

Correlation for Vapor-Liquid Equilibrium Data for Binary Solutions Unsaturated with Salts

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Experimental data are presented on the isobaric vapor-liquid equilibrium of the system propionic acid-water containing several inorganic salts. A correlation is developed which permits prediction of the salt effect from a minimum amount of experimental data.

MOST INVESTIGATIONS concerned with the effect of salt addition in the vapor-liquid equilibrium of binary systems are limited to presentation of experimental data with no attempt to develop correlations. Among these are the works of Bogart and Brunges (1), Butler (2, 3), Chen (4), Costa and Tarraso (5), Craven (7), Garwin and Hutchison (11), Guyer, Guyer, and Johnsen (12), Johnson, Ward, and Furter (15), Johnson and coworkers (15), Jost (16), Kyrides and coworkers (17), Mariller and Coutant (20), Rieder and Thompson (22), Samadder and Nandi (23), Yamamoto and coworkers (26).

The ultimate purpose of the present work was development of a correlation to make possible prediction of salt effect in binary vapor-liquid equilibrium from a minimum amount of experimental data. A few previous investigations have been concerned with development of such correlations. Among these are the works of Tursi and Thompson (24), Fogg (9), Lu (18), and Johnson and Furter (10, 13, 14). In nearly all these cases saturated salt solutions were employed, with the idea that under these conditions a more pronounced effect would be observed. Although this is true, it was recognized in this investigation that the use of saturated salt solutions makes the attempts to obtain correlations considerably more difficult. The fact that the solutions are saturated with respect to the salt is easily ascertained by operating the vapor-liquid equilibrium still under such conditions that presence of some precipitated salt at the bottom of the still is observed at all times. This, however, implies varying the concentration of dissolved salt along the binary liquid composition range, since the solubility of the salt is usually not the same in the two liquid components.

In this investigation it was decided to avoid as much as possible saturated salt solutions. The salt concentration in solution was a constant parameter within each system studied. A correlation is proposed which permits prediction of the salt effect from a minimum of experimental data. 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 is presented.

THE PROPOSED CORRELATION

The data obtained in this investigation as well as data from Furter (10, 14) were successfully correlated by use of reference-system charts (Figure 1) 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 vs. the abscissa at corresponding

equal values of the liquid composition x . Each line corresponds to the indicated concentration of dissolved salt.

Since for the systems studied the difference between the boiling points of the binary system without salt and with salt are small, the charts thus constructed are essentially equal temperature reference-system plots.

Figure 1 (a,b) shows these charts for two of the systems studied at different molal concentration of the salts. Similar graphs were plotted for all the other systems investigated.

Examination of these reference diagrams shows that for a given concentration of dissolved salt, straight lines are obtained. 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. The salt concentration parameters, therefore, are not meaningful after saturation is reached.

Examination of Figure 1a corroborates the choice of unsaturated salt systems—after saturation occurs a considerable scatter of points is encountered and no correlation is possible. No scatter is shown in Figure 1b, since all pertinent data were taken in the unsaturated region.

The straight lines shown appear to be parallel with a slope approaching unity.

Theoretical Justification for the Reference-System Charts. Johnson and Furter (10, 13, 14) indicated that it is rational to seek a correlation for salt effect in vapor-liquid equilibrium in the altering of the chemical potentials of the two volatile components by the salt.

From several basic assumptions which are discussed in their work (14) these authors arrived at the following equation:

$$T \ln \frac{\alpha_s}{\alpha} = CN \quad (1)$$

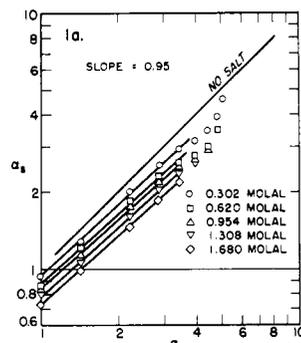


Figure 1a. Sodium nitrate-propionic acid-water

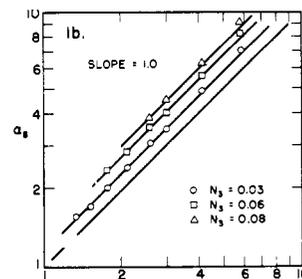


Figure 1b. Ammonium chloride-ethanol-water
Data from Johnson & Furter (10, 14)

