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LIQUID-LIQUID EQUILIBRIA OF THE WATER+ETHANOL+DIMETHYL ADIPATE TERNARY SYSTEM

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ABSTRACT

Liquid-liquid equilibrium data for the ternary system water+ethanol+dimethyl adipate (dibasic ester) have been determined experimentally at 298.15±0.20, 308.15±0.20 and 318.15±0.20 K. Tie-line compositions were correlated by Othmer-Tobias method. The UNIFAC method was used to predict the phase equilibrium in the system using the interaction parameters determined from experimental data between the CH_3, CH_2, *OH*, CH_3COO *and* H_2O *groups. Distribution coefficients and separation factors were evaluated for the immiscibility region.*

KEYWORDS: ethanol, dimethyl adipate, liquid-liquid extraction, ternary systems

RESUMO

Dados experimentais de equilíbrio foram determinados experimentalmente para o sistema ternário água-etanol -dimetiladipato a 298.15 , 308.15 e 318.15 K . As composições das linhas de união foram correladas com o método de Othmer-Tobias. O método UNIFAC foi usado para predizer equilíbrio entre fases para o sistema, usando parâmetros de interação determinados experimentalmente de dados considerando os grupos CH_3, CH_2, *OH,* CH_3COO *e* H_2O. *Coeficientes de distribuição e fatores de separação foram avaliados na região de imiscibilidade.*

INTRODUCTION

In the scope of investigating more benign solvents as potential replacements for chlorocarbons or aromatic hydrocarbons and as new solvents for separations, we have concentrated on the dibasic esters (dimethyl adipate, dimethyl glutarate, dimethyl succinate and mixture these three esters) which have excellent properties for industrial applications. They are powerful solvents, and as such they are already widely used in the paint, coating, and polymer industry and as industrial cleaners. They have low toxicity, great stability, rather high boiling points (463-573 K), and viscosity and density that are close to those of water. The dibasic esters also be used as novel solvents in separation techniques[1].

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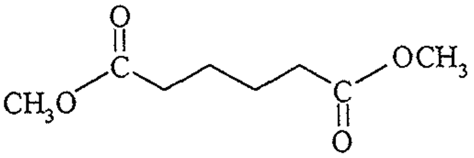
Dimethyl adipate is a colourless liquid, produced from adipic acid esterification. Its formulae is as follows:



dimethyl adipate

The properties of dimethyl adipate are excellent solvency, high boiling point, high flash point, low miscibility with water (beneficial for waste water treatment), high miscibility with organic solvents (safe diluent for classified solvents) and readily biodegradable. Dimethyl adipate is used in paint, lacquers, varnishes, in plasticizers for cellulose type resins, and in paint strippers. It is offer as an alternative to hazardous solvents[2].

In order to separate the ethanol from fermentation product, traditional distillation processes are frequently used, but these processes are very energy intensive. On the other hand, liquid-liquid extraction is a technique known to separate the ethanol from water mixtures and it is an alternative to distillation. In addition, liquid-liquid extraction allows to obtain high-standard ethanol. This also lowers the energy cost of the process in comparison to distillation[3-10].

The real behaviour of fluid mixtures can be calculated with the help of activity coefficients. The correct description of the dependence on temperature, pressure and composition in multicomponent systems requires reliable thermodynamic models, which allow the calculation of these properties from available experimental data[3,6]. The UNIFAC method (UNIFAC Functional Group Activity Coefficient) was developed by Fredenslund et al.[11]. It is one of the best methods in the estimating activity coefficient that has been established to date. The UNIFAC method for estimation of activity coefficients is based on the concept that a liquid mixture may be considered a solution of structural units from which the molecules are formed rather than a solution of the molecules themselves. This type of procedure is known as group contribution method. It has the advantage of being able to form a very large number of molecules from a relatively small set of structural units. The structural units in the calculation method are called subgroups. The mole fractions, X_i^E and X_i^R of liquid-liquid equilibrium phase can be calculated using the following equations.

$$\gamma_i^E X_i^E = \gamma_i^R X_i^R \qquad (1)$$

In this study, the predicted interaction parameters between CH_3, CH_2, OH, CH_3COO and H_2O groups were used to estimate the activity coefficients by the UNIFAC method.

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 study, in order to evaluate dimethyl adipate as an agent for the extraction of ethanol from dilute aqueous solutions, we reported liquid-liquid equilibrium results at temperatures 298.15, 303.15 and 318.15 K for the ternary system water+ethanol+dimethyl adipate. Dependence on temperature was studied by evaluating distribution coefficients and separation factors for each case.

