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## Salt Effects in Liquid-Liquid Equilibria

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The effect 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. has been investigated. The method of Hand, originally developed for ternary systems, was used to correlate the distribution data for quaternary systems containing salt. A regression in two variables was used to express the slope and the intercept of the Eisen-Joffe Equation as linear functions of salt concentration. The order of decreasing salting out, on a weight basis, is



for all systems studied. On a mole basis, the effect of lithium chloride diminishes with increase in the number of carbon atoms in the carboxylic acid.

INVESTIGATIONS of salt effects in liquids have dealt primarily with the solubilities of nonelectrolytes, such as benzene, in water. Excellent summaries of this work appear in the literature (9, 11, 14). The effect of salts on the distribution of a solute between two immiscible solvents, a problem having engineering applications, has received very little attention.

There is general agreement on the physical phenomena responsible for the salt effects (1). The mathematical interpretation of these phenomena has resulted in several relationships which are, at best, semiquantitative. The limited applicability of these expressions emphasizes the complexity of the salt effects.

### THEORIES OF THE SALT EFFECT

Three principal theories have been advanced to explain the salt effect. The hydration theory assumes that each salt ion binds a constant number of water molecules as a shell of oriented water dipoles surrounding the ion. This "bound" water is then unavailable as solvent for the nonelectrolyte. Considering the wide variation in hydration numbers reported in the literature, it appears that this concept permits only a qualitative estimate of the magnitude of the salt effect.

The electrostatic theory, which considers only the action of coulombic forces and omits other factors, was used by

Debye and McAulay (7) to compute the partial free energy of a molecule relative to the pure solvent from the reversible electrical work. Because of simplifications and approximations made in its derivation, the Debye-McAulay equation is a limiting equation and can be regarded as a first approximation only. Butler (4), using a similarly simplified model, obtained an equation virtually identical with that of Debye and McAulay. Later Debye (6), taking into account the heterogeneity of the mixture of water and neutral solute, expressed the total free energy of the system, including the contribution due to the field of the ion, as a function of distance from the ion.

Since the electrostatic interaction between an ion and a neutral molecule is short range in nature, additional interaction terms of the London or van der Waals type must be considered more fully. These terms involve the polarizability of salt ions, solvent molecules, and nonelectrolyte solute molecules, as well as the special force fields originating from any component dipoles that may be present.

McDevit and Long (12), applying the "internal pressure" concept of Tammann (17) to nonpolar nonelectrolytes, calculated the free energy of transfer of the latter from pure water to the salt solution.

### PREVIOUS WORK

The Setschenow equation (15)

$$\ln \frac{C^0}{C} = k_s X, \quad (1)$$

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is generally valid for salt concentrations as high as 2 or 3 molar, although, under certain conditions, it fails in dilute solutions. In applying this equation to distribution data,  $C^o$  and  $C$  must be aqueous phase solute concentrations in equilibrium with the same solvent phase solute concentration. It is assumed that neither salt nor water enter the solvent phase, a condition which would change the activity of the solute in the solvent phase. Swabb and Mongan (16), studying the effect of sodium sulfate on the distribution of acetic acid between benzene and isopropyl ether, were able to correlate their results using the Setschenow Equation.

#### CORRELATION OF RESULTS

Tie line correlations for ternary systems fall into two general categories—graphical and mathematical. The graphical methods, summarized by Treybal (18), require much data for their successful application. Mathematical correlations (2, 3, 5, 10, 13) permit tie-line data to be expressed as a linear function of two concentration variables. However, only in the Hand correlation

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

does the distributed solute  $C$  appear as a variable. By expressing the constants  $\log A_0$  and  $B_0$  as linear functions of the salt concentration, the Eisen-Joffe equation, applicable to quaternary systems containing salt, is obtained. In this equation

$$\log \frac{X_{CB}}{X_{BB}} = a + b X'_i + (c + d X'_i) \log \frac{X_{CA}}{X_{AA}} \quad (3)$$

$a$ ,  $b$ ,  $c$ , and  $d$  are constants which depend on the nature of the acid, the nature of the salt, and temperature, but which are independent of salt concentration.

