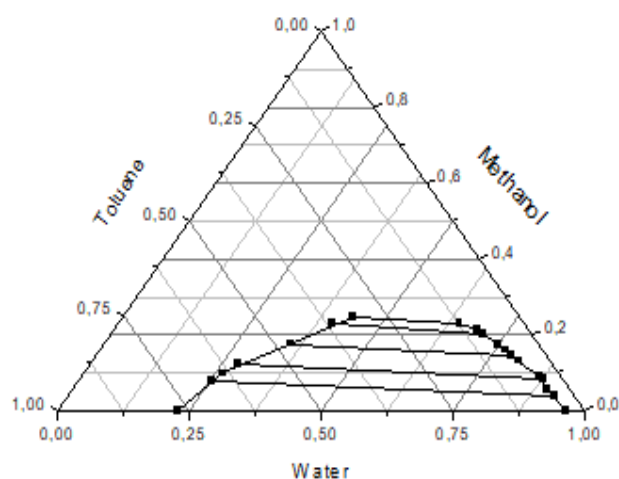
III.   Results and discussion

A. Liquid-liquid extraction results

The experimental results of the ternary systems water/methanol/n-hexane, water/methanol/toluene are shown in Figures 1 and 2.
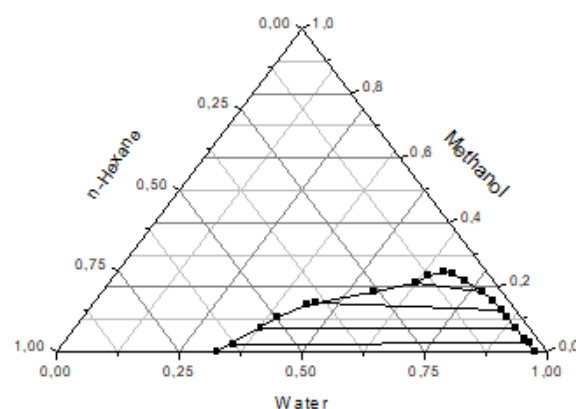
Figure 1. Solubility curve and tie lines data for water/methanol/n-hexane

Figure 2. Solubility curve and tie lines data for Water/Methanol/Toluene

Figures 1 and 2 show clearly that the two curves behave a type I according to Treybal classification [8], since (methanol - water and methanol - solvent) are two liquid pairs which are completely miscible and the only liquid pair (water - organic solvent : n-hexane, toluene) is partially miscible.

The slopes of the equilibrium lines obtained show that at the beginning the methanol is almost of the same order of solubility in water and in n-hexane, the tie lines are aligned, this may be due to the existing of intermolecular forces by hydrogen bonds [9]. Then they are emerged a little on the methanol-n-hexane side. Also methanol is more soluble in toluene than in water, this is clearly confirmed by the tie lines which are more emerged on the methanol-toluene side and approximated on the methanol-water side.

B. Partition coefficient and selectivity factor

The partition coefficient and the selectivity factor are two important criteria for evaluating the effectiveness of the solvent used. The partition coefficient refers to the solvent dosage, and selectivity factor is relative to the product purity. A solvent with higher values of these last is more suitable for an extraction system [2].

The partition coefficient and the selectivity, separation, factor are calculated respectively as follows [5]:

$$D_i = \frac{x_{i3}}{x_{i1}} \qquad (1)$$

$$S = \frac{D_{Methanol}}{D_{water}} = \frac{D_1}{D_2} \qquad (2)$$

D_1 (x_{13}/x_{11}) and D_2 (x_{23}/x_{21}) are the partition coefficients of methanol and water respectively. x_{13}, x_{23} are the molar fractions of methanol and water in the organic rich phase (extract). x_{11}, x_{21} are the molar fractions of methanol and water in the aqueous phase (raffinate). S is the selectivity factor. The partition coefficients and selectivity factors for each system are summarized in Table 2.

Table 2. Experimental partition coefficients and selectivity factors

Water/methanol/n-hexane		
D_1	D_2	S
0.9248	0.3643	2.5387
1.0344	0.4207	2.4586
1.1726	0.5365	2.1857
1.1629	0.8044	1.4456
Water/methanol/toluene		
2.0114	0.2746	7.3252
1.4277	0.3205	4.4538
1.1891	0.4483	2.6526
1.1375	0.5758	1.9754

According to Table 2, in all cases the calculated values of S are greater than the unity which means that the two selected solvents are effective for the extraction of methanol from aqueous solution. It can be also concluded that methanol has a greater affinity for toluene compared with n- hexane.