EXPERIMENTAL PROCEDURE

Materials. Ethanol and dimethyl adipate were purchased from Merck Co. with purities of 99.98 % (W/W) and 99 % (W/W). Ethanol and dimethyl adipate were used without further purification. Deionized water was further distilled before use. The measured physical properties are listed in Table I, along with literature values[12].

Table I. Densities (d), refractive indices (n_D) and boiling points (B.P.) of the pure compounds.

	d (298.15 K) g.cm^{-3}		n_D (298.15 K)		B.P. (101.325 kPa/K)	
Compound	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
Water	1.0000	0.99704	1.3324	1.3325	373.18	373.21
Ethanol	0.7851	0.78493	1.3593	1.3594	351.16	351.17
Dimethyl adipate	1.0610	1.06301	1.4278	1.4285	505.23	505.15

Procedure. Three different temperatures were fixed to study the ternary equilibrium system in order to observe the evolution of the tie lines. At each temperature, (298.15±0.20, 308.15±0.20 and 318.15±0.20 K) tie-line data were obtained by preparing ternary mixtures (water+ethanol+dimethyl adipate) of known overall compositions lying within the two phase region after being stirred vigorously and allowed to reach equilibrium in the isothermal conditions at constant temperatures at the Figure 1.

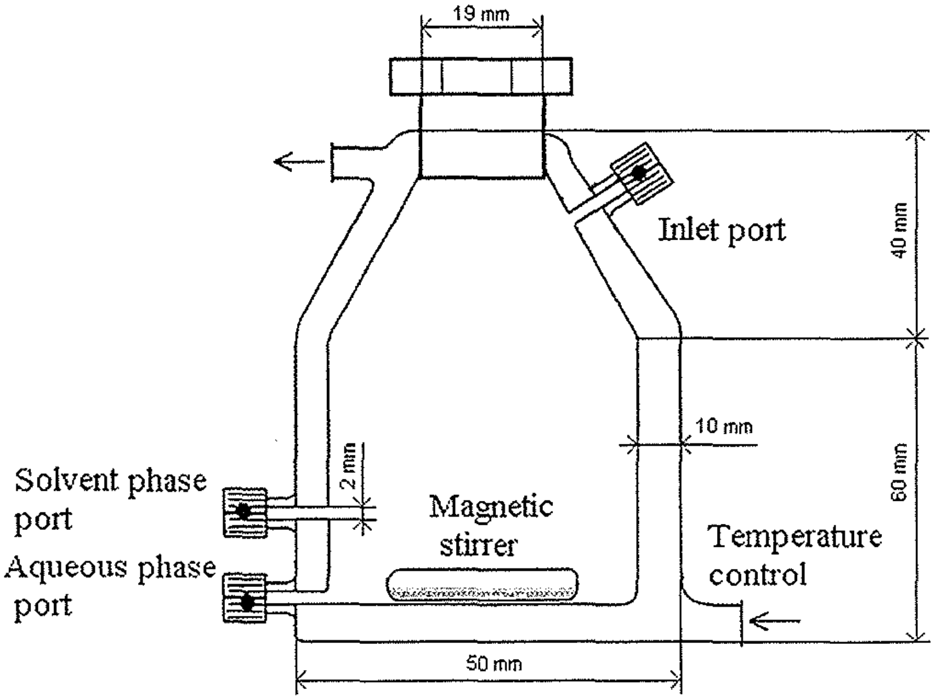


Figure 1. Liquid-liquid equilibrium cell.

The suitable stirring time for the attainment of equilibrium was 4 hours. 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 Proportional-Integral-Derivative (PID) controlled thermostat with a precision of 0.02 K. All mixtures were prepared by weighing with a Mettler balance with an accuracy of ± 0.0001 g.

Analysis. The liquid samples were analysed using a Gas Chromatograph (Hewlett Packard GC, Model 6890 Series), equipped with a Thermal Conductivity Detector (TCD) for the quantitative determination of water, ethanol and dimethyl adipate. A 15-m long HP-Plot Q column (320-micrometer diameter with a 20-micrometer film thickness) was used with a temperature programmed analysis. The oven temperature was fixed at 523.15 K. The detector temperature was kept 523.15 K, while injection-port temperature was held at 473.15 K. The flow rate of carrier gas, nitrogen was kept 6 mL/min. Samples of single phase with known compositions were used to calibrate the instrument in the composition range of interest.

