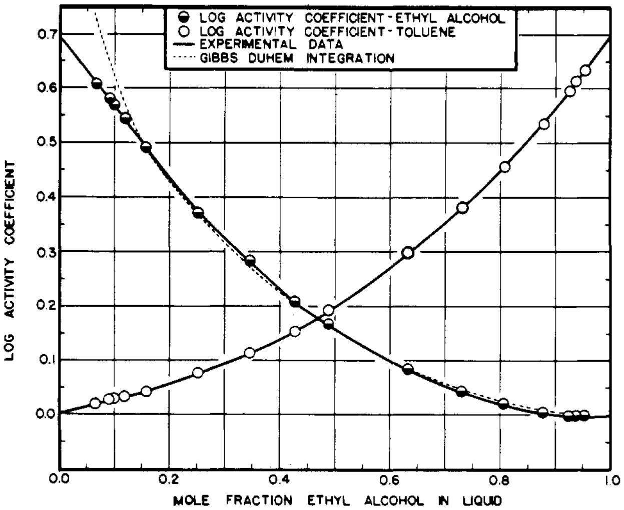

Figure 7. Diagram of log activity coefficient vs. composition for toluene–ethyl alcohol system at 765 mm. of mercury

data measured at 25°C. (9). The resulting curve lies approximately half-way between the experimental curve and the Gibbs-Duhem curve.

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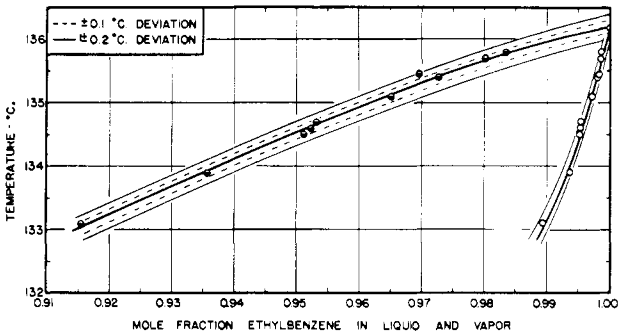

Figure 8. Temperature-composition diagram for ethylbenzene-*n*-propyl alcohol system

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Salt Effects in Aqueous Vapor-Liquid Equilibria

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The addition of a salt to an aqueous solution of a volatile nonelectrolyte has a marked effect upon the vapor-liquid equilibria of the solution. The presence of the salt may either raise or lower the relative volatility of the nonelectrolyte or, in extreme cases, cause the formation of two liquid phases. The observed effects depend upon the nature and concentration of both the salt and nonelectrolyte.

Various experimental studies of the salt effect in vapor-liquid equilibria have been reported, but no concerted effort has been made to fit the results into a correlating framework.

THEORY

A charged particle superimposes many complications on the already complex water-nonelectrolyte interactions. The ions tend to attract and orient solvent molecules in a hydration shell around the ion, promote or destroy the short-range ordered structure of the water, and increase the internal pressure of the solution.

Theoretical explanations of the salt effect have been based upon various physical phenomena, notably electrostatic interactions, hydration, van der Waals forces, and internal pressure. These theoretical attempts, although not successful in describing the salt effect quantitatively except in severely restricted situations, are useful for interpreting data.

Electrostatic Effects. The first attempt to treat salting out as an electrostatic phenomenon was made by Debye and McAuley (*2*). Considering the ion as a perfect sphere of radius *b*, the Helmholtz work function, ΔA, is equal to the difference in the work of charging and discharging the ion in media of dielectric constants D and D_0, respectively, and the work done against the potential due to the ionic atmosphere. This leads to an equation which expresses the activity coefficient of the nonelectrolyte as a function of the ratio of charge to ionic radius, the ion concentration, and the decrement in the dielectric constant of the aqueous solution due to nonelectrolyte.

The equation of Debye and McAuley is based upon the assumptions that: the dielectric constant of the solution can be expressed as a linear function of salt concentration and nonelectrolyte concentration; salting out is due only to alterations in the dielectric constant of the solution; and the solution is dilute in both nonelectrolyte and salt. Estimation of the ionic radius in solution is very difficult, especially at moderate to high ion concentrations.

The electrostatic theory gives fairly good results for many dilute systems. However, it always predicts salting out and cannot account for salting in.