Utilizing Equation 1, examine two different points at the same salt concentration in the unsaturated salt region,

$$\text{Point 1: } T \ln \frac{\alpha_s}{\alpha} = CN \quad (2)$$

$$\text{Point 2: } T' \ln \frac{\alpha'_s}{\alpha'} = CN \quad (2a)$$

If the two relationships are assumed equal to the same function of salt concentration one could write:

$$T \ln \frac{\alpha_s}{\alpha} = T' \ln \frac{\alpha'_s}{\alpha'} \quad (3)$$

By rearrangement Equation 3 becomes

$$\frac{T' \ln \alpha'_s - T \ln \alpha_s}{T' \ln \alpha' - T \ln \alpha} = 1.0 \quad (4)$$

Equation 4 indicates that a plot (on rectangular coordinates of $T \ln \alpha_s$ vs. $T \ln \alpha$ with salt concentration as a parameter would yield a straight line of unit slope. This would be unquestionably the case if salt concentration were zero, as this would result in a 45° line passing through the origin.

In this investigation data for the system ethanol-water-ammonium chloride (10, 14) were plotted on a reference diagram, Figure 2, as suggested by Equation 4. In this case Equation 4 represents the system quite accurately as lines of constant salt concentration have a unit slope.

If the temperature range $T - T'$ is small, Equation 4 can be simplified to yield:

$$\frac{\ln \alpha'_s - \ln \alpha_s}{\ln \alpha' - \ln \alpha} = 1.0 \quad (5)$$

This suggests that a plot of $\ln \alpha_s$ vs. $\ln \alpha$, such as the ones shown in Figure 1, should yield straight lines with slopes approaching unity, assuming all restrictions made in arriving at Equation 5 to be valid.

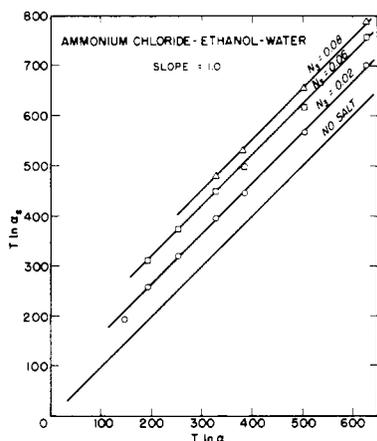


Figure 2. Relative volatility reference-system diagram. Data from Johnson and Furter (10, 14)

APPARATUS

The vapor-liquid equilibrium still employed was an 800-ml. improved Othmer still manufactured by The Emil Greiner Co., New York, Catalogue No. G-7373. The still was modified to include a U-tube projection for external heating (21).

Systematic errors were minimized by proper equipment design and control. To prevent refluxing on the inside still wall an electrothermal heating tape was wound around

the upper portion of the still body and the delivery tube to the condenser. Care was taken to wind the tape 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 covering of Styrafoam insulation was placed around the heating tape and over the top of the still. A thermometer graduated in 1° C. divisions placed between the still wall and the heating tape was useful in controlling the heat input from the tape.

To reduce the condensate receiver volume which is approximately 40 ml., 3-mm. glass beads were placed in the receiver. The condensate volume was thus reduced to approximately 23 ml. thus decreasing the time necessary for reaching equilibrium.

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 is not possible. The apparatus developed by Cottrell (6) and later modified by Washburn and Read (25) was utilized for the boiling point determinations. A calibrated partial immersion thermometer with graduations of 0.2° C. was employed. The thermometer could be read to the nearest 0.1° C.

Manostatic control was provided from both the equilibrium still and boiling point apparatus. All experimental data were taken at 760 ± 2.0 mm. of mercury.

Performance tests such as ability to reproduce data for well known binary systems, approach to steady-state, and liquid entrainment tests were conducted and indicated satisfactory operation of the equipment.

EXPERIMENTAL

The system propionic acid-water was chosen as a model. All substances employed in this investigation were analytical grade chemicals. Vapor-liquid and boiling point data for this system without addition of salts were determined and compared favorably with reliable data available in the literature. The salts sodium nitrate, potassium nitrate, potassium bromide, and lead nitrate were chosen to provide systems which are as simple as possible for correlation and analysis. All of the above salts are very soluble in water and extremely insoluble in propionic acid. One would thus expect a more pronounced change in vapor-liquid equilibrium data than would be the case for salts fairly soluble in both binary liquid components. These salts do not form hydrates and do not salt out the organic acid to form two immiscible liquid phases at the boiling temperature. These salts provide a wide range of molar concentrations because of the large differences in their molecular weights. For each salt system vapor-liquid and boiling point data were collected at salt concentrations of approximately 2.5%, 5%, 7.5%, 10%, and 12.5% by weight.

