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# Salt Effect in Isobaric Vapor-Liquid Equilibria of Acetic Acid-Water System

**A. S. Narayana, S. C. Naik,* and P. Rath**

*Department of Chemical Engineering, Regional Engineering College, Rourkela-769008, India*

**Experimental data are reported on the vapor-liquid equilibria of acetic acid-water system with the nonvolatile salts KCl, $Na_2SO_4$, and $K_2SO_4$ at atmospheric conditions of 740 ± 2 mmHg and also without salt. Solubility data are reported for these salts at boiling points of the system. An empirical correlation of the type log $(Y_s/Y_\infty) = KW$ fits the data well for the salt effect. All the three salts studied are found to have salting out effect for acetic acid in varying degrees.**

The presence of a salt can either raise or lower the relative volatility between the components of a system. These phenomena are known as salting out or salting in, respectively. As the molecular interactions between a salt and a binary liquid system are very complex in nature, no rigorous theory concerning quantitative aspect of salt effects has yet been published. A number of data on salt effects in both aqueous and nonaqueous binary systems are available in the literature suggesting simple empirical correlations (*1-6*).

## Experimental Section

***Materials.*** Analytical grade acetic acid, succinic acid, sodium hydroxide, potassium chloride, potassium sulfate, and sodium sulfate were used. Acetic acid and succinic acid were supplied by *Sarabhai M Chemicals, sodium hydroxide by Smith Stances* and Blackwood Hodge, and the other three salts by Oster Chemicals and Pharmaceutical Works. Distilled water was prepared in the laboratory. All these reagents were of the

**Table I. Vapor-Liquid Equilibrium Data for Water (1)-Acetic Acid (2) System at 740 ± 2 mmHg without Salt**

| $x_1$ | $y_1$ | $T$, °C | $x_1$ | $y_1$ | $T$, °C | $x_1$ | $y_1$ | $T$, °C |
|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 117.1 | 44.59 | 59.59 | 105.8 | 78.89 | 86.52 | 101.2 |
| 11.0 | 20.0 | 112.6 | 55.05 | 68.86 | 103.7 | 90.18 | 93.2 | 99.8 |
| 26.0 | 40.56 | 109.2 | 64.14 | 76.36 | 102.5 | 97.05 | 97.96 | 99.6 |
| 26.43 | 41.63 | 109.4 | | | | 100 | 100 | 99.3 |

**Table II. Vapor-Liquid Equilibrium Data for Water (1)-Acetic Acid (2) System with KCl at 740 ± 2 mmHg**

| $x_1$ | $y_1$ | $T$, °C | wt % KCl | |
|---|---|---|---|---|
| 100 | 100 | 108.2 | 55.32 | (S)[a] |
| 97.05 | 95.27 | 107.2 | 50.0 | (S) |
| 97.05 | 96.47 | 105.2 | 29.8 | |
| 89.42 | 86.99 | 106.3 | 35.0 | (S) |
| 89.83 | 92.55 | 100.8 | 2.0 | |
| 89.42 | 92.16 | 100.9 | 4.0 | |
| 89.16 | 91.24 | 101.8 | 8.0 | |
| 89.42 | 90.67 | 102.6 | 12.0 | |
| 89.42 | 88.50 | 104.6 | 23.9 | |
| 78.1 | 79.03 | 105.9 | 20.5 | (S) |
| 78.89 | 86.04 | 101.7 | 2.0 | |
| 78.77 | 85.02 | 102.8 | 4.0 | |
| 78.65 | 82.66 | 103.5 | 8.0 | |
| 78.1 | 82.2 | 104.4 | 12.0 | |
| 78.1 | 81.55 | 105.1 | 16.8 | |
| 60.29 | 67.29 | 106.8 | 12.0 | (S) |
| 60.29 | 67.81 | 106.4 | 9.32 | |
| 54.7 | 67.45 | 104.8 | 2.0 | |
| 59.53 | 68.22 | 105.8 | 4.0 | |
| 26.0 | 37.8 | 110.5 | 1.0 | |
| 26.0 | 33.52 | 110.0 | 1.5 | (S) |
| 11.0 | 19.08 | 113.0 | 0.2 | (S) |
| 0 | 0 | 117.1 | 0 | |

[a] (S) = saturated at boiling point.

