| | |
|---|---|
| $K$ | viscometer calibration constants |
| $L$ | viscometer tube length, m |
| $P$ | pressure, Pa |
| $R$ | tube radius, m |
| $R^0$ | McAllister equation constant |
| $t$ | time, s |
| $T$ | temperature, K |
| $V$ | mole volume, $m^3$/mol |
| $V$ | volume, $m^3$ |
| $x$ | mole fraction |
| $\bar{z}$ | average hydrostatic level, m |

*Greek Letters*

| | |
|---|---|
| $\Gamma$ | Gunn–Yamada parameter |
| $\gamma$ | shear force, g/($cm^2 \cdot s$) |
| $\Delta$ | change in (e.g., $\Delta P$ = pressure change) |
| $\mu$ | viscosity, mPa·s |
| $\nu$ | kinematic viscosity, $m^2$/s |
| $\rho$ | fluid density, kg/$m^3$ |
| $\omega$ | acentric factor |

*Subscripts*

| | |
|---|---|
| c | critical point |
| C | calibration constant |
| E | excess viscosity property, kinetic energy constant |
| $i$, $j$ | refers to components i, j |
| m | mixture |
| r | reduced |
| sc | scaling parameter |
| 123 | refers to ternary mixture |
| 1, 2, 3 | refers to pure components 1, 2, 3 |
| 21, 12 etc. | indicates binary mixture interaction |

*Superscripts*

| | |
|---|---|
| 0 | referring to an ideal mixture |
| 0 | at zero pressure |
| R | at the reference point |
| L | of mixture |

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# Liquid–Liquid Equilibrium for the Ternary System 1,3-Dioxolane–Ethyl Acetate–Ethylene Glycol at $T$ = 291.15, 301.15, and 311.15 K

**Bianca Bubani and Romolo Francesconi***

*Istituto Chimico "G. Ciamician", 40126 Bologna, Italy*

**Ternary liquid–liquid equilibrium data for the 1,3-dioxolane–ethyl acetate–ethylene glycol system are obtained at 291.15, 301.15, and 311.15 K and are correlated by the Bachman, Hand, Othmer–Tobias, and selectivity plots. We conclude that ethylene glycol can be used as a solvent for extracting ethyl acetate from its binary mixtures with 1,3-dioxolane, a separation not obtained by distillation since 1,3-dioxolane and ethyl acetate are a closely boiling pair.**

## Introduction

The wide use of ethylene glycol (G) in technology justifies the extensive study of its chemical properties, with particular regard to solubility. It is well-known that G is slightly soluble in hydrocarbons or similar compounds and in many esters, whereas alcohols, aldehydes, and ketones are good solvents for G (*1*). Reference *2* in the literature reports data on ternary mixtures of G with a good solvent and with a compound practically insoluble in G.

The aims of the present paper are the following:

1. To study the ternary mixtures of G with ethyl acetate (A) and 1,3-dioxolane (D) on account of the good solubility of D in the other two compounds and in their binary mixtures.

2. To find the experimental conditions that will allow the use of G as a solvent for extracting A from the binary mixtures with D: separation of these compounds via distillation indeed would be difficult since their boiling points are nearly the same ($T$ = 351.15 K at 102 kPa and $T$ = 350.21 K at 103.1 kPa for D and A, respectively) (*3*).

## Experimental Section

***Chemicals.*** 1,3-Dioxolane, Fluka product (analytical grade 99%), was purified by refluxing on sodium under inert gas flow

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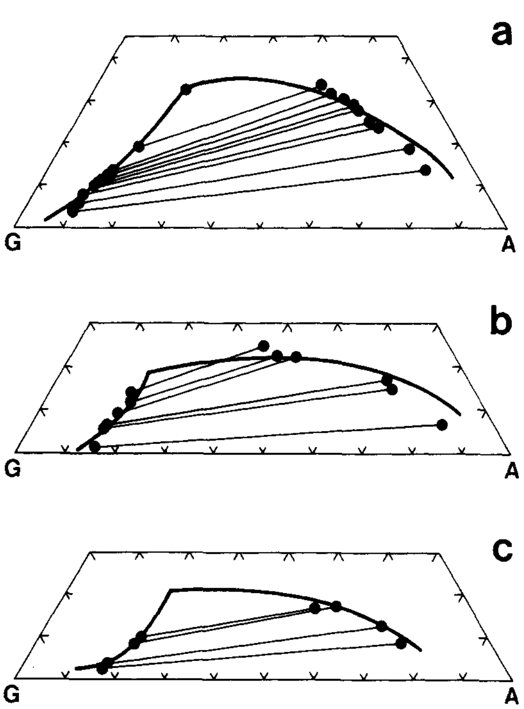

