V^E = excess volume of mixing
x_2 = mole fraction of propylene oxide

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Salt Effects in Liquid-Liquid Equilibria

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The effect of magnesium chloride on the distribution of acetic acid, propionic acid, and butyric acid between benzene and water at 25° C has been studied. The Eisen-Joffe equation has been employed to relate distribution data to salt concentration. Compared with previous work, the order of decreasing salting out, on a weight basis, is

$$MgCl_2 > LiCl > NaCl > KCl$$

for all systems studied. The ternary system acetic acid–benzene–water exhibits solutropy upon the addition of magnesium chloride.

The effect of salts on the solubilities of nonelectrolytes in water has been extensively studied (*5*). Several theories have been advanced to explain this complex effect (*1, 6, 7*). However, the mathematical characterization of the salt effect has been semiquantitative at best, because of limitations of the theories or simplifying assumptions made in the derivation of the equations.

The effect of salts on the distribution of a solute between two relatively immiscible solvents has received little attention. Setschenow (*8*) correlated distribution data with the equation

$$\ln C^\circ/C = k_s X_s \qquad (1)$$

which was valid for salt concentrations up to 3*M*. For a given solvent phase solute concentration, C and C^0 are aqueous phase solute concentrations with and without salt present, respectively. This equation was used by Swabb and Mongan (*9*) to correlate the effect of sodium sulfate on the distribution of acetic acid between benzene and isopropyl ether. The Hand (*4*) Equation,

$$\log \frac{X_{CB}}{X_{BB}} = \log A_0 + B_0 \log \frac{X_{CA}}{X_{AA}} \qquad (2)$$

which gives excellent results in correlating ternary distribution data, was adapted by Eisen and Joffe (*3*) to quaternary systems containing salt. In the Eisen-Joffe Equation,

$$\log \frac{X_{CB}}{X_{BB}} = a + bX_s' + (c + dX_s) \log \frac{X_{CA}}{X_{AA}} \qquad (3)$$

a, *b*, *c*, and *d* are constants which depend on the nature of the system, the nature of the salt, and temperature, but which are independent of salt concentration. The effects of lithium chloride, sodium chloride, and potassium chloride on the distribution of acetic acid, propionic acid, and butyric acid between benzene and water at 25° C were previously correlated using the Eisen-Joffe Equation (*2*).

EXPERIMENTAL

One to 60 ml of acid, 20 ml of aqueous magnesium chloride solution, and 20 ml of benzene were added to a tared polyethylene-stoppered Erlenmeyer flask. The weights of the respective solutions were read to ±0.1 mg on a Sartorius analytical balance. The composition of this initial mixture was then calculated, the composition of the magnesium chloride solution having been previously determined. The flasks were attached to a shaker and allowed to equilibrate for 24 hr in a constant-temperature bath maintained at 25.00 ± 0.02° C.

Two-milliliter aliquots of the aqueous phase and the organic phase were transferred to separate, tared 125-ml stoppered flasks and immediately weighed. Each aliquot was titrated with standard sodium hydroxide solution to the phenolphthalein end point, using 5-ml, 10-ml, and 50-ml class A burets. The percent of acid in the aqueous and organic phases was then calculated. A second aliquot of the organic phase was weighed and titrated with standardized Karl Fischer reagent using an electrometric "dead stop" end point indicator. The salt content of the organic phase was too low to produce a visible color change using dichlorofluorescein indicator. In previous work (*2*), a quantity of standard sodium chloride solution was added to the organic phase aliquot to improve the detection of the end point. Even then, the organic phase salt concentration could be determined only to within ±10%. In the present work, several organic phase samples were analyzed for salt

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Table I. Correlation of Results

$\log A_0 = a + bXs'$

System	a	b	$s(\log A_0)$	r	p	DF
HOAc-$MgCl_2$	-1.0623	0.05124	0.08499	0.9788	<0.001	4
HOPr-$MgCl_2$	0.0634	0.13167	0.04603	0.9990	<0.001	4
HOBu-$MgCl_2$	1.5715	0.20160	0.41769	0.9675	<0.001	4

Table II. Correlation of Results

$B_0 = c\ '\ dXs'$

System	c	d	$s(B_0)$	r	p	DF
HOAc-$MgCl_2$	1.2966	0.01497	0.08284	0.8200	0.05	4
HOPr-$MgCl_2$	1.2785	0.05992	0.04574	0.9954	<0.001	4
HOBu-$MgCl_2$	1.7111	0.07103	0.27002	0.9017	0.02	4