#### EXPERIMENTAL PROCEDURE

To a tared, polyethylene-stoppered Erlenmeyer flask were added 20 ml. of salt solution, 20 ml. of benzene, and 1 to 60 ml. of acid. The weight of each component was read to  $\pm 0.1$  mg. using a Sartorius analytical balance. The composition of this initial mixture then was calculated, the salt solution composition having been determined previously. Constant temperature baths consisted of 10-gallon aquaria insulated on all six sides with 2-inch sheets of styro-foam. By using glass cooling coils immersed in the bath and a Bronwill constant temperature circulating system, a temperature of  $25.00 \pm 0.02^\circ \text{C}$ . was maintained. The flasks were attached to a Burrell Shaker fitted with shaker arms designed by the author and allowed to equilibrate for at least 24 hours.

Two-milliliter aliquots of the acid phase and the organic phase were transferred to separate, tared, 300-ml. polyethylene-stoppered flasks containing 15 ml. of distilled water. The flask and contents were weighed immediately and the weight of the aliquot was calculated. Each aliquot was titrated with standard sodium hydroxide solution to the phenolphthalein end point, using class A burets of 5 ml., 10 ml., and 50 ml. capacity. The pH of this organic phase aliquot then was adjusted to 4.5 with 3% nitric acid, and a weighed quantity of standard sodium chloride solution was added. To prevent coagulation of the precipitate particles, 0.1 gram of dextrin was added. The mixture was titrated

Table I. Correlation of Results

System	$\log A_0 = a + b X'_i$			$r$	$p$	D.F.
	$a$	$b$	$s(\log A_0)$			
HOAc-LiCl	-0.9949	0.02877	0.00668	0.9997	<0.001	5
HOAc-NaCl	-0.9947	0.01403	0.00545	0.9987	<0.001	4
HOAc-KCl	-0.9929	0.00492	0.00750	0.9798	<0.001	4
HOPr-LiCl	0.3694	0.11093	0.09167	0.9956	<0.001	4
HOPr-NaCl	0.2672	0.07756	0.15081	0.9760	<0.001	4
LOWER LINE						
HOBu-LiCl	2.3690	0.08969	0.11670	0.9891	<0.001	5
HOBu-NaCl	2.3149	0.07707	0.03986	0.9982	<0.001	5
HOBu-KCl	2.2879	0.03687	0.05709	0.9841	<0.001	5
UPPER LINE						
HOBu-LiCl	4.8518	0.14911	1.56723	0.6389	0.15	5
HOBu-NaCl	4.2232	0.21392	1.89591	0.8956	0.01	5
HOBu-KCl	3.9827	0.10799	0.88568	0.7231	0.10	5

Table II. Correlation of Results

System	$B_0 = c + d X'_i$			$r$	$p$	D.F.
	$c$	$d$	$s(B_0)$			
HOAc-LiCl	1.2291	-0.01149	0.03769	0.9361	0.01	5
HOAc-NaCl	1.2329	-0.01223	0.01973	0.9778	<0.001	4
HOAc-KCl	1.2046	-0.00314	0.01559	0.8364	0.05	4
HOPr-LiCl	1.5301	0.04352	0.06003	0.9878	<0.001	4
HOPr-NaCl	1.4199	0.02866	0.12996	0.8872	0.01	4
LOWER LINE						
HOBu-LiCl	2.1706	+0.006320	0.05501	0.7081	0.10	5
HOBu-NaCl	2.1546	+0.006525	0.03074	0.8793	0.01	5
HOBu-KCl	2.1421	-0.001672	0.03973	0.3398	0.50	5
UPPER LINE						
HOBu-LiCl	4.4262	-0.001511	1.06497	0.0124	...	5
HOBu-NaCl	3.9625	+0.05984	0.68755	0.6034	0.20	5
HOBu-KCl	3.7466	+0.29825	0.78486	0.3102	0.50	5