Acid concentration in the distillate was found by titration with a standard sodium hydroxide solution. Duplicate analyses were performed in each case and the results averaged.

Determination of liquid residue composition was made by a material balance, a method used previously by Furter and coworkers (10, 14). The validity of this technique was verified by comparing data obtained by direct titration and that calculated by material balance. Each run was started with a fresh charge in the still.

DATA OBTAINED

Due to space limitations only a sample of the $x-y-t$ data obtained for a specific system is presented in Figures 3 and 4. Similar diagrams were constructed for all systems

studied in this investigation and are available (8). Data are also available in tabular form. A total of 352 determinations of vapor-liquid and boiling point data were performed in this investigation.

The data could not be checked for thermodynamic consistency because of the fact that propionic acid is associated in both liquid and vapor phases. Marek and

Standart (19) have rigorously derived relationships for activity coefficients which are corrected for association in both the liquid and vapor phases. These authors have applied these relationships in determination of consistency checks for the system acetic acid-water. The application of their equations involves use of association equilibrium constants between monomers and dimers. Such data are not available for the systems studied in the present investigation.

Correlation and Prediction of Salt-Effect Data. The proposed reference-system relative volatility diagram has been discussed, and presented in Figure 1 for two systems. Similar diagrams for all other systems studied are available from the authors.

The following slopes for the families of parallel straight lines were found:

- (a) Propionic acid-water- NaNO_3 0.95
 - (b) Propionic acid-water- KNO_3 0.91
 - (c) Propionic acid-water-KBr..... 0.95
 - (d) Propionic acid-water- $\text{Pb}(\text{NO}_3)_2$ 0.98
 - (e) Ethanol-water- NH_4Cl 1.00
- [data from Furter (10)]

Equation 12 better approximates the behavior of the ethanol-water-ammonium chloride system than the propionic acid-water-salt systems. This is possibly due to the fact that the largest temperature range encountered in the unsaturated region of the former system is approximately 5°C ., whereas that encountered in the latter systems is approximately 20°C .

Since the lines in the reference-system diagrams are parallel, this suggested the possibility of a simple relationship between the ordinate intercepts and the salt concentration. This plot is shown in Figure 5 for the four salts used in this investigation. Four straight lines passing through the origin are obtained.

The ordinate intercept corresponds to a point where $\ln \alpha = 0$ or $\alpha = 1$, which is the relative volatility at the azeotropic composition. If the system does not exhibit an azeotrope or the azeotrope does not occur within the unsaturated region of the x - y diagram, intercepts at some other line of constant α may be chosen to construct the intercept *vs.* salt concentration diagram. It is possible to construct Figures 1 and 5 from a minimum amount of experimental determinations and utilize them in the prediction of data for the unsaturated region of the x - y diagram. This is illustrated by Figure 6 for the two systems corresponding to Figures 1a and 1b.