Internal Pressure. A contraction in volume usually follows the addition of a salt to water. By application of the principle of Tammann (*17*), an internal pressure, P_e, is defined. This principle proposes that a given amount of water in solution behaves like the same amount of pure water under a pressure greater than atmospheric. The work done in introducing a volume of nonelectrolyte V_i into a solution is then given by $P_e V_i$ and can be related to the Helmholtz-free-energy change.

It was shown (*13*) that as a result of these considerations the following expression can be obtained:

$$\lim_{\substack{C_s \to 0 \\ n \to 0}} \frac{d \ln \gamma'}{dC_s} = \frac{\bar{V}_i^0 (V_s - \bar{V}_s^0)}{RT\beta_0} \qquad (1)$$

where

γ' = rational activity coefficient for nonelectrolyte
C_s = molar concentration of electrolyte
$\bar{V}_i^0$ = partial molar volume of nonelectrolyte at infinite dilution
V_s = molar volume of pure (liquid) electrolyte
$\bar{V}_s^0$ = partial molar volume of electrolyte at infinite dilution
R = gas constant
β_0 = compressibility of pure water
T = absolute temperature
n = molar concentration of salt

Equation 1 is useful only for regions of low salt and low nonelectrolyte concentrations. The terms $\bar{V}_s^0$, V_s, and $\bar{V}_i^0$ are, in general, not known although they can frequently be estimated quite closely.

The internal-pressure approach leads to a simple physical interpretation of salting out. A contraction in total volume which occurs on mixing salt and water can be thought of as a compression of the solvent. This compression makes it more difficult to insert a molecule of nonelectrolyte and results in salting out. An increase in total volume upon the addition of a salt would produce the counter effect known as salting in.

van der Waals Forces. Electrostatic attractions between ions and a neutral molecule are to a large extent short-range forces. Other short-range forces, such as dispersion forces, may also be of considerable importance.

Long and McDevit (*13*) proposed the semiempirical equation,

$$\ln \gamma' = A \sum_j z_j^2 C_j - B \sum_j a_j C_j \qquad (2)$$

where

A and B = empirical constants dependent upon both nonelectrolyte and electrolyte
a_j = polarizability of ion j
C_j = molar concentration of ion of type j
z_j = valence of ion of type j

The first term in Equation 2 accounts for changes in the activity coefficient due to electrostatic interactions; the second term reflects the effect of dispersion forces.

Hydration. A convenient physical picture of the salting-out effect is given by the hydration theory. Salting out must largely be due to a preferential attraction between water molecules and ions. The hydration theory thus assumes that each ion ties up its share of water molecules, thereby decreasing the activity of the water. The main objection to this theory is its assumption that the salt affects only the water and has no effect upon the nonaqueous component. Therefore the hydration theory can not explain the frequently observed phenomenon of salting in, which results in a decrease rather than an increase in the relative volatility of the nonelectrolyte.

The hydration theory, however, has considerable success when it is applied to aqueous solutions of nonpolar nonelectrolytes such as gases. Philip (*15*) postulated that the decrease in solubility of gases upon the addition of a salt is due to two factors:

Only water dissolves the gas. Therefore an absorption factor calculated upon amount of water present rather than total volume of solution would be constant.

Ions hydrate with water, thereby decreasing the effective amount of water for absorption of a gas. The hydration of water per molecule of electrolyte can be calculated by differences in absorption coefficients. The values of hydration numbers obtained from these calculations compare favorably with those obtained by transference measurements.

Table I lists hydration numbers for various anions and cations.

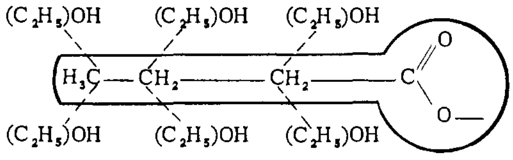
For potentially ionizable polar nonelectrolytes, a modified hydration theory has been proposed by Harned and Owen (*10*). This theory explains the differences in effects due to solutes and ions by assuming that each ion orients water molecules in a definite direction. This type of hydration is called "vector" hydration to differentiate it from "scalar" hydration in which orientation plays no part in determining the degree of salting out. If the orientation is "favorable" to the nonelectrolyte molecules, salting in occurs; an "unfavorable" orientation produces salting out.