**Figure 1.** Ternary liquid equilibrium diagrams for the 1,3-dioxolane (D)–ethyl acetate (A)–ethylene glycol (G) system at $T$ = 291.15 (a), 301.15 (b), 311.15 K (c); —, calculated by means of Hand, Othmer–Tobias, and selectivity correlation expressions.

and fractionated on a Vigreux column following the procedure given in a previous paper (*4*). Ethylene glycol, Merck "pro analysi", and ethyl acetate, Merck "Uvasol", were used without purification.

***Apparatus and Procedure*.** To obtain the ternary liquid–liquid data, a sample of the mixed solvents was placed in a double-walled glass flask thermostated with circulating water, vigorously shaken to ensure thermal equilibration, and then stored quiet for over 15 h. The cell volume was about 100 mL. The bath temperature was regulated within ±0.1 K. A sample of each layer was taken from the cell and diluted with isobutyl alcohol ensuring complete miscibility of the mixture at room temperature, different from that of the bath, without altering the amount of A, D, and G. Next, the composition of the sample was determined by means of a Perkin-Elmer Sigma 3 gas chromatograph connected to a Perkin-Elmer Sigma 10 integrating recorder. The operating conditions were as follows: 2 m × 2 mm stainless column Carbowax 20M, 10% on Chromosorb w, 80–100 mesh; carrier gas, nitrogen; flow rate 50 mL min$^{-1}$. The column temperature was programmed so as to have an initial temperature of 333.15 K, held for 5 min, followed by an increase to the final temperature of 473.15 K, held also for 5 min, through a heating rate of 10 K min$^{-1}$.

In order to obtain a correct chromatographic response for the different ratios of mixture concentrations at the equilibrium, the solubility curves were previously determined by the method of titration; using these approximate curves, it has been possible to evaluate the useful range for the chromatographic standards.

The experimental uncertainties in the molar fractions, estimated to be about 1%, are due mainly to an unfavorable set of retention times of the components. Table I and Figure 1 show mutual solubility and tie-line data for our system at $T$ = 291.15, 301.15, and 311.15 K. These data are the averaged results of at least three separated experiments.

## Correlation of Ternary Liquid–Liquid Equilibrium Data

The tie-line data of the mixture 1,3-dioxolane–ethyl acetate–ethylene glycol were correlated by means of the methods of

