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SALT EFFECT IN VAPOR-LIQUID EQUILIBRIUM
METHANOL-TOLUENE SYSTEM

BY

LINUS ENEMMOR ANEKE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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MASTER OF SCIENCE THESIS

OF

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1966

ABSTRACT

Vapor-liquid equilibrium data for the system methanol-toluene saturated with sodium bromide were determined at 760 mm Hg in an improved Othmer equilibrium still. The importance of salt-effect and the role of salt as a third component are discussed.

Analytical data for methanol-toluene solutions saturated with sodium bromide at 25^{o}C. are reported in the form of a refractive index-composition curve. Compositions were expressed on a salt-free basis.

Experimental vapor-liquid equilibrium data for the system methanol-toluene saturated with sodium bromide are reported over the entire composition range. The data were obtained in an atmosphere of helium at 760 mm Hg total pressure. Relative volatilities and activity coefficients were calculated and reported from the experimental equilibrium data. The significance of the relative volatilities and the activity coefficients was discussed. The data obtained by Burke and co-workers (8) for the binary system methanol-toluene were compared with those obtained in this study.

The experimental data were tested by the method of Redlich and Kister (56) and found to be thermodynamically consistent. A summary of the work done in salt-effect in vapor-liquid equilibrium is presented and suggestions for future work are made.

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I. INTRODUCTION AND THEORY

A. The Problem

The objective of this study was to investigate the effect of a dissolved salt on the vapor-liquid equilibrium of a binary system comprised of liquid components. Salt-effect in vapor-liquid equilibrium depends on the solubility characteristics of the salt and on the solvent properties of the liquid. Extensive studies have been made over the years of the effect of different salts on the vapor-liquid equilibrium of several binary organic mixtures. The interaction of a binary liquid mixture and a salt can fall into one of three categories:

1. The salt may be soluble in the high-boiling component and insoluble in the low-boiling one.
2. The salt may be soluble in the low-boiler and insoluble in the high-boiler.
3. The salt may be appreciably soluble in both components.

The first type is illustrated by the investigations of Rieder and Thompson (57) who studied the system ethanol-water saturated with potassium nitrate. The work of Tursi and Thompson (70), who used the system ethanol-water saturated with sodium sulfate, potassium sulfate and sodium nitrate, also comes under this type. From their findings these investigators came to two conclusions:

1. The addition of a salt which is relatively soluble only in the high-boiling component will cause a greater ease of separation between the components of a binary mixture.

2. The ease of separation increases as the solubility of the salt in the high-boiling component increases.

The second type is illustrated by the work of Ciesla (15) on the system ethanol-water-dimethylglyoxime. Dimethylglyoxime is relatively soluble in ethanol and insoluble in water. The relative volatility curve for this system shows a decrease in the volatility of ethanol as a result of the addition of the salt.

The third case is exemplified by the work of Chen (11), who investigated the system glycerol-water-sodium chloride. Sodium chloride is soluble in glycerol as well as water.

In the systems mentioned above, the binary liquid mixtures were saturated with salt. A summary of the work to date on vapor-liquid equilibrium with salt as a third component is given in Table X in the Appendix.

The present investigation was carried out on a system in which the salt was relatively soluble only in the low-boiling liquid component.

B. System Investigated

The system studied was methanol-toluene, saturated with sodium bromide. Mixtures of methyl alcohol and toluene are used in chemical processing. These solvents are frequently recovered or repurified by distillation. Vapor-liquid equilibrium data have been determined for this binary system by Burke and co-workers (8) and by Benedict and co-workers (2). The work of these investigators showed that a minimum-boiling azeotrope is formed at approximately 0.885 mole fraction methanol and a temperature of 63.6°C.

The purpose of the present work was to see what effect, if any, a salt such as a sodium halide would have on the vapor-liquid equilibrium of the system methanol-toluene. Sodium halides are very soluble in methyl alcohol but practically insolube in toluene. This work had the further purpose of trying to establish whether the salt would "break" or shift the azeotrope and make possible a more complete separation of the binary mixture by distillation.

Many investigations into salt-effect in vapor-liquid equilibrium have established that, for any appreciable effect on the vapor-liquid equilibrium to be observed, the salt must be reasonably soluble in the system. In other words, the influence exerted on the system increases as the solubility of the salt in the system increases. Sodium iodide was initially used in this study because it was very soluble in methanol. Other salts such as calcium nitrate, cupric chloride and sodium bromide, which are soluble in methanol, were also available.

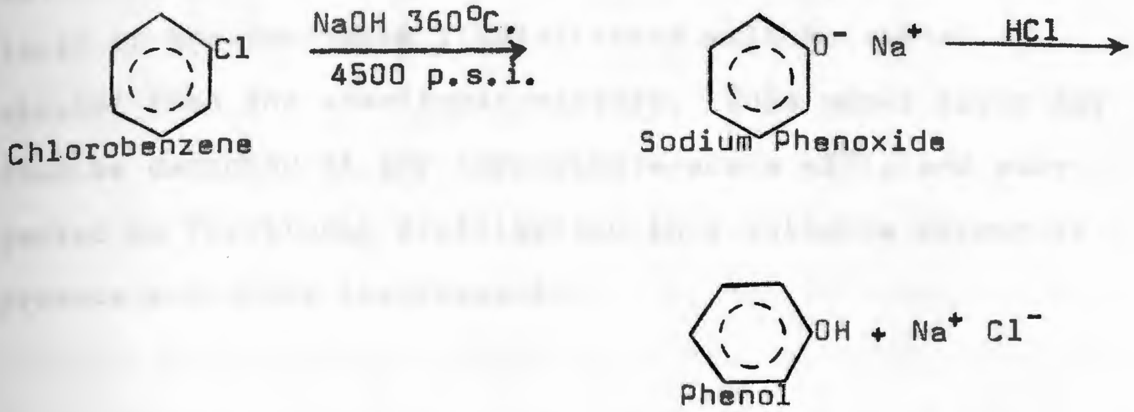
The use of sodium iodide was discontinued because it is one of those salts which are so soluble in methanol that the binary mixture of methanol and toluene separated into two liquid phases. Sodium iodide, calcium nitrate and cupric chloride all produced this effect at room temperature while, with sodium iodide, the two liquid phases persisted even at elevated temperatures. In this study, a two-phase liquid system was obviously undesirable because the improved Othmer still had no provision for sampling a two-phase liquid system either in the still-pot or in the condensate trap. Thus, although it was recognized that a two-phase liquid system would have made a very interesting study, it was not practical. The problem was eventually solved by substituting sodium bromide for sodium iodide. The former is much less soluble in methanol than the latter and therefore does not break the binary liquid mixture into two phases. The solubilities of several salts in methanol are presented in Table XI in the Appendix for comparison.

C. Importance of Salt-Effect

Salt-effect in vapor-liquid equilibrium is of definite industrial importance. This may be the reason for the research efforts already undertaken on the effect of various salts on the vapor-liquid equilibria of several binary mixtures and of ways of correlating and estimating salt-effect in vapor-liquid equilibrium. Extractive and azeotropic distillation are already widely used in industry in the separation of mixtures whose components boil so close together that they cannot be economically separated by fractional distillation. These special techniques have also been successfully used in separating mixtures which form azeotropes. In a similar manner, the addition of a salt to a binary mixture produces changes in relative volatility of the systems which can be adapted to separate the mixture into its components. Since the addition of a salt soluble in the high-boiling component increases the relative volatility of the more volatile component, it has been suggested (15) that an industrial application would be to add a salt directly to the still-pot of a fractionating column to increase the separation. The salt-effect, however, is not limited to increasing relative volatility. This was noted in the work of Garwin and Hutchison (22), in which acetic acid was separated from water. In this case a condition of reversed relative volatility was observed because of the presence of calcium chloride. In the fractional distillation of a binary mixture of water and acetic acid, water is recovered in the overhead and acetic acid in the bottoms. By saturating the mixture with calcium chloride, acetic acid is recovered in the overhead and water in the bottoms. An advantage of this reversed relative volatility is that acetic acid, which now appears at the top of the column, may be recovered from dilute solutions of acetic acid in water with a small amount of heat and therefore reduced costs.

Several investigators (23,24,68,69), have proposed a method for the recovery of inorganic salts from aqueous solutions by the addition of a liquid organic solvent to crystallize out the salt. For such a process to be commercially feasible, the solvent must be cheaply recovered. Since this is usually done by distillation, the effect of the salt on the vapor-liquid equilibrium of the system would have to be known.

Many organic syntheses involve an alkali or acid hydrolysis of an intermediate compound resulting in an organic-water-salt mixture from which the valuable organic product must be separated. In many such cases, distillation affords the most economical means of separating the components. The presence of the salt will affect the vapor-liquid equilibrium relationship of the system. Its effect must therefore be determined. The large scale manufacture of phenol involves an alkaline hydrolysis of chlorobenzene. In this process, known as the Dow process (45), chlorobenzene is allowed to react with aqueous sodium hydroxide at a temperature of about 360°C. and a pressure of 4500 p.s.i.



The product is sodium phenoxide which is neutralized by hydrochloric acid to yield a phenol-water-salt solution. It is very difficult to isolate phenol in this synthesis. Bogart and Brunjes (4) have shown that recovery becomes commercially feasible, by distillation, in the presence of a salt. The salt performs a function comparable to a solvent in extractive distillation.

Another application of the salt-effect in vapor-liquid equilibrium is in attempting to "break" or shift the azeotrope of a binary mixture. Mariller and Coutant (41) successfully used this technique to produce anhydrous ethanol from an ethanol-water mixture by the addition of mercuric chloride as a third component. Kyrides and co-workers (36) used the alkali salts of high-boiling alcohols, glycols, and glycerol for the dehydration of the lower-boiling alcohols which are difficult to dehydrate by ordinary means, although it was not possible to obtain absolute alcohol by this method. Thompson and Molstad (68) proposed a method for producing anhydrous isopropanol. They found that if an isopropanol-water mixture is saturated with ammonium nitrate above 41°C., the upper layer of the two-phase liquid formed will be richer in alcohol than the azeotropic mixture. This upper layer may then be decanted at any temperature above 41°C. and subjected to fractional distillation in a suitable column to produce anhydrous isopropanol.

D. The Role of a Salt as a Third Component

The usual ternary liquid system relationships do not apply to binary liquid mixtures saturated with salts, because of the non-volatile nature of the salts. Furthermore, the physical laws of solutions are inapplicable to solutions of electrolytes, especially concentrated solutions of electrolytes, since many of these physical laws are based on the assumption of ideal behavior and are generally applicable only to dilute solutions (17). The role of a salt as a third component in a binary liquid mixture can be correlated in terms of the four colligative properties of solutions: vapor-pressure reduction, boiling-point elevation, freezing-point depression, and osmotic pressure, which are closely inter-related. The most obvious relation would be between the lowering of the solvent vapor-pressure upon addition of a solute and a corresponding reduction in the volatility of the solvent. Thus, a salt that is soluble in the less volatile component of a binary system and insoluble in the more volatile component would effectively increase the relative volatility of the more volatile component and make separation easier. Conversely, if the salt is soluble in the more volatile component, separation would be more difficult.

Another factor which must be considered in a quantitative study of salt-effect is the extent of dissociation or association of the solutes in solution. If there is dissociation, the vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure will be increased over the values expected for a non-dissociating solute. For an associating solute, these quantities will be decreased (17). In order to avoid complications, most of the quantitative study on solutions have been restricted to dilute solutions of solutes which do not dissociate or associate in solution (17). Another problem that may arise is the possibility of intermolecular reaction or ionic-molecular attraction between the salt ions and the molecules of one or both of the solvents. It seemed reasonable to postulate that inter-ionic forces, ion-molecule forces, polarity of the solvents, dielectric constants of the solvents, and perhaps many other phenomena play some part in determining the effect of any salt on any binary system. However, Fogg (20) has stated that the concentration of the salt would be the primary factor in determining the magnitude of the salt-effect, whereas the relative solubilities of the salt in the two liquid components would control the direction of the change of relative volatility.

In cases where normal distillation methods are impractical, a third component is introduced into a distillation charge to improve the separation. This difficulty of separation may be a result of azeotrope formation or of very low relative volatility over a wide concentration range. Therefore by adding a third component which will reduce the partial vapor pressure of the higher-boiling component without affecting the other, the relative volatility of the mixture will be enhanced and separation by distillation will be easier. Most industrial applications of this technique in extractive and azeotropic distillation have employed a liquid as a third component. Walker and his colleagues (74) suggested a modification of this method by the addition of a material which is very soluble in one but not in the other component. Such a material would obviously lower the vapor pressure of the first component but not the second. The work of Rieder and Thompson (57), and Tursi and Thompson (70), and others, have verified that the relative volatility of a binary mixture is increased by the addition of a salt soluble in the high-boiling component and insoluble in the low-boiling.

The non-ideality of a given mixture is indicated by the activity coefficients. Therefore the effect of the third component can be observed by noting the difference between the activity coefficients of this mixture and that of the corresponding binary mixture. Studies by several investigators (57) confirm that the addition of a salt to a binary liquid mixture increases the non-ideality of the system. However, there are other factors contributing to the non-ideality of a system besides the salt-effect. These include:

1. Differences in "internal pressure" or molecular attraction force which favor positive deviations.

2. Compound-formation between two components or a marked difference in size, giving negative deviations.

E. Correlating Salt-Effect in Vapor-Liquid Equilibrium

Several investigators have attempted to develop correlations for the prediction of salt effect in binary vapor-liquid equilibrium. Notable among these are Ramalho and Edgett (54), Tursi and Thompson (70), Fogg (20), Lu (37), and Johnson and Furter (31,32).

Lu (37) proposed a method which uses, as primary information, the vapor-pressure lowering of the pure components resulting from addition of salt, and vapor-liquid equilibrium data under salt-free conditions. The proposed empirical method is limited to the following conditions:

1. The salt does not have any chemical effect on the components, such as the formation of hydrate or alcoholate with the liquid components.