Table I. Hydration Numbers

Ion	No. of Molecules of Water Associated with an Ion
Li^+	6
Na^+	5
K^+	3
Rb^+	2
F^-	5
Cl^-	3
Br^-	2
I^-	0

Hydrotropism. Salting in can be thought of as a congregation of nonelectrolyte molecules around the ions at the expense of the water molecules. A large ion with an unsymmetrical charge distribution and a prominent nonpolar region will result in this favored congregation. Complex organic salts which would be expected to produce this hydrotropic effect do, in fact, cause salting in in many cases (*6*).

As an example, consider the system sodium butyrate-water-ethyl alcohol as illustrated below. The large butyrate ion attracts nonelectrolyte molecules to its nonpolar end, thus decreasing the concentration of alcohol molecules at points away from the ion. This, in effect, causes salting in of the alcohol.



Solubility of Salts in Nonelectrolyte. If a salt is more soluble in the nonelectrolyte than in water, salting in will occur. Glasstone (*5*) noted an increase in the solubility of ethyl acetate in water when lithium and ammonium iodides were added. These iodides are more soluble in ethyl acetate than in water. The salting in may be due to a preferential association of ions and nonelectrolyte or of undissociated salt and nonelectrolyte.

A general analysis of the salt effect indicates that salting out decreases with rising dipole moment; that hydration effects are scalar for nonpolar, but vector for polar nonelectrolytes; that salting-out effects of small ions are in the order indicated in Table II; that large ions cause small salting in due to hydrotropism; and that salting in results when a salt is more soluble in the nonelectrolyte than in water.

EXPERIMENTAL

Extensive experimental data on the salting-out effect in liquid-liquid equilibria have been reviewed by Long and McDevit (*13*) but little information is available on the salt effect in vapor-liquid equilibria (Table III).

It is convenient to divide nonelectrolytes into a polar

Table II. Salting-Out Effects in Decreasing Order for Small Ions

A. Nonpolar and neutral polar nonelectrolytes

Cation. Mg^{++}, Na^{+}, K^{+}, Be^{++}, Li^{+} [a], Cs^{+}, NH_4^{+}
Anion. SO_4^{--}, F^{-}, NO_3^{-}, I^{-}

B. Acidic nonelectrolyte

Cation. Li^{+}, Na^{+}, NH_4^{+}, Rb^{+}
Anion. Cl^{-}, Br^{-}, NO_3^{-}

C. Basic nonelectrolyte

Cation. K^{+}, Na^{+}, Li^{+}
Anion. Cl^{-}, Br^{-}, NO_3^{-}, I^{-}

[a] Li^{+} ion is an anomaly and in many cases produces less salting out than would be expected from an ion of its size.

Table III. Previously Published Salt Effect Data

Nonelectrolyte	Lit. Ref.	Salt	Range of Salt Concn.	Salt Effect[a]
Ethyl alcohol	(*16,18*)	$NaNO_3$	Satd.	SO
		KNO_3	Satd.	SO
		Na_2SO_4	Satd.	WO
		K_2SO_4	Satd.	WO
	(*12*)	$CaCl_2$	100 grams/liter	SO
	(*19*)	$CaCl_2$	Satd.	SO
		NH_4Cl	Satd.	SO
		KCl	Satd.	SO
		$NaNO_3$	Satd.	SO
	(*11*)	$HgCl_2$	Satd.	In
	(*14*)	$CuCl_2$	Satd.	Out
		$KC_2H_3O_2$	Satd.	SO
Ethylene glycol	(*3*)	Na_2SO_4	Satd.	WO
		KCl	Satd.	Out
		KBr	Satd.	Out
Acetic acid	(*4*)	$CaCl_2$	0–60 wt. %	SO
Formic acid	(*9*)	$CaCl_2$	$F^{b} = 2.4$ to 5.3	SO
		$MgCl_2$	$F = 2.4$ to 3.0	SO
		NaCl	$F = 4.8$	WO
		$CaCl_2$	Satd.	None
		Na_2SO_4	$F = 5.6$	None
		$(NH_4)_2SO_4$	$F = 6.4$	WI
		$Ca(CHO_2)_2$	Satd.	None
		$Mg(CHO_2)_2$	Satd.	None
		$NaCHO_2$	$F = 5.4$ to 36.5	In
		NH_4CHO_2	11 wt. %	In
Phenol	(*1*)	NaCl	10–17 wt. %	Slight salting out

[a] SO = strong salting out; WO = weak salting out; WI = weak salting in.
[b] F = weight ratio of water to salt.