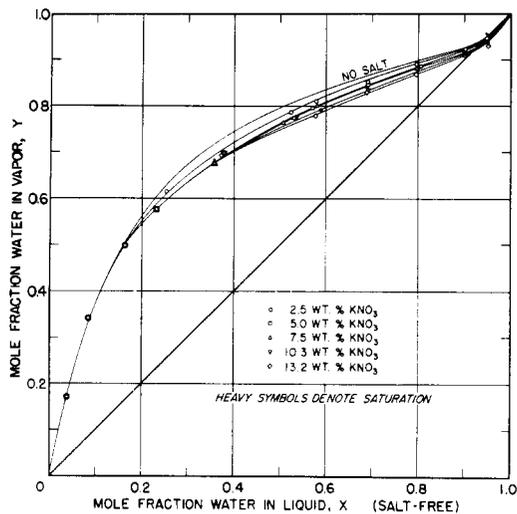


Figure 3. Vapor-liquid equilibrium of propionic acid-water- KNO_3

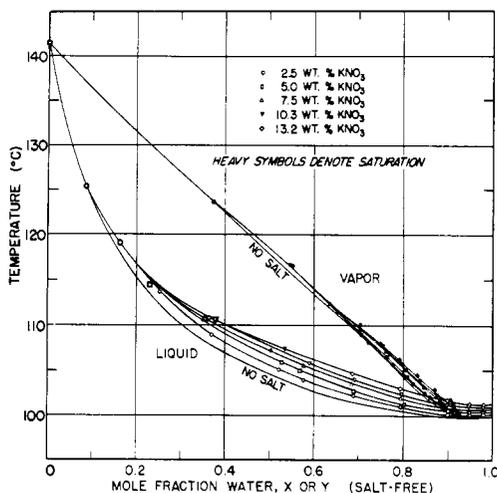


Figure 4. Boiling point diagram of propionic acid-water- KNO_3

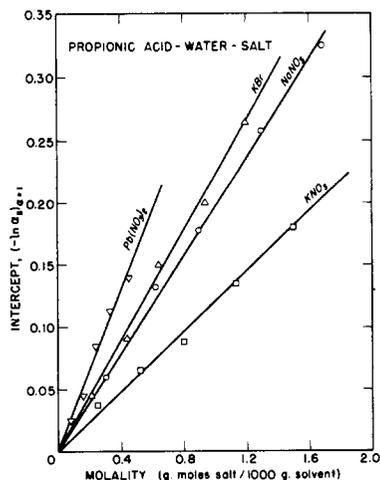


Figure 5. Intercept-molality diagram

LIMITATIONS OF PROPOSED CORRELATION

The proposed correlation is only applicable to unsaturated salt regions of the vapor-liquid equilibrium composition diagram.

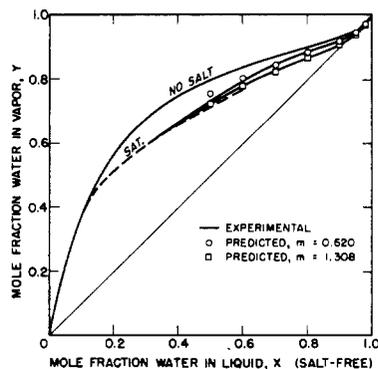


Figure 6a. Experimental and predicted x - y data from the system propionic acid-water- NaNO_3

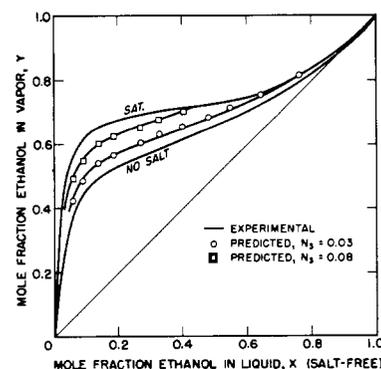


Figure 6b. Experimental and predicted x - y data from the system ethanol-water- NH_4Cl

The method gives no information for determining exactly the liquid concentration at which salt saturation occurs. The saturation point for any particular salt concentration can, however, be easily found experimentally.

The prediction cannot be used successfully for systems exhibiting nearly constant relative volatilities. In this case the straight lines in Figure 1 will be very short and the method becomes inaccurate.

NOMENCLATURE

- c, k = empirical constants
 m = molality, g. moles salt/1000 g. solvent
 N = mole fraction of salt based on total residue composition
 T = absolute temperature
 x = mole fraction of the more volatile component in the liquid phase at equilibrium (salt-free basis)
 y = mole fraction of the more volatile component in the vapor phase at equilibrium
 α = relative volatility

Subscript

- s = system with salt added

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Equations of State for Propyne

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P-V-T data for propyne have been fitted using the Martin-Hou and the Benedict-Webb-Rubin equations of state. The Martin-Hou equation, with its constants calculated from the critical constants and a vapor pressure point for the gas, fits up to 1.1 to 1.5 times the critical density with deviations of less than 1%. The Benedict-Webb-Rubin equation, with its constants calculated by the method of Joffe, resulted in somewhat greater deviations in the low pressure region than did the Martin-Hou equation; however, it also provided a better approximation of the data at high pressures and lower temperatures. The best over-all fit was obtained using the B-W-R equation with its constants determined by a multiple non-linear regression technique, to give a least squares fit to the data themselves.

EXTENSIVE *P-V-T* DATA for propyne were recently obtained by Vohra and coworkers (8). These data included over 350 observations, covering the range of 50–200° C. and 6–315 atm. The experimental work has not extended to temperatures above 200° C. because of the polymerization of propyne at these conditions.

The propyne *P-V-T* data were fitted by two equations of state, the Martin-Hou equation (6) and the Benedict-Webb-Rubin equation (3). This paper presents the results of this work.

MARTIN-HOU EQUATION

The nine constants in the Martin-Hou equation were calculated from the critical values determined by Vohra (8) and from the normal boiling point (2). The calculations were carried out using an IBM 1620 computer, following the procedure presented in the literature (6, 7). Following the suggestion of Martin and Hou, the constants were

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