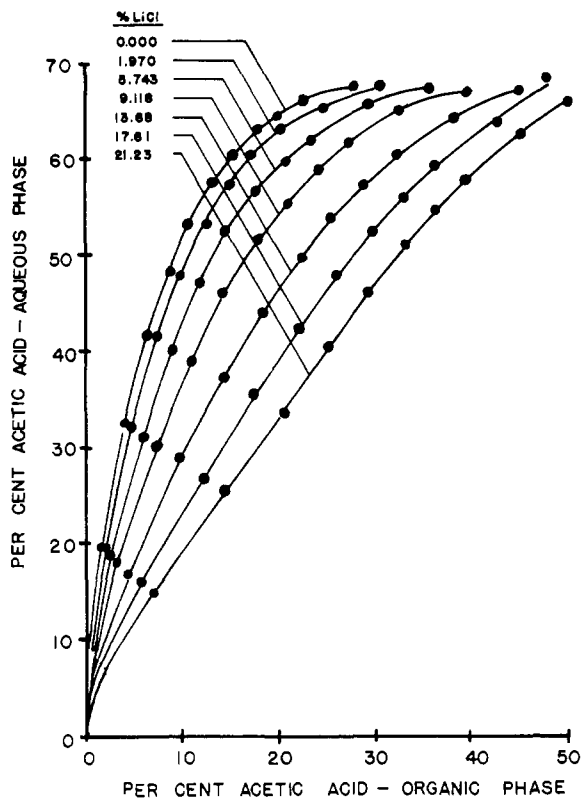


Figure 1. Effect of lithium chloride on the distribution of acetic acid

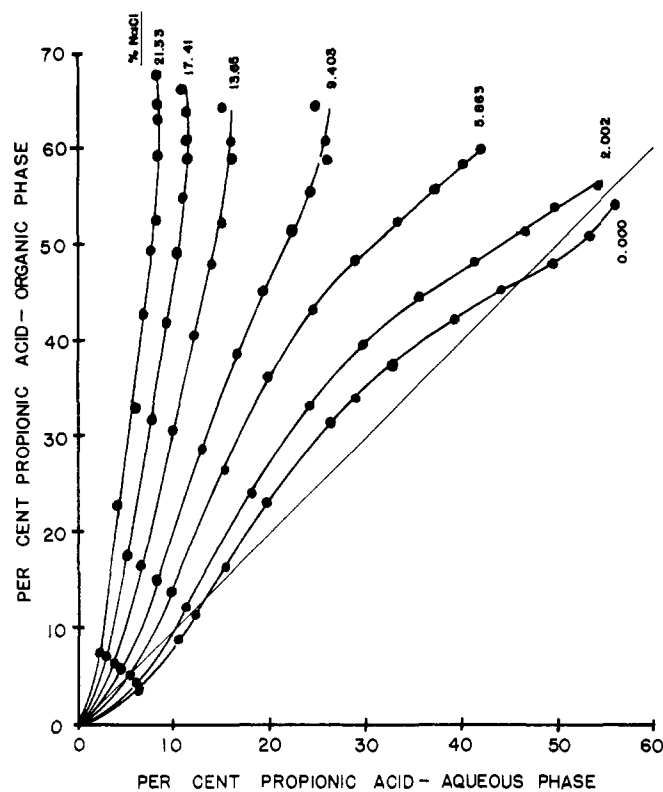


Figure 2. Effect of sodium chloride on the distribution of propionic acid

with standard silver nitrate solution from a 5-ml. class A microburet to the dichlorofluorescein end point. (The salt content of the organic phase was too low to produce a visible color change in the dichlorofluorescein indicator. This change occurs at the surface of the colloidal precipitated particles, and the color intensity depends on the number of particles present. A quantity of standard sodium chloride added to the organic phase aliquot prior to titration yielded a satisfactory end point. A study of the effect of pH on the end point showed that the sharpest color change occurred at a pH of approximately 4.5. The presence of phenolphthalein indicator did not interfere with the end point.) A 5-ml. hypodermic syringe with stainless steel needle was used to extract a second aliquot of the organic phase. After being weighed, the sample was titrated with standardized Karl Fischer reagent, using an electrometric "dead stop" end point detector.

As the acid, water, and salt content of the organic phase had been analytically determined, the benzene content was found by difference. A material balance on the acid gives the weights of the aqueous and organic phases. By material balances on the other components, the composition of the aqueous phase was calculated.

