

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

Salt-induced Medium Effects. I. Salt Effects on the Activity Coefficients of Naphthalene and 1-Naphthoic Acid in 50 Wt. % Dioxane-Water<sup>1a,b</sup>BY ERNEST GRUNWALD<sup>1c</sup> AND ARTHUR F. BUTLER

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From solubility measurements in 50 wt. % dioxane-water at 25°, salt-non-electrolyte interaction coefficients,  $k_{24}$ , have been evaluated, using naphthalene and 1-naphthoic acid as sample non-electrolytes (component 3) and NaCl, KCl, KBr, KI, HCl, NaClO<sub>4</sub>, KClO<sub>4</sub>, (CH<sub>3</sub>)<sub>4</sub>NCl and 2-C<sub>10</sub>H<sub>7</sub>SO<sub>3</sub>Na as salts (component 4);  $k_{24} = (\partial \log \gamma_3 / \partial c_4)_{c_3}$  in dilute solution, where  $\gamma$  is the molar activity coefficient and  $c$  the concentration. The following empirical facts emerge concerning  $k_{24}$ : (i) Values of  $k_{24}$  are highly specific ranging from positive values for NaClO<sub>4</sub> and KClO<sub>4</sub> to negative values for NaCl and (CH<sub>3</sub>)<sub>4</sub>NCl. (ii) There seems to be a well-defined "salting-order." Values of  $k_{24}$  for C<sub>10</sub>H<sub>8</sub> vary linearly with corresponding values for C<sub>10</sub>H<sub>7</sub>COOH as the salt is varied. (iii) The salting-order for the simple inorganic salts in 50% dioxane-water is almost exactly the reverse of the order in water. (iv) Values of  $k_{24}$  for simple inorganic salts vary in a roughly linear manner with  $dF_{4m}^0/dZ_1$ , where  $F_{4m}^0$  is the standard partial molal free energy of the salt and  $Z_1$  the mole fraction of water in the solvent. (v) Values of  $k_{24}$  for the salts with large organic ions are of the same order of magnitude in 50% dioxane-water as in water. Observations iii and iv are interpreted on the basis of a theory of salt-induced medium effects in which the salt and the non-electrolyte interact indirectly through their effects on the internal pressure and on the water/dioxane activity ratio of the solution. A simple approximate equation for this effect is tested, and a more rigorous thermodynamic approach is described. In this connection, partial molal volumes have been measured in 50 wt. % dioxane-water at 25° for 1-naphthoic acid, NaClO<sub>4</sub>, HClO<sub>4</sub>, KI, NaCl, NaOH and (CH<sub>3</sub>)<sub>4</sub>NCl.

In this paper we are reporting salt effects on the activity coefficients of naphthalene and 1-naphthoic acid in 50 wt. % dioxane-water. This study was undertaken because information concerning the activity coefficients of non-electrolytes in the presence of salts is surprisingly incomplete for water-organic solvent mixtures, and because any information gained might find immediate application in chemical kinetics and in the elucidation of reaction mechanism.

The most relevant previous studies of salt effects on non-electrolytes are those of Bockris and Egan.<sup>2</sup> These authors measured the solubility of benzoic acid in various water-organic solvent mixtures, both with and without added 1 M NaCl. While benzoic acid is salted out by NaCl in pure water, the salting-out gradually changes toward salting-in as an organic solvent component, such as ethanol or dioxane, is added, even though the dielectric constant of the medium is decreasing. Having convinced themselves that, for one-component solvents, a decrease in the dielectric constant would normally result in increased salting-out as required by simple electrostatic theory,<sup>2,3</sup> Bockris and Egan then explained the "anomalous" results for the mixed solvents on the assumption that the ions of NaCl are solvated preferentially by water molecules. This would have the effect of increasing the average concentration of ethanol or dioxane in the remainder of the solvent and could result in a net observation of salting-in, since in the absence of salt the solubility of benzoic acid increases rapidly with increasing concentration of ethanol or dioxane.

We now supplement these observations by studying the salt-non-electrolyte interaction in detail in a single two-component solvent. The salts range from simple inorganic ones to salts with large organic ions; the analytical form of the relationship between solubility and salt concentration is examined; and "salting constants" for the salt-non-electrolyte interaction are discussed from the point of view of salt-induced medium effects.

## Results

**Relationship between Solubility and Concentration.**—We shall use the subscripts noted to denote the components of our system: 1, water; 2, dioxane; 3, non-electrolyte; 4, electrolyte. In water, salt effects on the solubility,  $S_3$ , of a slightly soluble non-electrolyte are described as a function of salt concentration,  $c_4$ , by the Setschenow equation, 1

$$\log (S_3^0/S_3) = k_s c_4 \quad (1)$$

where  $S_3^0$  is the solubility in the absence of salt. The "salting constant,"  $k_s$ , is a specific parameter for each salt and non-electrolyte. Equation 1 represents the data well up to salt concentrations of the order of 1 M and fits surprisingly well even at several molar.<sup>4,5</sup>

By comparison, the solubility data in 50 wt. % dioxane-water fall into the following pattern. For the majority of salts, eq. 1 fits the data within the experimental error up to concentrations of the order of 0.5 M. However, in several cases there is slight but significant curvature, and the data are described by eq. 2.

$$\log (S_3^0/S_3) = k_s c_4 + l_s c_4^2 \quad (2)$$

Examples of linear and curved relationships are shown in Fig. 1. Values of the parameters,  $k_s$  and  $l_s$ , were computed by the method of least squares and are listed in Table I. It is seen that

(4) For a recent review, see F. A. Long and W. F. McDevitt, *Chem. Revs.*, **81**, 119 (1962).

(5) M. A. Paul, *THIS JOURNAL*, **75**, 2513 (1953).

(1) (a) A preliminary communication was published in *THIS JOURNAL*, **77**, 1706, 6727 (1955). (b) Work supported by Office of Naval Research; reproduction in whole or in part is permitted for any purpose of the United States government. (c) Alfred P. Sloan fellow, 1959.

(2) J. O'M. Bockris and H. Egan, *Trans. Faraday Soc.*, **44**, 151 (1948); *Experientia*, **2**, 453 (1947).

(3) (a) P. Debye and J. McAulay, *Physik. Z.*, **26**, 22 (1925); (b) J. A. V. Butler, *J. Phys. Chem.*, **33**, 1015 (1929); (c) see, however: E. G. Thoria, *Z. physik. Chem.*, **89**, 689 (1915); R. W. Wright, L. S. Stuber and P. S. Albrecht, *THIS JOURNAL*, **61**, 238 (1939).