RESULTS AND DISCUSSION

The experimental tie line data of water+ethanol+dimethyl adipate ternaries at temperatures 298.15, 303.15 and 318.15 K, are given in Table II.

It was found that dimethyl adipate was only slightly soluble in water but miscible with ethanol. The experimental and predicted tie-lines for the system at each temperature were plotted and shown in Figures 2-4.

Table II. Experimental Tie-Line Data of Water (1)+Ethanol (2)+Dimethyl adipate (3) at temperatures of 298.15, 308.15 and 318.15 K.

	water-rich phase (W/W, %)			solvent-rich phase (W/W, %)		
Temp. (K)	**water**	**ethanol**	**dimethyl adipate**	**water**	**ethanol**	**dimethyl adipate**
298.15	88.91	7.08	4.01	3.66	1.88	94.46
	86.21	9.42	4.37	4.22	2.66	93.12
	82.20	13.15	4.65	4.73	4.05	91.22
	78.48	16.15	5.37	6.37	5.81	87.82
	77.71	17.50	5.49	6.42	6.69	86.89
	73.66	19.65	6.69	7.78	8.63	83.59
308.15	88.96	7.11	3.83	3.96	2.11	93.93
	86.25	9.42	4.33	4.43	2.91	92.66
	82.81	12.87	4.32	5.02	4.32	90.66
	78.84	15.65	5.51	6.18	5.95	87.87
	75.99	17.81	6.20	7.28	7.46	85.26
	72.78	19.55	7.67	8.53	8.94	82.53
318.15	88.68	6.72	4.60	4.10	2.14	93.76
	86.73	9.05	4.22	4.30	3.11	92.59
	82.87	12.41	4.72	5.16	4.55	90.29
	79.60	15.51	4.89	6.19	6.11	87.70
	77.13	17.47	5.40	7.26	7.46	85.28
	74.22	19.32	6.46	8.85	9.05	82.10