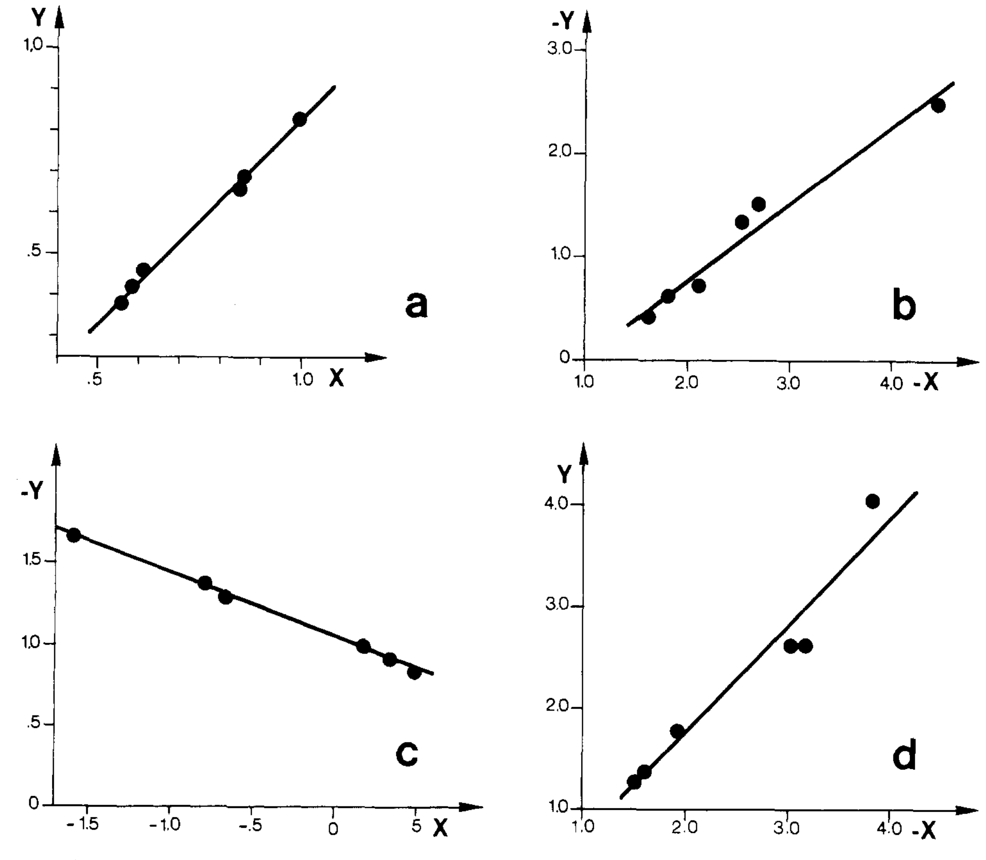

**Figure 2.** Correlation of tie-line data of the mixture 1,3-dioxolane–ethyl acetate–ethylene glycol at $T$ = 301.15 K by the methods of Bachman (a), Hand (b), Othmer–Tobias (c), selectivity (d). Y axis is the left-hand side of eq 1–4. X axis is given by $X_{AA}/X_{44}$ (Bachman), ln $X_{D4}/X_{44}$ (Hand), ln $(1 - X_{AA})/X_{AA}$ (Othmer–Tobias), and ln $X_{GG}X_{AA}/X_{AG}X_{GA}$ (selectivity); — calculated with the parameters of Table II.

**Table I. Mutual Solubilies and Tie-Line Data for the System 1,3-Dioxolane (D)-Ethyl Acetate (A)-Ethylene Glycol (G) at $T$ = 291.15, 301.15, and 311.15 K**[a]

| $T$ = 291.15 K | | | | $T$ = 301.15 K | | | | $T$ = 311.15 K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_{AA}$ | $X_{DA}$ | $X_{GG}$ | $X_{DG}$ | $X_{AA}$ | $X_{DA}$ | $X_{GG}$ | $X_{DG}$ | $X_{AA}$ | $X_{DA}$ | $X_{GG}$ | $X_{DG}$ |
| 0.767 | 0.137 | 0.862 | 0.037 | 0.830 | 0.069 | 0.840 | 0.010 | 0.522 | 0.171 | 0.700 | 0.096 |
| 0.706 | 0.188 | 0.840 | 0.056 | 0.689 | 0.150 | 0.799 | 0.055 | 0.563 | 0.175 | 0.706 | 0.094 |
| 0.618 | 0.246 | 0.827 | 0.073 | 0.664 | 0.174 | 0.785 | 0.062 | 0.674 | 0.133 | 0.805 | 0.036 |
| 0.592 | 0.255 | 0.785 | 0.093 | 0.455 | 0.226 | 0.749 | 0.091 | 0.727 | 0.092 | 0.817 | 0.029 |
| 0.555 | 0.281 | 0.780 | 0.122 | 0.418 | 0.228 | 0.715 | 0.117 | | | | |
| 0.546 | 0.288 | 0.767 | 0.112 | 0.382 | 0.251 | 0.698 | 0.138 | | | | |
| 0.519 | 0.307 | 0.749 | 0.119 | | | | | | | | |
| 0.488 | 0.319 | 0.725 | 0.136 | | | | | | | | |
| 0.453 | 0.339 | 0.645 | 0.193 | | | | | | | | |

[a] $X_{ij}$ = molar fraction of component i in the j-rich phase.