TABLE I  
SALTING CONSTANTS FOR NAPHTHALENE AND 1-NAPHTHOIC ACID IN 50.00 WT. % DIOXANE-WATER, 25.00°

Electrolyte	Range of $c_4$	$k_s$	$l_s$	$\bar{k}_s^a$	$k_{34}$	$k_{34m}$
Naphthalene						
NaClO <sub>4</sub>	0-0.71	0.190	0.000	0.190	0.167	0.175
KClO <sub>4</sub>	0- .06	.166	.000	.166	.146	.126
KI	0- .38	.072	.060	.087	.076	.059
HCl	0- .74	.053	.000	.053	.047	.041
KBr	0- .37	.011	.000	.011	.010	-.003
KCl	0- .26	-.051	-.174	-.083	-.073	-.086
NaCl	0- .25	-.062	-.125	-.085	-.075	-.084
(CH <sub>3</sub> ) <sub>4</sub> NCl	0- .23	-.086	-.208	-.124	-.109	-.157
1-Naphthoic acid						
NaClO <sub>4</sub>	0-0.70	0.320	0.000	0.320	0.299	0.311
KClO <sub>4</sub>	0- .06	.270	.000	.270	.252	.236
KI	0- .45	.158	.000	.158	.148	.133
HCl	0-1.15	.139	-.009	.136	.127	.124
KBr	0-0.36	-.003	.000	-.003	-.003	-.017
NaCl	0- .50	-.048	-.145	-.096	-.090	-.099
KCl	0- .43	-.142	.000	-.142	-.133	-.148
(CH <sub>3</sub> ) <sub>4</sub> NCl	0- .47	-.119	-.096	-.149	-.139	-.188
$\beta$ -Naph-SO <sub>2</sub> Na	0- .22	-.199	.000	-.199	-.186	-.253

<sup>a</sup>  $\Sigma \log (S_3^0/S_3)/\Sigma c_4$ .

$l_s$  is different from zero often enough so that eq. 1 may be assumed to be generally valid only if  $c_4$  is less than 0.1 M.

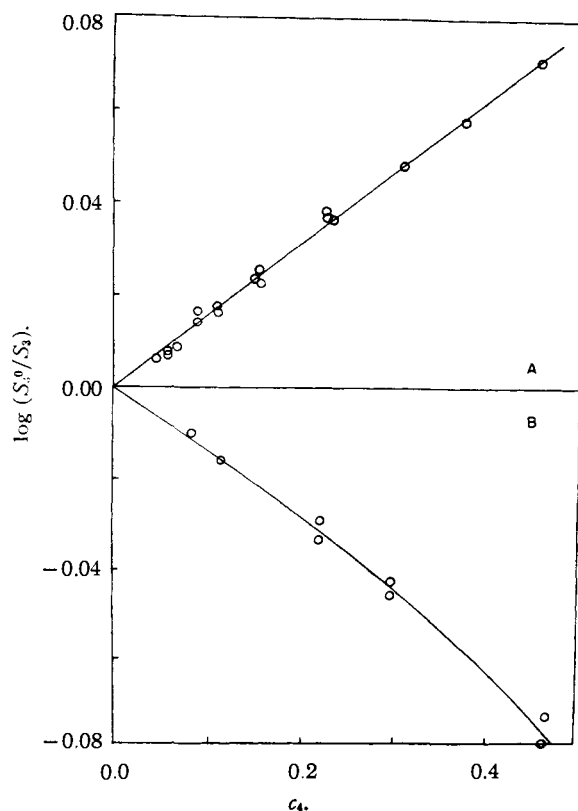


Fig. 1.—Typical plots of  $\log (S_3^0/S_3)$  vs.  $c_4$  in 50 wt. % dioxane-water at 25°: A,  $\alpha$ -naphthoic acid and potassium iodide; B,  $\alpha$ -naphthoic acid and tetramethylammonium chloride.

In the subsequent discussion we shall be interested in the theoretical interpretation of  $k_s$ . When the plot of  $\log (S_3^0/S_3)$  vs.  $c_4$  is straight, this

parameter is evaluated with good accuracy. However, when a two-parameter fit is required (eq. 2), the accuracy of  $k_s$  is rather poor. We have tried, therefore, to get a better estimate by computing the quantity

$$\bar{k}_s = \Sigma \log (S_3^0/S_3)/\Sigma c_4 \quad (3)$$

This calculation involves only a single parameter, and the data for the lowest salt concentrations are overweighted slightly. Values of  $\bar{k}_s$  are included in Table I.

**Salt-Non-electrolyte Interaction Coefficients.**—Some relevant thermodynamic data for solvent, salts and non-electrolytes are collected in Tables II, III and IV. At moderate concentrations, the molar activity coefficient,  $\gamma_3$ , is given by eq. 4<sup>4</sup>

$$\log \gamma_3 = k_{33}c_3 + k_{34}c_4 \quad (4)$$

where  $k_{33}$  is the self-interaction coefficient of the non-electrolyte, and  $k_{34}$  is the salt-non-electrolyte interaction coefficient. It can then be shown that, when  $(S_3^0 - S_3)/S_3^0$  is small, eq. 5 expresses the relationship between  $k_s$  and interaction coefficients in good approximation.

$$k_{34} = k_s(1 + 2.303 k_{33}S_3^0) \quad (5)$$

Using the values of  $k_{33}$  listed in Table IV, values of  $k_{34}$  have been computed from  $\bar{k}_s$  and are given in Table I.

For the purpose of correlation with other thermodynamic properties, it is more convenient to employ molal rather than the more conventional molar concentration units. Equation 6 is the analog of eq. 4, with  $\gamma_3$  being the molal activity coefficient.

$$\log \gamma_3 = k_{33m}m_3 + k_{34m}m_4 \quad (6)$$

The thermodynamic relationships between the two kinds of interaction coefficients are given in eq. 7, the unknown symbols being defined below. Values of  $k_{34m}$  for our systems, based on the data in Tables I-III, are listed in Table I.

$$k_{33m} = \left( k_{33} - \frac{V_3}{2303} \right) d_0; k_{34m} = \left( k_{34} - \frac{V_4}{2303} \right) d_0 \quad (7)$$

**Additional Thermodynamic Data.**—Thermodynamic data to be used in the subsequent discussion of interaction coefficients are summarized in Tables II–IV. In addition to standard symbols and symbols already defined, we use this notation