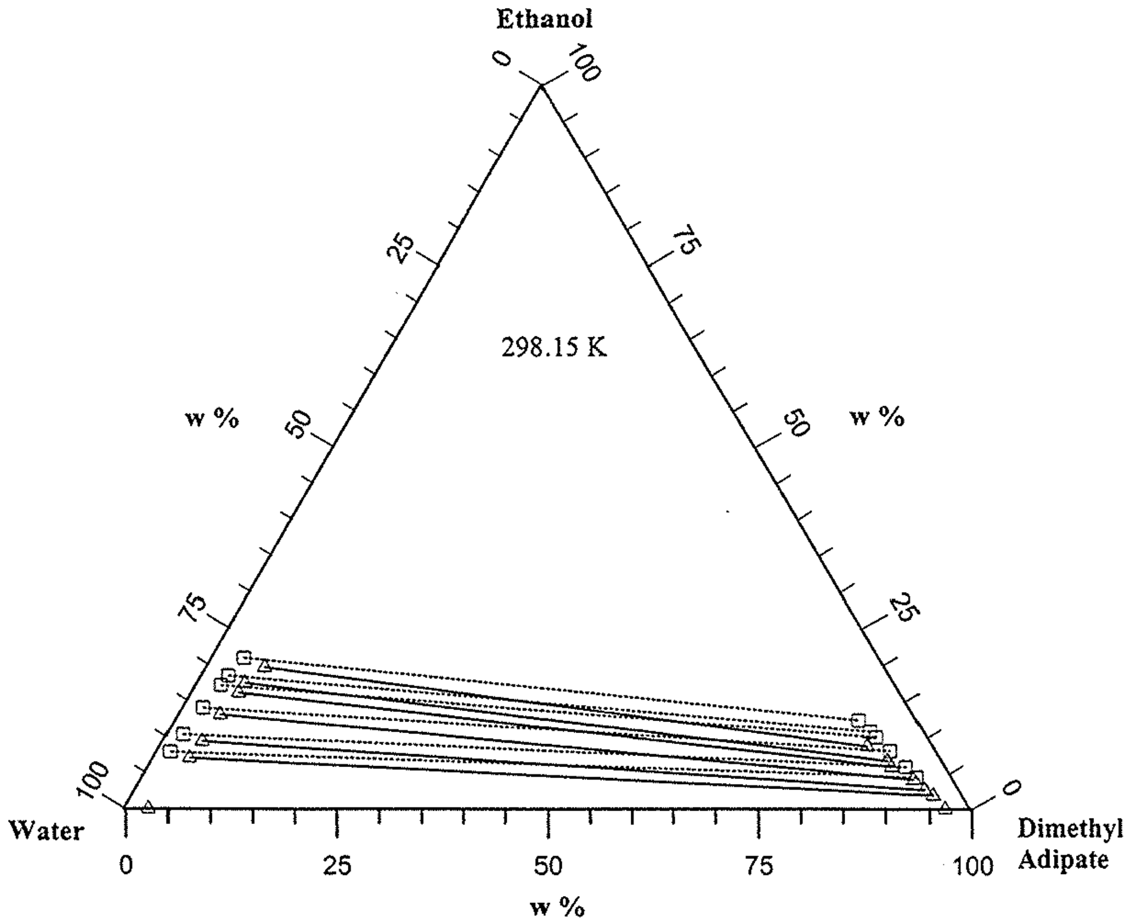


Figure 2. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 298.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

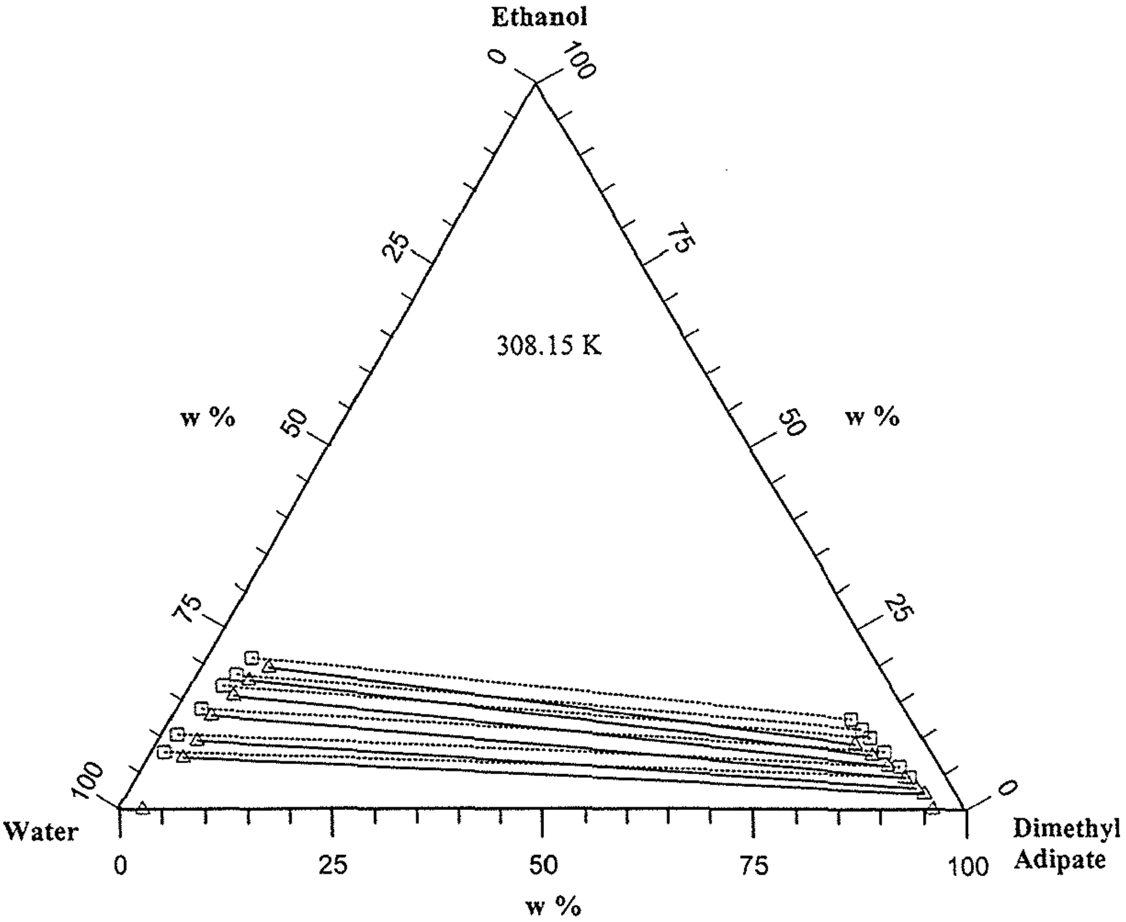


Figure 3. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 308.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