Table IV. New Experimental Data

Nonelectrolyte	Salt	Range of Salt Concn.	Salt Effect
Dioxane	NaCl	$F^{a} = 3.3$ to 10	Out
	$KC_7H_5O_2$	$F = 3.3$ to 10	Out
	$NaC_2H_3O_2$	$F = 6.5$	Out
Isopropyl alcohol	NaCl	$F = 3.3$	Out
	$KC_7H_5O_2$	$F = 3.3$	None
Pyridine	NaI	$F = 2.5$	Slight salting in at low pyridine concentrations and moderate salting out at high pyridine concentrations
	Na_2SO_4	$F = 5.0$	

[a] F = weight ratio of water to salt.

Table V. Vapor-Liquid Equilibria Data

Salt	Water/Salt, Wt. Ratio	Temp., °C.,	Mole Per Cent Nonelectrolyte (Salt-Free)	
			Liquid phase	Vapor phase
		Water-Dioxane		
$KC_7H_5O_2$	10	98.8	1.1	13.0
		89.2	16.4	41.4
		88.8	32.4	45.2
		88.1	43.8	48.3
		88.1	52.0	49.4
		90.3	65.6	54.4
		91.0	76.4	60.8
		93.6	84.8	69.4
		96.2	90.2	83.2
NaCl	3.3	93.0	3.7	40.0
		88.5	5.9	52.0
		88.5	8.0	52.0
		88.5	30.0	52.0
		88.5	87.2	52.0
NaCl	10	101.3	0.1	3.5
		97.9	1.0	16.4
		94.2	3.8	28.2
		90.9	6.2	34.8
		89.1	8.2	45.1
		89.1	24.0	45.1
		89.1	58.0	45.1
		89.1	78.3	45.1
$NaC_2H_3O_2$	6.3	95.2	1.8	24.0
		88.6	20.8	45.4
		88.2	35.0	47.5
		88.2	72.0	47.5
		88.2	90.0	47.5
No salt		97.3	0.8	9.2
		96.3	1.2	15.2
		88.9	23.0	41.6
		88.2	36.0	47.2
		97.5	44.9	47.2
		...	72.2	54.4
		89.4	82.8	63.0
		93.4	83.0	66.6
		98.5	89.2	75.2
		97.0	91.8	80.0
		Water-Isopropyl Alcohol		
NaCl	3.3	...	1.5	31.1
		...	11.2	58.1
		...	26.0	64.0
		...	53.1	64.0
		...	72.4	64.0
		...	85.8	64.0
$KC_7H_5O_2$	3.3	92.2	1.7	30.5
		82.7	14.5	55.5
		82.7	25.3	55.5
		82.7	71.2	55.5
		80.7	74.0	71.2
		Water-Pyridine		
NaI	2.5	...	7.5	19.0
		...	25.7	44.1
		97.0	56.6	42.5
		93.8	81.3	7.7
		94.3	89.8	78.5
		97.0	96.8	88.8
Na_2SO_4	5.0	...	5.4	11.4
		...	18.8	33.0
		...	40.2	52.5
		...	60.3	66.5
		...	90.1	78.0
No salt		104.0	13.2	34.1
		102.3	29.5	48.0
		97.2	45.1	58.2
		96.0	54.1	65.0
		94.5	62.6	70.2
		94.2	72.1	74.5
		94.2	83.6	77.0
		94.5	90.6	77.6
		95.0	95.0	80.6

