Esterification of Butanol in a Two-Phase Liquid-Liquid System

Part I: Quaternary Phase Equilibria Studies

The phase equilibria of the systems are discussed:

(i) n-butanol-acetic acid-water and n-heptane
(ii) Water-acetic acid-benzene and carbon tetrachloride
(iii) Water-methanol-p.cresol and methyl naphthalene have been studied and a correlating procedure has been developed that utilizes binary and ternary experimental data to predict the composition of the quaternary equilibrium mixtures. Allowance is made for the different salting effects and the agreement between the experimental and predicted quaternary data is in all cases very good.

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SCOPE

In recent years, mixed solvents have been employed in solvent extraction operations so that the system under consideration is, in reality, a double binary quaternary system which cannot be represented graphically on a triangular diagram. In addition, a small number of batch and continuous extractive-reaction processes have recently been described in which the two parent solvents contain the reactants and possibly products together with a liquid catalyst. Usually, the liquid catalyst is not distributed so that this system is, in fact, a single binary quaternary which, again, cannot be represented graphically subsequent to the analysis of the particular process.

Furthermore, these processes are most conveniently analyzed by computer but this entails the development of reliable correlations that will represent the phase equilibria accurately over a wide range of conditions. These correlations must accommodate the different "salting" effects that will arise due to the presence of different concentrations of the different components in each phase. These anomalies complicate the prediction procedure based on conventional activity coefficients and it is more propitious to resort to the development of correlations, based on experimental binary and ternary data that can be obtained relatively easily in the laboratory, and, which may be incorporated in the form of subroutines in the overall analysis of the process. This approach has been adopted in this investigation of the batch and continuous esterification of n-butanol with acetic acid in the presence of sulphuric acid in a two-phase aqueous-heptane solvent system.

The system studied consisted originally of the two reactants; acetic acid and n.butyl alcohol with water and n-heptane in addition to a limited amount of sulphuric acid catalyst. As the chemical reaction proceeded ester was formed which increases the number of components to six. Therefore, the correlation derived must take into consideration the interaction between all these components. This has been accomplished in a form suitable for incorporation into the form of a subroutine in a program of an extractive-reaction process.

CONCLUSIONS AND SIGNIFICANCE

The phase equilibria of the system n-butanol, acetic acid, butyl acetate, n-heptane and water have been studied in order to develop a mathematical correlation that may be applied to analyse the feasibility of the two-phase batch and continuous esterification processes. The correlation procedure developed utilizes ternary experimental data only to predict double binary quaternary compositions and ternary experimental data with a limited amount of quaternary data to correlate the single binary quaternary compositions.

The correlation procedure has been tested, using the experimental results of Prince (1954) for the system: water-acetic acid-benzene and carbon tetrachloride and that of Prutton (1950) for the system: water-methanol-p.cresol and methylnapthalene and with both of these systems the agreement between their experimental results and the predicted data were very good and, significantly, available in the form that can be assimilated readily into an overall analysis of an overall reaction extraction process.

INTRODUCTION

Phase equilibria in liquid-liquid systems may be approached in one of two ways. These are based on: (i) thermodynamics and the phase rule; and (ii) the laws of distribution.

For the design or analysis of a solvent extraction process and other applications where data are required about the equilibria of a particular two-phase liquid system the approach involving the laws of distribution is frequently of more practical importance. These laws, as applied to liquid-liquid systems, include the various empirical correlations that attempt to systematize the relationship between the concentrations of the various components in the different phases of the system. Most frequently,

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the equilibria of a three component partially miscible liquid system are represented on triangular coordinates, and the binodal curve is important in determining the solubilities. However, it is the tie-lie data which is of primary interest in determining the distribution of the various components between the two phases and this distribution may be represented graphically or by algebraic correlations.

Geometrical methods for interpolation and extrapolation of tie-line data have been devised by Brancker, Hunter and Nash (1940), Sherwood (1937), Hand (1930) and others. These methods are entirely graphical and are useful for extrapolation. They lack the flexibility of mathematical formulations required for the analysis of solvent extraction processes, particularly by computer, and therefore only the mathematical relationships are considered in the following paper.

The first empirical equation describing the distribution of components in a three component two-phase liquid system was due to Bachman (1940). He proposed that:

$$x_{BB} = r + b(x_{BB}/x_{AA}) \tag{1}$$

where r and b are constants.

Later Othmer and Tobias (1942) showed that Eq. 1 is limited in application since it is based on ternary systems composed of practically immiscible nonconsulute components in the absence of the consulute component. They modified Bachman's equation so that a plot of the conjugate values of:

$$\left(\frac{1 - x_{AA}}{x_{AA}}\right) \cdot v \cdot \left(\frac{1 - x_{BB}}{x_{BB}}\right)$$

on logarithmic coordinates produced straight lines. However, the Othmer and Tobias method also suffers from the fact that it does not include the concentration of the distributed component and it would appear that the most useful formula is that of Hand (1930) which correlates the concentration of the solute in the two conjugate solutions.

Hand's equation is represented by:

$$\left(\frac{x_{CA}}{x_{AA}}\right) = K\left(\frac{x_{CB}}{x_{BB}}\right)^r \tag{2}$$

i.e., the logarithmic plot of (x_{CA}/x_{AA}) against (x_{CB}/x_{BB}) is rectilinear.

Four dimensional geometrical models are necessary to represent four component systems and one method due to Brancker, Hunter and Nash (1940) makes use of a regular tetrahedron. Two types of quaternary two-phase liquid systems are possible. The first type is formed when one pair of components is partially miscible; i.e., when two solutes are distributed between two solvents. The other type is formed when one component is partially miscible with two of the others; i.e., when one solute is distributed between one of the solvents in one phase and with two "mixed" solvents in the other phase. These two types of quaternary system have been termed "Single binary quaternaries" and "Double binary quaternaries," respectively, and an example of a single binary quaternary, studied by Brancker et al. (1940) and Hunter (1942), is the system acetone-acetic acid-chloroform-water. Geometrical correlations were deduced for quaternary tie-lines and the saturation surface obtained from the different ternary data.

