ganic acids by washing with dilute aqueous sodium carbonate and then with water, the benzene solution was allowed to evaporate at room temperature. The 0.160 g. (69%) of oxide, m.p. 66–67°, which remained was crystallized at 0° from 40–60° petroleum ether, yielding analytically pure material, m.p. 67.5–68.0°.

Anal. Calcd. for $C_6H_8Br_2O$: C, 28.14; H, 3.13. Found: C, 28.56; H, 3.28.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

COMMUNICATIONS TO THE EDITOR

SALT EFFECTS ON NON-ELECTROLYTES IN PARTIALLY AQUEOUS MIXED SOLVENTS[1]

Sir:

Previous work on kinetic salt effects[2,3] had led us to the belief that salt effects on non-electrolytes in mixed, partly aqueous solvents might be quite different from corresponding effects observed in water.

This belief has been borne out by some data recently obtained from solubility measurements in 50% dioxane at 25°, as tabulated in Table I.

TABLE I

Non-electrolyte	Solvent	Salt	*k*
Benzoic Acid	Water[4]	NaCl	0.182
		HCl	.121
		KCl	.093
		KI	.041
α-Naphthoic Acid	50% Dioxane	HCl	.011
		KI	.017
		NaCl	− .12
		KCl	− .15
Naphthalene	Water[5]	NaCl	.260
		KCl	.204
	50% Dioxane	NaCl	− .09
		KCl	− .08

The data show that the salting order of various electrolytes in 50% dioxane is quite different from that generally observed in water.[3] This can be seen by comparing the values of *k* in Table I, which were obtained by plotting log $\frac{S^\circ}{S}$ versus C_S and measuring the slope. A positive *k* is associated with salting-out while a negative *k* results from salting-in of the non-electrolyte by the salts present. For example, NaCl and KCl, which in water are usually better salting-out agents than HCl and KI, in 50% dioxane actually cause salting-in.

A qualitative understanding of the effect of the mixed solvent on the salting order of electrolytes may be reached on the basis of the preferential hydration of the electrolytes. Consider, for example, the effects due to KCl. In water, hydration of KCl leaves less solvent for the non-electrolyte to dissolve in; hence, salting-out. In 50% dioxane, preferential solvation by water leaves an effective solvent richer in dioxane. When the non-electrolyte solubility increases with dioxane content, the net effect may be salting-in. The solubility data for naphthalene and α- naphthoic acid in Table II suggest this as a partial explanation.

TABLE II

Nonelectrolyte	Dioxane, %	Solubility (g./100 ml.)
α-Naphthoic Acid	40	0.89
	50	2.91
	60	7.57
Naphthalene	40	0.44
	50	0.79

The present data suggest that previous treatments of kinetic salt effects as colligative functions of ionic strength, or even on the basis of the Setschenow equation, may be oversimplified in partly aqueous solvents.

CHEMISTRY DEPT.
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA

ARTHUR F. BUTLER
ERNEST GRUNWALD

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AN INVESTIGATION OF THE HYPOTHETICAL ION PAIR INTERMEDIATE IN THE REARRANGEMENT OF 9-DECALYL HYDROPEROXIDE BENZOATE USING OXYGEN-18

Sir:

Recently, ion pairs have been considered as intermediates in a variety of organic reactions.[1,2,3] The degree of separation of the ions in many of these reactions, particularly those ion pairs which have been dubbed "intimate" or "internal," has remained obscure. We wish to report the results of an oxygen-18 tracer study of the rearrangement of the benzoate of 9-decalyl hydroperoxide (I), a reaction which has the properties of an intimate ion pair reaction.[4,5]

Benzoyl chloride-O^{18}, prepared from benzoic acid-O^{18}, was allowed to react with 9-decalyl hydroperoxide to form I. I was rearranged in both methanol and acetic acid to give 1-benzoyl-1,6-epoxycyclodecane (III) which was reduced with lithium aluminum hydride to benzyl alcohol

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