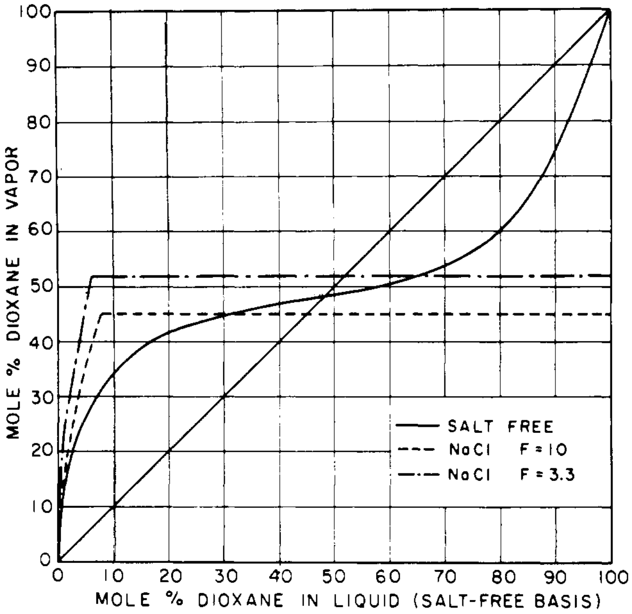


Figure 1. Vapor-liquid equilibrium data for dioxane-water-sodium chloride at atmospheric pressure

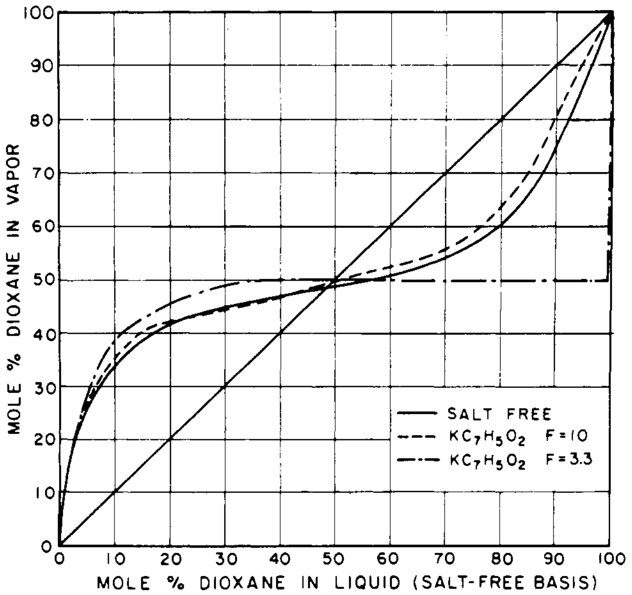


Figure 2. Vapor-liquid equilibria data for dioxane-water-potassium benzoate at atmospheric pressure

and nonpolar category, which can further be subdivided into neutral, acidic, and basic. In the five systems studied (Table III), the nonelectrolyte of the first two is neutral nonpolar but those of the remaining three are acidic polar. To supplement these data it seemed appropriate to make experimental studies of systems containing one of three types of nonelectrolyte: nonpolar, basic polar, or a neutral polar having a dipole moment larger than that of ethyl alcohol.

Dioxane was chosen as the nonpolar, isopropyl alcohol as the neutral polar, and pyridine as the basic polar nonelectrolyte. All vapor-liquid equilibrium measurements were made in a modified Gillespie still using an external heater. The three chosen aqueous' systems were first studied in the absence of salt and good agreement was obtained with previously published results. Samples were analyzed by refractive index measurements.

In determining the vapor-liquid equilibria for the salt-containing systems the salt had to be removed from the liquid sample before analysis. This separation was performed by a high vacuum distillation operating at a pressure near 0.1 micron of mercury and using liquid nitrogen to condense the distilled vapor.

Special precautions were taken to prevent entrainment in both the still and the vacuum distillation apparatus. Spot tests for salt content in the condensed vapor samples were always negative.

All data were taken at atmospheric pressure. A constant ratio of water to salt, *F*, was used in all the experimental data taken as recommended by Guyer, Guyer, and Johnson (*9*). This was done to explore more completely the regions of high nonelectrolyte concentrations where the solubility of the salt may be very low.

A summary of the new salt-effect data is given in Table IV. The detailed data are given in Table V.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental results can be best interpreted in terms of the classification of nonelectrolytes as suggested by theoretical considerations.