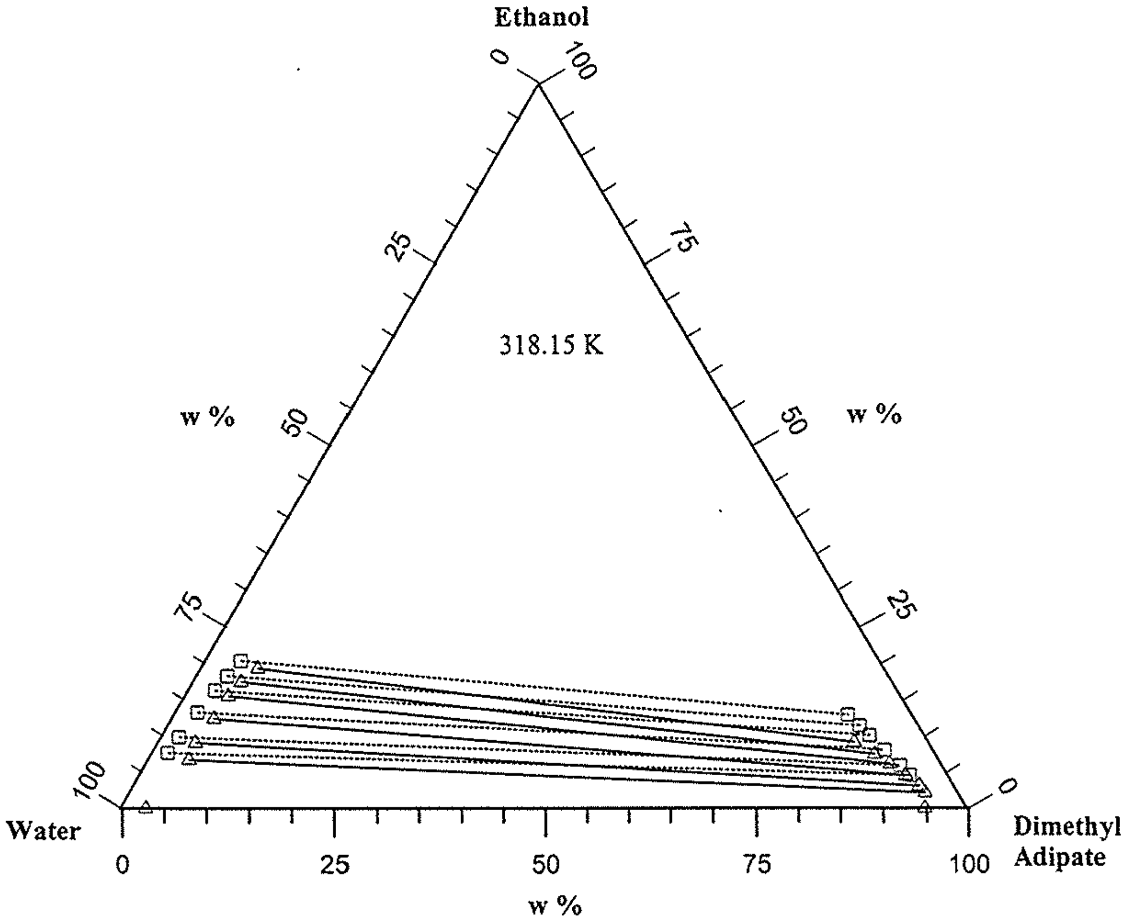


Figure 4. Ternary diagram for experimental LLE of water (1) + ethanol (2) + dimethyl adipate (3) at 318.15 K; –Δ– experimental tie-line data, --□-- calculated (UNIFAC) tie-line data.

Distribution coefficients, D_i, for ethanol (i=2) and water (i=1) and separation factors, S, were determined as follows:

$$D_i = \frac{\text{Weight fraction in solvent phase } (W_{i3})}{\text{Weight fraction in aqueous phase } (W_{i1})} \tag{2}$$

$$S = \frac{D_2}{D_1} \tag{3}$$

The distribution coefficient, D_2 of ethanol was calculated according to the Equation 2. The distribution coefficients and separation factors for the each temperature are given in Table III.

Table III. Distribution Coefficients, D_i of Water (1)-Ethanol (2) and Separation Factors at 298.15, 308.15 and 318.15 K.