**Table III. Vapor-Liquid Equilibrium Data for Water (1)-Acetic Acid (2) with $Na_2SO_4$ at 740 ± 2 mmHg**

| $x_1$ | $y_1$ | $T$, °C | wt % $Na_2SO_4$ | |
|---|---|---|---|---|
| 100 | 100 | 105.1 | 38.8 | |
| 98.6 | 98.38 | 101.6 | 15.0 | |
| 98.4 | 97.61 | 102.0 | 32.0 | (S) |
| 95.6 | 96.7 | 100.3 | 2.0 | |
| 95.6 | 96.5 | 100.6 | 4.0 | |
| 95.6 | 96.0 | 100.9 | 8.0 | |
| 95.6 | 95.15 | 101.7 | 16.0 | |
| 95.6 | 94.6 | 101.9 | 23.0 | (S) |
| 95.07 | 94.0 | 102.2 | 22.0 | (S) |
| 91.15 | 93.64 | 101.2 | 3.0 | |
| 91.15 | 92.78 | 101.6 | 6.0 | |
| 91.15 | 92.1 | 102.1 | 9.0 | |
| 91.15 | 91.7 | 102.2 | 12.6 | |
| 91.15 | 91.5 | 102.3 | 15.0 | (S) |
| 86.8 | 88.7 | 102.3 | 8.0 | (S) |
| 86.8 | 91.08 | 101.6 | 1.0 | |
| 81.8 | 87.3 | 102.3 | 2.0 | |
| 81.8 | 86.53 | 102.4 | 4.5 | |
| 81.8 | 86.2 | 102.5 | 6.5 | (S) |
| 73.98 | 81.65 | 102.6 | 1.0 | |
| 73.98 | 80.97 | 103.0 | 3.0 | |
| 66.14 | 74.77 | 103.4 | 1.3 | (S) |
| 28.1 | 39.67 | 109.6 | 0.5 | (S) |
| 5.92 | 12.2 | 115.2 | 0.03 | (S) |
| 0 | 0 | 117.1 | 0 | |

**Table IV. Vapor-Liquid Equilibrium Data for Water (1)-Acetic Acid (2) System with $K_2SO_4$ at 740 ± 2 mmHg**

| $x_1$ | $y_1$ | $T$, °C | wt % $K_2SO_4$ | |
|---|---|---|---|---|
| 5.92 | 12.2 | 115.1 | 0.02 | (S) |
| 28.1 | 39.67 | 109.4 | 0.3 | (S) |
| 50.66 | 62.56 | 104.5 | 0.5 | (S) |
| 69.16 | 78.94 | 102.2 | 0.5 | |
| 69.16 | 78.67 | 102.5 | 1.0 | |
| 69.16 | 78.52 | 102.5 | 2.0 | |
| 68.16 | 78.1 | 102.7 | 2.5 | (S) |
| 78.95 | 85.9 | 101.5 | 1.0 | |
| 78.96 | 85.66 | 102.2 | 2.0 | |
| 78.95 | 85.2 | 102.4 | 3.0 | (S) |
| 90.04 | 92.7 | 100.8 | 2.0 | |
| 90.04 | 92.5 | 101.4 | 4.0 | |
| 90.08 | 92.2 | 102.2 | 10.5 | (S) |
| 95.825 | 96.3 | 101.7 | 18.0 | (S) |
| 97.5 | 98.22 | 100.2 | 2.0 | |
| 97.5 | 98.17 | 100.5 | 4.0 | |
| 97.5 | 98.1 | 100.9 | 6.0 | |
| 97.5 | 98.0 | 101.0 | 8.0 | |
| 97.5 | 97.96 | 101.2 | 10.0 | |
| 97.5 | 97.97 | 101.4 | 12.0 | |
| 97.5 | 97.81 | 101.5 | 14.0 | |
| 97.5 | 97.75 | 101.6 | 16.0 | |
| 97.5 | 97.8 | 101.7 | 18.0 | (S) |
| 98.05 | 98.28 | 100.8 | 21.0 | (S) |
| 98.27 | 98.69 | 100.0 | 2.0 | |
| 98.27 | 98.6 | 100.2 | 4.0 | |
| 100.0 | 100 | 102.0 | 23.8 | |