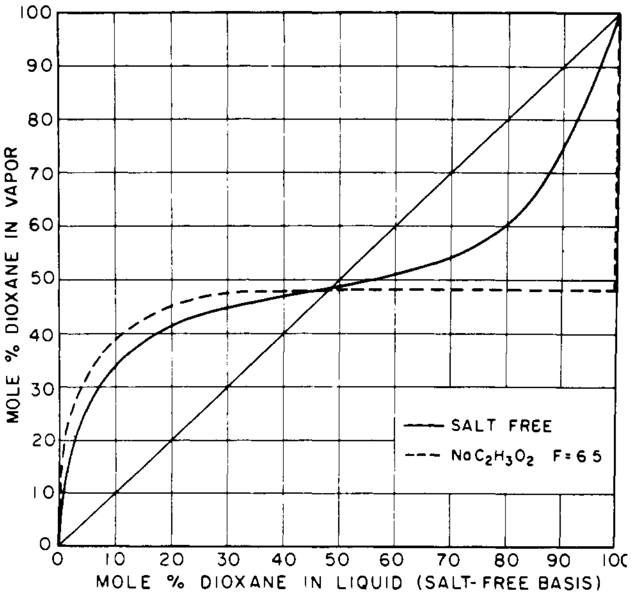


Figure 3. Vapor-liquid equilibrium data for dioxane-water-sodium acetate at atmospheric pressure

Dioxane, the nonpolar nonelectrolyte, has a zero dipole moment. The salting out of dioxane by sodium chloride was sufficiently strong to cause separation into two liquid phases, as shown in Figure 1. High concentrations of potassium benzoate also caused two-phase formation but at a higher dioxane concentration. At moderate potassium benzoate concentrations salting out was observed, but not phase separation, due to the hydrotropic effect of benzoate ion. Sodium acetate produced results of the same order of magnitude as those reported for potassium benzoate. These effects are presented in Figures 2 and 3. The especially severe salting out obtained for the dioxane-water system is caused by the low dipole moment of the dioxane.

Isopropyl alcohol (dipole moment, 1.76 debyes), ethyl alcohol (dipole moment, 1.5 debyes), and ethylene glycol (dipole moment, 1.68 debyes) are the only neutral, polar nonelectrolytes for which experimental data are now available. Sodium chloride caused salting out of the isopropyl alcohol, as is shown in Figure 4, but the salting out is of smaller degree than that observed with dioxane. Potassium benzoate produced no significant effect upon the relative volatility of isopropyl alcohol.

The more complete data for ethyl alcohol provide support for the validity of the theoretically developed criteria for

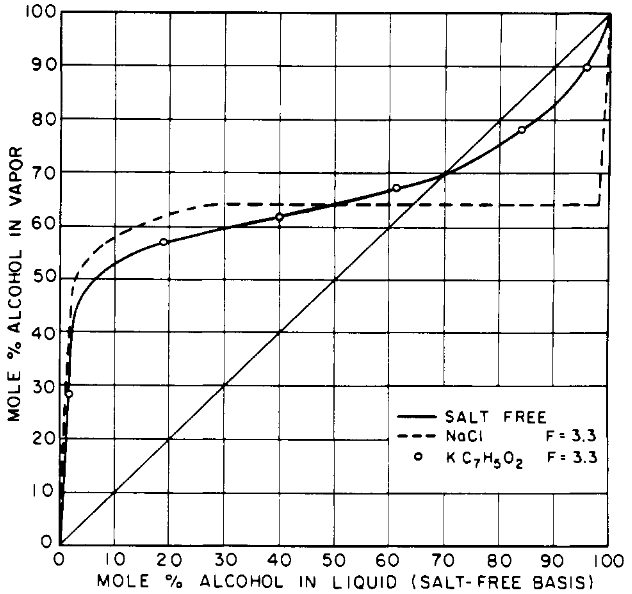


Figure 4. Vapor-liquid equilibrium data for isopropyl alcohol-water with salts at atmospheric pressure

salt effects in a neutral polar system. These data show that the order of salting out for saturated solutions is $NaNO_3 > KNO_3 > Na_2SO_4 > K_2SO_4$. Sodium and potassium nitrates have approximately the same solubility in water; and, from surface charge calculations, the sodium ion increases the relative volatility of the alcohol to a greater degree than the potassium ion. The experimental evidence bears this out. Similarly, the sulfate ion should cause more salting out than the nitrate ion, which is difficult to discern with these data due to the rather large difference in solubility between sulfates and nitrates. Nonelectrolyte solubility decrement measurements at equal salt concentrations (*7,8*) show that the salting-out effect of the sulfate ion is much greater than that of the nitrate ion. Jost (*12*), using calcium chloride in a concentration of 100 grams per liter, observed strong salting out for the ethyl alcohol-water system and has shifted the azeotrope significantly. Novella and Tarraso (*14*) observed salting out with saturated solutions of cupric chloride and potassium acetate; in both cases the azeotrope was shifted to higher alcohol concentrations. The salting-out effect for potassium acetate was larger because of its greater solubility in water. The solubilities of these salts in ethyl alcohol are about the same.