$a_1, a_2$	thermodynamic activity of solvent components
$d_0$	density of solvent
$F_{3m}^0, F_{4m}^0$	standard partial molal free energy, on the $m$ -scale—a function of $Z_1$ [ $F_{im}^0 = \lim_{m_i \rightarrow 0} (\bar{F}_i - RT \nu_i \ln m_i)$ ] $_{Z_1}$
$g_3, g_4$	constants in eq. 23
$M$	molecular weight
$M_{12}$	$Z_1 M_1 + Z_2 M_2$
$n_i$	mole number of $i$ -th component
$P$	applied pressure
$P_i, P_{i,0}$	internal pressure of solution, solvent
$P'$	"effective" pressure [= $P + P_i - P_{i,0}$ ]
$V_i$	partial molal volume of $i$ -th component at infinite dilution
$V_{12}$	$Z_1 V_1 + Z_2 V_2$
$\phi V_i$	apparent molal volume of solute
$W$	$n_1 M_1 + n_2 M_2$
$x$	$a_1/a_2$
$Z_1(Z_2)$	mole fraction water (dioxane) in the solution, not counting the solute <sup>8</sup> [ $Z_1 = n_1/(n_1 + n_2)$ ]
$\beta_0$	coefficient of isothermal compressibility of the solvent
$\epsilon$	dielectric constant

TABLE II

THEMODYNAMIC DATA FOR 50.00 WT. % DIOXANE-WATER AT 25.00°

$Z_1$	0.8302
$d_0$	1.03324 <sup>a</sup>
$V_1$	17.8 ml. <sup>7</sup>
$V_2$	83.6 ml. <sup>7</sup>
$d \ln a_1/d Z_1$	0.624 <sup>8</sup>
$d \ln a_2/d Z_1$	-3.054 <sup>8</sup>
$M_{12}$	29.92
$\beta_0^b$	$45.8 \times 10^{-6}$ atm. <sup>-1</sup>

<sup>a</sup> Measured by William B. Brogden, Jr. <sup>b</sup> Calculated from  $\beta_0 = 1/d_0 V^2 + T(d\beta_0/dT)^2/d_0^3 C_p$ , where  $V$  is the sound velocity in the medium; numerical data from ref. 9 and 12.

Of the new data reported in Tables II–IV, only the partial molal volumes  $V_4$  require comment. Solvent and solution densities were measured with an accuracy of 0.003% by William B. Brogden, Jr., of this Laboratory. The measurements were most extensive for NaOH, NaClO<sub>4</sub> and (CH<sub>3</sub>)<sub>4</sub>NCl, where numerous solutions, with  $c_4$  ranging up to 0.3  $M$ , were studied. The resulting values of  $\phi V_4$  were then fitted to equations of the form predicted by the interionic attraction theory<sup>12</sup>

$$\phi V_4 = V_4 + Bc_4^{1/2} + Cc_4 \quad (8)$$

In eq. 8,  $V_4$  and  $C$  are parameters characteristic

(6) The symbol  $Z_1$  is used rather than a more conventional symbol for mole fraction to emphasize that  $Z_1 = n_1/(n_1 + n_2)$  rather than  $n_1/(n_1 + n_2 + n_3 + n_4)$ .

(7) F. Hovorka, R. A. Schaefer and D. Dreisbach, *THIS JOURNAL*, **58**, 2264 (1936); **59**, 2753 (1937).

(8) Based on data given by A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

(9) (a) C. J. Burton, *J. Acoust. Soc. Amer.*, **20**, 186 (1948); (b) R. D. Stallard and E. S. Amis, *THIS JOURNAL*, **74**, 1781 (1952).

(10) (a) E. Grunwald, G. Baughman and G. Kohnstam, *ibid.*, submitted for publication; values reported by these authors have been converted to the  $m$ -scale; (b) E. Grunwald and G. Baughman, *J. Phys. Chem.*, **64**, 933 (1960).

(11) Calculated from group volumes according to M. N. Papadopoulos and E. L. Derr, *THIS JOURNAL*, **81**, 2285 (1959).

(12) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapter 8, p. 545.

of the electrolyte, but  $B$  should depend solely on the charge-type of the electrolyte and on solvent properties.<sup>12</sup> The values obtained for these parameters by the method of least squares are listed in Table III. The value of  $B$ , +14.6 for 1:1 electrolytes in 50 wt. % dioxane-water at 25°, is of the same sign as the corresponding quantity in water, and appears to be of a reasonable magnitude. (Some of the solvent properties required for comparing this parameter with interionic attraction theory are not known.) Values of  $C$  range from -4.0 for NaClO<sub>4</sub> to -13.1 for (CH<sub>3</sub>)<sub>4</sub>NCl, with a mean value of -9.2.

Less numerous data for KI, NaCl and HClO<sub>4</sub>, obtained at concentrations below 0.1  $M$ , were also treated by eq. 8, but did not suffice to evaluate all the parameters. The values of  $V_4$  listed for these electrolytes in Table III were obtained on the assumption that  $B = 14.6$  and  $C = -9.2$ .

Values of  $V_4$  for the other electrolytes were estimated by assuming (i) that the partial molal volume for the electrolyte is the sum of ionic partial molal volumes, and (ii) that ( $V_{K^+} - V_{Na^+}$ ) and ( $V_{Br^-} - V_{Cl^-}$ ) have the same values as in water.<sup>13</sup>

As shown in Table IV, the solubilities of naphthalene and 1-naphthoic acid are rather sensitive to changes in solvent composition.

### Discussion

**Is there a Salting Order?**—The values of  $k_{34}$  for naphthalene and for 1-naphthoic acid in 50 wt. % dioxane-water are highly specific, ranging from positive values for some salts to negative values for others. However, just as there is a more-or-less definite salting order in water,<sup>4,14</sup> so there is here. When values of  $k_{34}$  for a given salt obtained for naphthalene are plotted *vs.* the corresponding values for 1-naphthoic acid, a good straight line is obtained, as shown in Fig. 2. This linear correlation is expressed in eq. 9.

$$k_{34}(\text{C}_{10}\text{H}_7\text{COOH}) = 1.68_1 k_{34}(\text{C}_{10}\text{H}_8) + 0.018 \quad (9)$$

Perhaps even more striking than the *existence* of a salting order is the *sequence* of the salting order for the *inorganic salts*, because it is almost exactly the reverse of the order in water. Thus for benzoic acid in water, values of  $k_{34}$  are in the sequence NaCl > KCl > KBr > HCl > KI  $\approx$  NaClO<sub>4</sub> > KClO<sub>4</sub>,<sup>4</sup> while for 1-naphthoic acid in 50% dioxane-water the sequence is NaClO<sub>4</sub> > KClO<sub>4</sub> > KI > HCl > KBr > NaCl > KCl; see Fig. 3. Or again, for benzene and naphthalene in water the sequence is similar to that for benzoic acid,<sup>4,15</sup> while for naphthalene in 50% dioxane-water this sequence is again approximately reversed.