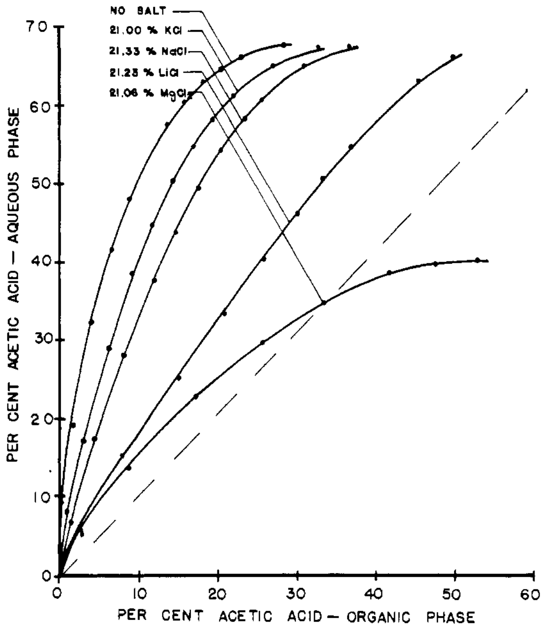

Figure 1. Effect of magnesium chloride on the distribution of acetic acid

and the results compared with those for lithium chloride. For a given acid, the organic phase salt-to-water ratio in the magnesium chloride systems was very close to that of the corresponding lithium chloride systems and was almost constant over the range of salt concentrations investigated. Salt-to-water ratios for lithium chloride solutions were used to calculate organic phase magnesium chloride concentrations based on the experimentally measured organic phase water concentration. The maximum magnesium chloride concentration was 0.09% in acetic acid systems, 0.15% in propionic acid systems, and 0.04% in butyric acid systems.

The water, salt, and acid concentrations of the organic phase having been determined, the benzene concentration was found by difference. A material balance on the acid allows calculation of the relative weights of the organic and inorganic phases. Material balances on the other components permit the complete determination of the aqueous phase composition.

The complete experimental data have been deposited with the National Auxiliary Publications Service (*11*).

RESULTS

A CDC 3300 computer was used to determine the values of the constants *a*, *b*, *c*, and *d* in Equation 3. Tables I and II also list *s* (log A_0), the standard error of estimate of log A_0; *r*, the correlation coefficient; *p*, the probability level and the degrees of freedom (DF) for the correlation. The probability level is the chance of obtaining as large a value of the correlation coefficient when no correlation exists. The correlation of the intercept, log A_0, was more reliable than that of the slope.

DISCUSSION

The three ternary systems studied, consisting of benzene, water, and one carboxylic acid, contain one pair of slightly miscible components, benzene and water. Addition of moderate amounts of magnesium chloride produces a second pair of slightly miscible components, carboxylic acid and water, in each system. Addition of magnesium chloride also decreases the acid concentration in the aqueous phase. With no salt present, an organic phase containing 10%