Yamamoto's results (*19*) for ethyl alcohol-water are substantially in agreement with those of the other investigators. However, Yamamoto was not able to produce a significant change in the azeotropic composition, contrary to Jost's results.

The vapor-liquid equilibria for the system ethyl alcohol-water saturated with mercuric chloride have been studied by Johnson and Furter (*11*). The system is rather unusual since mercuric chloride is more soluble in ethyl alcohol than in water. The solubility of mercuric chloride in water is 6.9 grams per 100 ml. of water at 25 °C., and that in ethyl alcohol is 33 grams per 100 ml. of ethyl alcohol at 30 °C. The observed salting in appears to be due to the high solubility of mercuric chloride in ethyl alcohol.

Fogg (*3*) studied the salt effect in aqueous solutions of ethylene glycol; his data are for saturated solutions of sodium sulfate, potassium chloride, and potassium bromide. This is an interesting system because water is the more volatile component over the entire composition range, no azeotrope being formed. All three salts lowered the relative volatility of the water, the effect being larger for the potassium salts.

Acidic systems for which data have been reported are acetic acid (*4*), formic acid (*9*), and phenol (*1*). Garwin and Hutchison (*4*) report salting out for the system calcium chloride-water-acetic acid. The salting out was so large that the relative volatility of the acetic acid was increased from 0.6 to 9.0. The unusually large increase in relative volatility can be ascribed to large electrostatic and hydration effects due to high calcium chloride concentrations in both water and acetic acid.

The system formic acid-water was studied by Guyer, Guyer, and Johnson (*9*) who used various organic and inorganic salts. At approximately equal salt concentrations the chlorides of magnesium, calcium and sodium caused salting out in the order of Mg > Ca > Na. This order agrees with that predicted on the basis of ionic charge and radius. Calcium sulfate and sodium sulfate do not affect the relative volatility of formic acid. There appears to be a cancellation of ionic effects since anions and cations both hydrate strongly. According to the concept of vector hydration the positively charged cation causes salting out, the negatively charged anion, salting in. Each effect tends to cancel the other.

Formic acid is salted in by ammonium sulfate. This is due to the presence of the sulfate ion, as the large univalent ammonium ion does not produce any primary effects upon the solution's vapor-liquid equilibrium.

Calcium and magnesium formates also have little effect upon the relative volatility of the acid. In these cases the cancellation of anionic and cationic interactions may be due to antagonistic interplay of hydrotropism and salting out. For the case of formate ion in aqueous formic acid it is not known whether or not there is a common-ion effect in solution, nor is it known what consequence this has on the vapor-liquid equilibria of the system. Salting in was observed with ammonium formate, the effect of the formate ion outweighing that due to the ammonium.

Salting out was observed for the system phenol-water-sodium chloride. This is in agreement with the vector hydration theory for acidic polar nonelectrolytes.

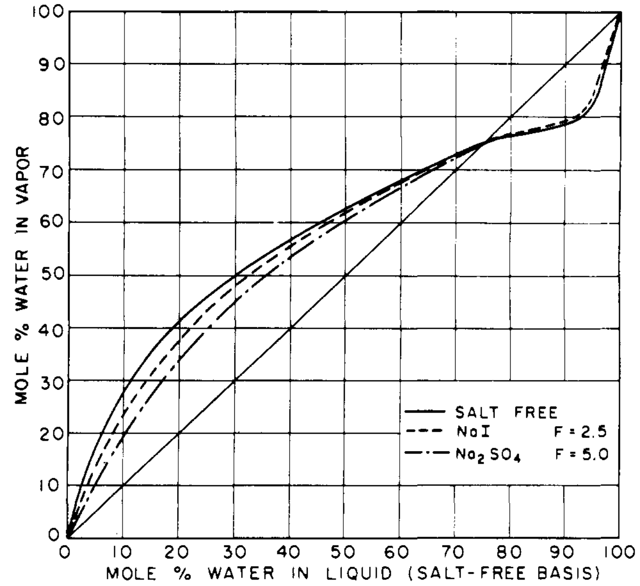


Figure 5. Vapor-liquid equilibrium data for pyridine-water with inorganic salts at atmospheric pressure

The salt effect on the vapor-liquid equilibria of a basic aqueous system has been investigated only for pyridine-water (Figure 5). Pyridine has a pK_B of 5.