2. The salt-free binary system does not deviate much from ideality.

3. The salt solution is saturated. In dilute salt solutions, the vapor-pressure lowering of the pure solvents is related to the concentration through Raoult's Law.

$$x_s = \frac{p^0 - p}{p^0} \qquad (1)$$

where x_s is mole fraction of the solute; p^0 is the vapor pressure of the pure solvent; and p is the vapor pressure of the solution at the same temperature. For binary vapor-liquid equilibrium calculations, under salt-free conditions, and assuming that the vapor phase is an ideal mixture, the total pressure is given by

$$\pi = x_1 \gamma_1 p_1^0 + x_2 \gamma_2 p_2^0 \qquad (2)$$

where γ refers to activity coefficient and subscripts 1 and 2 refer to components 1 and 2 respectively. For saturated solutions, Equation 1 often does not apply. Hence Lu defined a pseudo mole fraction of the solute using Equation 1. When salt is added, the liquid mole fraction terms in Equation 2 are modified as follows:

$$x_1' = \frac{x_1}{x_1\left(\frac{p_1^0}{p_1}\right) + x_2\left(\frac{p_2^0}{p_2}\right)} \qquad (3a)$$

$$x_2' = \frac{x_2}{x_1\left(\frac{p_1^0}{p_1}\right) + x_2\left(\frac{p_2^0}{p_2}\right)} \qquad (3b)$$

where p_1 and p_2 are vapor pressures of the solutions, salt plus pure liquid 1 and salt plus pure liquid 2, respectively, at the boiling point; p_1^0 and p_2^0 are the vapor pressures of the pure components 1 and 2, respectively, at the same temperature. According to Equation 1, $\frac{p^0}{p} = \frac{1}{1 - x_s}$.

Using 1 mole of salt free solution, the ratio $\frac{p^0}{p}$ gives the total number of moles of salt solution available (number of moles of salt and 1 mole of salt-free liquid). In Equation 3, the term $\frac{p_1^0}{p_2^0}$, means the number of moles of salt solutions per mole of salt-free liquid component 1, and the term $x_1\left(\frac{p_1^0}{p_1}\right)$ represents the number of moles of salt solution contributed from liquid component 1. Similarly, $\frac{p_2^0}{p_2}$ means the number of moles of salt solution per mole of salt-free liquid component 2 while the term $x_2 \frac{(p_2^0)}{(p_2)}$ represents the number of moles of salt solution contributed from liquid component 2. In both cases, pseudo mole fraction of the salt is employed. Thus the quantities x_1' and x_2' in Equation 3 may be considered as the effective mole fractions of the liquid components. The quantities γ_1 and γ_2 may be taken from the salt-free vapor-liquid data at the corresponding x_1 and x_2. Thus the boiling point corresponding to the given total pressure π can be determined by the equation

$$\pi = x_1'\gamma_1 \; p_1^0 + x_2'\gamma_2 \; p_2^0 \qquad (4)$$

The equilibrium vapor compositions are evaluated by

$$y_1 = \frac{x_1'\gamma_1 \; p_1^0}{\pi} \qquad (5a)$$

$$y_2 = \frac{y_2'\gamma_2 \; p_2^0}{\pi} \qquad (5b)$$

The correlation proposed by Ramalho and Edgett (54) is interesting because it was designed to apply only to non-saturated solutions. In nearly all the correlations proposed by previous investigations, saturated salt solutions were employed so that a more pronounced effect would be observed. Ramalho and Edgett, however, decided to avoid saturated solutions, but made the salt concentration in solution a constant parameter for each system studied. They proposed a correlation which would permit prediction of the salt effect from a minimum of experimental data. The authors also presented a theoretical justification for the proposed correlation, based upon consideration of the change of chemical potentials of the two volatile components due to salt addition. The correlation consisted of the use of reference-system charts with the following **coordinates.**

Ordinate: Relative volatilities (α_s) for the system 1-2-salt, where 1 and 2 are the liquid components.

Abscissa: Values of the relative volatilities (α) for the reference system 1-2.

The ordinates are plotted versus the abscissa at corresponding equal values of the liquid composition x. Several straight lines are obtained corresponding to the several different concentrations of dissolved salt. The straight line relationship fails only after saturation is reached. When this happens, the concentration of dissolved salt is no longer constant since salt-precipitation occurs. This means that there is a variation in the concentration of dissolved salt over the binary liquid composition range. This is due to the fact that the solubility of the salt is usually not the same in the two liquid components at all compositions, even though the liquid mixture may be saturated at the different binary compositions.

Fogg (20) proposed an empirical correlation which relates the fractional change in the activity coefficients of both components, caused by addition of a salt, to the solubility of the salt in the pure components. From this correlation, he believed that the effect of any salt on a binary system can be predicted under the following conditions:

1. Experimental data are available for the effect of three or four representative salts on the system.

2. The salts do not react with the liquid components.

3. The salts exhibit similar ionic properties.

II. EXPERIMENTAL

A. Chemicals Used

Toluene. The toluene used in this work was of analytical reagent grade, purchased from the Mallinckrodt Chemical Works. The boiling point of the chemical was quoted as 110.6°C. which is the literature value of the normal boiling point of toluene. The maximum impurities were listed as 0.03%. The boiling point of the toluene was experimentally determined in the apparatus of this investigation to be 110.6°C. As a further check of the purity of this reagent, a sample was analyzed on a gas chromatograph. No impurities were detected at the highest sensitivity of the instrument. As a final check for purity, the refractive index of the toluene was determined and found to be $n_D^{25} = 1.49420$. This value is in good agreement with the literature value $n_D^{25} = 1.49428$ reported by Burke and co-workers (8). The toluene was therefore used without further purification.

Methanol. The methanol, also purchased from the Mallinckrodt Chemical Works, was of analytical reagent grade. It was specified to be anhydrous and acetone-free, with a boiling point of 64.6°C. The minimum assay was quoted as 99.5% methanol by volume and the water content was guaranteed to be no more than 0.10%. Refractive index measurements and gas chromatographic analysis showed that further purification was necessary. In the gas chromatographic analysis of the methanol, a small peak, other than that for methanol, was observed. A few drops of water were deliberately added to the methanol sample and another analysis was carried out. Peaks were observed at the same places as before except that the impurity peak was considerably increased. This simple test indicated that the impurity was water. The methanol was therefore distilled over calcium oxide and the middle cut was retained. The boiling point was found to be 64.7°C. which is the value given in the literature for pure methanol (30). The refractive index (n_D^{25}) of the methanol was found to be 1.32690 at 25°C. This value is very close to that determined by Burke and co-workers (8), $n_D^{25} = 1.32691$. Chromatographic analysis of the distilled methanol showed only one peak, obviously that for methanol. This indicated that the methanol had been successfully purified.

<u>Sodium Bromide</u>. The sodium bromide used in this study was a product of the General Chemical Division of the Allied Chemical Company. The salt was of reagent grade and in granular form. It was used as received without further purification.

B. Apparatus

The vapor-liquid equilibrium still employed was an 800-ml. improved Othmer still shown in Figure 1. This type of still has been widely used with great success by several investigators (11,15,54,57,70). Moreover, the improved Othmer type was rated very high by Fogg (20) in his comparison of equilibrium stills. However, it was recognized that a recycling type of equilibrium still like this one, also known as a continuous distillation equilibrium still, has advantages as well as disadvantages. The main advantages are that it is simple and that the unit can be placed in operation and allowed to come to a steady state without any great amount of attention (60). The disadvantages which may lead to serious errors are (60):

1. Partial condensation of the vapors, thereby increasing the concentration of the more volatile component in the vapor.

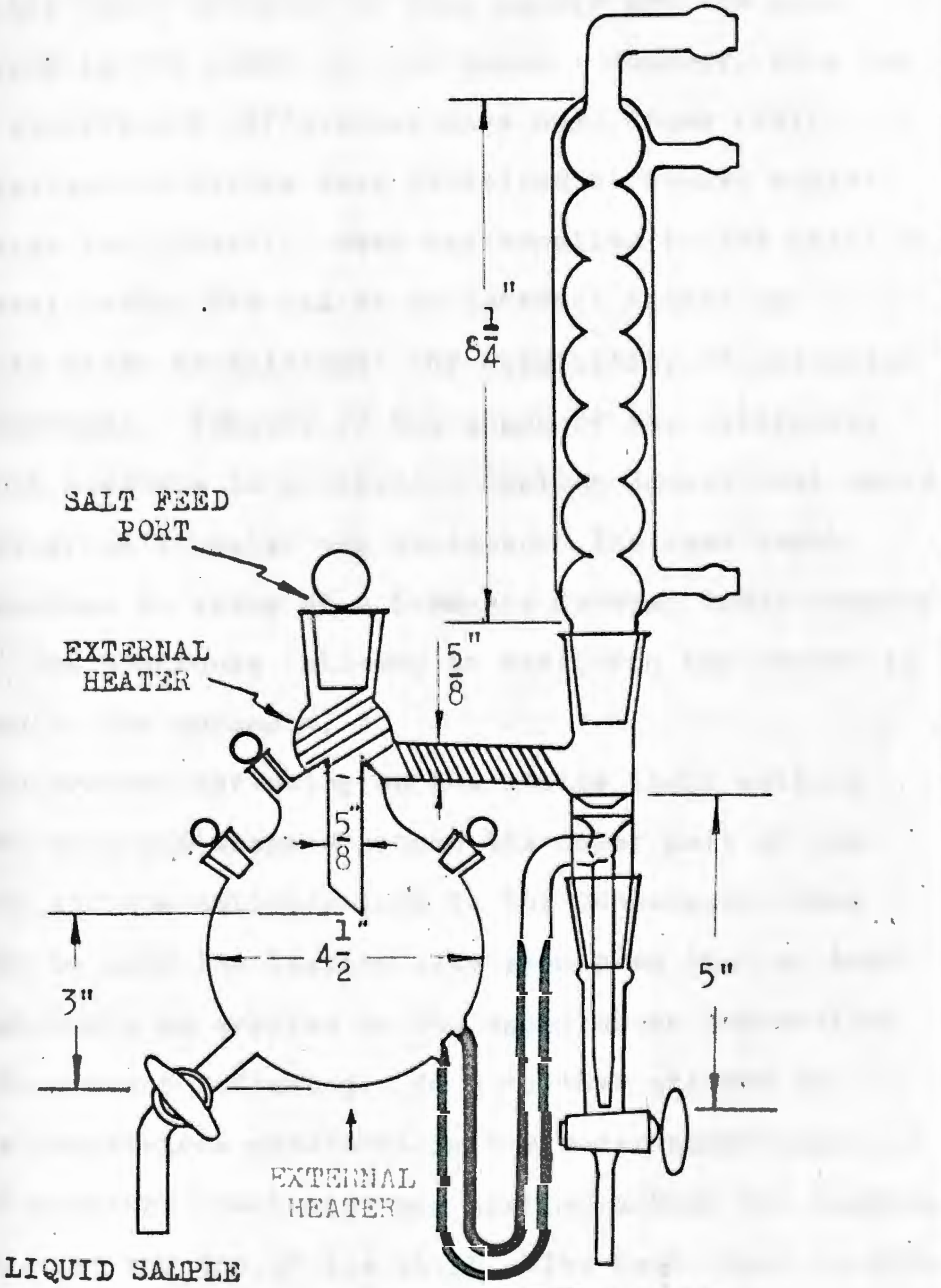
2. Entrainment of liquids in the vapor leaving the still-pot, thus increasing the concentration of the less volatile component in the vapor.

3. Inadequate or slow mixing of the returning condensate with the liquid in the still-pot causing the condensate, which is of a different composition from the liquid in the still and, in general, of a lower boiling point to flash as soon as it meets the hot liquid. The vapor obtained in this case is not an equilibrium vapor.

4. This method assumes that the vapor obtained by boiling a liquid is in equilibrium with the liquid. There

FIGURE 1

IMPROVED OTHMER STILL


SALT FEED PORT
EXTERNAL HEATER
$8\frac{1}{4}$"
$\frac{5}{8}$"
$\frac{5}{8}$"
$4\frac{1}{2}$"
3"
5"
EXTERNAL HEATER
LIQUID SAMPLE
VAPOR SAMPLE

has been no adequate proof of this assumption. Some theoretical considerations would tend to indicate that equilibrium should not be obtained (60). Available experimental data indicate that the difference in composition between the vapor obtained in this manner and the true equilibrium is not great in most cases. However, in a few systems significant differences have been found (60).

Systematic errors were minimized by proper equipment design and control. Heat was supplied to the still by an external heater. The use of an internal heater was avoided in order to eliminate the possibility of oxidation of the methanol. Because of the shape of the still-pot, it was not possible to purchase a heating jacket that would fit. Therefore a heater was designed. The heat input was controlled by means of a 5-ampere General Radio Company Variac. The procedure followed in designing the heater is presented in the Appendix.

To prevent refluxing on the inside still wall, a length of wire was wrapped around the upper part of the still-pot and the delivery tube to the condenser. Care was taken to wind the heating wire evenly so that an even superheat could be applied to the vapor above the boiling liquid to prevent refluxing. In a further attempt to minimize temperature gradients in the superheated vapor, a layer of asbestos insulation was applied around the heating wire and over the top of the still. The heat input to this heating wire was controlled by another 5-ampere Variac made by the General Radio Company. The still was enclosed in a large wooden box, which was open at the top and was equipped with glass doors at the front so that the still could be observed from outside. With these precautions the effects of air currents were minimized and the still was assumed to operate under adiabatic conditions.