On the other hand, salts with large organic ions appear to be in a class all by themselves. Values of  $k_{34}$  for the interaction of non-electrolytes with salts such as (CH<sub>3</sub>)<sub>4</sub>NCl or NaO<sub>3</sub>SC<sub>10</sub>H<sub>7</sub> in water are generally quite negative.<sup>4,16</sup> Thus, if the reversal of salt effects noted for the inorganic salts were applicable to salts with large organic ions, values of  $k_{34}$  for the latter should be impressively

(13) B. Lundén, *Z. physik. Chem.*, **192**, 345 (1943).

(14) M. Randall and C. F. Failey, *Chem. Revs.*, **4**, 285 (1927).

(15) M. A. Paul, *THIS JOURNAL*, **74**, 5274 (1952).

(16) E. Larsson, *Z. physik. Chem.*, **A153**, 299 (1931); R. L. Bergen and F. A. Long, *J. Phys. Chem.*, **60**, 1131 (1956).

TABLE III  
THERMODYNAMIC DATA FOR ELECTROLYTES IN 50.00 WT. % DIOXANE-WATER AT 25.00°\*

Electrolyte	$dF_{4m}^0/dZ_1,^{18a}$ kcal.	$V_1, \text{ml.}$	B	C	$(V_1, \text{solid} - V_1, \text{ml.})$	
					$\text{H}_2\text{O}^{18a}$	$50\% \text{ diox.} - \text{H}_2\text{O}^c$
$\text{NaClO}_4$	-6.8	42.6	14.6	-4.0	7.5	6.4
$\text{KClO}_4$	-6.8	(52.7)	..	....	5.0	4.1
KI	-11.3	43.2	14.6	(-9.2)	5.5	7.7
HCl	-10.7	(16.4)	..	....	2.5	4.1
KBr	-14.1	(30.8)	..	....	8.0	10.9
NaCl	-16.6	13.6	14.6	(-9.2)	12.5	15.4
KCl	-16.6	(23.7)	..	....	10	12.8
$(\text{CH}_3)_4\text{NCl}$	-16.3	99.6	14.6	-13.1	(-13.5)	(-6.1)
$\beta\text{-Naph}\cdot\text{SO}_3\text{Na}$	-7.3	(136) <sup>b</sup>	..	....	.....	.....
NaOH	....	-4.3	14.6	-10.6	24.5	22.3
$\text{HClO}_4$	....	45.4	14.6	(-9.2)	-1.5	-3.4

\* Values in parentheses are estimated; see text. <sup>b</sup> Less accurate than other values. <sup>c</sup> Values of  $V_1, \text{solid}$  from ref. 23.

large and positive in 50% dioxane-water. For example, on the basis of the line drawn through the data for inorganic salts in Fig. 3, one would expect  $k_{34}$  for the interaction of  $(\text{CH}_3)_4\text{NCl}$  with 1-naphthoic acid to be greater than +0.8! Yet the actual

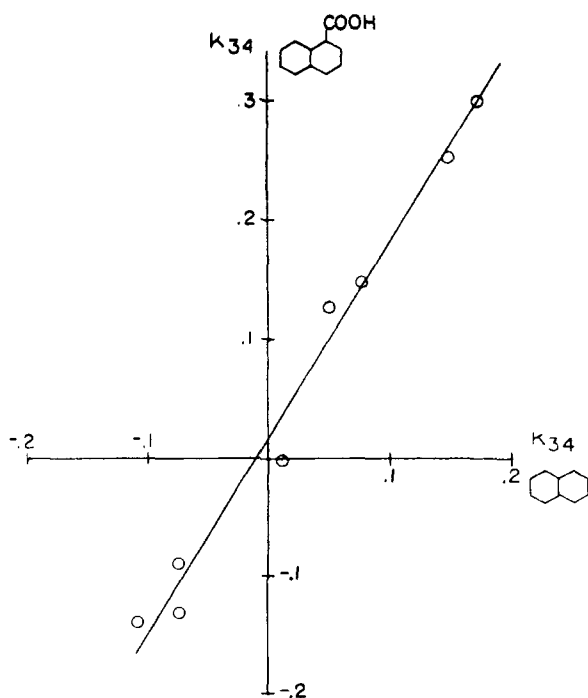


Fig. 2.—Plot of  $k_{34}$  for  $\alpha$ -naphthoic acid vs.  $k_{34}$  for naphthalene, 50% dioxane-water, 25°.

values for  $(\text{CH}_3)_4\text{NCl}$  and  $\text{NaO}_3\text{SC}_{10}\text{H}_7$  are quite negative, being of the same order of magnitude as in water.<sup>4,16</sup> One is tempted to think that this qualitative difference between the medium effects on  $k_{34}$  for inorganic salts and for salts with large organic ions is the result of a fundamental difference in the nature of the molecular interactions that are responsible for  $k_{34}$ .

**Salt-induced Medium Effects. Correlation with  $dF_{4m}^0/dZ_1$  for Inorganic Salts.**—Previous theoretical models for the salt-non-electrolyte interaction may be classified as follows: (i) Electrostatic models. In these models,  $k_{34}$  is calculated by considering coulombic interactions only. This might be the difference in the charging energy of the ions in the pure solvent (dielectric constant  $\epsilon_0$ ) and in

TABLE IV  
THERMODYNAMIC DATA FOR NON-ELECTROLYTES IN THE SYSTEM DIOXANE-WATER, 25.00°

Property	Wt. % dioxane in solvent	Value for		
		$Z_1$	Naphthalene	1-Naphthoic acid
$S_2^0 (M)$	46.319	0.8500	0.0412	0.1071 <sup>a</sup>
	50.000	.8302	.0614	.1689
	53.422	.8100	.0970	.2382 <sup>a</sup>
$k_{23}$	50.00	.8302	-.83 <sup>a</sup>	-.17 <sup>a</sup>
$V_1, \text{ml.}$	50.00	.8302	119 <sup>11</sup>	148
$M_1$	...	...	128.2	172.1
$dF_{3m}^0/dZ_1, \text{kcal.}$	50.00	.8302	11.17 <sup>a</sup>	10.92 <sup>a</sup>