The distribution curve plotted in rectangular coordinates and represents the variation of the solute composition in the extract as a function of the solute composition in the raffinate, as shown in
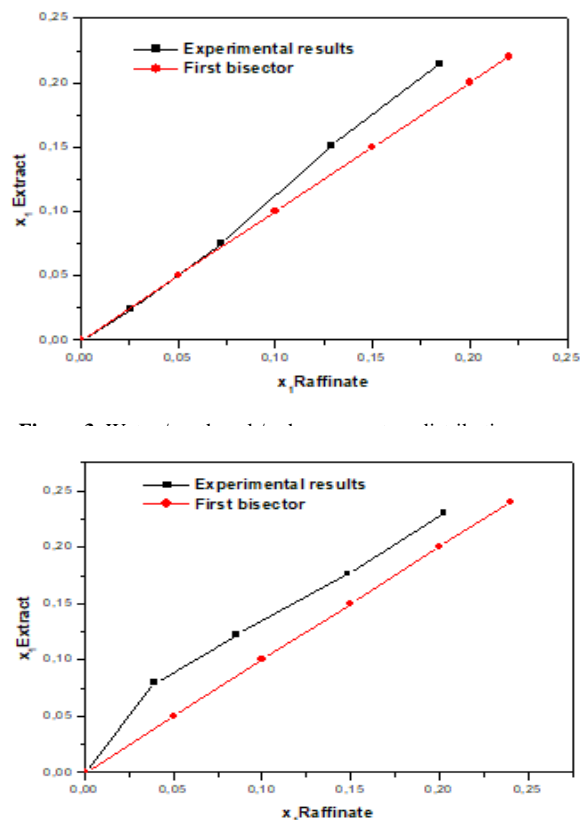
Figure 4. Water / methanol / toluene system distribution curve

For the case of a water / methanol / n-hexane system (Figure 3) we note that, between $0.0239 \leq x_1$ raffinate <0.0295 the distribution curve is located slightly below the first bisector, meaning that methanol is slightly more soluble in water (raffinate) than in n-hexane (extract) [5]. Then we notice the presence of a point that intercepts the bisector: x_1 raffinate $= 0.0295$ meaning the presence of a solutropy (x_1Extract $= x_1$Raffinate). After this value the curve is reversed, indicating a migration of the solute to the extract phase and improved methanol extraction, this is clearly confirmed by the slopes of the tie lines.

For the water / methanol / toluene system the distribution curve is above the bisector indicating that toluene is a good solvent for the extraction of methanol (methanol is concentrated in the extract phase).

The selectivity diagram on a solvent-free basis is obtained by plotting the content of solute,

methanol, in the extract as a function of that in the raffinate for each solvent, which estimates the ability of a solvent to extract solute better than another solvent.
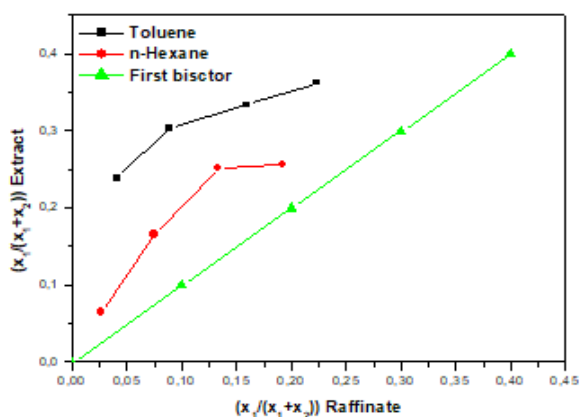

Figure 5. Comparative selectivity diagram of two studied systems

Figure 5, shows clearly that the black curve representative of the variation of the methanol content in the extract using toluene as solvent, is further from the first bisector than that using n-hexane as solvent, thus indicating that the amount of methanol in the toluene-rich phase is greater than that rich in n-hexane, this is clearly confirmed by the selectivity factor values of the toluene which are the highest values, meaning that toluene is a preferable solvent and it is more selective to methanol than n-hexane.

IV. Conclusion

Liquid -liquid extraction of methanol from aqueous solution was studied at atmospheric pressure and ambient temperature. The results of this study show that the solubility curves for the two studied systems: (water / methanol / n-hexane) and (water / methanol / toluene) behave a type I, where one of the binary mixtures has a miscibility gap. The slopes of the tie lines obtained show that methanol was almost of the same order of solubility in water and in n-hexane, and it was more soluble in toluene than in water. The selectivity factor and partition coefficient for the used solvents were calculated and compared. The experimental results indicate that toluene was the preferred or the best solvent for the extraction of methanol from its aqueous solution, as well as the selectivity curves which were determined to guide the choice of solvent.

List of symbols:

D_i: partition coefficient of constituent i

D_1: partition coefficient of methanol

D_2: partition coefficient of water

x_{13}: molar fraction of methanol in the organic rich phase

x_{23}: molar fraction of water in the organic rich phase

x_{11}: molar fraction of methanol in the aqueous phase

x_{21}: molar fraction of water in the aqueous phase

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