Temperature, (K)	D_1	D_2	S
298.15	0.0412	0.2655	6.4505
	0.0490	0.2824	5.7687
	0.0575	0.3080	5.3523
	0.0812	0.3598	4.4322
	0.0834	0.3823	4.5856
308.15	0.0445	0.2968	6.6667
	0.0514	0.3089	6.0145
	0.0606	0.3357	5.5371
	0.0784	0.3802	4.8502
	0.0958	0.4189	4.3722
318.15	0.0462	0.3185	6.8879
	0.0496	0.3436	6.9313
	0.0623	0.3666	5.8883
	0.0778	0.3939	5.0658
	0.0941	0.4270	4.5366

The separation factor (S) is greater than unity for all temperatures reported. This means extraction of ethanol using dimethyl adipate is possible. Hovewer, it is not constant over the whole two-phase region. The extracting power of the solvent at each temperature, plots of D_2 *vs.* W_{21} and S *vs.* W_{21} are given in Figure 5 and 6, respectively.

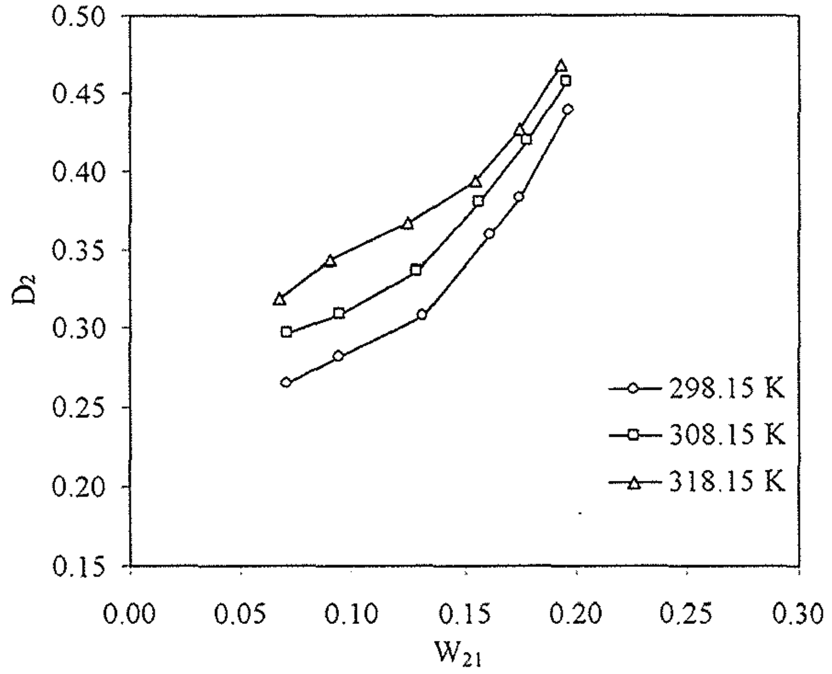


Figure 5. Distribution coefficient, D_2 of ethanol as a function of the mass fraction W_{21} of ethanol in aqueous phase.

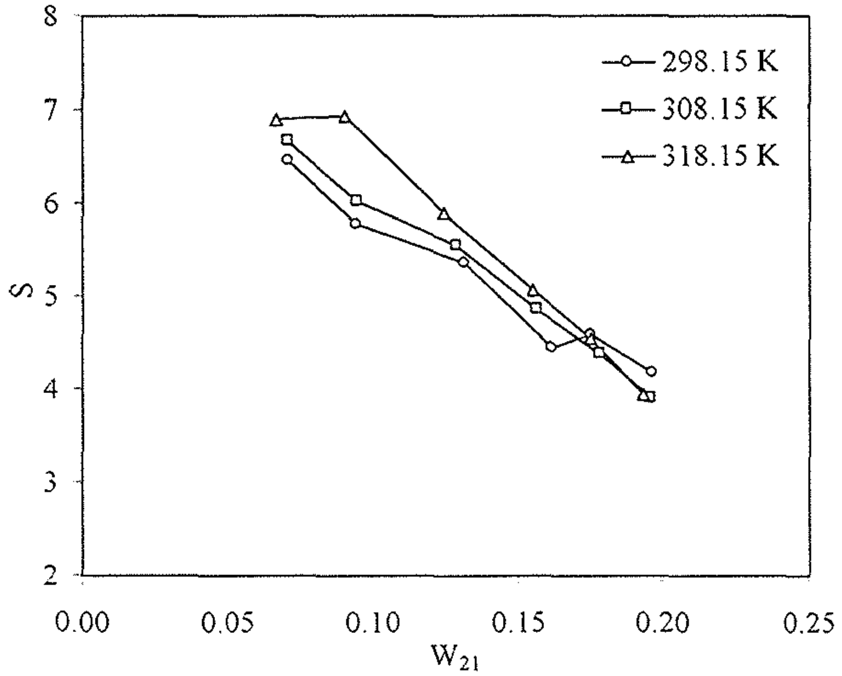


Figure 6. Separation factor, S as a function of the mass fraction W_{21} of ethanol in the aqueous phase.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer-Tobias correlation Equation 4 at each temperature[13].