An example of a double binary quaternary system, consisting of acetic-acid-water-benzene-carbon tetrachloride has been studied by Prince (1954). He deduced two correlations from the quaternary saturation surface and ternary data, one was algebraic and the other geometrical, and he claimed that these two correlations could predict the equilibrium of the quaternary systems. Prince's model is a combination of a geometrical correlation of experimental data and an empirical relation which makes it complicated and possibly unreliable if applied to other systems. In addition, it is not a complete prediction of quaternary data from the constituent ternaries since experimentation with the quaternary system is still required to determine the saturation surface. Therefore, an attempt has been made to develop a prediction method using only the constituent ternary data and the results obtained are presented in the following paragraphs.

EXPERIMENTAL

The system under investigation consisted originally of two reactants; acetic acid and n-butyl alcohol with water and the solvent heptane, as well as a limited amount of sulphuric acid catalyst. As chemical reaction proceeded, ester was formed which increased the total number of components to six. Therefore the experimental data must enable a mathematical model to be produced that will take into consideration the interaction between all these components, and the following experimental work was undertaken with these objectives in mind.

Saturation Composition. Data for the binodal curves of the component ternary systems were determined using the cloud point method described by Al-Saadi (1978), and the tie-line data of the different systems were determined by agitating known amounts of the constituents vigorously for at least three hours at 20.0°C. Then the phases were allowed to settle and separate analytical determinations of the different constituents were performed as follows:

1) Acetic acid was determined by titration with 0.1 N NaOH solution.
2) n-Heptane, n-butyl-alcohol and n-butyl acetate was determined by gas-liquid chromatography. A standard pye analytical column (PEG 400) was used. The stationary phase was polyethylene glycol MW 400 and detection was made by a flame ionisation detector together with an integrator.

Water was determined from the material balance or was read directly on the binodal curve in the case of ternary systems.

Correlation and the Phase Distribution of a Multicomponent Two-Phase System

Geometrical representation of four or more components of a liquid system was considered to be inadequate and therefore a mathematical expression was constructed to systematize the relationships between the concentrations of the various components in the two phases. The problem was approached on the basis of the experimental data for the different combinations that could be built up into an overall equation for all the components. Apart from the different ternaries, the system consisted of two kinds of quaternaries; viz., the double binary quaternary and the single binary quaternary. Hence, it was necessary to express both types and a combination of the two models gave a model for the five component system.

In the following analysis, let X and x denote the mole fractions in the quaternary and ternary systems respectively. X_{BA} denotes the mole fraction of B in a "A rich" phase. A-N represent the different components considered and are identified in the nomenclature.

Ternary Systems

Hand's formula adequately predicted the concentration of a solute B in the water phase (A) for any combinations of A, B and D (where D is a solvent) provided that the concentration of A in phase D and D in phase A was negligible. Parameters k and r were determined from a regression analysis of the experimental data, hence:

$$\frac{B_1}{A} = k\left(\frac{B - B_1}{D}\right)^r \tag{3}$$

where B_1 is the fraction of B in phase A.

Equation 3 is easily solved for B_1 by an iteration process, e.g., the reguli-falsi or Newton-Raphson methods.

Quaternary Systems

Two types of quaternary system are to be considered, i.e., the "single binary quaternary" of water-acetic acid-n-butyl alcohol and n-heptane (or n butyl acetate) and the "double binary quaternary" of water, acetic acid (or n butyl alcohol), n-butyl acetate and n-heptane. Each type was treated differently.

Correlation of a Single Binary Quaternary System

In a four component system of two solutes B and C in two solvents A and D; the components B and C will influence each other's distribution;

i.e., there is likely to be a mutual "salting" effect which will be proportional to the total amount of each component present. A measure of the distribution of any solute, e.g., solute B between A and D is the ratio of its concentration in the phase rich in A to its concentration in the phase rich in D and this ratio will be affected by the total amount of B as well as the salting effect of a fourth component C.

For the purpose of mathematical representation, the "total amount" can be represented by the sum of the concentrations in the two phases. However, in order to modify the distribtion of B between A and D in the absence of C, a term must be included which will account for ternary distribution and the salting effect. Hence, the equation to describe the single binary quaternary distribution will be of the form:

$$\frac{X_{BA}/X_{AA}}{X_{BD}/X_{DD}} = \frac{x_{BA}/x_{AA}}{x_{BD}/x_{DD}} + K\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{m} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{n} \quad (4)$$

where K, m and n are constants for the quaternary system.

The first term on the right hand side of Eq. 4 is obtained from the ternary data and the second is introduced to account for the modification resulting from the salting effect of component C. K will be positive if C salts out B from phase D into phase A and negative if C salts out B from A in D.

Similarly for solute component C.

$$\frac{X_{CA}/X_{AA}}{X_{CD}/X_{DD}} = \frac{x_{CA}/x_{AA}}{x_{CD}/x_{DD}} + K'\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{m'} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{n} \quad (5)$$

K, K', m, m', n and n' can be found from a regression analysis of the experimental quaternary data. Hence, two simultaneous nonlinear algebraic equations for X_{BA} and X_{CA} are obtained which can be solved by a suitable iteration procedure to predict the quaternary equilibria from a limited number of experimental results, since the ternary data can be obtained from Hand's equation.

As for ternary systems, this method is suitable when the solubilities of A in phase D and D in phase A are negligible since, in the iteration process, it is assumed that all A remains in phase A while all D remains in phase D.

Correlation of a Double Binary Quaternary System

In this case a solute B or C is distributed between phase A which consists of water, with negligible amounts of D and E and an organic phase of $(D + E)$ with negligible amounts of water. The concentration of B in phase A is represented by (B_1/A) and is likely to change as the ratio of D to E is changed. At one extreme, when E is zero, (B_1/A) is the ternary concentration for the system A, B, D. On the other hand if D is zero (B_1/A) is the concentration for the ternary system A, B, E. If $(D$-$E)$ solution is ideal, each component of its mixture can be expected to "contribute" a share to the distribution proportional to its mole fraction.