**Table II. Results of the Least-Squares Analysis for the System 1,3-Dioxolane-Ethyl Acetate-Ethylene Glycol at $T$ = 291.15, 301.15, and 311.15 K**[a]

| | $T$ = 291.15 K | | | $T$ = 301.15 K | | | $T$ = 311.15 K | | |
|---|---|---|---|---|---|---|---|---|---|
| correlation | $a_k$ | $b_k$ | $\rho$ | $a_k$ | $b_k$ | $\rho$ | $a_k$ | $b_k$ | $\rho$ |
| 1. Bachman | -0.4198 | 1.342 | 0.958 | -0.1554 | 0.9853 | 0.998 | -0.6191 | 1.517 | 0.976 |
| 2. Hand | 0.7837 | 0.7625 | 0.977 | 0.7036 | 0.7442 | 0.979 | 0.0668 | 0.5959 | 0.962 |
| 3. Othmer-Tobias | -0.9917 | 0.8027 | 0.944 | -1.068 | 0.3749 | 0.986 | -0.7419 | 0.8143 | 0.979 |
| 4. selectivity | -0.0691 | 0.8366 | 0.978 | 0.3756 | 1.058 | 0.970 | -0.5569 | 1.097 | 0.987 |

[a] $a_k$, $b_k$ are the adjustable parameters of eq 1-4 ($k$ = 1-4). $\rho$ is the correlation coefficient for the straight lines expressed by eq 1-4.

Bachman, Hand, and Othmer-Tobias. Also the correlation of selectivity ($\beta$) was tried (*5*)

$$X_{AA} = a_1 + b_1 \frac{X_{AA}}{X_{GG}} \quad \text{Bachman correlation} \quad (1)$$

$$\ln\left(\frac{X_{DA}}{X_{AA}}\right) = a_2 + b_2 \ln\left(\frac{X_{DG}}{X_{GG}}\right) \quad \text{Hand correlation} \quad (2)$$

$$\ln\left(\frac{1 - X_{GG}}{X_{GG}}\right) = a_3 + b_3 \ln\left(\frac{1 - X_{AA}}{X_{AA}}\right) \quad \text{Othmer-Tobias correlation} \quad (3)$$

$$\ln \beta = a_4 + b_4 \ln \frac{X_{GG}X_{AA}}{X_{AG}X_{GA}} \quad \text{selectivity correlation} \quad (4)$$

$$\beta = \frac{X_{DA}X_{GG}}{X_{GA}X_{DG}}$$

where $X_{ij}$ = molar fraction of component i in the j-rich phase.

The parameters $a_k$ and $b_k$ ($k$ = 1, ..., 4) of eq 1-4 were obtained by means of least-squares procedure starting from the data of Table I.

Table II reports the values of the estimated parameters together with the correlation coefficients of the straight lines. Figure 2 shows the straight lines calculated with the parameters of Table II at $T$ = 301.15 K, as an example.

To evaluate the plait point at each temperature, three of the four correlation expressions 1-4, that is, Hand, Othmer-Tobias, and selectivity, were taken and the system of these independent nonlinear equations was solved in the unknowns $X_{AA}$, $X_{DA}$, and $X_{DG}$, with $X_{AG}$ chosen as the independent variable. The mixture composition corresponding to $X_{AA} = X_{AG}$ and $X_{DA} = X_{DG}$ gives the plait point. Practically the same plait point value resulted from Bachman, Hand, and selectivity correlation equations. Figure 1 shows calculated limit curves and, at their intersection, the plait point.

## Conclusions

The Bachman correlation is found to fit better the experimental data for the ternary system 1,3-dioxolane-ethyl acetate-ethylene glycol in the range 291.15-311.15 K.

From the analysis of the experimental points of this study it is seen that ethylene glycol can be used to separate 1,3-dioxolane and ethyl acetate via solvent extraction at temperatures not exceeding 291.15 K, whereas no phase splitting occurred in this system above 318.15 K.

## Acknowledgment

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## Glossary

| | |
|---|---|
| A | ethyl acetate |
| $a_1$, $a_2$, $a_3$, $a_4$ | parameters in the correlation eq 1-4 |
| $b_1$, $b_2$, $b_3$, $b_4$ | parameters in the correlation eq 1-4 |
| D | 1,3-dioxolane |
| G | ethylene glycol |
| $X_{ij}$ | molar fraction of component i in the j-rich phase |
| $\beta$ | molar fractions ratio in the selectivity correlation eq 4 |
| $\rho$ | correlation coefficient |

**Registry No.** 1,3-Dioxolane, 646-06-0; ethyl acetate, 141-78-6; ethylene glycol, 107-21-1.

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