A Cartesian Manostat, Model #8, made by Greiner Scientific Corporation, was used to maintain the system at a constant pressure of 760 mm Hg. A tank of helium was used to supply pressure to the system while vacuum was obtained with a water aspirator. With this type of manostat there was no need for a surge tank because the instrument responded immediately to any slight pressure rise in the system. All experimental data were taken at 760 ± 2.0 mm of mercury. The manometer was made by the Meriam Company of Cleveland, Ohio. Mercury was the manometric fluid.

Vapor temperatures in the still were measured with a mercury-in-glass thermometer whose scale is in 0.2°C. divisions. Because of the superheat required to prevent refluxing, accurate measurement of the boiling temperature in the still was not possible. Rather, boiling point data were obtained in a 2000 ml. three-necked flask, which was kept approximately one-half full with saturated solution. A condenser was inserted into the center neck so that boiling could be done under total reflux. The top of the condenser was connected to the pressure controller described above so that the normal boiling points of the mixtures could be obtained. In one side neck a calibrated thermometer was immersed in the liquid so that the boiling temperature of the latter could be determined. In the other side neck another calibrated thermometer was located approximately one inch above the surface of the liquid in order to give the temperature of the vapor assumed to be in equilibrium with the boiling liquid. The effect of radiation on the thermometers was assumed negligible. Corrections were made for the emergent stem of the thermometer.

Ten ml. Weld-type, capped specific gravity bottles were used to weigh the liquid mixtures used in preparing the refractive index-composition calibration curve for the system methanol-toluene saturated with sodium bromide. Special 75-ml. narrow-necked bottles were used for all liquid samples for the refractive index analysis.

C. Analytical Technique

Refractive index-composition data have been reported for the system methanol-toluene by Burke and co-workers (8). Three main reasons indicated the use of refractive index measurements as the analytical technique: high accuracy; relatively short times required to analyze each sample; and the need of only small samples for each analysis. In addition to the above reasons, it was intended to use the data of Burke and co-workers to plot a calibration curve of refractive index versus composition for the system methanol-toluene containing no salt. Because the data of Burke and co-workers were determined at 25°C., all refractive index measurements made in the present study were at 25°C.

For the refractive index measurements, a Bausch and Lomb precision refractometer was employed. Using this instrument, it was possible to reproduce refractive index measurements with a precision of ± 0.00005, but the values were reported to only four decimal places. The temperature of the prism was maintained at 25 ± 0.05°C. by a precision constant temperature bath. Burke and co-workers (8) claimed that the refractometer yielded analyses with an estimated maximum error of ± 0.03 mole % absolute. Their claim seems to be too optimistic. The data from the present study, like those of Burke et al., are reported to the nearest 0.1 mole %.

The General Electric Sodium Lab-Arc, which is installed as a permanent part of the precision refractometers, was used as a light source in the determination of the basic index values. A type NB Colora Ultra-Thermostat constant temperature bath was used. It has a built-in pump which circulates the bath water through the refractometer prisms. Typically, only a few trials of cooling water flow rate were required. Once the right flow rate was established and steady operation was obtained, the temperature was constant at 25 ± 0.05°C.

In order to obtain reproducible results, it was necessary to transfer samples to the refractometer as quickly as possible. This was accomplished by the use of medicine droppers. The number of drops of sample used tended to make a slight difference in the sharpness of the dividing line which consequently affected the results obtained. In order to obtain reprodubible results, two, or at the most three, drops were used each time. As a final precaution any drops suspended at the tip of the dropper were absorbed on blotting paper. This was necessary because drops exposed to the atmosphere partially evaporated during transfer to the refractometer. This made it very difficult to obtain reproducible results.

In analyzing salt-saturated samples, some authors (20,71) first separated the salt from the liquid samples, and then analyzed the salt-free liquids; others (15,70) determined its density at a known temperature; while at least one author (11) determined the refractive index of a binary liquid mixture saturated with a salt.

In this work, the analyses of salt-saturated liquid samples were accomplished by refractive index measurements. A calibration curve for the methanol-toluene system saturated with sodium bromide was prepared at 25°C. The system methanol-toluene saturated with sodium bromide may be suitably analyzed by refractive index measurements. In the first place sodium bromide is not excessively soluble in the system methanol-toluene (64). Thus precipitation of sodium bromide on the refractometer prisms would not cause difficulties provided the prisms are properly cleaned and dried after each analysis. Secondly, the methanol-toluene mixtures saturated with sodium bromide are optically clear over the whole range of compositions. Hence they can be analyzed by refractive index measurements (51).

In order to obtain refractive index-composition data, mixtures of methanol and toluene were accurately weighed in ten ml. Weld-type specific gravity bottles. Hypodermic syringes were used when necessary to inject the required amounts of the liquids into the bottles. The weighing instrument was a Sartorius Balance. The compositions of the samples were first checked by measuring their refractive indices at 25°C. The solutions were then saturated with sodium bromide and kept in the constant temperature bath at 25°C. for several hours for thermal equilibrium to be reached.

The results of this work together with the refractive index of methanol-toluene solutions are plotted in Figure 2. The plot for the salt-saturated system is on a salt-free basis. The experimental data of refractive index of methanol-toluene-sodium bromide solutions at 25°C. are listed in Table I. In addition, the refractive

FIGURE 2

REFRACTIVE INDICES OF MIXTURES OF METHANOL AND TOLUENE AT 25°C.

(EXPERIMENTAL DATA)

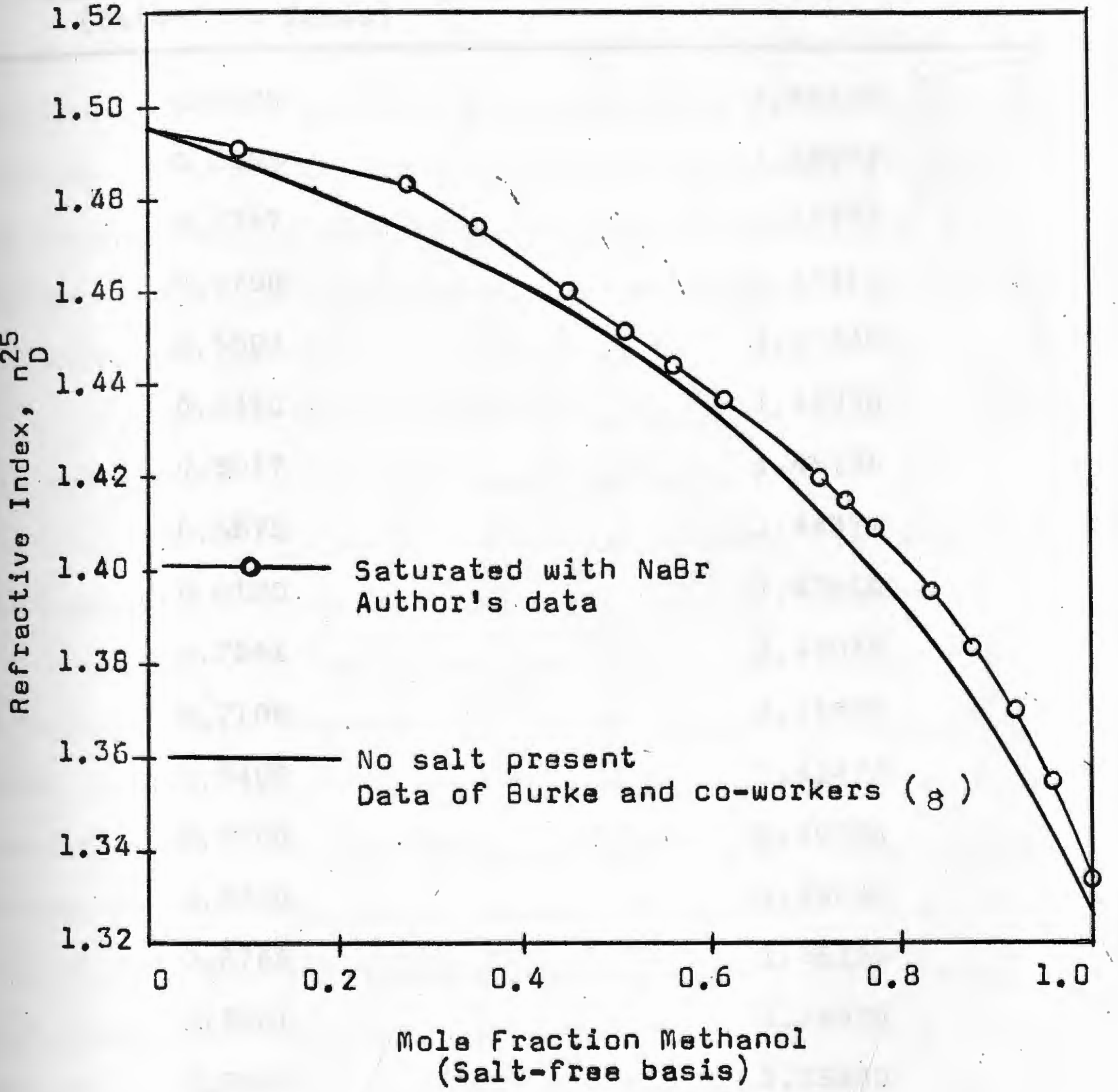

1.52
1.50
1.48
1.46
1.44
1.42
1.40
1.38
1.36
1.34
1.32
Refractive Index, n_D^{25}
0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol
(Salt-free basis)
Saturated with NaBr
Author's data
No salt present
Data of Burke and co-workers (8)

TABLE I

REFRACTIVE INDEX-COMPOSITION DATA AT 25°C. FOR METHANOL-TOLUENE SOLUTIONS SATURATED WITH SODIUM BROMIDE

Mole Fraction Methanol (Salt-free Basis)	Refractive Index
0.0000	1.49430
0.0953	1.48972
0.2727	1.48272
0.2780	1.48210
0.3504	1.47340
0.4420	1.45930
0.5017	1.45106
0.5575	1.44371
0.6100	1.43610
0.7061	1.42045
0.7100	1.41990
0.7400	1.41470
0.7700	1.40890
0.8300	1.39520
0.8769	1.38330
0.9201	1.36970
0.9603	1.35400
1.0000	1.33260

index composition data for methanol-toluene solutions at $25^{o}C$. are given in Table VIII in the Appendix. These data are those reported by Burke and co-workers (8).

Gas Chromatography was seriously considered as a method of analysis since it has definite advantages for binary liquid mixtures saturated with inorganic salts. An obvious advantage is that, since the salt is non-volatile, only one calibration curve would be required to analyze the liquid and the vapor samples. Refractive index measurement was chosen over gas chromatography for the following reasons:

1. A refractive index-composition calibration curve for methanol-toluene was already available.

2. The refractive index measurements were simpler and quicker than gas chromatography.

3. Gas chromatography is not as accurate as refractive index measurement. Lu et al. (38) estimated an error of ± 0.2 mole% using a Bausch and Lomb Abbe-3L precision refractometer and an error of ± 0.5 mole% using a Perkin-Elmer Model 154-C Vapor Fractometer. Bowden (6), however, thought the error-estimate on the Perkin-Elmer instrument was optimistic, and suggested a minimum error of 2-5%.

D. Experimental Procedure

Performance tests such as ability to reproduce data for well-known binary systems, approach to steady-state, and liquid entrainment tests were conducted. Equilibrium points were determined for ethanol-water and methanol-toluene systems at atmospheric pressure. The values obtained checked very well with those presented by Chu (14), and those of Burke et al. (8).

1. Charging the Still

The still was charged with approximately 300 ml. of solution in each run. Saturation was assured by adding enough salt so that an excess was always observed at the bottom of the still. Initially the still was charged with approximately 250 ml. of pure methanol. Then the concentration of the mixture was varied by adding toluene or methanol to the mixture from the previous run. For higher methanol concentrations, the alcohol and salt were added directly to the still. For higher toluene concentrations, it was necessary to empty the contents of the still into a beaker, add the toluene and reintroduce the mixture into the still, leaving some of the salt in the beaker. In this way, the salt precipitated when toluene is added is prevented from plugging the liquid sample cock. The still was operated for at least four hours to insure the attainment of equilibrium. The criterion for equilibrium was a constant temperature for the particular run. During this study the vapors were superheated by 5-10°C. by supplying heat to the insulated portion of the still so that no refluxing would be observed in the vapor channel.

2. Pressure Control

Atmospheric pressure was measured by means of a mercury column barometer located in the same building as the apparatus. The pressure in the still was adjusted to 760 mm Hg with the manostat. Pressure was controlled only after the addition of all components, and after it had been established that the mixture was saturated. With the pressure adjusted and no abnormal behavior such as leakage observed in the system, the timing of the experimental run was begun.

3. Temperature Measurements

Vapor temperatures in the still were measured with a mercury-in-glass thermometer calibrated against an A.S.T.M. thermometer. The thermometer was read at frequent intervals throughout the course of each run in order to keep track of the approach of the system to equilibrium. In most cases the temperature remained constant after the still had been operated for about two hours. It was then allowed to run for another two hours before samples were taken.

4. Sampling Technique

After the minimum time of four hours had elapsed, the following standard procedure was followed for taking the samples:

1. Clean sample bottles were taken from the oven and allowed to cool in a desiccator at room temperature.
2. The sample outlets were cleaned and dried with a pipe cleaner.

3. All heating elements were turned off.

4. The system was vented to the atmosphere.

5. About ten ml. of the condensate were drained off in order to flush the stopcock bore.

6. The vapor sample bottle was immersed in an ice bath. About 10 ml. of condensate were collected and the sample bottle was immediately stoppered and labelled.

7. Approximately 20 ml. of liquid were drained from the still-pot in order to flush the stopcock bore.

8. Sodium bromide was introduced into the liquid sample bottle. This was to ensure that the liquid samples would still be saturated.

9. The liquid sample bottle was immersed in an ice bath. About 20 ml. of liquid sample were collected, and the bottle was immediately stoppered and labelled.

10. Both samples were refrigerated until they were transferred to the constant temperature bath.

By strictly following the above procedure, the errors introduced by sampling were reduced to a minimum.