Sodium sulfate and sodium iodide have similar effects on the pyridine-water phase equilibrium; at high pyridine concentrations there is considerable salting out but at high water concentrations these salts produce slight salting in.

These experiments indicate that the basic pyridine molecule orients water molecules such that acidic and neutral salts cause more salting out than basic ones. The opposite effect was observed for the case of acidic nonelectrolytes.

An acid salt such as ammonium chloride may form a complex ion with pyridine. Formation of such a complex causes a decrease in the effective pyridine concentration and would result in the salting in of pyridine.

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Boiling Point – Composition Diagrams for the Systems 2-Ethoxyethanol–Ethyl Acetate and 2-Ethoxyethanol–Propyl Acetate

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In an investigation of the solvent properties of mixtures of 2-ethoxyethanol-ethyl acetate and 2-ethoxyethanol-propyl acetate in which moderately active metal salts were to be electrolyzed, it seemed desirable to determine the boiling point-composition diagrams for these systems. Especially because azeotrope formation has been noted in the 2-ethoxyethanol-butyl acetate system (*1,4*) it was of interest to determine whether azeotropes would form between 2-ethoxyethanol and ethyl or propyl acetate solutions.

MATERIALS

C.P. ethyl and propyl acetate were purified by the procedure of Hurd and Strong (*3*) and distilled twice from a 3-foot, all-glass column (*7*); in each case the center fraction was taken. The refractive indices at 25° for ethyl and propyl acetate, respectively, were $n_D^{25} = 1.3698$ and $n_D^{25} = 1.3821$.

C.P. 2-ethoxyethanol was fractionally distilled twice from a 3-foot, all-glass column and the center fractions were retained. The refractive index at 25° was found to be $n_D^{25} = 1.4059$.

ANALYTICAL METHODS

Vapor and liquid samples were analyzed by means of index of refraction, using a Bausch & Lomb refractometer with a sodium lamp as the source of illumination. The composition of the samples was determined from a refractive index-composition curve determined from samples of known composition. Standard samples were prepared by direct weighing in glass-stoppered flasks. The refractometer cell was maintained at a constant temperature of 25° ± 0.05° by pumping water from a constant temperature bath through the instrument. Four or five measurements were taken on each sample and the average refractive index was taken.

PROCEDURE

The determinations were carried out in an Othmer equilibrium still (*5*) manufactured by the Emil Greiner Co. The pressure was maintained at 760 mm. of mercury by means of

Table I. Boiling Point-Composition Data for 2-Ethoxyethanol-Ethyl Acetate System at 760 Mm. of Mercury Pressure

	Composition, Mole % of 2-Ethoxyethanol	
B.P., °C.	Vapor	Liquid
77.1	0.0	0.0
80.6	3.75	18.75
82.3	5.0	26.25
84.2	6.25	33.5
87.1	8.75	42.0
90.5	13.25	54.75
95.4	18.25	65.25
97.6	21.0	68.5
106.8	34.25	80.7
113.1	47.0	86.7
119.3	59.1	91.75
125.9	74.0	95.0
128.6	80.4	96.8
130.6	83.75	98.0
135.0	100.0	100.0

Table II. Boiling Point-Composition Data for 2-Ethoxyethanol-Propyl Acetate System at 760 Mm. of Mercury Pressure

	Composition, Mole % of 2-Ethoxyethanol	
B.P., °C.	Vapor	Liquid
101.6	0.0	0.0
103.1	4.75	11.0
104.0	6.5	15.75
105.3	11.0	20.5
107.2	15.75	37.5
109.55	21.5	48.5
111.8	27.0	59.0
114.6	34.5	68.75
117.5	42.5	76.5
120.6	48.6	81.5
126.3	67.6	90.4
129.5	77.0	93.75
131.4	84.1	96.4
133.85	95.6	98.5
135.0	100.0	100.0

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