<sup>a</sup> Measurement by George Baughman.<sup>16b</sup>

a solution containing the non-electrolyte (dielectric constant  $\epsilon$ )<sup>8</sup>; the sorting of molecules in a medium consisting of two or more non-electrolytes owing to the electrostatic field of the ions<sup>17,18</sup>; and interac-

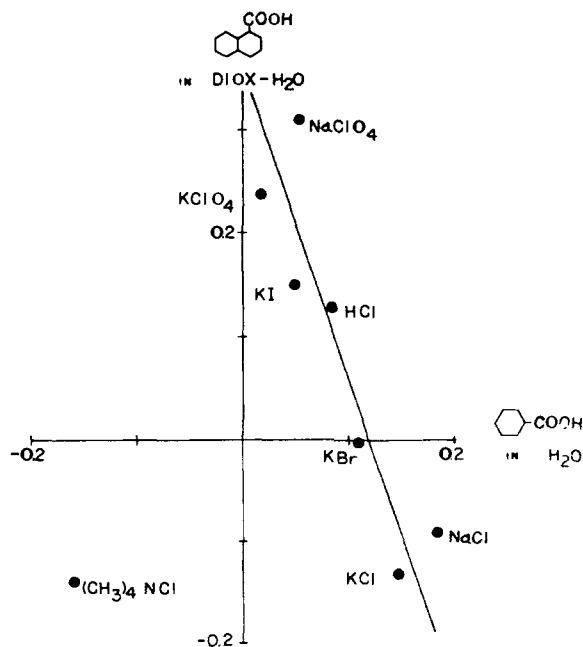


Fig. 3.—Reversal of salting sequence for inorganic salts: ordinate,  $k_{34}$  for  $\alpha$ -naphthoic acid in 50% dioxane-water, 25°; abscissa,  $k_{34}$  for benzoic acid in water, 25°. Note the isolated point for  $(\text{CH}_3)_4\text{NCl}$ .

(17) P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

(18) (a) G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941); (b) H. S. Frank, *ibid.*, **23**, 2023 (1955).

tions of dipolar molecules with their ionic atmospheres.<sup>19,20</sup> These models predict that values of  $k_{24}$  are either completely independent of the nature of the salt for electrolytes of a given valence type,<sup>20</sup> or else that they vary but slightly.<sup>21</sup> (ii) Specific short-range interaction between salt and non-electrolyte. Models of this type have been developed particularly to account for the salting-in of non-polar non-electrolytes by large organic ions.<sup>22</sup> Roughly speaking, the kind of interaction envisioned is similar to that leading to the solubilization of non-electrolytes by micelle-forming salts. (iii) Salt-induced medium effects. These models have been invented because the values of  $k_{24}$  vary much more with the nature of the salt than one would expect from the electrostatic models,<sup>21</sup> yet perhaps not enough with the nature of the non-electrolyte to suggest that specific short-range interaction is important. It is significant, for example, that the sequence of salt effects for simple inorganic salts is very nearly independent of the non-electrolyte. To explain this fact, the salt is thought to affect the activity of the non-electrolyte not by short-range interaction, but only indirectly by its effect on certain properties of the solvent.

A particularly lucid description of such a model has been given by McDevit and Long for aqueous solutions.<sup>23</sup> It has long been recognized<sup>24</sup> that the addition of salt to water raises the internal pressure. Thus "when salt is added to an aqueous solution of a non-electrolyte, the increase in internal pressure resulting from ion-solvent interaction "squeezes out" the non-electrolyte molecules."<sup>23</sup> According to McDevit and Long,<sup>23</sup> the contribution of this effect to  $k_{24}$  is given by eq. 10

$$k_{24}(\text{internal pressure}) = V_1(V_{4,\text{solid}} - V_4)/2.3\beta_0 RT \quad (10)$$

where  $(V_{4,\text{solid}} - V_4)$  is a measure of the electrostriction produced by the salt. Equation 10 represents the variation of  $k_{24}$  with salt quite well for aqueous solutions.<sup>4</sup> However, even a cursory inspection of the values of  $(V_{4,\text{solid}} - V_4)$  listed in Table III indicates that the internal pressure concept alone cannot account for the observed salt effects in 50% dioxane-water. In spite of quantitative differences, the sequence of values of  $(V_{4,\text{solid}} - V_4)$  is much the same as in water, whereas the sequence of  $k_{24}$  values is almost exactly reversed.

In two-component solvents, one can conceive of plausible additional mechanisms for salt-induced medium effects. Thus, as stated before,<sup>1a,2</sup> if the average composition of the "tight" solvation shells surrounding the ions were different from that of the nominal solvent, the compensating change in the average composition outside the solvation shells could produce distinctive changes in solubility. It is desirable to develop a theory of this effect which is independent of any specific model of ionic solvation.

(19) J. G. Kirkwood, *Chem. Revs.*, **24**, 233 (1939).

(20) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(21) F. A. Long, W. F. McDevit and F. B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813 (1951).

(22) J. O'M. Bockris, J. Bowler-Reed and J. A. Kitchener, *Trans. Faraday Soc.*, **47**, 184 (1951).

(23) W. F. McDevit and F. A. Long, *THIS JOURNAL*, **74**, 1773 (1952).

(24) C. Tammann, *Z. anorg. allgem. Chem.*, **158**, 25 (1926).

In the present work, we therefore propose to use the water/dioxane activity ratio,  $x$ , as a macroscopic index of the effective composition of the solvent in which the non-electrolyte exists. This quantity changes in a striking and characteristic way when salt is added at constant  $Z_1$ . For example, NaCl "salts-out" dioxane to a much greater extent than does NaClO<sub>4</sub>, the sequence of this effect for various salts being similar to the salting order in water.