5. Refractive Index Measurement

The samples were analyzed as soon as possible after completion of a run. The samples were left overnight in the constant temperature bath in order to ensure thermal equilibrium and saturation of the liquid sample. In every run the vapor sample was analyzed before the liquid sample. The refractometer prisms were carefully washed with methyl alcohol, allowed to dry, and cleaned with lens paper. Any specks of foreign material were removed with camel-hair brush.

III. EXPERIMENTAL RESULTS

A. Experimental Vapor-Liquid Equilibrium Data

The following factors were determined experimentally for each run: duration of run, total pressure, vapor composition expressed as mole fraction methanol, and liquid composition expressed as mole fraction methanol on a salt-free basis. These values are given in Table II. The equilibrium data for the system methanol-toluene saturated with sodium bromide are shown in Figure 3. The data obtained for methanol-toluene by Burke et al. (8), listed in Table VII in the Appendix, are also plotted on the same curve for comparison.

TABLE II

EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA OF METHANOL-TOLUENE-SODIUM BROMIDE SYSTEM (under Helium)

Run No.	Duration of Run, Hours	Total Pressure mm Hg	Mole Fraction Liquid x_1	Mole Fraction Vapor y_1
1-5	Preliminary Runs			
6	6.0	760 ± 2.0	0.912	0.877
7	6.5	760 ± 2.0	0.930	0.905
8	5.5	760 ± 2.0	0.953	0.939
9	5.5	760 ± 2.0	0.343	0.783
10	5.5	760 ± 2.0	0.011	0.051
11	6.0	760 ± 2.0	0.288	0.770
12	5.0	760 ± 2.0	0.121	0.721
13	5.0	760 ± 2.0	0.155	0.731
14	4.5	760 ± 2.0	0.600	0.821
15	6.0	760 ± 2.0	0.517	0.813
16	4.5	760 ± 2.0	0.690	0.824
17	5.5	760 ± 2.0	0.829	0.840
18	6.0	760 ± 2.0	0.888	0.860
19	7.0	760 ± 2.0	0.926	0.892
20	6.0	760 ± 2.0	0.886	0.858
21	6.0	760 ± 2.0	0.446	0.814
22	6.5	760 ± 2.0	0.018	0.144
23	6.5	760 ± 2.0	0.071	0.560
24	6.0	760 ± 2.0	0.120	0.690
25	6.0	760 ± 2.0	0.032	0.214
26	6.5	760 ± 2.0	0.095	0.660

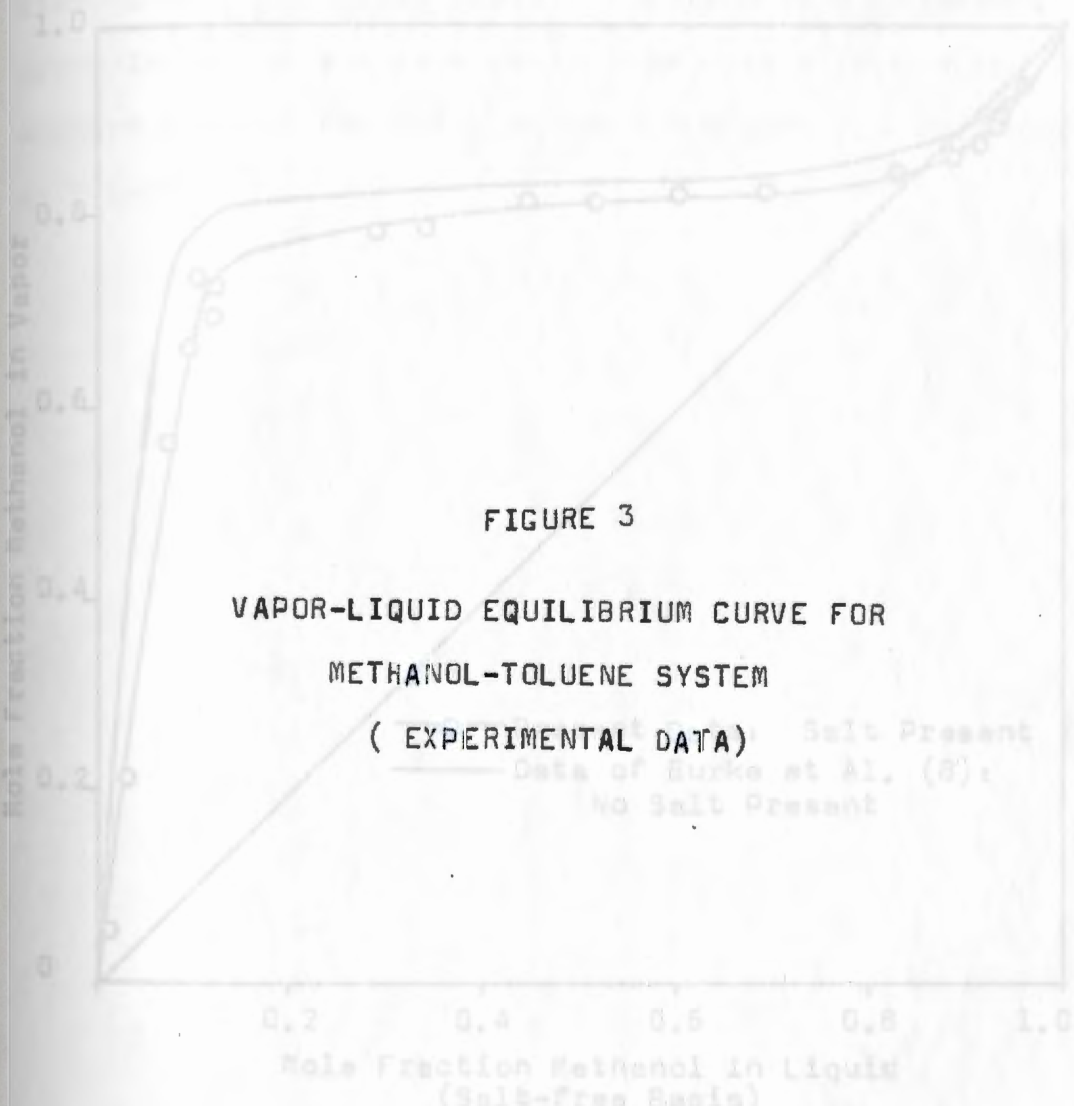
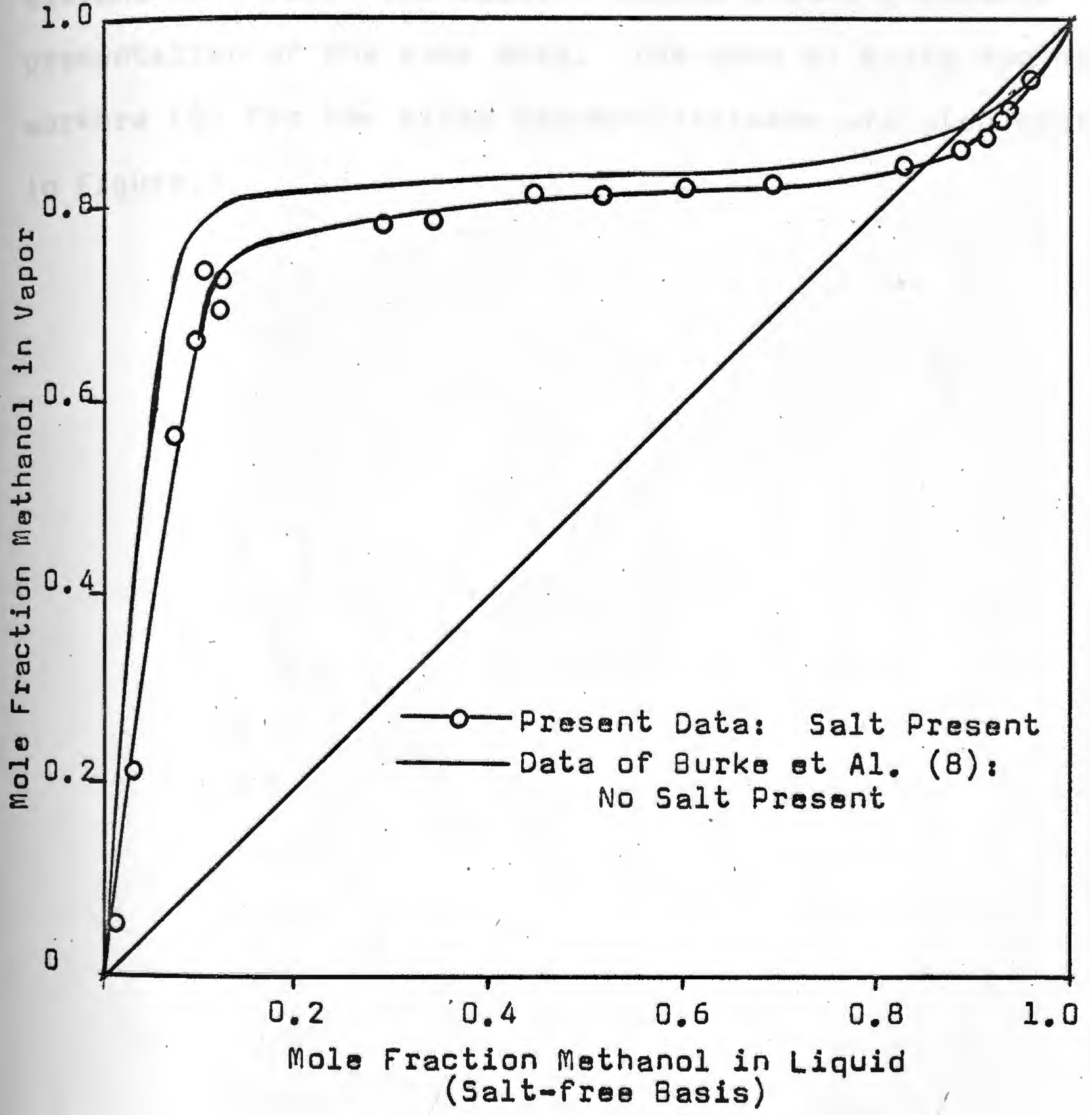


FIGURE 3

VAPOR-LIQUID EQUILIBRIUM CURVE FOR
METHANOL-TOLUENE SYSTEM
(EXPERIMENTAL DATA)


1.0
0.8
0.6
0.4
0.2
0
Mole Fraction Methanol in Vapor
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol in Liquid
(Salt-free Basis)
Present Data: Salt Present
Data of Burke et Al. (8): No Salt Present

B. Boiling Point-Composition Data

The experimental boiling point data for methanol-toluene mixtures saturated with sodium bromide are presented in Table III with the corresponding liquid compositions on a salt-free basis. Figure 4 is a graphical presentation of the same data. The data of Burke and coworkers (8) for the ystem methanol-toluene are also plotted in Figure 4.

TABLE III

BOILING POINTS AT ATMOSPHERIC PRESSURE OF METHANOL-TOLUENE SOLUTIONS SATURATED WITH SODIUM BROMIDE

Mole Fraction Methanol Liquid, x_1	Temperature, ^{0}C. Liquid
0.000	110.6
0.012	107.3
0.108	74.5
0.155	72.4
0.180	71.2
0.244	69.4
0.323	67.2
0.368	66.5
0.425	65.9
0.480	65.6
0.563	65.5
0.625	65.4
0.685	65.2
0.768	65.1
0.838	65.0
0.892	65.1
0.928	65.7
0.944	66.1
0.948	66.4
1.000	67.4