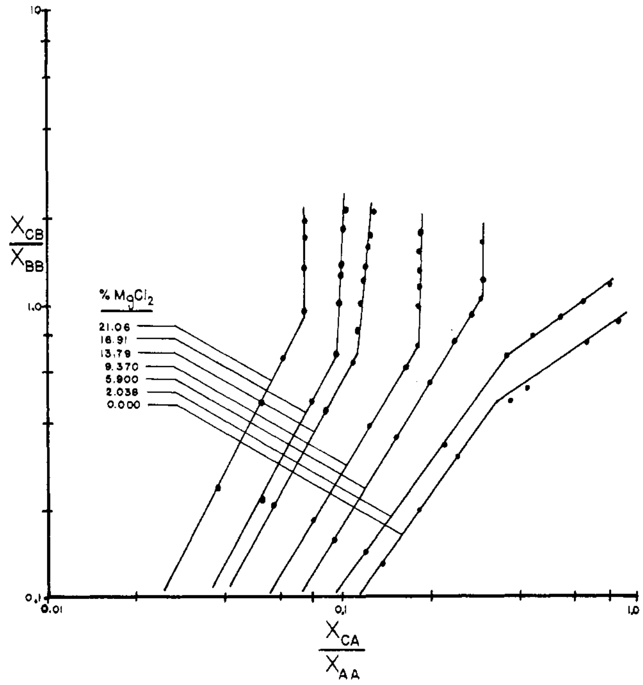

Figure 2. Hand plot, butyric acid–benzene–water–magnesium chloride

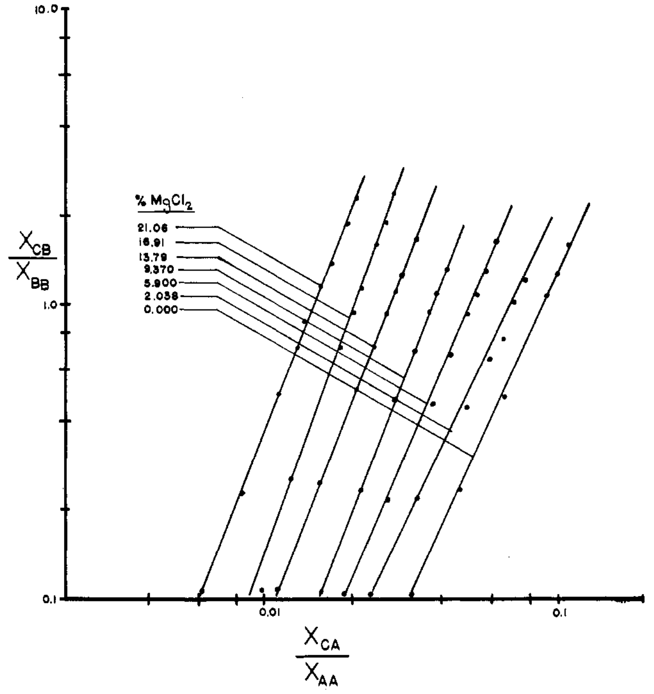

Figure 3. Hand plot, propionic acid–benzene–water–magnesium chloride

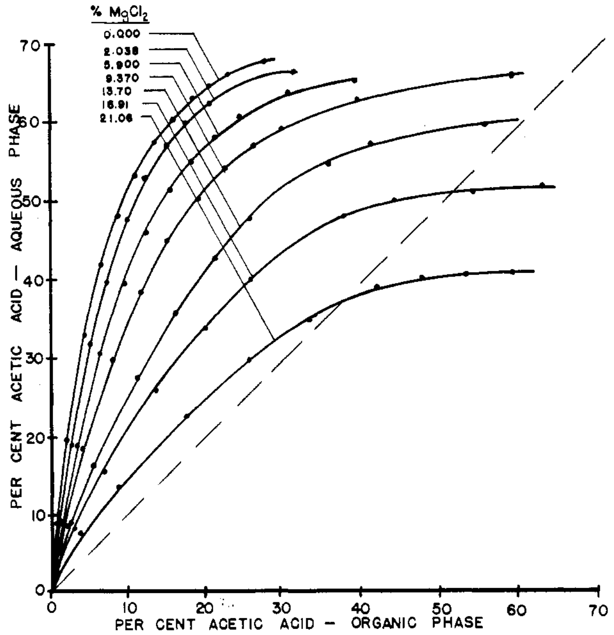

Figure 4. Effect of chlorides on the distribution of acetic acid

acetic acid is in equilibrium with an aqueous phase containing 51.7% acetic acid. Addition of 21.06% magnesium chloride reduces the equilibrium aqueous phase acid concentration to 15.8%.

Two aspects of solutropy, a phenomenon in which a solute favors one phase at low solute concentration and the other phase at high concentration, were observed. First, the addition of magnesium chloride removed both solutropes in the propionic acid–benzene–water ternary systems, an effect which has been reported (*3, 10*). Second, the addition of magnesium chloride to the acetic acid ternary system produced a solutrope at salt concentrations above 16.91% (Figure 1). The Hand plots for the acetic acid and butyric acid ternary systems consisted of a family of single straight lines differing markedly in intercept but only slightly in slope (Figure 2). The correlation for the propionic acid system (Figure 3) required two straight lines for each salt concentration. The Eisen-Joffe equation, which has been applied only to the lower line of this system, is valid for X_{CB}/X_{BB} below 0.8. The effects of 21% solutions of lithium, sodium, potassium, and magnesium chlorides, respectively, on the distribution of acetic acid between benzene and water are compared in Figure 4. When salt concentrations are expressed as moles salt/100 grams salt plus water, the order of salting out effectiveness is

$$\mathrm{MgCl_2} > \mathrm{LiCl} > \mathrm{NaCl} > \mathrm{KCl}$$

NOMENCLATURE

a, b, c, d = constants in Equation 3
$\log A_0, B_0$ = constants in Equation 2
C^0 = concentration of nonelectrolyte in water, no salt present, moles/liter
C = concentration of nonelectrolyte in water, salt present, moles/liter
k_s = salting out constant, liters/mole salt
X_s = salt concentration, moles salt/liter
X_s' = salt concentration, grams salt per 100 grams salt plus water
X_{AA} = mass fraction water in aqueous phase
X_{BB} = mass fraction solvent in organic phase
X_{CA} = mass fraction solute in aqueous phase
X_{CB} = mass fraction solute in organic phase

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