$$\ln\left(\frac{1-W_{33}}{W_{33}}\right) = a + b\ln\left(\frac{1-W_{11}}{W_{11}}\right) \tag{4}$$

The linearity of the plot indicates the degree of consistency of the data. Othmer-Tobias plots were made of the $\ln((1-W_{33})/W_{33})$ *vs.* $\ln((1-W_{11})/W_{11})$. The parameters of the Othmer-Tobias correlation are in Table IV.

Table IV. Othmer-Tobias Equation Constants for Water + Ethanol + Dimethyl Adipate System.

Temperature, (K)	a	b	R^2
298.15	0.4137	0.8630	0.9880
308.15	0.4633	0.9135	0.9931
318.15	0.2736	0.8489	0.9928

Prediction of Equilibria by the UNIFAC Method. The equilibrium data of the ternary mixture were predicted by UNIFAC method[11] using the interaction parameters between CH_3, CH_2, OH, CH_3COO and H_2O obtained by Magnussen et al.[14]. UNIFAC parameters for LLE prediction are summarised in Table V.

Table V. UNIFAC group parameters for prediction tie lines data[14].

	CH_3	CH_2	OH	CH_3COO	H_2O	R_k	Q_k
CH_3	0	0	156.4	114.8	300	0.9011	0.848
CH_2	0	0	156.4	114.8	300	0.6744	0.54
OH	986.5	986.5	0	245.4	-229.1	1	1.2
CH_3COO	232.1	232.1	101.1	0	72.87	1.9031	1.728
H_2O	1318	1318	353.5	200.8	0	0.92	1.4

We observe, in Figures 2-4, how the UNIFAC method predicts the equilibrium data (dashed lines in Figures 2-4). The discrepancy between the experimental and predicted solubilities do not change with temperature because the predicted and experimental data are practically independent of temperature.

The temperature effect on the distribution coefficients was found to be slightly positive. The experimental and UNIFAC model predictions were fitted according to the following equation.

$$D_2 = A\exp(-E_A / RT) \tag{5}$$

The experimental and predicted UNIFAC values are shown in Figure 7.

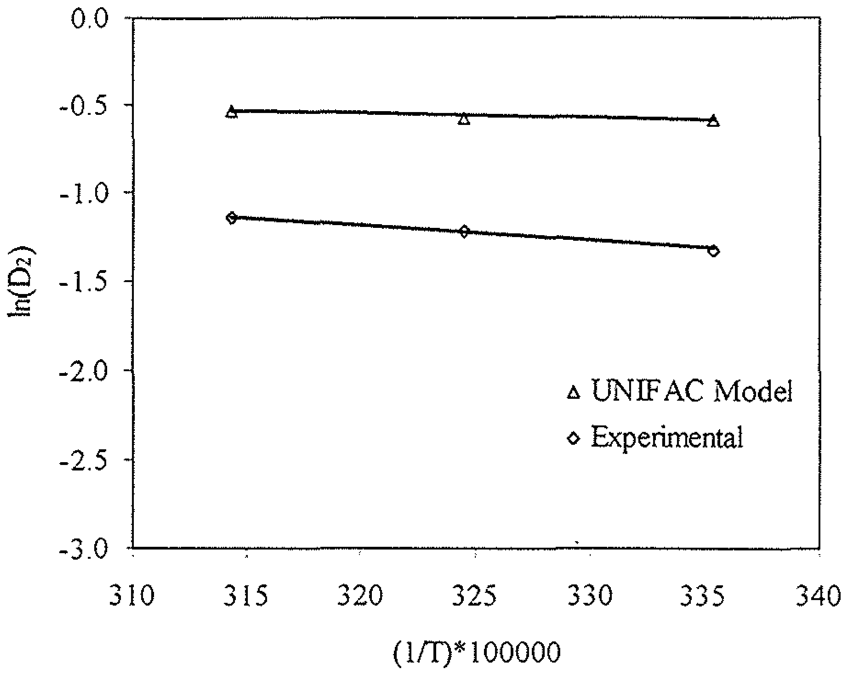


Figure 7. Temperature effect on the distribution coefficient, D_2 of ethanol.