## RESULTS

A digital computer was used to determine the values of the constants  $a$ ,  $b$ ,  $c$ , and  $d$  in Equation 3. Values of the correlation coefficient  $r$ , the probability level  $p$ , the degrees of freedom D.F., and the standard error of estimate of  $\log A_0$  and  $B_0$  also are given in Tables I and II. Complete data for each quaternary system at six salt concentrations have been tabulated (8). The correlation of intercept,  $\log A_0$ , was more reliable than that for the slope  $B_0$ . The slope for the upper line of the butyric acid-lithium chloride quaternary system showed no correlation.

## DISCUSSION

The ternary systems studied—carboxylic acid-benzene-water—are each type 1, containing one pair of slightly miscible components, benzene and water. Butyric acid favors the organic phase at all concentrations, while acetic acid favors the aqueous phase (Figure 1). The propionic acid ternary system exhibits double solutropy (Figure 2).

Salt affects the mutual solubility of the carboxylic acid and water and the distribution of the carboxylic acid. Addition of sufficient quantities of each of the three salts to the butyric acid ternary results in a type 2 system containing the additional slightly miscible pair butyric acid and water. Lithium chloride and potassium chloride similarly affect the propionic acid ternary. Type 2 systems are not produced in the acetic acid ternary nor by potassium chloride in the propionic acid ternary. Addition of salt removes the solutropes in the propionic acid ternary, a phenomenon observed with other solutropes (19).

Salts alter the distribution by decreasing the carboxylic acid concentration in the aqueous phase. With no salt present, an organic phase containing 10.0% acetic acid is in equilibrium with an aqueous phase containing 51.7% acetic acid. Addition of 21.23% lithium chloride reduces the equilibrium aqueous phase acetic acid concentration to 18.6%. When salt concentrations are expressed as grams of salt per 100 grams salt plus water, the order of effectiveness in salting the carboxylic acid out of the aqueous phase is



On a corresponding mole basis, lithium chloride is more effective than sodium chloride for acetic acid, as effective for propionic acid, and less effective for butyric acid.

Correlation of distribution data using the Eisen-Joffe equation produces two types of Hand plots. Addition of salt to the acetic acid ternary results in a family of single straight lines differing markedly in intercept but only