To be specific, consider the change in  $\bar{F}_3$  when a very small amount of salt is added to a salt-free highly dilute solution of a non-electrolyte at constant  $Z_1$ ,  $T$  and  $P$ . The added salt will produce changes in the water/dioxane activity ratio and in the internal pressure, which in turn lead to changes in  $\bar{F}_3$ . According to the simplest possible model (the incompleteness of which will be criticized in the next section), the non-ideal part of the change in  $\bar{F}_3$  due to the added salt may be equated to the actual change in  $\bar{F}_3$  produced in the absence of salt by an equivalent change in external pressure and solvent composition. Thus

$$\delta \bar{F}_3 = \left( \frac{\partial \bar{F}_3}{\partial \ln x} \right)_{m_4=0} \times \delta \ln x + \left( \frac{\partial \bar{F}_3}{\partial P} \right)_{m_4=0} \delta P' \quad (11)$$

$$= \left[ \frac{\left( \frac{\partial \bar{F}_3}{\partial Z_1} \right)_{m_4} \left( \frac{\partial \ln x}{\partial m_4} \right)_{Z_1, m_4}}{\left( \frac{\partial \ln x}{\partial Z_1} \right)_{m_4}} + \left( \frac{\partial \bar{F}_3}{\partial P} \right)_{m_4} \left( \frac{\partial P'}{\partial m_4} \right)_{Z_1, m_4} \right]_{m_4=0} \delta m_4 \quad (12)$$

Equation 12 is in a form suitable for calculation. Using standard thermodynamic equations, including the previously-derived<sup>28</sup> eq. 13

$$\left( \frac{\partial \ln x}{\partial m_4} \right)_{Z_1, m_4=0} = \frac{M_{12}}{1000 RT} \frac{dF_{3m}^0}{dZ_1} - \frac{M_1 - M_2}{1000} \quad (13)$$

and evaluating  $\partial P'/\partial m_4$  according to McDevit and Long<sup>23</sup> (eq. 10 and 7), we obtain

$$k_{24,m} = \frac{M_{12}(dF_{3m}^0/dZ_1)(dF_{3m}^0/dZ_1)}{2303 R^2 T^2 (d \ln x/dZ_1)} + \frac{V_1(V_{4,\text{solid}} - V_4)d_0}{2303 RT \beta_0} - \frac{V_4 d_0}{2303} - \frac{(M_1 - M_2)(dF_{3m}^0/dZ_1)}{2303 RT (d \ln x/dZ_1)} + A_{24} \quad (14)$$

The term  $A_{24}$  is added to eq. 14 to allow for any and all interactions other than those considered so far. Explicit values for the various terms in 14 are shown for 1-naphthoic acid in Table V. The equation succeeds in showing why the sequence of

TABLE V  
TERMS IN EQ. 14 EVALUATED FOR 1-NAPHTHOIC ACID IN  
50.00 WT. % DIOXANE-WATER, 25°

Salt	$k_{24,m}$	$\frac{0.01007}{(dF_{3m}^0/dZ_1)}$	$\frac{0.000400}{(V_{4,\text{solid}} - V_4)}$	$A_{24}^a$
NaClO <sub>4</sub>	0.311	-0.75	0.38	0.55
KClO <sub>4</sub>	.236	-0.75	.24	.61
KI	.133	-1.24	.46	.79
HCl	.124	-1.18	.24	.91
KBr	-.017	-1.55	.64	.75
NaCl	-.099	-1.83	.91	.67
KCl	-.148	-1.83	.76	.78

<sup>a</sup>  $(V_4 d_0/2303)$  ranges from 0.026 to 0.026;  $(M_1 - M_2)(dF_{3m}^0/dZ_1)/(2303 RT d \ln x/dZ_1) = -0.153$ .

(25) E. Grunwald and A. L. Bacarella, *THIS JOURNAL*, **80**, 3840 (1958).

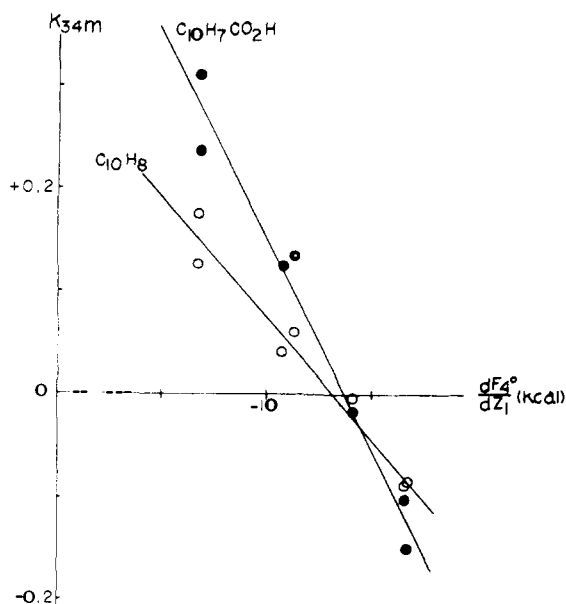


Fig. 4.—Correlation of  $k_{34m}$  with  $dF_{4m}^0/dZ_1$ ; data for 50 wt. % dioxane–water at 25°.

$k_{34m}$  values in water is the reverse of that in 50% dioxane–water. The last three terms in the equation are relatively insensitive to the nature of the salt, so that we shall consider only the first two terms. (Although no physical interpretation is given,  $A_{34}$  is of such a magnitude that it could be ascribed largely to electrostatic interactions.) When  $Z_1 = 1$ ,  $d \ln x/dZ_1$  is infinite; hence the first term vanishes when the solvent is pure water. As dioxane is added to the solvent, the magnitude of  $(V_{4, \text{solid}} - V_4) d_0/\beta_0$  at first changes only slightly, since  $\beta_0$  and  $d_0$  are quite constant up to at least 50 wt. % dioxane,<sup>9,12</sup> and since our data (Table III) indicate that the same is true for  $(V_{4, \text{solid}} - V_4)$ . The second term in 14 is therefore quite constant for small values of  $Z_2$ . On the other hand, the first term, which is zero in water, becomes negative as dioxane is added, passes through a minimum at some intermediate composition, and finally increases to zero as  $Z_2$  approaches unity. Moreover, as long as  $Z_2$  is small, the values of  $dF_{4m}^0/dZ_1$  may be expected to vary in proportion to  $(V_{4, \text{solid}} - V_4)$ . This relationship follows from eq. 10, since  $dF_{4m}^0/dZ_1 \approx 2.3 RT k_{24m}$ , where  $k_{24m}$  is the interaction constant for the salting-out of dioxane from dilute aqueous solution. For small values of  $Z_2$ , the first two terms may therefore be written in the form

$$(\alpha - \zeta)(V_{4, \text{solid}} - V_4) \quad (15)$$

where  $\alpha = (V_3 d_0/2303 RT \beta_0)_{\text{H}_2\text{O}}$ , and  $\zeta$  is a positive number which increases with  $Z_2$ . The salting sequence reverses when  $\zeta > \alpha$ . Apparently this happens somewhere between 0 and 50 wt. % dioxane.