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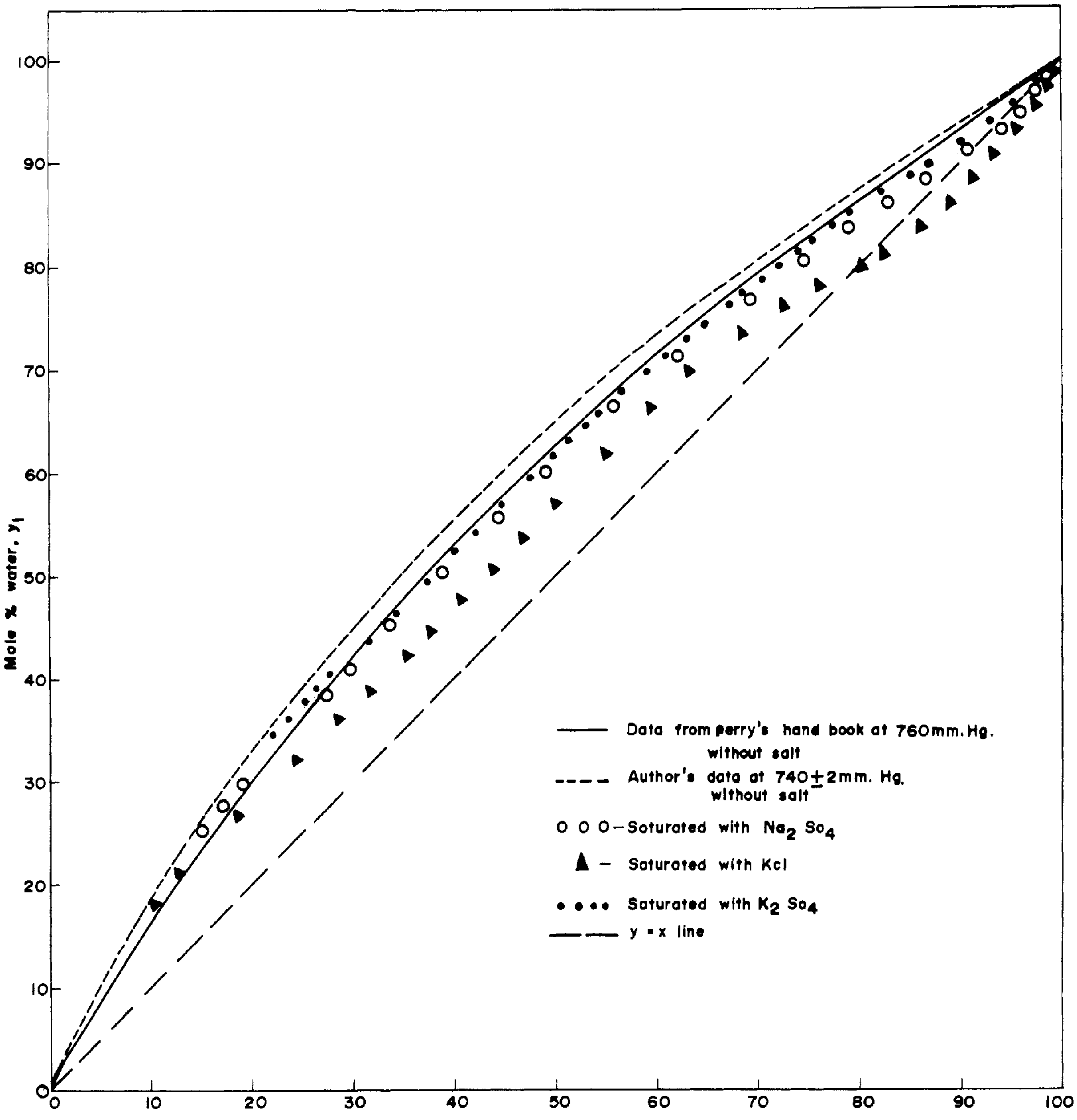

Figure 1. Equilibrium curves ($y_1$ vs. $x_1$).