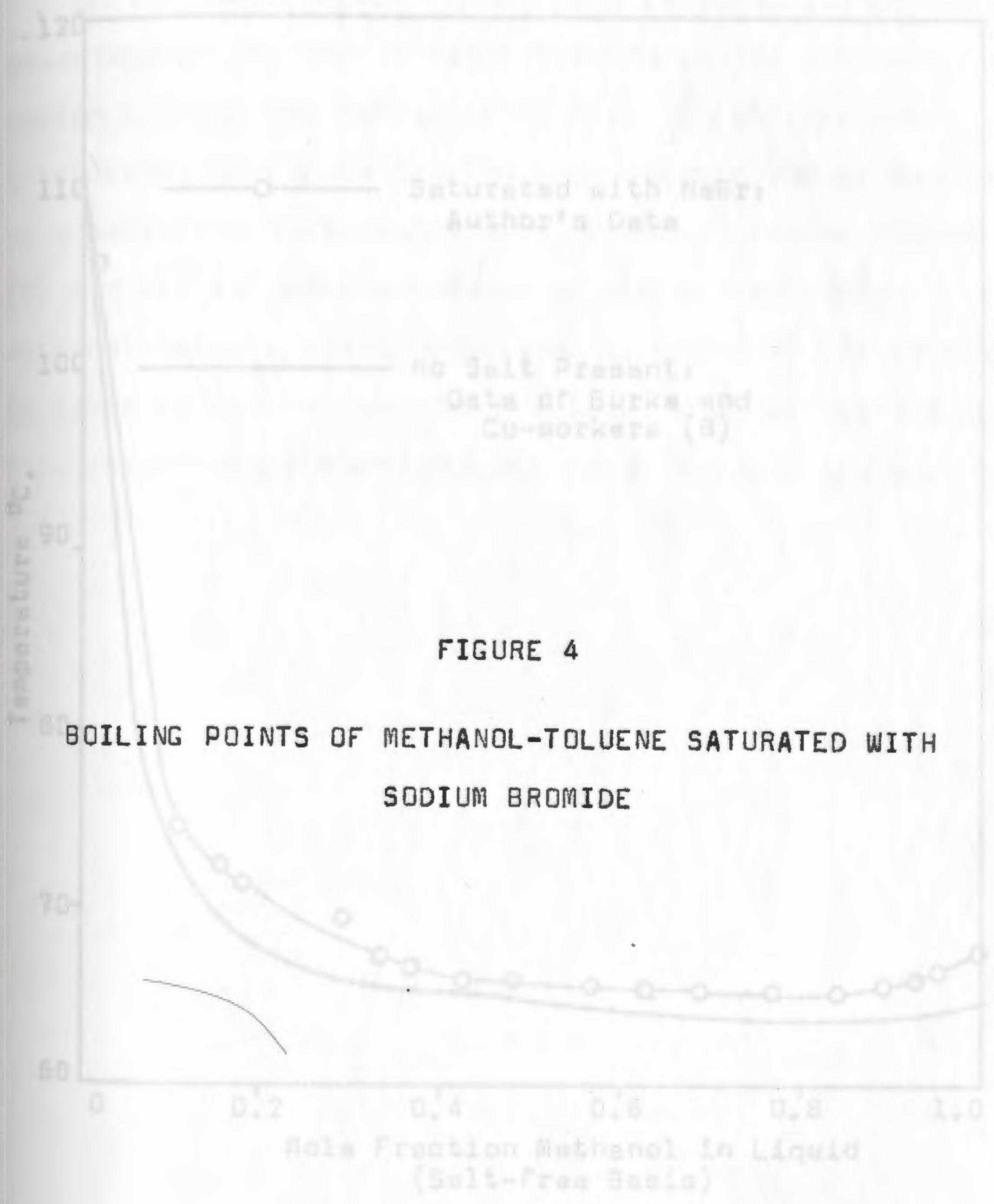
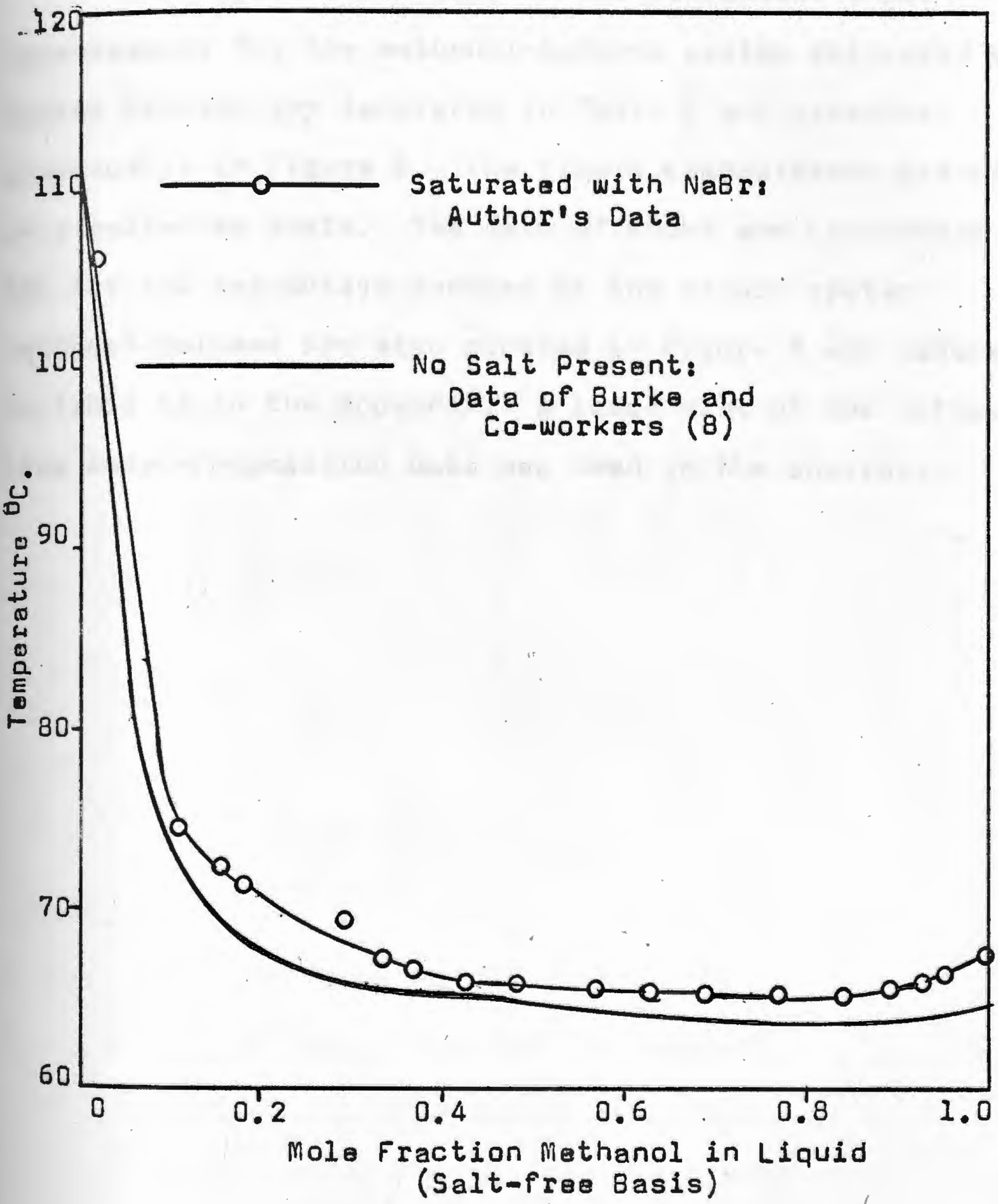


FIGURE 4

BOILING POINTS OF METHANOL-TOLUENE SATURATED WITH SODIUM BROMIDE


120
110
100
90
80
70
60
Saturated with NaBr: Author's Data
No Salt Present: Data of Burke and Co-workers (8)
Temperature °C.
0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol in Liquid
(Salt-free Basis)

C. Refractive Index-Composition Data at 25°C.

The experimental data of the refractive index measurements for the methanol-toluene system saturated with sodium bromide are tabulated in Table I and presented graphically in Figure 2. The liquid compositions are given on a salt-free basis. The data of Burke and co-workers (8) for the refractive indices of the binary system methanol-toluene are also plotted in Figure 2 and tabulated in Table XI in the Appendix. A large plot of the refractive index-composition data was used in the analysis.

IV. CALCULATED RESULTS

A. Mole Fraction

In order to prepare the refractive index-composition calibration curve, solutions of methanol and toluene of accurately known compositions were saturated with sodium bromide. The compositions, initially expressed as weight fraction methanol on a salt-free basis were converted to the corresponding mole-fractions. The mole fractions were calculated from the weight fractions by the following relation:

$$x_{MeOH} = \frac{\frac{X_{MeOH}}{32.04}}{\frac{X_{MeOH}}{32.04} + \frac{(1 - X_{MeOH})}{92.13}}$$

$$= \frac{X_{MeOH}}{0.328 + 0.672\, X_{MeOH}}$$

where

x_{MeOH} = mole fraction of methanol

X_{MeOH} = weight fraction of methanol

32.04 = molecular weight of methanol

92.13 = molecular weight of toluene

B. Relative Volatility

The volatility of any substance in a homogeneous liquid is defined as its partial pressure in the vapor in equilibrium with that liquid, divided by its mole fraction in the liquid (60). The relative volatility of a mixture is the ratio of the volatilities of the components. For a binary mixture containing components A and B, the relative volatility is defined as:

$$\alpha_{AB} = \frac{v_A}{v_B}$$

$$= \frac{\frac{p_A}{x_A}}{\frac{p_B}{x_B}}$$

If the vapor phase is assumed to follow Dalton's law of partial pressures, the final expression for the relative volatility is:

$$\alpha_{AB} = \frac{y_A \, x_B}{x_A \, y_B}$$

where

α_{AB} = volatility of "A" with respect to "B"

x = mole fraction in the liquid phase

y = mole fraction in the vapor phase

A = lower boiling component

B = higher boiling component

v_A = volatility of "A"

v_B = volatility of "B"

Relative volatility is a direct measure of the ease of separation of two or more components by the distillation process. The more separable a mixture is the larger is the value of the relative volatility. If the relative volatility, α, is unity, no separation is possible since the composition of the liquid is identical with that of the vapor.

Relative volatilities were calculated from the experimental equilibrium data for the system methanol-toluene saturated with sodium bromide. The calculated values are listed in Table IV. The values calculated for the binary system methanol-toluene according to the data of Burke et al. (8), are listed in the Appendix in Table XII. Both sets of data are plotted in Figure 5.

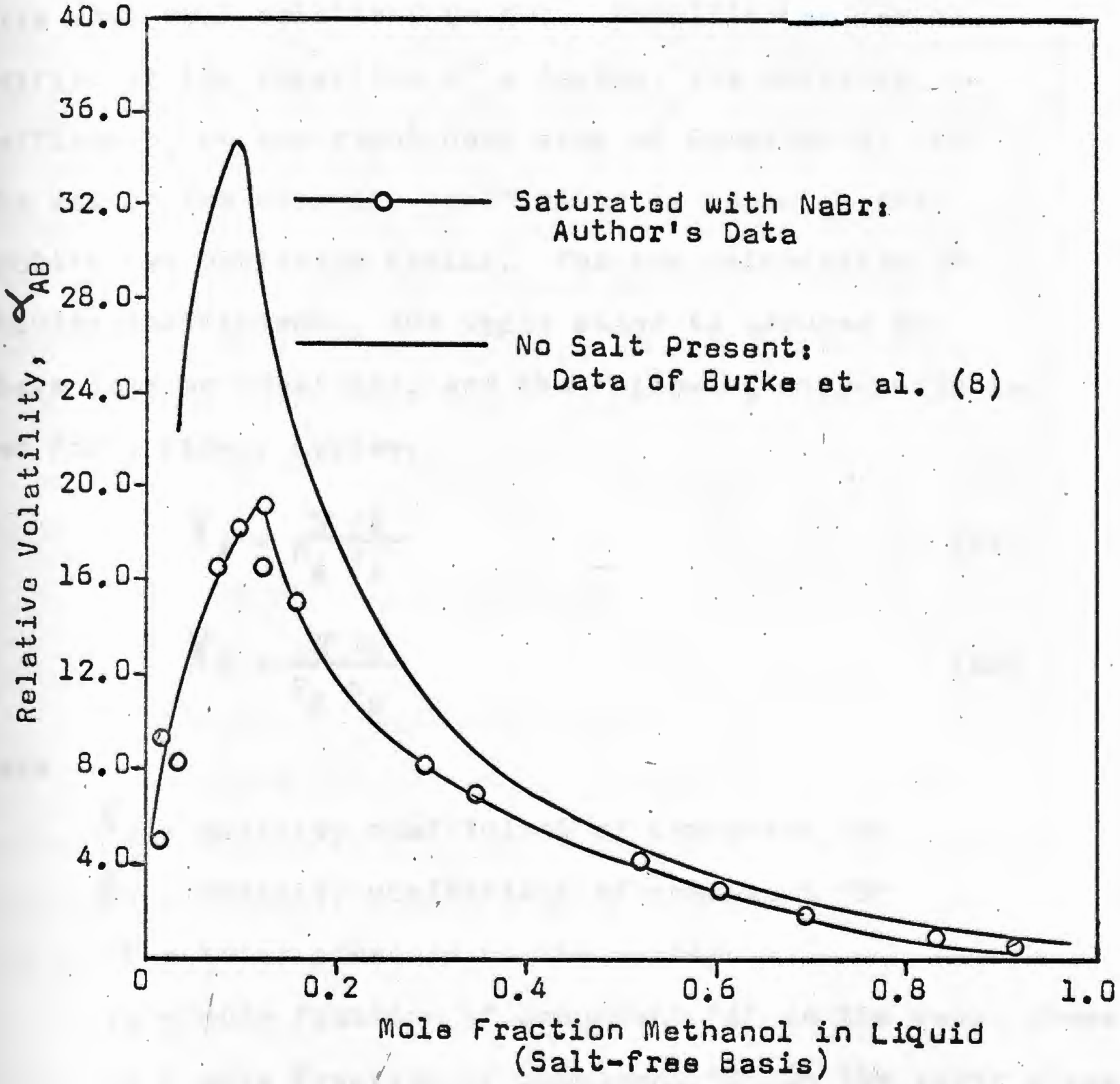
TABLE IV

RELATIVE VOLATILITIES OF METHANOL-TOLUENE SATURATED WITH SODIUM BROMIDE

Mole Fraction	Methanol	Relative Volatility
x_1	y_1	
0.912	0.877	0.687
0.930	0.905	0.715
0.953	0.939	0.758
0.343	0.783	6.945
0.011	0.051	5.000
0.288	0.770	8.303
0.121	0.721	19.181
0.155	0.731	15.048
0.600	0.821	3.065
0.517	0.813	4.083
0.690	0.824	2.107
0.829	0.840	1.083
0.888	0.860	0.774
0.926	0.892	0.660
0.886	0.858	0.776
0.446	0.814	5.350
0.018	0.144	9.400
0.071	0.560	16.774
0.120	0.690	16.405
0.032	0.214	8.280
0.095	0.660	18.656

FIGURE 5

RELATIVE VOLATILITY OF METHANOL-TOLUENE MIXTURES


40.0
36.0
32.0
28.0
24.0
20.0
16.0
12.0
8.0
4.0
Relative Volatility, α_{AB}
Saturated with NaBr: Author's Data
No Salt Present: Data of Burke et al. (8)
0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol in Liquid
(Salt-free Basis)

C. Activity Coefficients

The activity coefficients of a system are used to compare the properties of real solutions with those of an ideal solution (27). Ideal solutions follow Raoult's Law while most real solutions do not. Raoult's Law can be modified by the insertion of a factor, the activity coefficient, on the right hand side of Equation 6. For this reason the activity coefficient is known as the Raoult's Law Deviation Factor. For the calculation of activity coefficients, the vapor phase is assumed to behave like an ideal gas, and the following expression is used for a binary system:

$$\gamma_A = \frac{\pi y_A}{P_A x_A} \tag{6a}$$

$$\gamma_B = \frac{\pi y_B}{P_B x_B} \tag{6b}$$

where

γ_A = activity coefficient of component "A"

γ_B = activity coefficient of component "B"

π = total pressure on the system

y_A = mole fraction of component "A" in the vapor phase

y_B = mole fraction of component "B" in the vapor phase

P_A = vapor pressure of pure component "A" at the temperature for which the equilibrium data were determined

P_B = vapor pressure of pure component "B" at the temperature for which the equilibrium data were determined

x_A = mole fraction of component "A" in the liquid phase

x_B = mole fraction of component "B" in the liquid phase

Vapor pressure data for both methanol and toluene were obtained from Chemical Engineers' Handbook (51). In Figure 6 the logarithms of the vapor pressures are plotted against the reciprocals of the absolute temperatures. The reciprocals of the absolute temperatures have been multiplied by 10^3 for convenience in plotting. Since the temperature range is not too wide, these data follow the Equation (17):

$$\log P = A + \frac{B}{T} \tag{7}$$

where

P = vapor pressure in mm Hg

A and B = constants

T = absolute temperature in ^oK

By presenting the graphical dependence of vapor pressure on temperature in such a way that a straight line is obtained, vapor pressures can be read off the graph with greater accuracy.