Hence, it would be expected that the distribution of a solute in a double binary quaternary could be described by an equation of the form:

$$\frac{X_{BA}}{X_{AA}} = \left(\frac{D}{D+E}\right)\left(\frac{x_{BA}}{x_{AA}}\right)_{D} + \left(\frac{E}{D+E}\right)\left(\frac{x_{BA}}{x_{AA}}\right)_{E} \quad (6)$$

where: $(x_{BA}/x_{AA})_D$ is obtained from experimental data for the ternary system A, B, D and corrected for the quaternary composition by multiplying by the ratio [moles of D/moles of $(D + E)$]; and $(x_{BA}/x_{AA})_E$ is obtained from experimental data for the ternary system A, B, E and corrected for the quaternary composition by multiplying by the ratio [mol of E/mol of $(D + E)$]. That is, application of Eq. 6 enables the quaternary data to be estimated from the ternary data alone.

Computation Details

The regression analysis was performed by inserting the data into the ICL 1900 statistical analysis package XDS3 and Eqs. 4 and 5 were solved by the Newton-Raphson's method for partial derivatives.

RESULTS

The two single-binary quaternary systems of water-acetic acid-n butanol-n heptane, and water-acetic acid-n butanol-n butyl acetate as well as two double binary quaternary systems of water-acetic acid-n heptane-n butyl acetate and water-butanol-n heptane-n butyl acetate were investigated experimentally and the data was evaluated to test the proposed equations for predicting the solute compositions. In addition, the data of Brancker et al. (1940) and Prutton et al. (1950) for the single binary quaternary and the data of Prince (1954) for a double quaternary were also tested by the same equations.

Ternary Systems

The complete data for all the different ternaries investigated experimentally have been reported by Al-Saadi (1978) and the results of regression analysis of the ternaries solubility data, based on Hand's formula resulted in Eqs. 7 to 10. The data reported by Brancker (1940) yielded the correlations (Eqs. 11 and 12) while correlations (Eqs. 13 and 14) were obtained from the data of Prince (1954). Prutton's (1950) data yielded Eqs. 15 and 16:

Water-Acetic acid-n heptane System:

$$\frac{x_{BA}}{x_{AA}} = 7.82\left(\frac{x_{BD}}{x_{DD}}\right)^{0.89} \quad (7)$$

Water-butanol-n heptane System:

$$\frac{x_{CA}}{x_{AA}} = 0.02\left(\frac{x_{CD}}{x_{DD}}\right)^{0.18} \quad (8)$$

Water-acetic acid-n butyl acetate System:

$$\frac{x_{BA}}{x_{AA}} = 0.25\left(\frac{x_{BE}}{x_{EE}}\right)^{0.85} \quad (9)$$

Water-butanol-n butyl acetate System:

$$\frac{x_{CA}}{x_{AA}} = 0.014\left(\frac{x_{CE}}{x_{EE}}\right)^{0.65} \quad (10)$$

Water-acetic acid-chloroform ternary:

$$\frac{x_{BA}}{x_{AA}} = 0.595\left(\frac{x_{BJ}}{x_{JJ}}\right)^{0.913} \quad (11)$$

Water-acetone-chloroform ternary:

$$\frac{x_{IA}}{x_{AA}} = 0.055\left(\frac{x_{IJ}}{x_{JJ}}\right)^{1.194} \quad (12)$$

Water-acetic acid-benzene system:

$$\frac{x_{BA}}{x_{AA}} = 1.616\left(\frac{x_{BF}}{x_{FF}}\right)^{0.827} \quad (13)$$

Water-acetic acid-carbontetrachloride system:

$$\frac{x_{BA}}{x_{AA}} = 2.18\left(\frac{x_{BG}}{x_{GG}}\right)^{0.794} \quad (14)$$

Water-methanol-methylnaphthalene system:

$$\frac{x_{LA}}{x_{AA}} = 137.0\left(\frac{x_{LM}}{x_{MM}}\right)^{1.85} \quad (15)$$

Water-p cresol-methylnaphthalene system:

$$\frac{x_{NA}}{x_{AA}} = 0.00273\left(\frac{x_{NM}}{x_{MM}}\right)^{0.274} \quad (16)$$

Single Binary Quaternary Systems

Water-Acetic Acid-Butanol-Heptane System. Regression analysis of the variables based on Eqs. 4 and 5 led to the following correlations for this system.

$$\frac{X_{BA}/X_{AA}}{X_{BD}/X_{DD}} = \frac{x_{BA}/x_{AA}}{x_{BD}/x_{DD}} - 10.85\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{0.21} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{0.16} \quad (17)$$

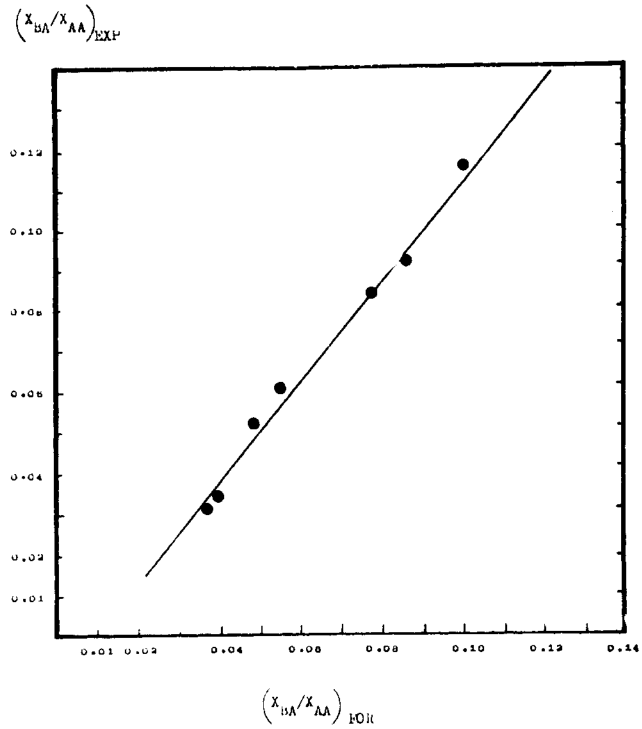

Figure 1. Distribution of acetic acid in water-acetic acid-butanol heptane quaternary.