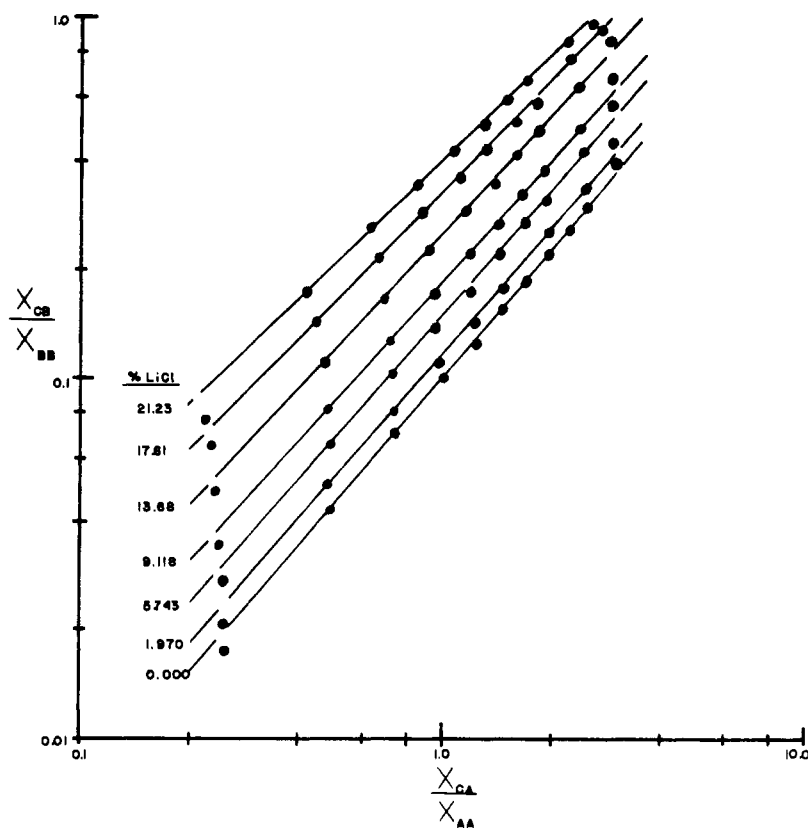


Figure 3. Hand plot. Acetic acid-benzene-water-lithium chloride

slightly in slope. In contrast, the correlation for the butyric acid ternary requires two straight lines. The Eisen-Joffe equation for the lower line is valid for  $X_{CB}/X_{BB}$  below 1.35 with lithium chloride, 1.15 with sodium chloride, and 1.00 with potassium chloride. For the propionic acid ternary, two straight lines occur when a type 1 system prevails, while a single line correlates the type 2 system.

#### COMPARISON OF EISEN-JOFFE CORRELATION AND SETSCHENOW EQUATION

The equation of Setschenow, as employed by Swabb and Mongan, may be written

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} = k_w \left[ \frac{X_{DA}}{X_{AA}} \right] \quad (4)$$

where the salt concentration was expressed as grams of salt per gram of water in the aqueous phase.

The Eisen-Joffe equation is written for the salt-free system (Equation 5) and for the system containing salt (Equation 6).

$$\log \left[ \frac{X_{CB}}{X_{BB}} \right]_{sf} = \log A_{osf} + B_{osf} \log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} \quad (5)$$

$$\log \left[ \frac{X_{CB}}{X_{BB}} \right]_s = \log A_{os} + B_{os} \log \left[ \frac{X_{CA}}{X_{AA}} \right]_s \quad (6)$$

Equations 5 and 6 are solved in terms of  $X_{CA}/X_{AA}$ .

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} = -\frac{1}{B_{osf}} \log A_{osf} + \frac{1}{B_{osf}} \log \left[ \frac{X_{CB}}{X_{BB}} \right]_{sf} \quad (7)$$

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_s = -\frac{1}{B_{os}} \log A_{os} + \frac{1}{B_{os}} \log \left[ \frac{X_{CB}}{X_{BB}} \right]_s \quad (8)$$

Equation 8 is subtracted from Equation 7 and rearranged.

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} = \frac{1}{B_{osf}B_{os}} \left\{ B_{osf} \log A_{os} - B_{os} \log A_{osf} + B_{os} \log \left[ \frac{X_{CB}}{X_{BB}} \right]_s - B_{osf} \log \left[ \frac{X_{CB}}{X_{BB}} \right]_s \right\} \quad (9)$$

But

$$\left[ \frac{X_{CB}}{X_{BB}} \right]_{sf} = \left[ \frac{X_{CB}}{X_{BB}} \right]_s \quad (10)$$

For the salt-free systems,  $X'_s = 0$ .

$$B_{osf} = (c + dX'_s)_{sf} = c \quad (11)$$

$$B_{os} = (c + dX'_s)_s \quad (12)$$

$$\log A_{osf} = (a + bX'_s)_{sf} = a \quad (13)$$

$$\log A_{os} = (a + bX'_s)_s \quad (14)$$

The final equation is

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} = \frac{X'_s}{c(c + dX'_s)} \left\{ cb - ad + d \log \left[ \frac{X_{CB}}{X_{BB}} \right]_s \right\} \quad (15)$$

Since  $X'_s = \frac{X_{DA}}{X_{AA} + X_{DA}} \times 100$ , multiplication of Equation 4 by

$\frac{X_{AA}}{X_{AA} + X_{DA}}$  and introduction of a new constant  $k'_s$  gives

$$\log \left[ \frac{X_{CA}}{X_{AA}} \right]_{sf} = k'_s X'_s \left[ \frac{X_{CA}}{X_{AA}} \right]_s \quad (16)$$