The calculated values of the activity coefficients for the system methanol-toluene saturated with sodium bromide are listed in Table V and plotted in Figure 7. The activity coefficients reported for the system methanol-toluene by Burke and co-workers are listed in Table IX in the Appendix and plotted in Figure 7.

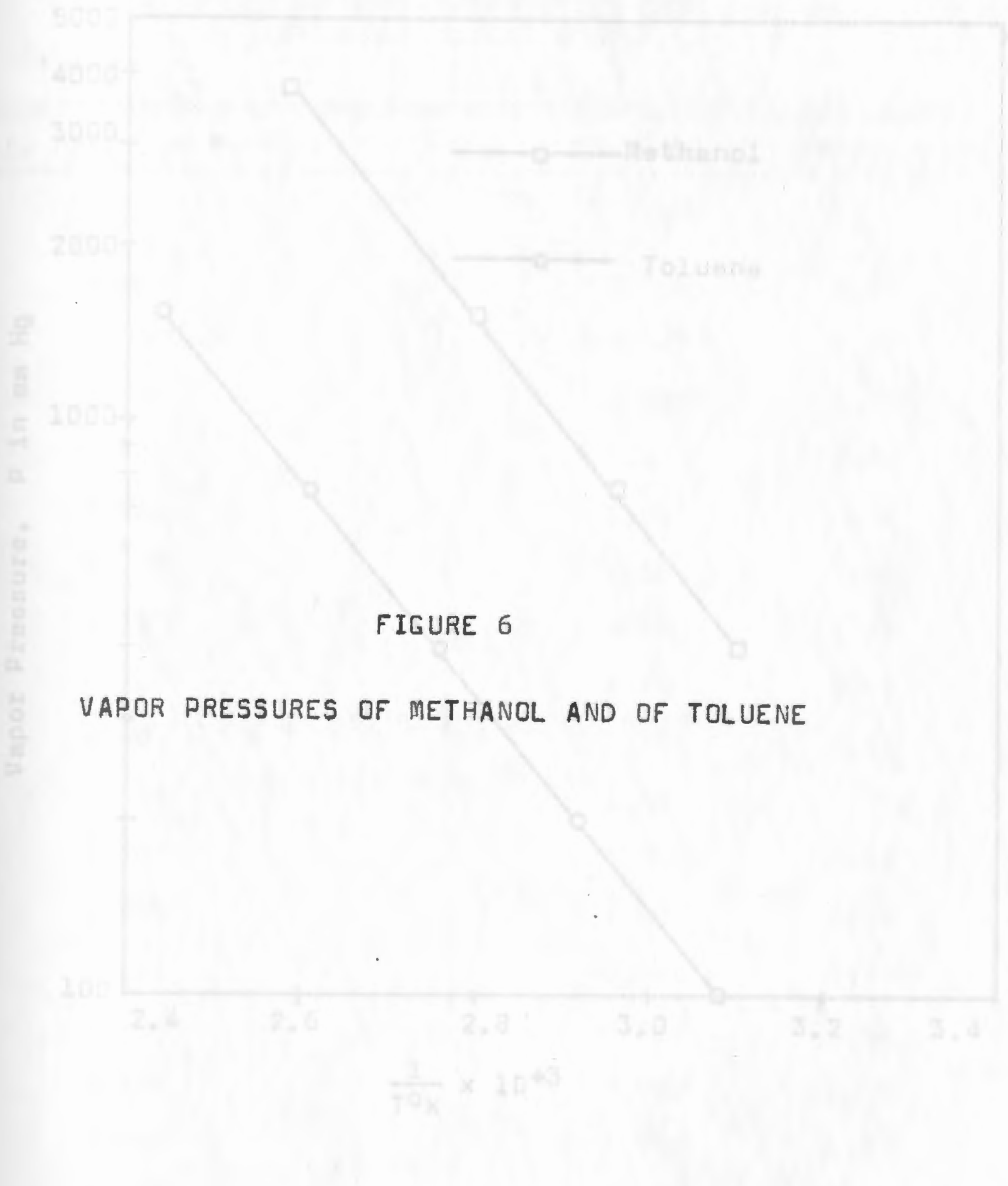


FIGURE 6

VAPOR PRESSURES OF METHANOL AND OF TOLUENE

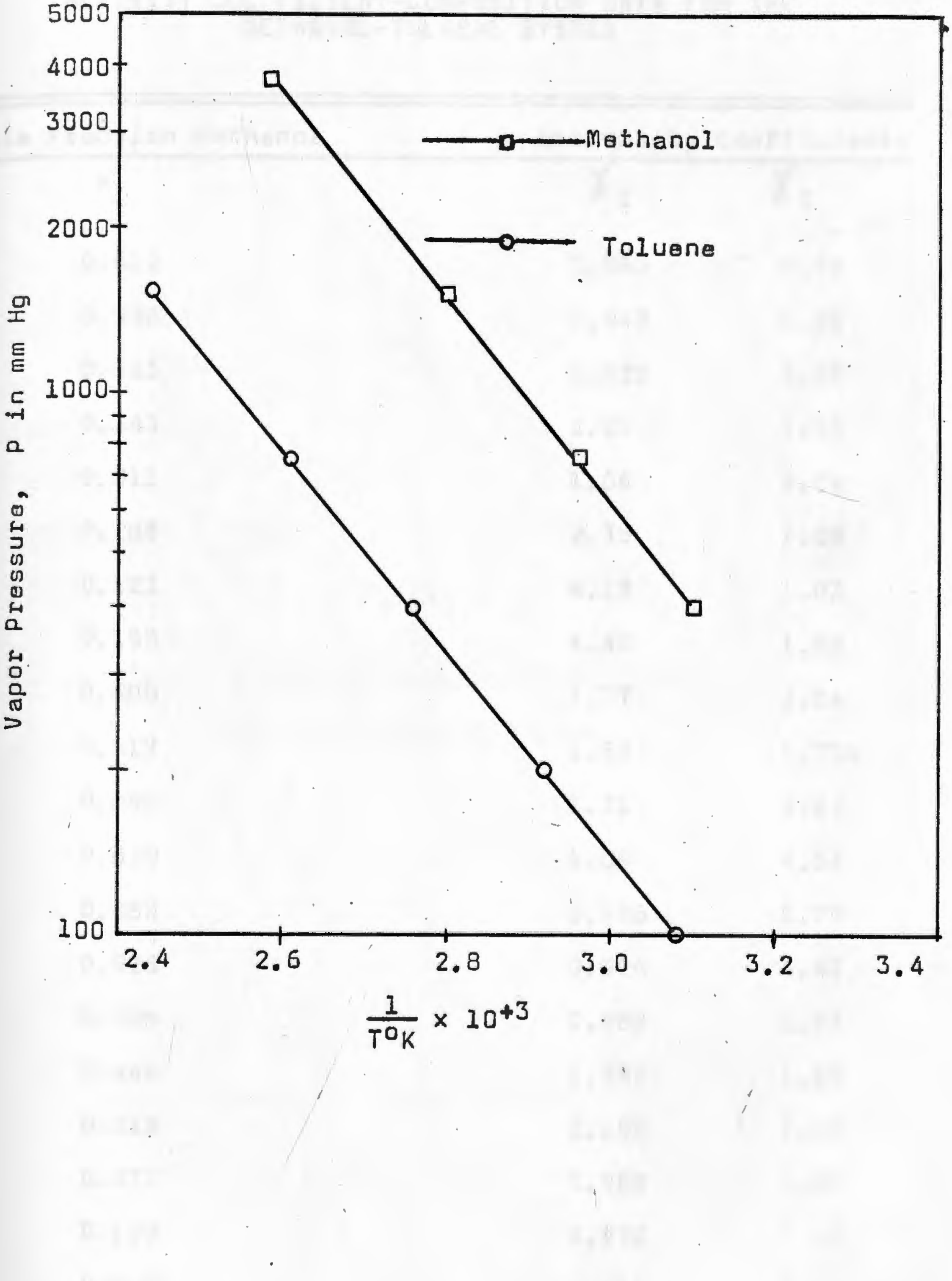

5000
4000
3000
2000
1000
100
Vapor Pressure, p in mm Hg
2.4
2.6
2.8
3.0
3.2
3.4
$\frac{1}{T^{o}K} \times 10^{+3}$
Methanol
Toluene

TABLE V

ACTIVITY COEFFICIENT-COMPOSITION DATA FOR THE METHANOL-TOLUENE SYSTEM

Mole Fraction Methanol	Activivity Coefficients	
x_1	γ_1	γ_2
0.912	0.963	6.36
0.930	0.947	6.06
0.953	0.925	5.59
0.343	2.05	1.36
0.011	1.06	1.04
0.288	2.35	1.09
0.121	4.19	1.03
0.155	4.48	1.08
0.600	1.37	2.04
0.517	1.54	1.730
0.690	1.21	2.62
0.829	1.09	4.34
0.888	0.986	5.79
0.926	0.926	6.41
0.886	0.968	5.74
0.446	1.950	1.48
0.018	2.150	1.09
0.071	3.960	1.08
0.120	4.270	1.19
0.032	2.110	1.11
0.095	4.55	1.07