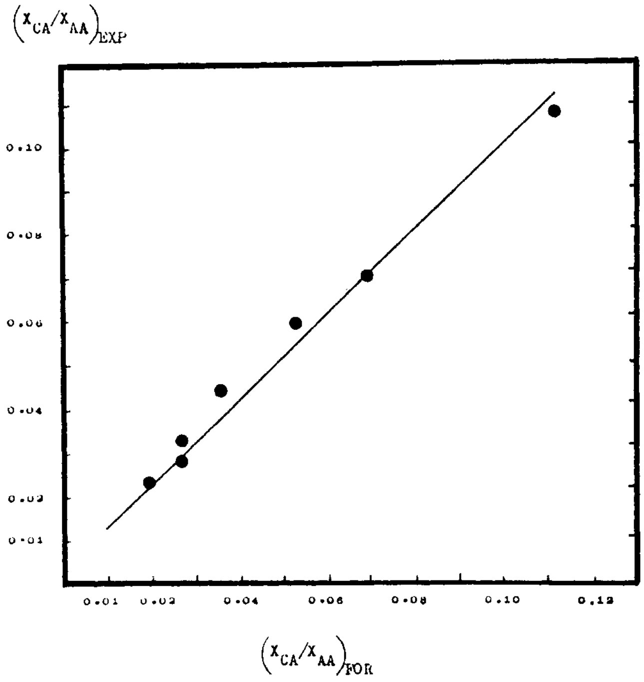

Figure 2. Distribution of butanol in water-acetic acid-butanol-n heptane quaternary.

$$\frac{X_{CA}/X_{AA}}{X_{CD}/X_{DD}} = \frac{x_{CA}/x_{AA}}{x_{CD}/x_{DD}} + 0.20\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BD}}{X_{DD}}\right)^{2.00} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CD}}{X_{DD}}\right)^{-2.20} \qquad (18)$$

Equations 17 and 18 demonstrate the salting effect between acetic acid and butanol in the water-heptane systems. The distribution of acetic acid relative to the aqueous phase is depressed in accordance with Eq. 17 and enhancement of the alcohol distribution in the aqueous phase is indicated by Eq. 18.

A computer program was written to solve Eqs. 17 and 18 and the results of the computer calculations of the acid and alcohol concentrations relative to water are plotted against the experimental values in Figures 1 and 2 and as can be seen good agreement was achieved; the average deviation between experimental and calculated values was about 10%.

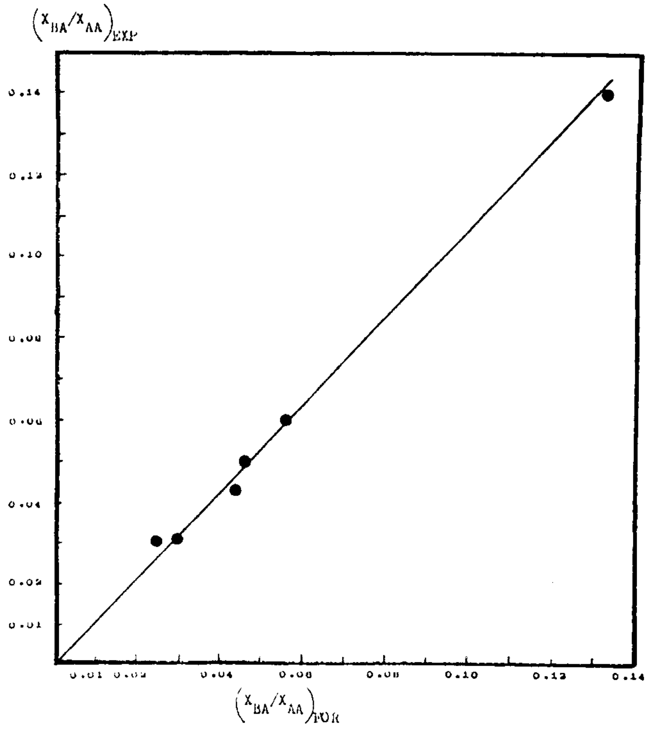

Figure 3. Distribution of acetic acid in water-acetic acid-butanol-ester quaternary system.

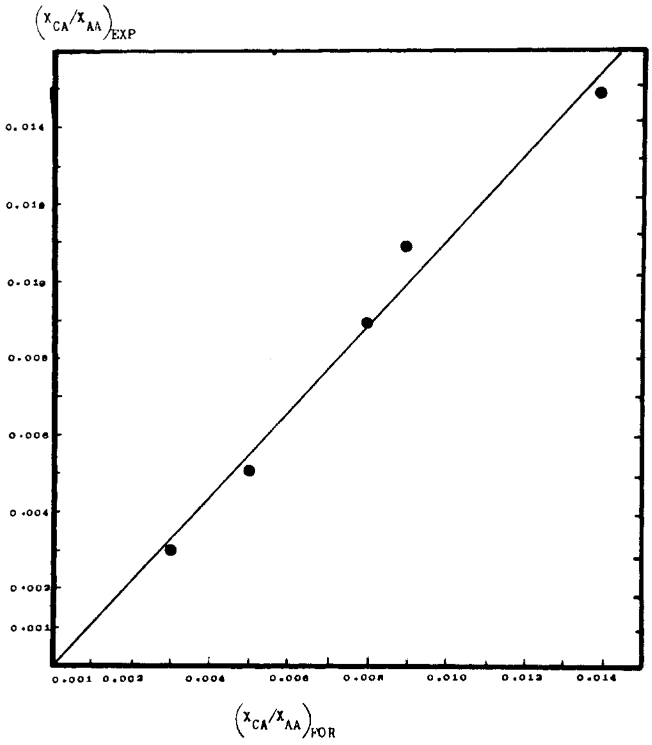

Figure 4. Distribution of butanol in water-acetic acid-butanol-ester quaternary system.