The experimental activation energy (E_A) and the frequency factor (A) were found as -0.0715 J.mol^{-1} and 1.5763, respectively. The calculated (UNIFAC) activation energy (E_A) and the frequency factor (A) were found as -0.0216 J.mol^{-1} and 1.3306, respectively.

Selectivity. Selectivity diagrams on a solvent-free basis are obtained by plotting $W_{23}/(W_{23}+W_{13})$ *vs.* $W_{21}/(W_{21}+W_{11})$ for 298.15, 308.15 and 318.15 K in Figure 8. The effect of temperature change on the selectivity values was found to be insignificant.

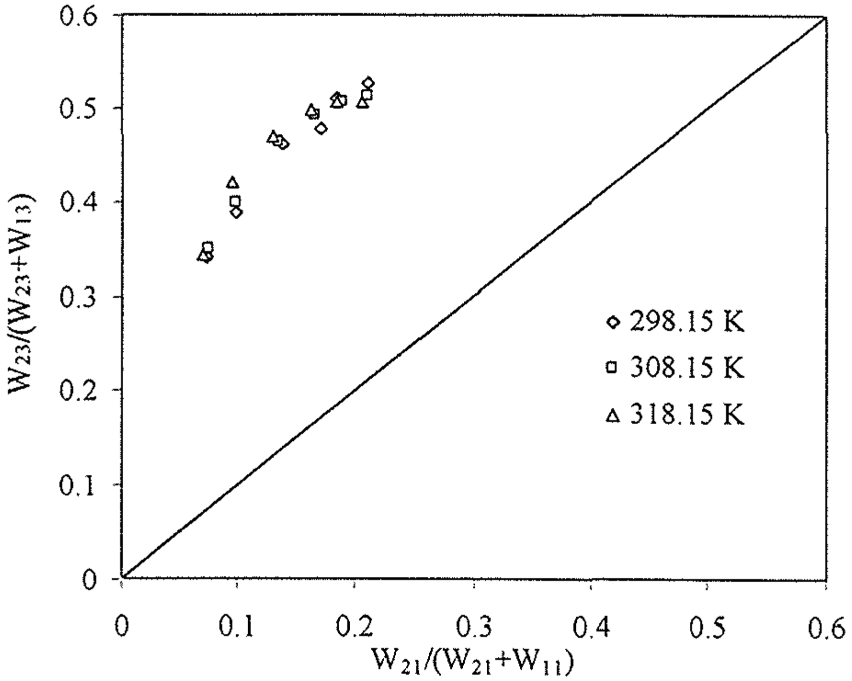


Figure 8. Selectivity diagram at investigated temperatures (free-solvent basis)

CONCLUSION

Dimethyl adipate was chosen on the basis of its suitability for industrial applications. It is concluded that because dimethyl adipate shows low solubility in water it may serve as an adequate solvent to extract ethanol from dilute aqueous solutions. The tie-lines in Figures 2-4 show, as was expected, that ethanol is more readily soluble in the water phase than in the dimethyl adipate phase. It was found the UNIFAC method predictions were satisfactory and agreed qualitatively with the experimental data.

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NOMENCLATURE

A	: frequency factor, Equation 6
d	: density, (g.cm^{-3})
D_i	: distribution coefficient of the ith component, Equation 2
E	: extract (solvent) phase
E_A	: activation energy, J.mol^{-1}
I	: component number of water (1), ethanol (2) and solvent (dimethyl adipate) (3)
R	: raffinate (aqueous) phase and universal gas constant, Equation 6
S	: separation factor, Equation 3
T	: temperature, K
W_i	: weight fraction of the ith component

W_{11} : weight fraction of water (1) in the aqueous phase
W_{21} : weight fraction of ethanol (2) in the aqueous phase
W_{31} : weight fraction of dimethyl adipate (3) in the aqueous phase
W_{13} : weight fraction of water (1) in the solvent-rich phase
W_{23} : weight fraction of ethanol (2) in the solvent-rich phase
W_{33} : weight fraction of dimethyl adipate (3) in the solvent-rich phase
X : mole fraction of the component
n_D : refractive index
γ : activity coefficients of the component

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