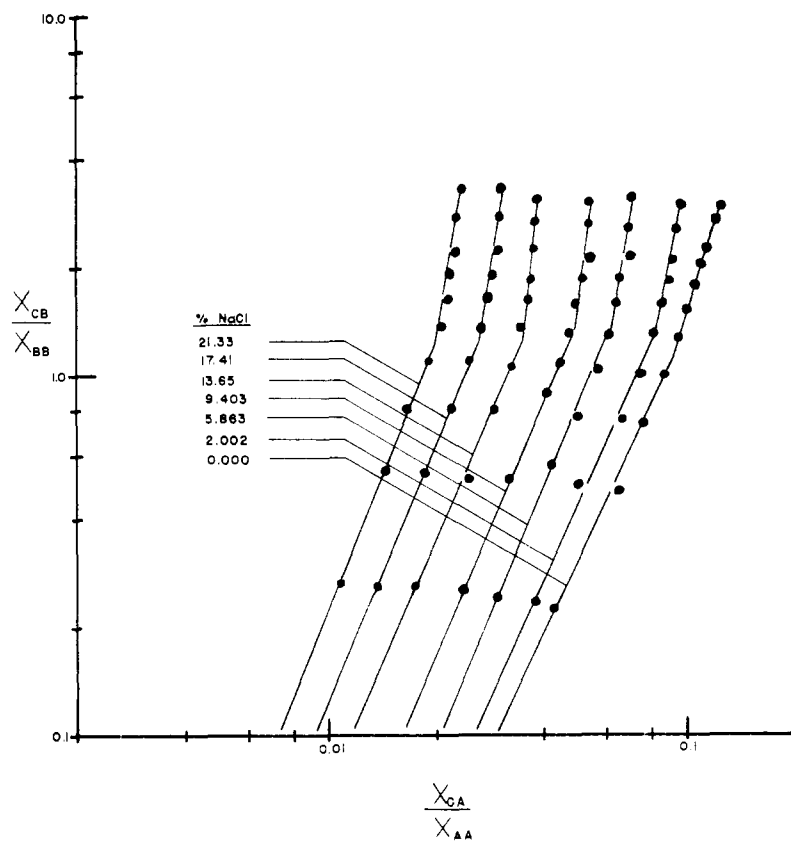


Figure 4. Hand plot. Butyric acid-benzene-water-sodium chloride

Combining Equations 15 and 16 shows that

$$k'_s = \frac{1}{c(c + dX')} \left\{ cb - ad + d \log \left[ \frac{X_{CB}}{X_{BB}} \right] \right\} \quad (17)$$

An attempt was made to correlate the data of this work using the method of Swabb and Mongan. The terms  $C^o$  and  $C$  in Equation 1 were defined by these investigators as grams of acid per gram of water in the aqueous phase, or  $X_{CA}/X_{AA}$ . This suggests that the salting-out constant can be expressed in terms of the empirical constants of the Eisen-Joffe Equation. This comparison, expressed by Equation 17, predicts that  $k_s$  is a function of salt concentration and of the ratio  $X_{CB}/X_{BB}$ . In short, it predicts that  $k_s$  is not a constant. The present data did not obey Equation 4. A quaternary system containing salt which obeys the Eisen-Joffe Equation will not obey the Setschenow Equation.

#### NOMENCLATURE

- $a, b, c, d$  = constants in Equation 3  
 $\log A, B$  = constants in Equation 2  
 $C^o$  = concentration of nonelectrolyte in water, no salt present, moles per liter  
 $C$  = concentration of nonelectrolyte in water, salt present, moles per liter  
 $k_s$  = salting out constant, liters per mole of salt  
 $k_{se}$  = salting out constant, mass fraction of water per mass fraction of salt  
 $k'_s$  = salting out constant, 100 grams of salt plus water per grams of salt  
 $X$  = salt concentration, moles of salt per liter  
 $X'$  = salt concentration, grams of salt per 100 grams of salt plus water  
 $X_{AA}$  = mass fraction of water in aqueous phase  
 $X_{BB}$  = mass fraction of solvent in organic phase  
 $X_{CA}$  = mass fraction of solute in aqueous phase

- $X_{CB}$  = mass fraction of solute in organic phase  
 $X_{DA}$  = mass fraction of salt in aqueous phase

#### Subscripts

- $sf$  = salt-free system  
 $s$  = salt-containing system

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