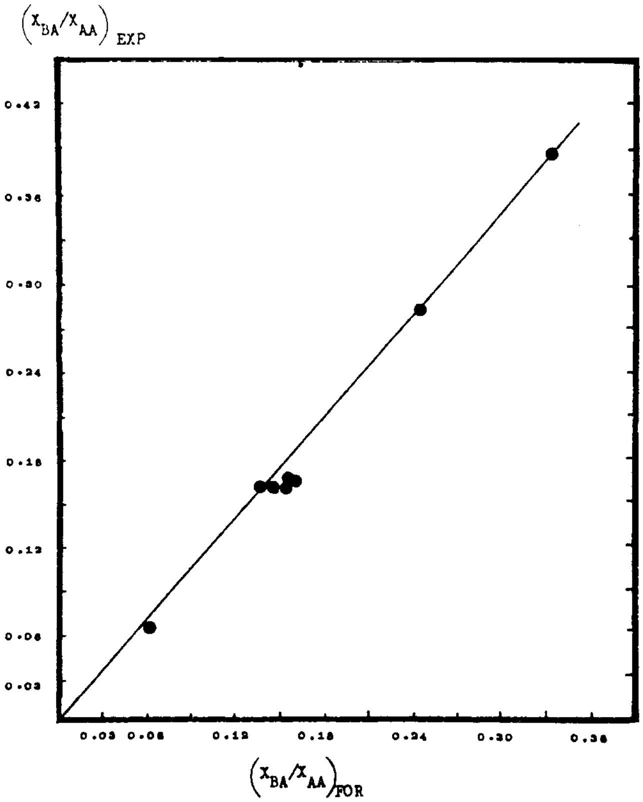

Figure 5. Distribution of acetic acid in the water-acetic acid-acetone-chloroform quaternary system.

Water-Acetic Acid-Butanol-n Butyl Acetate System. Regression analysis of the experimental ternary and quaternary distribution values led to the following correlations:

$$\frac{X_{BA}/X_{AA}}{X_{BE}/X_{EE}} = \frac{x_{BA}/x_{AA}}{x_{BE}/x_{EE}} - 0.20\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BE}}{X_{EE}}\right)^{-0.20} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CE}}{X_{EE}}\right)^{0.35} \qquad (19)$$

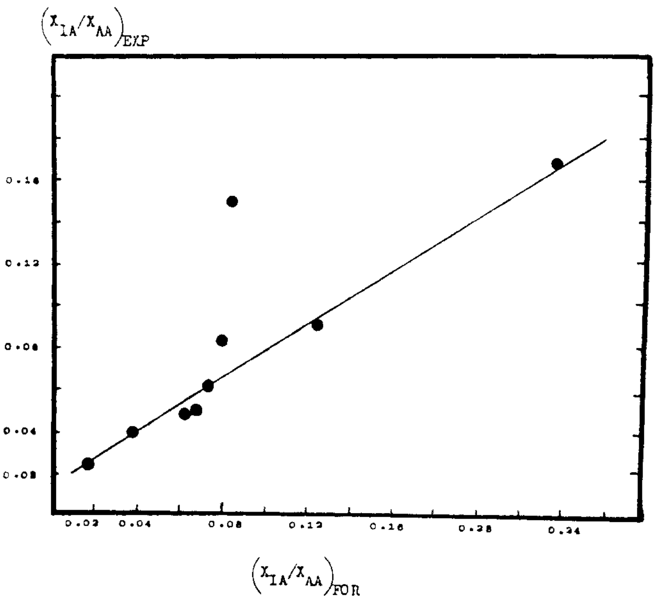

Figure 6. Solubility of acetone in the water-acetic acid-acetone-chloroform quaternary system.

$$\frac{X_{CA}/X_{AA}}{X_{CE}/X_{EE}} = \frac{x_{CA}/x_{AA}}{x_{CE}/x_{EE}} + 0.0021\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BE}}{X_{EE}}\right)^{2.06} \cdot \left(\frac{X_{CA}}{X_{AA}} + \frac{X_{CE}}{X_{EE}}\right)^{-2.02} \qquad (20)$$

The last term of Eq. 20 is very small indicating that the salting effect of acetic acid on butanol in water-n-butyl acetate systems is small and can, in practice, be neglected. Hence in programming, Eqs. 19 and 20, the last term of Eq. 20 was ignored. Thus,

$$x_{CA} = X_{CA}$$

$$x_{CE} = X_{CE}$$

and the concentration of butanol was calculated directly from the ternary correlation (Eq. 10).

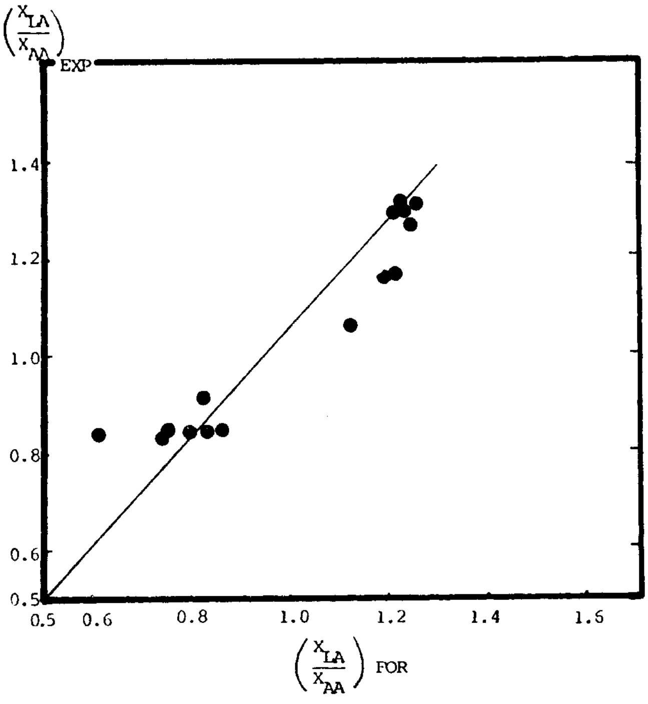

Figure 7. Distribution of methanol in water-methanol-p cresol-methylnaphthalene system.