In order to correlate  $k_{34m}$  in 50% dioxane with other thermodynamic properties it seems advisable, however, to choose  $dF_{4m}^0/dZ_1$  for the independent variable rather than  $(V_{4, \text{solid}} - V_4)$ . This is because the term involving  $dF_{4m}^0/dZ_1$  is by far the most important of the salt-specific terms in eq. 14,

and because  $dF_{4m}^0/dZ_1$  is known with better accuracy than  $(V_{4, \text{solid}} - V_4)$ . We have therefore tried to correlate  $k_{34m}$  according to eq. 16

$$k_{34m} = A_3 + B_3 (dF_{3m}^0/dZ_1)(dF_{4m}^0/dZ_1) \quad (16)$$

where  $A_3$  and  $B_3$  are parameters characteristic of the non-electrolyte and the solvent composition. As shown in Fig. 4, the hoped-for linear relationships are indeed observed to a rather good approximation. The least-squares lines representing the data (with  $F_{3m}^0$  and  $F_{4m}^0$  expressed in kcal./mole) are

$$\text{For } C_{10}H_8: k_{34m} = 0.310 + 0.00210 (dF_{3m}^0/dZ_1)(dF_{4m}^0/dZ_1) \quad (17a)$$

$$\text{For } C_{10}H_7COOH: k_{34m} = 0.559 + 0.00373 (dF_{3m}^0/dZ_1)(dF_{4m}^0/dZ_1) \quad (17b)$$

The success of the theory leading up to eq. 16 must be regarded as incomplete, however, since the slopes in eq. 17 agree with predictions based on the first two terms of eq. 14 only in order of magnitude. Moreover, the theory is intended to apply only to those cases where specific short-range interaction between the salt and the nonelectrolyte may be neglected. Since such short-range interaction appears to be important for salts with large organic ions, the data for  $(\text{CH}_3)_4\text{NCl}$  and  $2\text{-C}_{10}\text{H}_7\text{SO}_3\text{Na}$  have not been included in this correlation.

**Rigorous Treatment of Salt-induced Medium Effects.**—Furthermore, there is a fundamental objection to simple theoretical approaches such as those leading to eq. 10 or 12: The final expressions do not have the required symmetry with respect to subscripts 3 and 4. We therefore wish to describe a rigorous thermodynamic approach which does lead to expressions of the desired symmetry. The approach will be illustrated by applying it to salt-induced changes in  $x$  and  $P'$ .

Customarily, the free energy of a system of  $j$  components is represented as a function,  $T$ ,  $P$  and of the  $j$  mole numbers;  $T$  and  $P$  are intensive properties, and the mole numbers are extensive. However, there is no fundamental reason why additional intensive properties, such as  $Z_1$  or  $x$ , could not be used instead of the mole numbers, provided that at least one extensive property remains. In the present case, it is convenient to represent the free energy: (i) as a function of  $T$ ,  $P$ ,  $n_1$ ,  $n_3$ ,  $n_4$ , and  $W = n_1 M_1 + n_2 M_2$ ; (ii) as a function of  $T$ ,  $P'$ ,  $n_3$ ,  $n_4$ ,  $x$  and  $W$ . Thus, at constant  $T$

$$\begin{aligned} (\partial F/\partial n_3)_{n_4 x W P'} &= (\partial F/\partial n_3)_{n_1 n_4 W P'} + \\ &(\partial F/\partial n_1)_{n_3 n_4 W P'} (\partial n_1/\partial n_3)_{n_4 x W P'} + \\ &(\partial F/\partial P)_{n_1 n_3 n_4 W} (\partial P/\partial n_3)_{n_4 x W P'} \quad (17) \end{aligned}$$

It will be noted that

$$(\partial F/\partial n_3)_{n_1 n_4 W P} = (\partial F/\partial n_3)_{n_1 n_2 n_4 P} = \bar{F}_3 \quad (18)$$

$$(\partial F/\partial P)_{n_1 n_3 n_4 W} = (\partial F/\partial P)_{n_1 n_2 n_4} = V \quad (19)$$

However, neither  $(\partial F/\partial n_3)_{n_4 x W P'}$  nor  $(\partial F/\partial n_1)_{n_3 n_4 W P'}$  are chemical potentials as customarily defined. For example

$$\left(\frac{\partial F}{\partial n_1}\right)_{n_3 n_4 W P'} = \frac{M_2 \bar{F}_1 - M_1 \bar{F}_2}{M_2} \quad (20)$$

Since

$$2.3 RT k_{24m} = \left(\frac{\partial \bar{F}_3}{\partial m_4}\right)_{Z_1 P m_3} = \frac{W}{1000} \left(\frac{\partial^2 F}{\partial n_3 \partial n_4}\right)_{n_1 W P} \quad (21)$$

we define

$$2.3 RT k_{34}' = \frac{W}{1000} \left( \frac{\partial^2 F}{\partial n_3 \partial n_4} \right)_{xWP'} \quad (22)$$

Physically,  $k_{34}'$  is the value of the salt-non-electrolyte interaction constant if the measurements were done at constant  $x$  and  $P'$  rather than  $Z_1$  and  $P$ . In contrast to the simple treatment given before, the present treatment allows for the fact that changes in  $x$  and  $P'$  occur not only when the salt is added, but also when the non-electrolyte is added.

In order to find the relationship between  $k_{34}'$  and  $k_{34m}$ , both sides of eq. 17 are partially differentiated with respect to  $n_4$  at constant  $n_3$ ,  $x$ ,  $W$ ,  $P'$ , and the resulting partial differentials evaluated. The mathematics is straightforward but long and is therefore made available elsewhere.<sup>26</sup> If we write that, at constant  $Z_1$  and  $T$

$$P' = P + g_3 m_3 + g_4 m_4 \quad (23)$$

and define a quantity  $\phi$  by

$$\phi = RT \, d \ln x / dZ_1 \quad (24)$$

the expression finally obtained is

$$k_{34m} = k_{34}' + \frac{M_{12}(dF_{3m}^0/dZ_1)(dF_{4m}^0/dZ_1)}{2303 RT \phi} + \frac{g_4 V_3 + g_3 V_4}{2.303 RT} - \frac{(M_1 - M_2)^2 RT}{2.303 M_{12} \phi} - \frac{(g_4 + g_3)(M_1 - M_2)^2 V_{12}}{2.303 M_{12}^2 \phi} + \frac{1000g_3g_4}{2.303 RT} \left( \frac{\beta_0}{d_0} - \frac{(V_1 - V_2)(M_1 - M_2)V_{12}}{M_{12}^2 \phi} \right) + \frac{M_1 V_2 - M_2 V_1}{2.303 M_{12} RT \phi} \left( g_4 \frac{dF_{3m}^0}{dZ_1} + g_3 \frac{dF_{4m}^0}{dZ_1} + \frac{g_3 g_4 (V_2 - V_1) 1000}{M_{12}} \right) \quad (25)$$

Equation 25 has the required symmetry with respect to subscripts 3 and 4. Moreover, it shows that the rigorous calculation of solute-induced medium effects is considerably more complicated than one might have inferred from eq. 10 and 12, even if  $k_{34}'$  is (improbably) assumed to be negligibly small. In the simplest case,  $k_{34}' = 0$ ,  $Z_1 = 1$ , hence  $\phi$  is infinite and 25 reduces to 26.

$$k_{34}' = 0, Z_1 = 1: k_{34m} = \frac{g_4 V_3 + g_3 V_4}{2.303 RT} + \frac{1000g_3g_4\beta_0}{2.303 RT d_0} \quad (26)$$

Equation 26 becomes equivalent to 10 only in the unlikely event that  $g_3 = 0$ .