Table V. Solubility Data for KCl in Water (1)-Acetic Acid (2) System at 30 ± 1 °C (g of Salt/100 g of Salt-Free Solution)

| $x_1$ | wt % | $x_1$ | wt % | $x_1$ | wt % |
|---|---|---|---|---|---|
| 100 | 36.4 | 73.94 | 14.72 | 26.0 | 1.49 |
| 97.05 | 29.8 | 63.1 | 10.25 | 20.0 | 0.75 |
| 93.03 | 25.74 | 40.0 | 4.1 | 0 | 0 |
|  |  | 35.93 | 3.36 |  |  |

Table VI. Solubility Data for KCl in Water (1)-Acetic Acid (2) System at Boiling Point

| $x_1$ | wt % | $x_1$ | wt % | $x_1$ | wt % |
|---|---|---|---|---|---|
| 100 | 55.32 | 80.4 | 22.4 | 47.4 | 6.96 |
| 92.32 | 40.86 | 67.88 | 15.71 | 34.0 | 2.26 |
| 88.98 | 33.74 | 56.3 | 10.1 | 11.3 | 0.2 |
| 85.88 | 28.4 |  |  | 0 | 0 |

Table VII. Solubility Data for $Na_2SO_4$ in Water (1)-Acetic Acid (2) System at Boiling Point

| $x_1$ | wt % $Na_2SO_4$ | $x_1$ | wt % $Na_2SO_4$ | $x_1$ | wt % $Na_2SO_4$ |
|---|---|---|---|---|---|
| 100 | 38.8 | 86.25 | 8.0 | 72.67 | 1.882 |
| 97.46 | 29.6 | 83.53 | 6.695 | 59.26 | 0.987 |
| 93.66 | 19.8 | 79.45 | 4.7 | 11.3 | 0.05 |
| 89.2 | 11.8 |  |  | 0 | 0 |

Table VIII. Solubility Data for $K_2SO_4$ in Water (1)-Acetic Acid (2) System at Boiling Point

| $x_1$ | wt % $K_2SO_4$ | $x_1$ | wt % $K_2SO_4$ |
|---|---|---|---|
| 100 | 23.8 | 72.7 | 3.8 |
| 89.9 | 10.15 | 46.5 | 0.6 |
| 83.2 | 5.7 | 11.3 | 0.05 |
|  |  | 0 | 0 |

highest purity and failed to show presence of any significant impurities.

***Apparatus and Procedure.*** A modified Othmer still was used in this work. The volume of the liquid chamber was around 0.400 × $10^{-3}$ $m^3$ and that of the condensate chamber, 0.01 × $10^{-3}$ $m^3$. Recirculation was provided from condensate chamber to liquid chamber. Mercury-in-glass thermometers of 0.1 °C accuracy were used to measure temperatures. The thermometers were calibrated with the melting point of ice and boiling point of distilled water. Each observation was taken after running the still for at least 3 h.

***Analyses.*** The standard succinic acid solution was prepared by weighing solid succinic acid accurately and dissolving it in a known volume of distilled water. The sodium hydroxide solution was standardized by using standard succinic acid solution with phenolphthalein as indicator. Weight percent acetic acid in aqueous solution in vapor phase was estimated by titrating a known amount of solution against standardized sodium hydroxide solution with phenolphthalein as indicator. Weight percent acetic acid in the aqueous solution in the liquid phase was determined by material balance. The results were reproducible with a maximum error of 0.1%.

## Results and Discussion

Table I contains the experimental vapor-liquid equilibrium data for water (1)-acetic acid (2) solution without salt. Tables II-IV report the experimental data with the three salts at different salt concentrations. Tables V-VIII show the solubilities of the salts. Equilibrium curves at salt saturation are shown in Figure 1. The points in the figure are smoothed data points.