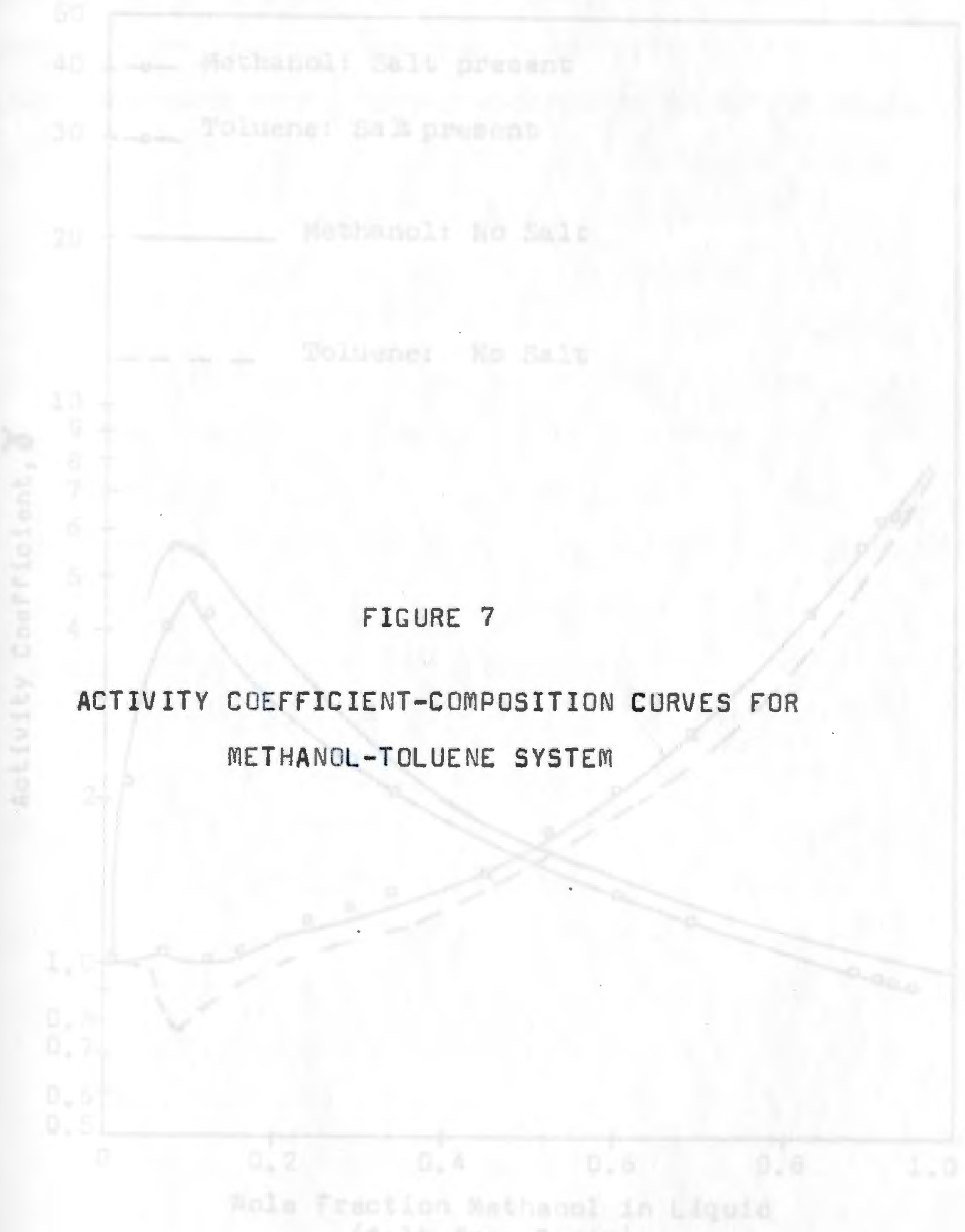
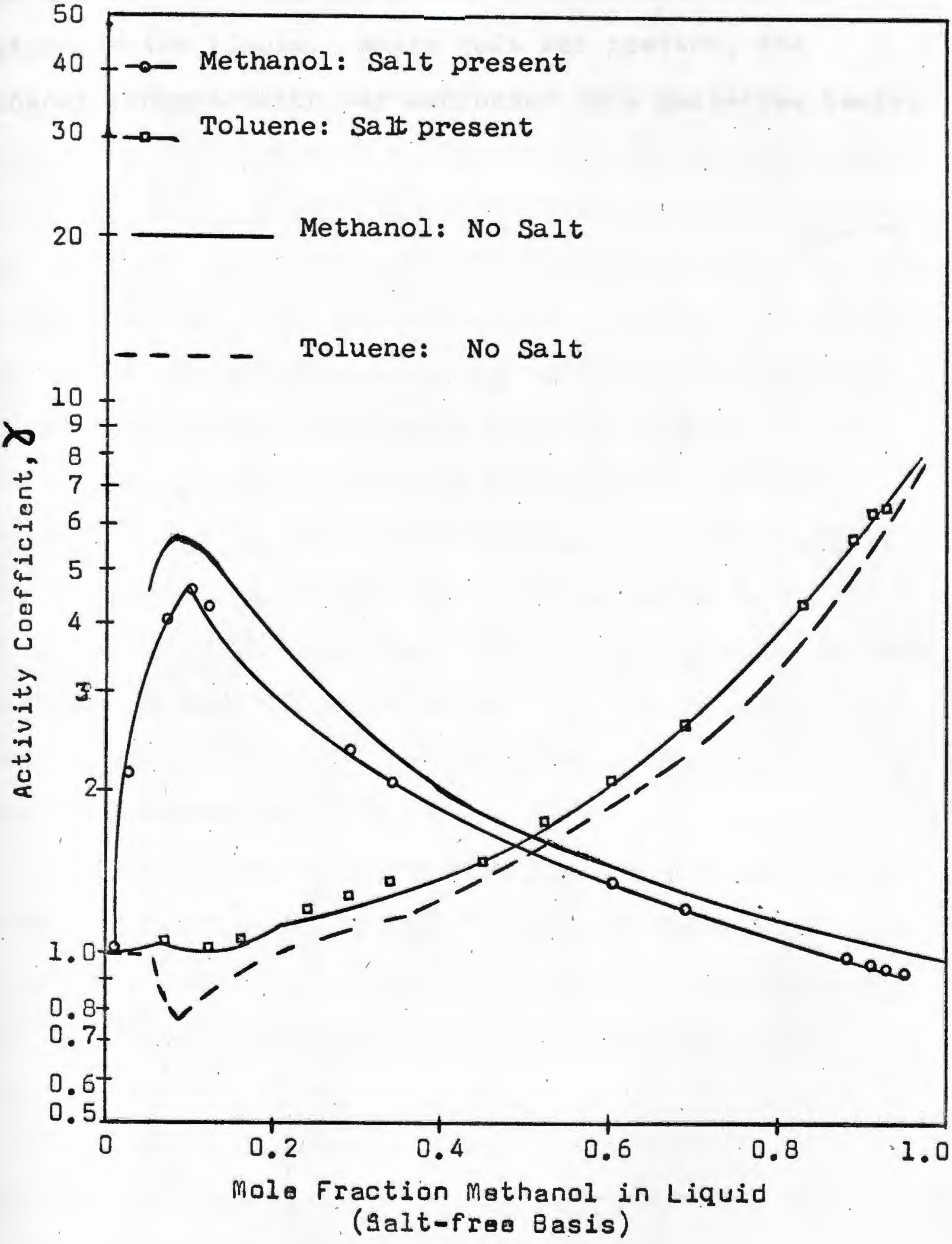


FIGURE 7

ACTIVITY COEFFICIENT-COMPOSITION CURVES FOR
METHANOL-TOLUENE SYSTEM


Methanol: Salt present
Toluene: Salt present
Methanol: No Salt
Toluene: No Salt
Activity Coefficient, γ
50
40
30
20
10
9
8
7
6
5
4
3
2
1.0
0.8
0.7
0.6
0.5
0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol in Liquid
(Salt-free Basis)

In both cases the activity coefficients were based on actual experimental data and are plotted versus methanol concentration in the liquid. Where salt was present, the methanol concentration was expressed on a salt-free basis.

V. TEST FOR THERMODYNAMIC CONSISTENCY

The experimental data were tested for thermodynamic consistency. The shapes and smoothness of the vapor-liquid equilibrium plot, Figure 3, and the activity coefficients plot, Figure 7, were criteria for thermodynamic consistency. In Figure 8, the $\ln \gamma_1$ curve exhibits a maximum at approximately 0.10 mole fraction methanol while the $\ln \gamma_2$ curve exhibits a minimum at 0.12 mole fraction methanol.

Burke and co-workers (8) state that at a concentration of 0.5 mole fraction the value of $\ln \gamma_1$ should be greater than that of $\ln \gamma_2$, since the value of $\ln \gamma_2$ at $x_1 = 1.0$ is greater than that for $\ln \gamma_2$ at $x_1 = 0$. In this investigation the opposite was found to be the case. The values obtained for $\ln \gamma_1$ and $\ln \gamma_2$ at $x_1 = 0.5$ were 0.438 and 0.525, respectively.

An additional thermodynamic check was made of the experimental data using a modification of the method of Redlich and Kister (56). The Redlich-Kister equation which is given below applies only to isothermal data.

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad (8)$$

Herington (28) extended the method to include isobaric data. In this case the integral of Equation 8 above does not equal zero and the condition necessary for thermodynamic consistency is:

$$D < J$$

where D is the percentage deviation from zero of the quantity calculated in Equation 8. D is calculated as follows:

$$D = \frac{100 \left| \int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1 \right|}{\left| \sum \text{Area} \right|}$$

where $\left| \sum \right|$ is the sum of the absolute values of the areas calculated by Equation 8. The quantity J is a function of the over-all boiling point range of the system and is defined by the following equation:

$$J = \frac{150 \ \theta}{T_{Min}}$$

where θ is the over-all range of boiling points of the system and T_{Min} is the lowest measured boiling point of the system in degrees Kelvin.

For the methanol-toluene-sodium bromide system investigated in this study, $D = 13.9$ and $J = 19.2$. Hence the data are thermodynamically consistent. Calculated values of $\frac{\gamma_1}{\gamma_2}$ are listed in Table VI. Figure 8 is a plot of $\log \frac{\gamma_1}{\gamma_2}$ versus x_1.

TABLE VI

VALUES CALCULATED FOR THERMODYNAMIC CONSISTENCY TEST

x_1	γ_1	γ_2	$\frac{\gamma_1}{\gamma_2}$
0.011	1.06	1.04	1.019
0.018	2.15	1.09	1.973
0.032	2.11	1.11	1.901
0.071	3.96	1.08	3.667
0.095	4.55	1.07	4.252
0.120	4.27	1.19	3.588
0.121	4.19	1.03	4.068
0.155	4.48	1.08	4.148
0.288	2.35	1.29	1.822
0.343	2.05	1.36	1.507
0.446	1.95	1.48	1.318
0.517	1.54	1.73	0.890
0.600	1.37	2.04	0.672
0.690	1.21	2.62	0.462
0.829	1.09	4.34	0.251
0.886	0.968	5.74	0.169
0.888	0.986	5.79	0.170
0.912	0.963	6.36	0.151
0.926	0.926	6.44	0.145
0.930	0.946	6.06	0.156
0.953	0.925	5.59	0.165

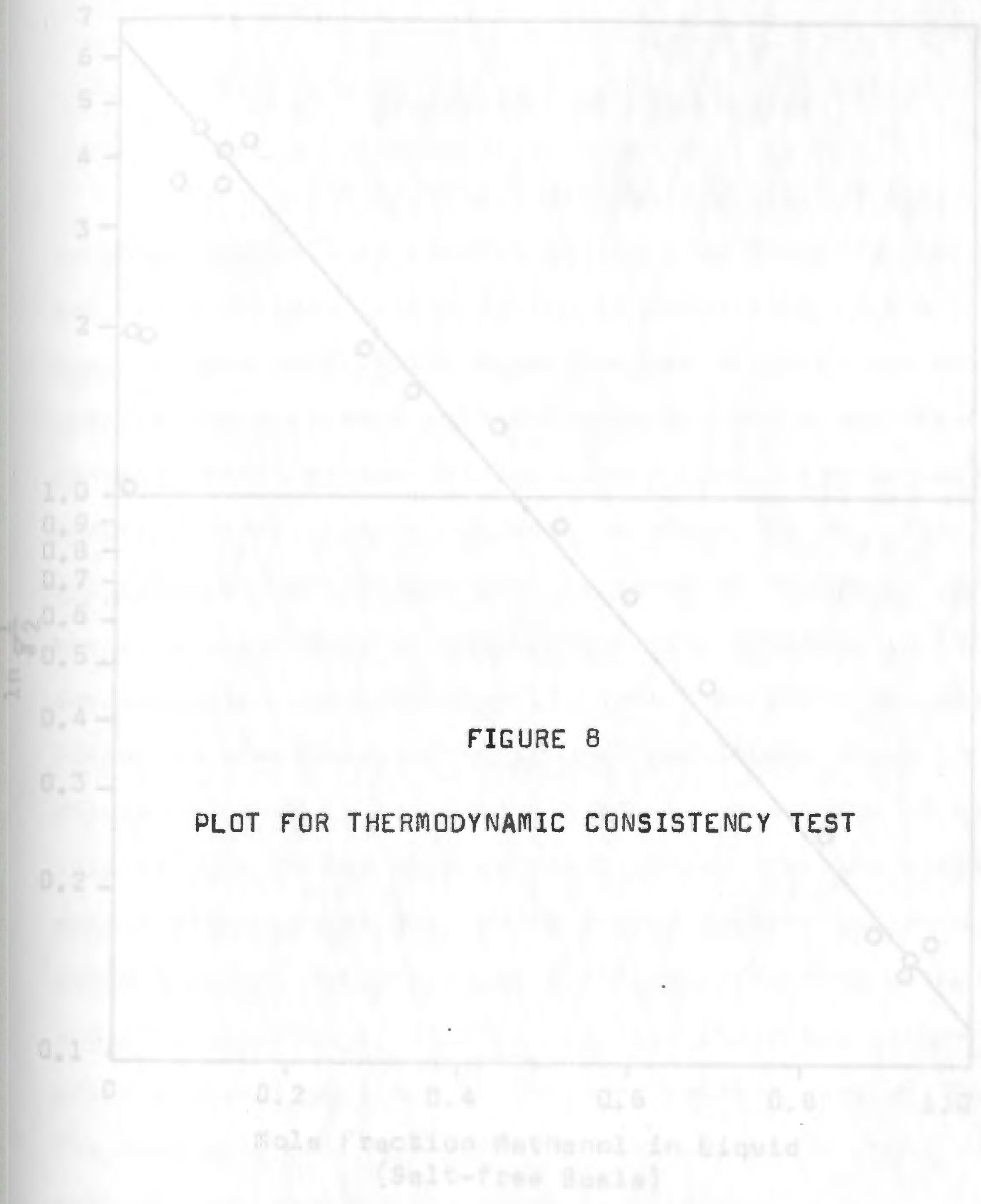
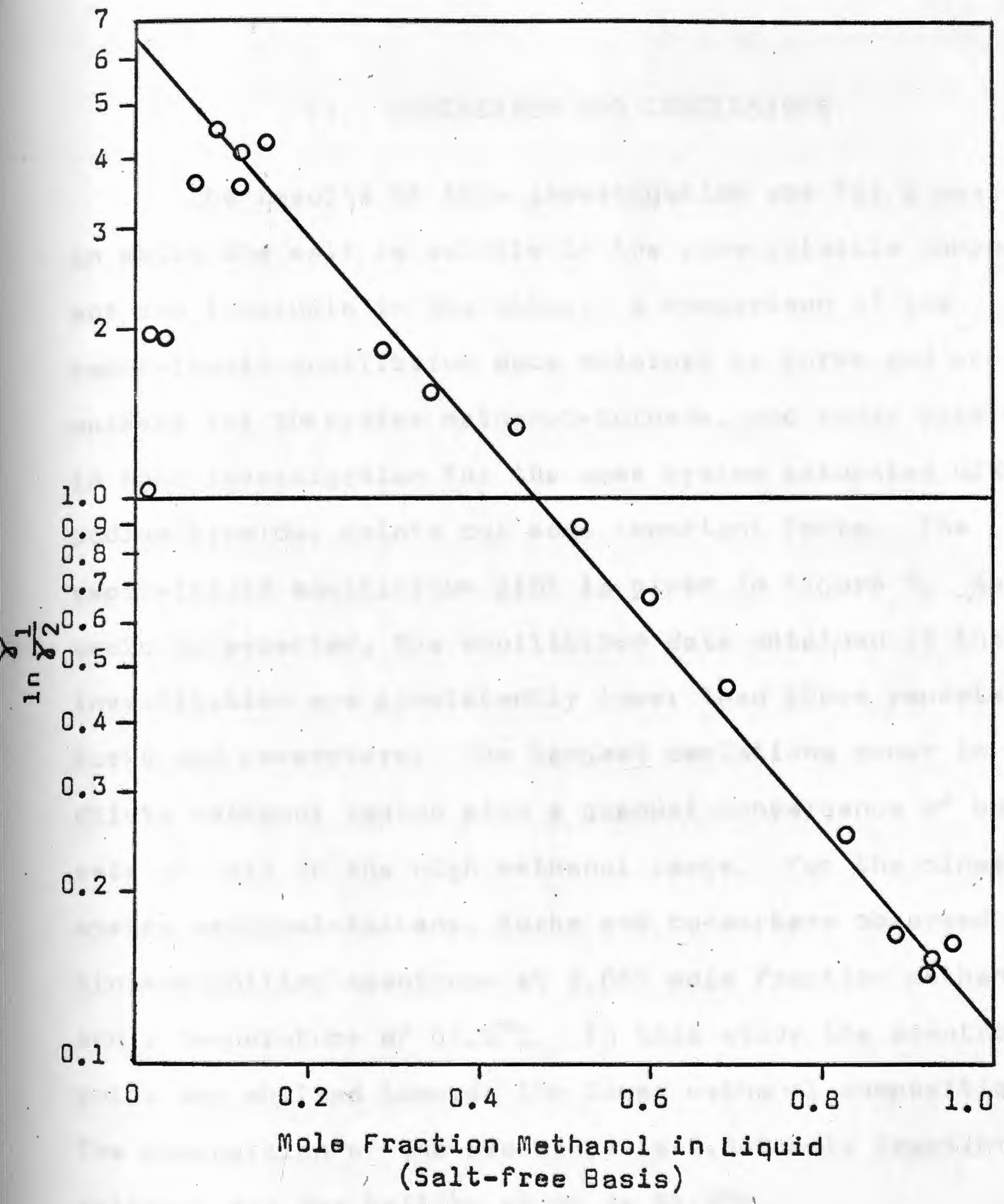