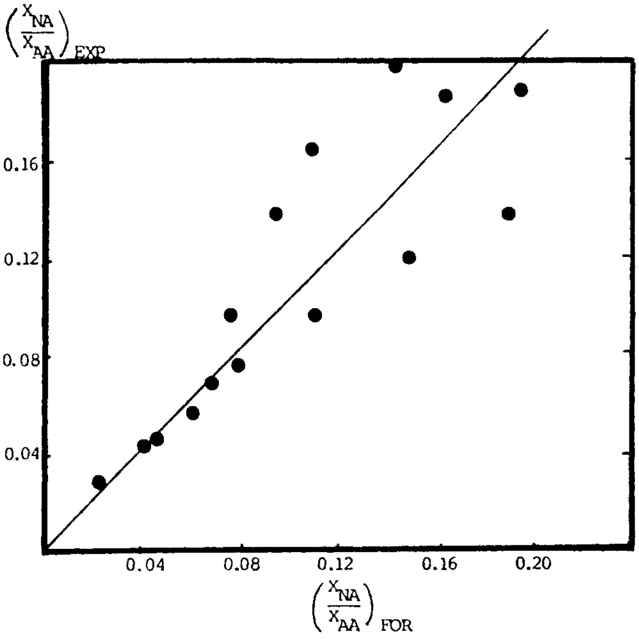

Figure 8. Distribution of p-cresol in water-methanol-p cresol-methylnaphthalene system.

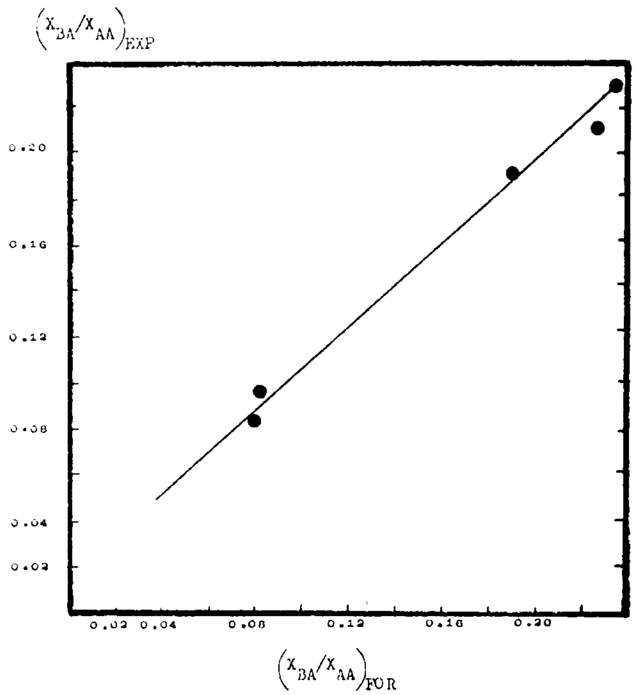

Figure 9. Distribution of acetic acid in the water-acetic acid-n heptane-ester quaternary system.

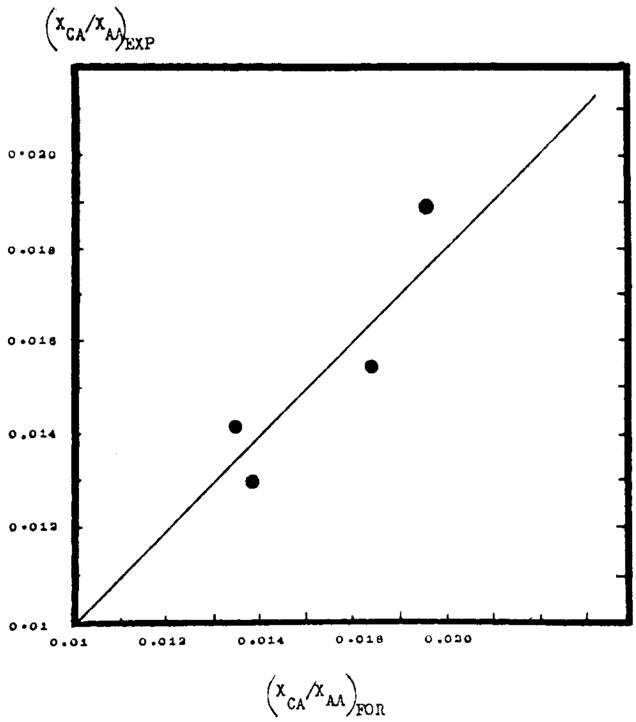

Figure 10. Distribution of butanol in water-butanol-n heptane-ester quaternary system.

The computed values together with the experimental values are plotted in Figures 3 and 4. Good agreement was achieved between the experimental and calculated values; the average difference being 7.7% for acetic acid and 4.0% for butanol.

Water-Acetic Acid-Acetone-Chloroform System. The data for this system was taken from the results of Brancker, Hunter and Nash (1942) and the regression analysis led to the following correlations for acetic acid and acetone concentrations:

$$\frac{X_{BA}/X_{AA}}{X_{BJ}/X_{JJ}} = \frac{x_{BA}/x_{AA}}{x_{BJ}/x_{JJ}}$$

$$- 0.132\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BJ}}{X_{JJ}}\right)^{0.181} \cdot \left(\frac{X_{IA}}{X_{AA}} + \frac{X_{IJ}}{X_{JJ}}\right)^{1.600} \tag{21}$$

$$\frac{X_{IA}/X_{AA}}{X_{IJ}/X_{JJ}} = \frac{x_{IA}/x_{AA}}{x_{IJ}/x_{JJ}}$$

$$+ 0.051\left(\frac{X_{BA}}{X_{AA}} + \frac{X_{BJ}}{X_{JJ}}\right)^{0.504} \cdot \left(\frac{X_{IA}}{X_{AA}} + \frac{X_{IJ}}{X_{JJ}}\right)^{1.348} \tag{22}$$

Equations 21 and 22 were solved to evaluate the concentration of acetic acid and acetone in the quaternary system. Results are plotted against the experimental values in Figures 5 and 6. In this case the average deviation for acetic acid was less than 10%. However, in the case of acetone, the agreement was poor; there being deviations of over 40% and an overall average of about 27%. Possible reasons for this are explained later.