Addition of KCl, $Na_2SO_4$, and $K_2SO_4$ results in "salting out" of acetic acid. Water-acetic acid solutions containing salts KCl and $Na_2SO_4$ above 80 and 91 wt % water on salt-free basis, respectively, form azeotropes. An equation of the type log $(Y_s/Y_{so}) = KW$ fits the data for the three salts studied in this system. Such an equation was proposed by Yoshida et al. (*4*) for the salts NaCl, $MgCl_2$, $NaNO_3$, $Na_2SO_4$, and $CaCl_2$. The constants obtained are KCl, $K = 8.2 \times 10^{-3}$; $Na_2SO_4$, $13.0 \times 10^{-3}$; $K_2SO_4$, $8.0 \times 10^{-3}$.

The thermodynamic consistency was assessed by applying Herrington's criteria (*7, 8*). Herington's isobaric consistency test is not very accurate for aqueous systems. The absolute value of $(D - J)$ to be less than 10 is good for systems having the ratio of the maximum value of heat of mixing to the maximum value of excees free energy of mixing, greater than or equal to three.

The values of $D$ and $J$ are

|  | $D$ | $J$ |
|---|---|---|
| without salt | 12.3 | 7.1 |
| saturated with KCl | 2.7 | 15.7 |
| saturated with $Na_2SO_4$ | 36.4 | 25.7 |
| saturated with $K_2SO_4$ | 28.3 | 24.0 |

## Glossary

|  |  |
|---|---|
| $D$ | percent deviation, $100\ I/\Sigma$ |
| $I$ | difference between the area above and below the abscissa when log $(\gamma_1/\gamma_2)$ is plotted against $x_i$ |
| $J$ | $150\theta/T_{\min}$ |
| $K$ | proportionality factor |
| $T_{\min}$ | lowest boiling point in the system, K |
| $W$ | weight percent of salt in liquid solution on salt-free basis |
| $x_i$ | mole fraction of component $i$ in liquid phase on salt-free basis |
| $y_i$ | mole fraction of component $i$ in vapor phase |
| $Y_s$ | mole fraction of organic solvent in vapor phase in salt solution |
| $Y_{so}$ | mole fraction of organic solvent in vapor phase in salt-free (without salt) solution |

*Greek letters*

|  |  |
|---|---|
| $\theta$ | difference in temperature between maximum and minimum boiling point, K |
| $\Sigma$ | total integral area |

*Subscripts*

|  |  |
|---|---|
| 1 | water |
| 2 | acetic acid |

**Registry No.** KCl, 7447-40-7; $Na_2SO_4$, 7757-82-6; $K_2SO_4$, 7778-80-5; acetic acid, 64-19-7.

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# Equilibrium Phase Compositions, Phase Densities, and Interfacial Tensions for $CO_2$ + Hydrocarbon Systems. 1. $CO_2$ + *n*-Butane

**Jack J.-C. Hsu, N. Nagarajan, and R. L. Robinson, Jr.***

*School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma 74078*

**An experimental facility has been established for measurements of equilibrium phase compositions, phase densities, and interfacial tensions in mixtures of interest in petroleum reservoir engineering. Data have been obtained on the system $CO_2$ + *n*-butane at 115, 160, and 220 °F at pressures to the critical point (interfacial tensions as low as 0.03 mN/m). The measured phase compositions and densities agree well with the work by Sage and Lacey. The interfacial tension data are in reasonable agreement with the measurements of Stegemeier (115 and 160 °F), with the present results extending to lower values of interfacial tension.**

## Introduction

The development of efficient, economical methods for secondary or tertiary recovery of petroleum reservoir fluids could substantially increase our nation's usable reserves and supply of energy. The use of carbon dioxide ($CO_2$) for the miscible displacement of petroleum is one such recovery method. The $CO_2$ flooding technique has proved sufficiently promising that it is currently under intensive laboratory and field study. However, the mechanisms by which $CO_2$ floods operate are not fully understood.

Evidence exists that so-called "miscible" displacements of oil by $CO_2$ actually operate, in substantial part, in the immiscible

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