FIGURE 8

PLOT FOR THERMODYNAMIC CONSISTENCY TEST


7
6
5
4
3
2
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
$\ln \frac{\gamma_1}{\gamma_2}$
0
0.2
0.4
0.6
0.8
1.0
Mole Fraction Methanol in Liquid
(Salt-free Basis)

VI. DISCUSSION AND CONCLUSIONS

The results of this investigation are for a system in which the salt is soluble in the more volatile component and insoluble in the other. A comparison of the vapor-liquid equilibrium data obtained by Burke and co-workers for the system methanol-toluene, and those obtained in this investigation for the same system saturated with sodium bromide, points out some important facts. The vapor-liquid equilibrium plot is given in Figure 3. As would be expected, the equilibrium data obtained in this investigation are consistently lower than those reported by Burke and co-workers. The largest deviations occur in the dilute methanol region with a gradual convergence of both sets of data in the high methanol range. For the binary system methanol-toluene, Burke and co-workers observed a minimum boiling azeotrope at 0.885 mole fraction methanol and a temperature of $63.6^{\circ}C$. In this study the azeotropic point was shifted towards the lower methanol compositions. The composition of the azeotrope is 0.845 mole fraction methanol and the boiling point is $65.0^{\circ}C$.

Figure 5 is a plot of the relative volatilities observed in this investigation and those calculated from the data of Burke et al. The graphs clearly show that the relative volatility is appreciably decreased by the addition of salt. The trend observed is similar to that previously noted for the vapor-liquid equilibrium plot in

Figure 3. The effect of the salt is more pronounced at the low methanol compositions and the two curves approach each other as the methanol composition increases.

In Figure 7 the activity coefficients determined from the data of this investigation are plotted along with those determined by Burke and co-workers. The plot shows that the activity coefficients of both methanol and toluene decreased by a constant value over the entire composition range as a result of the presence of the salt. The activity coefficient plot showed fairly smooth curves especially at high methanol compositions. At lower methanol compositions, however, the experimental points showed some scattering. Scattering was observed in the vapor-liquid plot and relative volatility plot at low methanol compositions. The shape of the equilibrium curve explains why such scattering should be anticipated. A small change in liquid composition in this range results in a disproportionately large change in vapor composition. Thus in this range of compositions it is more difficult to determine liquid and vapor compositions to a high degree of accuracy.

A comparison of the relative volatility plot, Figure 5, with the activity coefficients plot, Figure 7, indicates that the effect of the salt is greatest where non-ideality is greatest. This occurs at approximately 0.1 mole fraction methanol.

Comparison of the experimental results with Burke's data indicate that sodium bromide significantly affects the vapor-liquid equilibrium of methanol and toluene. As would be expected, the relative volatility of methanol with respect to toluene is decreased over the entire range of compositions. A comparison of the activity coefficients indicates that the presence of the salt makes the salt more ideal.

Although some scattering was observed in the low methanol range, satisfactory curves were obtained for the vapor-liquid equilibrium, boiling point-compositions, relative volatility, and activity coefficient plots. Moreover, the Redlich-Kister test showed the experimental data to be thermodynamically consistent. All this would then indicate that refractive index measurements can be reliably used not only to analyze binary organic mixtures but also mixtures saturated with salts.

VII. SUGGESTIONS FOR FUTURE WORK

It is suggested that the effects of other salts on the system methanol-toluene at 760 mm Hg should be investigated. Specifically, salts more soluble in methanol than sodium bromide should be employed. Since it is possible that a salt very soluble in methanol would break the binary system into a two phase liquid system, it is suggested that an equilibrium still be used which is designed to allow sampling of a two phase liquid system.

It would also be advantageous to investigate ways of increasing the relative volatility of the system methanol-toluene. This may have a direct industrial application if it breaks the azeotrope. In order to attempt to break the azeotrope, experimental vapor-liquid equilibrium data should be determined for the binary system methanol-toluene at lower pressures than atmospheric.

Finally, analysis of salt-saturated binary organic mixtures by refractive index measurements should be encouraged and used more widely in view of the many attendant advantages. There is a dearth of information in the literature concerning refractive index-composition data for ternary systems. More effort should be expended to fill this gap.

VIII. SUMMARY

Refractive index-composition data for methanol-toluene saturated with sodium bromide were obtained at $25^{\circ}C$. and used in the analysis of the samples taken in this experiment.

Vapor-liquid equilibrium and boiling-point-composition data at 760 mm Hg were obtained for the system methanol-toluene saturated with sodium bromide. An improved Othmer type equilibrium still was used. From the experimental vapor-liquid equilibrium data, relative volatilities and activity coefficients were calculated. The effect of sodium bromide on the relative volatilities and activity coefficients of the system was shown and discussed. The experimental data were tested by the method of Redlich and Kister and found to be thermodynamically consistent.

An extensive literature survey was made and a summary of the major published investigations on the subject of salt-effect in vapor-liquid equilibrium is presented in the Appendix and in the Bibliography.

IX. APPENDIX

Design of External Heater

Initially, the resistance of a wire was determined to be 7 ohms. Since the variac was a 5-ampere model, this fact was made the criterion for design.

Maximum Power = $I^2R = 5^2 \times 7 = 175$ watts

Maximum Voltage = $5 \times 7 = 35$ volts

At 30 volts, $I = \frac{V}{R} = \frac{30}{7} = 4.29$ watts

At 30 volts, Power = $I \times V = I^2R = 30 \times 4.29$

$= 4.29^2 \times 7$

$= 129$ watts

The heater was found to operate satisfactorily.

TABLE VII

EXPERIMENTAL EQUILIBRIUM DATA FOR METHANOL-TOLUENE AT 760 mm of Hg (Burke et al.)

Temperature °C.	Mole Fraction Methanol x_1	y_1
110.6	0.000	0.000
89.90	0.046	0.519
84.80	0.058	0.607
80.40	0.070	0.704
74.75	0.094	0.777
71.30	0.114	0.793
69.70	0.132	0.801
66.75	0.234	0.813
65.75	0.330	0.822
65.10	0.439	0.828
64.15	0.675	0.842
63.70	0.830	0.866
63.60	0.870	0.878
63.70	0.930	0.912
64.10	0.974	0.957
64.60	1.000	1.000

TABLE VIII

REFRACTIVE INDICES OF MIXTURES OF METHANOL-TOLUENE AT 25ºC.

Mole Fraction Methanol	Refractive Index
0.0000	1.49428
0.0967	1.48772
0.2246	1.47775
0.3507	1.46562
0.4829	1.45033
0.5312	1.44370
0.6037	1.43268
0.7025	1.41497
0.7289	1.40986
0.7663	1.40112
0.8426	1.38158
0.8861	1.36870
0.9296	1.35390
0.9685	1.33997
1.000	1.32691

TABLE IX

ACTIVITY COEFFICIENT-COMPOSITION DATA FOR METHANOL-TOLUENE (Burke et al.)

Mole Fraction Methanol	Activity Coefficients	
x_1	1	2
0.000	--	1.000
0.046	4.566	0.945
0.058	5.194	0.878
0.070	5.630	0.819
0.094	5.666	0.773
0.114	5.417	0.831
0.132	5.018	0.865
0.234	3.215	1.028
0.330	2.396	1.162
0.439	1.861	1.375
0.675	1.277	2.261
0.830	1.087	3.730
0.870	1.056	4.459
0.930	1.022	5.950
0.974	1.008	7.707
1.000	1.000	--

TABLE X

SUMMARY OF VAPOR-LIQUID EQUILIBRIUM DATA WITH SALT AS A THIRD COMPONENT

System	Salt	Composition Range in Mole %	Salt Concentration	Authors
Acetic Acid-Water	$CaCl_2$	0 - 100	10,20,30 40,50% wt.	Garwin and Hutchison (22)
Acetic Acid-Water	LiCl, NaCl, KCNS, Na_2SO_4 K_2SO_4, KNO_3 $NaC_2H_3O_2$	0.05 -0.4N	Saturated	McBain and Kam (43)
Acetic Acid-Water	NaCl, Na_2SO_4 $MgSO_4$	dilute	0-Saturated	Virtanen and Pulki (72)
Acetone Ethylmethyl Ketone	$CaCl_2$	0 - 100	Saturated	Jost (33)
Acetone-Methanol	$CaCl_2$	0 - 100	Saturated	Jost (33)
Ethanol-Water	NH_4Cl, NaCl			Maizlick and Tverdovsky (39)
Ethanol-Water	$CuCl_2$, CH_3COOK			Costa and Tarraso (16)
Ethanol-Water	$CuCl_2$	0 - 100	10 & 50 gm/100g solvent	Tarraso (16) Rouleau (62)
Ethanol-Water	$(CH_3 \cdot C:NOH)_2$	0 - 100	Saturated	Ciesla (15)

TABLE X (CONTINUED)

System	Salt	Composition Range in Mole %	Salt Concentration	Authors
Ethanol-Water	$CaCl_2$,KCl,NH_4Cl; $NaNO_3$	0 - 100	Saturated	75
Ethanol-Water	$CaCl_2$,NaOH,Na_2C_2, H_3O_2	91 - 100	Saturated	42
Ethanol-Water	Hg_2Cl_2	0 - 100	Saturated	31
Ethanol-Water	$HgCl_2$,$ZnCl_2$,KCl, NaCl,KOA_c			41
Ethanol-Water	KNO_3	0 - 100	Saturated	57
Ethanol-Water	K_2SO_4,$NaNO_3$	8 - 20	Saturated	70
Ethanol-Water	K_2CO_3	50 - 90	Saturated	36
Ethanol-Water	NaCl	0 - 100		31,33,63
Ethanol-Water	NaOR R = AlR_{yl} R = Ar_{yl}	89 - 98	Saturated	36
Ethylene Glycol Water	Na_2SO_4,KCl,KBr	0 - 100	Saturated	20
Ethylene Glycol Water	Na_2SO_4	0 - 100	Saturated	21
Formic Acid Caproic Acid	$LiCl_3NaCl$			53

TABLE X (CONTINUED)

System	Salt	Composition Range in Mole %	Salt Concentration	Authors
Formic Acid-Water	$CaCl_2$, $CaSO_4$, $MgCl_2$, $NaCl$ Na_2SO_4, $HCOOCa$, $HCOOMg$, $HCOONa$, $HCOONH_4$, $(NH_4)_2SO_4$	0 - 100	Saturated	26
Glycerol-Water	NaCl	0 - 100	Saturated	11
Methanol-Toluene	NaBr	0 - 100	Saturated	This work
Pyridine-Water	NaCl			73
Phenol-Water	NaCl	0 - 6	0 - 17 wt.%	4
Deuterium Oxide Water	Salts			25
Water-Hydrochloric Acid	Several			53
Water-Carboxylic Acid	Several			53
M-Xylene-p-Xylene	$SbCl_2$			

TABLE XI

SOLUBILITIES OF VARIOUS SALTS IN ALCOHOL AT ROOM TEMPERATURE in Gms/100 Gm SOLVENT

Solvent	NaI	$CuCl_2$	$Ca(NO_3)_2$
MEOH	83.3	36.5	65.5
ETOH	58.8	35.7	--
PROH	26.3	30.5	36.5

TABLE XII

RELATIVE VOLATILITIES OF METHANOL-TOLUENE MIXTURES
(Burke et al.)

Mole Fraction Methanol		Relative Volatility
x_1	y_1	
0.046	0.519	22.50
0.058	0.627	28.095
0.070	0.704	32.700
0.094	0.777	35.15
0.114	0.793	29.826
0.132	0.801	26.730
0.234	0.813	14.465
0.330	0.822	9.482
0.439	0.828	6.186
0.675	0.842	2.575
0.830	0.866	1.324
0.870	0.878	1.027
0.930	0.912	0.777
0.974	0.957	0.585

TABLE XIII

VAPOR PRESSURES OF METHANOL AND OF TOLUENE AT VARIOUS TEMPERATURES

Temperature, ^{o}C.	Vapor Pressure in mm Hg
	METHANOL
49.9	400
64.7	760
84.0	1520
112.5	3800
138	7600
	TOLUENE
40.3	60
51.9	100
69.5	200
89.5	400
110.6	760
136.5	1520

X. NOMENCLATURE

I = current

R = resistance

V = voltage

Subscript$_1$ = methanol

Subscript$_2$ = toluene

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