Water-Methanol-p Cresol-Methylnaphthalene System. This system had been studied by Prutton and co-workers (1950) at different temperatures. All the data adopted in this study are at 35°C; except that for the water-methanol-methylnaphthalene ternary which is at 25°C. There being no data at 35°C for this system. However, this is thought not to influence the quaternary calculations a great deal since the saturation curves given by Prutton et al. at 25 and 35°C are very close together. Following the above procedure yielded the correlations for these quaternary distributions:

$$\frac{X_{LA}/X_{AA}}{X_{LM}/X_{MM}} = \frac{x_{LA}/x_{AA}}{x_{LM}/x_{MM}}$$

$$- 11.33\left(\frac{X_{LA}}{X_{AA}} + \frac{X_{LM}}{X_{MM}}\right)^{-0.103} \cdot \left(\frac{X_{NA}}{X_{AA}} + \frac{X_{NM}}{X_{MM}}\right)^{0.291} \tag{23}$$

$$\frac{X_{NA}/X_{AA}}{X_{NM}/X_{MM}} = \frac{x_{NA}/x_{AA}}{x_{NM}/x_{mm}}$$

$$+ 0.148\left(\frac{X_{LA}}{X_{AA}} + \frac{X_{LM}}{X_{MM}}\right)^{0.432} \cdot \left(\frac{X_{NA}}{X_{AA}} + \frac{X_{NM}}{X_{MM}}\right)^{0.725} \tag{24}$$

Solution of Eqs. 23 and 24 gave the distribution values for

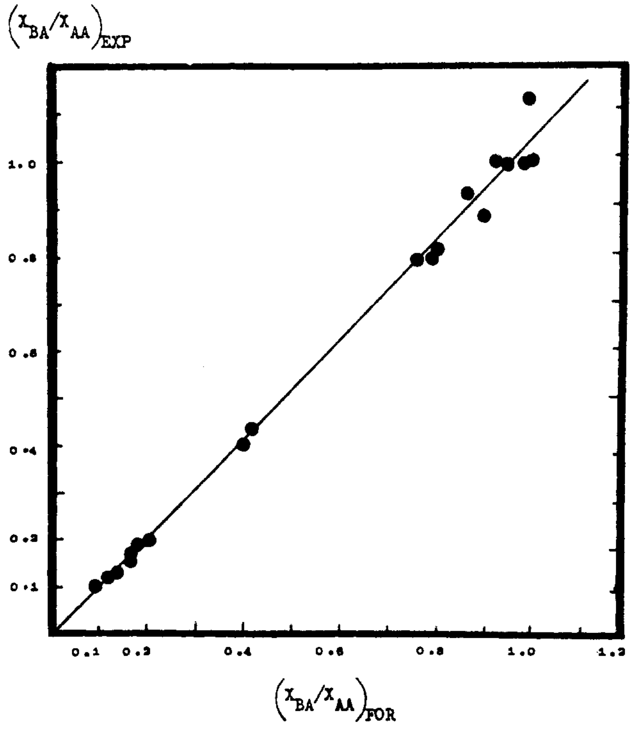

Figure 11. Distribution of acetic acid in water-acetic acid-benzene-carbon tetrachloride system.

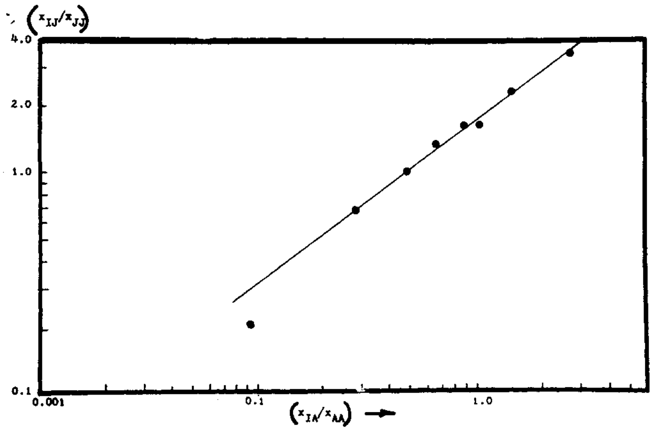

Figure 12. Hand coordinates for the ternary system water-acetone-chloroform.

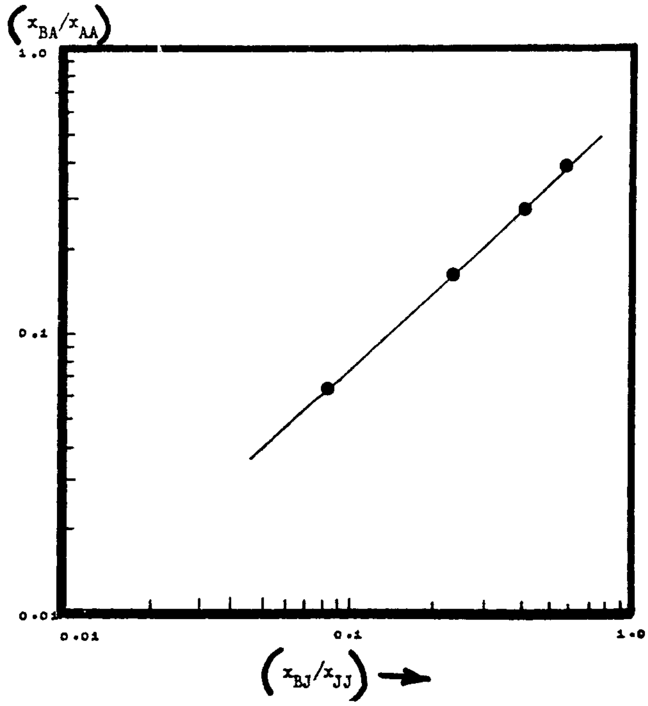

Figure 13. Hand coordinates for the ternary system water-acetic acid-chloroform.

methanol and p-cresol in the quaternary system. These values are plotted in Figures 7 and 8 where it can be seen that reasonably good agreement was achieved between the experimental and calculated values.

Double Binary Quaternary Systems

Equation 6 was applied to the data for the two systems studied experimentally. That is the water-acetic acid-heptane-n-butyl acetate and water-butanol-heptane-n-butyl acetate systems as well as the water-acetic acid-benzene-carbon tetrachloride system studied by Prince (1954). The factors $(x_{BA}/x_{AA})_D$ and $(x_{BA}/x_{AA})_E$ were found from the respective ternary correlations (Eqs. 7, 8, 9, 10, 13 and 14), and the mole fractions $(D/D + E)$ and $(E/D + E)$ were found from weight fractions of the two mixed solvents. The theoretical solute distribution values were then calculated and the results are plotted v. the corresponding experimental values in Figures 9 to 11. Excellent agreement was obtained between the experimental and predicted values in all three cases and it can be seen that the deviation was less than 10%.

DISCUSSION

Single Binary Quaternary Systems

The correlations for binary quaternary system represented by Eqs. 4 and 5, describes the distribution of two solutes between two immiscible solvents, e.g., water and an organic solvent. Application of this method to the two systems studied experimentally and a third system studied by Prutton (1950) showed good agreement between experimental and predicted distribution values for the two solutes. However, when this method was applied to a fourth system—that of water-acetic acid-acetone-chloroform studied by Brancker (1942), good agreement was achieved between predicted and experimental distribution values for acetic acid, while the agreement for acetone was very poor. This is thought to be due to peculiarities reported in the experimental values for acetone. Thus:

(1) All the ternaries studied with the exception of the data for the water-acetone-chloroform ternary fitted Hand's correlations very well. This is illustrated in Figure 12 where it can be seen that there is a considerable scattering of the experimental points on the double logarithmic coordinates, whereas in Figure 13 of the data obtained by the same workers show that the other ternary, viz., the water-acetic acid-chloroform ternary was much more "well behaved."

(2) Peculiarities were also seen in the acetone concentration values for the quaternary system data. This was evident from the difference between the term:

$$\left(\frac{X_{IA}/X_{AA}}{X_{IJ}/X_{JJ}}\right) \text{ and the term } \left(\frac{x_{IA}/x_{AA}}{x_{IJ}/x_{JJ}}\right)$$

which is a measure of the enhancement or the depression of the acetone concentration in the quaternary aqueous phase relative to the ternary aqueous phase due to the influence of the other solute (acetic acid). This difference was negative for two values indicating that acetic acid depresses acetone solubility in the aqueous phase. For the other seven values, the difference was positive indicating enhancement.

Double Binary Quaternary Systems

The correlation of a double binary quaternary system represented by Eq. 6 predicts algebraically the distribution of a solute between one solvent in one phase and two "mixed" solvents in the other phase. Equation 6 is similar in form to Raoults Law and is indeed based on the same principles.

The agreement between the predicted and experimental values for the two cases investigated experimentally, was very good and Eq. 6 appears to be an exact representation of the physical conditions prevailing in double binary quaternary systems. Equation 6 was tested on Prince's data (1954), for the water-acetic acid-benzene-carbon tetrachloride system and again the agreement between experimental and predicted distribution values was also very good. In this case the average deviation for 23 points was about 3%.

Determination of the solubilities of four component systems is a time consuming operation and is prone to experimental error. Hence, Eq. 6, which does not require any quaternary experimental values will find application in predicting the composition of double binary quaternary systems with only very limited experimentation on the quaternary for confirmation of the prediction procedure with the particular system.

It is very likely that the same equation can be used for systems of more than two "mixed solvents" by including a term for each solvent but this requires further study.

In conclusion, it may be stated that the distribution of two solutes between two solvents, i.e., in the single binary quaternary system can be correlated algebraically by a system of equations based on the difference between distribution ratios (i.e., salting effect) of the two solutes in the binary and quaternary cases.

In addition, the distribution of one solute between one solvent in one phase and two "mixed" solvents in the other phase, i.e., in the double binary quaternary system can be predicted by an equation similar to Raoult's Law when ternary data only is needed for predicting the distribution in the quaternary.

NOTATION

$A, B, C \ldots$ = components $A, B, C \ldots$, respectively; X_{AB} = mole fraction of A in B rich phase
A = water
B = acetic acid
b = constant
C = n-butyl alcohol
D = n-heptane
E = n-butyl acetate
F = benzene
G = carbon tetrachloride
I = acetone
J = chloroform
K, K' = constants
L = methanol
M = methylnaphthalene
N = p-cresol
m, m' = constants
n, n' = constants
r = constant
EXP = experimental
FOR = formula

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Manuscript received April 18, 1979; revision received October 14, and accepted October 24, 1980.

Part II: Reaction Rate Studies and the Analysis of Batch Esterification in two phase Systems

The kinetics of the esterification of n-butyl alcohol with acetic acid has been studied experimentally in concentrated solutions at near ambient temperature in the presence of a sulphuric acid catalyst and the rate constants for the forward and reverse reaction determined.

The rate data obtained from the homogeneous system has been applied to analyse the performance of a batch-extractive reactor using n-heptane as solvent. The rate of mass transfer of the ester was found to be significant and when introduced in a model of the reaction process gave good agreement with the experimental results.

SCOPE

Butyl acetate is manufactured by the esterification of n-butyl alcohol with acetic acid in the presence of sulphuric acid at temperatures of the order of 100°C and the ester is removed from the reaction mixture by distillation using live steam. The esterification reaction has therefore been studied extensively at these elevated temperatures and rate equations and rate constants have been published that accurately describe the course of the esterification under these conditions. However, no kinetic data is available describing this reaction near ambient conditions. Therefore, since the object of the overall study was to assess the feasibility of producing n-butyl acetate in an extractive reactor, it was necessary to ascertain the kinetics of this esterification reaction under conditions that would prevail in an extraction column containing an organic solvent. In this particular study n-heptane was selected as solvent.

The esterification reaction has been performed in a single phase batch reactor and the rate of esterification determined. The effect of catalyst concentration on the specific reaction rate has been investigated and the influence of butyl sulphate on the course of the reaction at near ambient conditions ascertained. The rate data obtained from the homogeneous reaction studies have been applied to evaluate the performance of a two phase batch reactor using heptane as the immiscible hydrocarbon solvent. The effects of the rate of mass transfer on the rate of esterification and particularly on the significance of the reverse reaction have been considered in order to develop a model predicting the course of the extractive-reaction under batch operation.

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