In view of the complexity of the problem, a semi-empirical approach such as that embodied in eq. 15 or 16 seems to be the only one that is practical at the present time.

### Experimental

**Solvents.**—Distilled water was redistilled from alkaline permanganate in an all-glass still protected by a soda-lime tube and was stored in a polyethylene bottle prior to use.

(26) A full derivation of eq. 25 has been deposited as Document number 6327 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm, by check or money order payable to: Chief, Photoduplication Service Library of Congress.

Dioxane (practical grade) was allowed to stand over  $\text{FeSO}_4$  for at least 24 hours with occasional shaking, filtered, and the filtrate purified according to Bacarella, Finch and Grunwald.<sup>8</sup>

**Non-electrolytes.**—Eastman Kodak Co. white label 1-naphthoic acid was decolorized with activated charcoal and recrystallized twice from toluene<sup>27</sup>; m.p. 162.5–163.0°; neutral equivalent 171.9 (obsd.), 172.2 (calcd.).

Naphthalene (practical grade) was decolorized with activated charcoal and recrystallized several times from 95% alcohol. The white crystalline product was dried over  $\text{P}_2\text{O}_5$  *in vacuo*, and before use was ground in an agate mortar to give smaller, more easily dissolvable crystals; m.p. 80.0–80.5°.

**Salts.**—Sodium chloride, potassium chloride, sodium perchlorate and potassium perchlorate were prepared from reagent grade chemicals according to methods given by Walton.<sup>28</sup> Constant-boiling hydrochloric acid was prepared as suggested by Kolthoff and Sandell.<sup>29</sup> The water content of the acid was calculated from data given by these authors.<sup>29</sup> Reagent grade potassium bromide and potassium iodide was recrystallized twice from water and dried over  $\text{P}_2\text{O}_5$  *in vacuo*. Each salt was ground in an agate mortar and dried at 120° for several hours just before use.

Eastman Kodak Co. white label tetramethylammonium chloride was recrystallized twice from water. The oven-dried (at 120°) salt was analyzed gravimetrically for chloride, and 99.96% of the calculated amount of silver chloride was obtained.

Sodium 2-naphthalenesulfonate was prepared from reagent grade sodium acetate, dissolved in a minimum amount of hot water, and a slight excess of 2-naphthalenesulfonic acid. Boiling water was added until the salt was dissolved, then hot alcohol until the first sign of precipitate appeared. The crystals obtained on cooling were washed with 95% alcohol, recrystallized from water-alcohol, filtered, and finally dried over  $\text{P}_2\text{O}_5$  *in vacuo*. *Anal.* Calcd.: C, 52.17; H, 3.07. Found: C, 52.05; H, 3.25.

**Solutions.**—Dioxane-water (50.00 wt. %) was prepared gravimetrically from freshly distilled dioxane and water and was used within 24 hours after preparation. The composition of each batch of solvent was checked by high-precision refractometry.

Salt solutions were prepared by standard analytical techniques from 50% dioxane-water and the dry salts. In the case of the hygroscopic salts,  $\text{NaClO}_4$  and  $(\text{CH}_3)_4\text{NCl}$ , the required amounts were dried to constant weight in tared weighing bottles, transferred immediately to calibrated volumetric flasks with the aid of 50% dioxane-water, and the solutions then made up to volume. In the case of HCl, a weight of pure dioxane, equal to the amount of water in the constant-boiling acid, was added, so that the final solution corresponded to anhydrous HCl in 50% dioxane-water.

**Solubility Measurements.**—A predetermined excess of the pure, solid non-electrolyte was weighed into each of a series of 75-ml. Pyrex ampoules. Each ampoule was then carefully flushed with pure dry nitrogen to remove most of the air, about 30 ml. of solvent or salt solution was added quickly, and the ampoule was sealed. The ampoules were then clamped onto a wrist-action shaker, beneath the surface in a 25.00° constant temperature bath, and were shaken at this temperature for at least 48 hr. To prove that this procedure resulted in saturated solutions, one ampoule was heated gently until most of the solid had dissolved; the ampoule was then cooled slowly until recrystallization was evident, and finally was shaken at 25.00° for 48 hours. The concentration of non-electrolyte in this ampoule was identical with that which is observed when equilibrium is approached from undersaturation.

After completion of the shaking, the excess solid was allowed to settle, the ampoules were opened, and aliquot portions were pipetted for analysis through a sintered glass filter. All these operations were carried out at 25°. A "control" consisting of non-electrolyte and 50% dioxane-

(27) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 426.

(28) H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948.

(29) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 545.

water was always run side-by-side with each series of salt solutions.

The saturated solutions were analyzed as follows: 1-naphthoic acid, by acid-base titration, using phenolphthalein as indicator. Potassium acid phthalate obtained from the U. S. Bureau of Standards served as primary acidimetric standard.

Naphthalene, by measurement of optical density at 3110 Å. with a Beckman model DU ultraviolet spectrophotometer, after 1:20 dilution of the saturated solutions with 50% dioxane-water. Using 1-cm. cells and a constant slit width of 0.7 mm. the optical densities were in the neighborhood of 0.5 and could be measured with a precision of better than 0.4%. Actual concentrations were obtained from the optical densities by interpolation on a large scale calibration curve, which was constructed using solutions of known concentration and identical instrument settings. (Under our experimental conditions there was some slight but significant deviation from Beer's law.)

The optical density of each undiluted salt solution was measured using 50% dioxane as a blank. No appreciable absorption was found with any of the salts in the region around 3110 Å., except with sodium 2-naphthalenesulfonate. This salt absorbed so strongly that it was not feasible to determine the naphthalene concentration in its presence.

Owing to the rapid change of solubility with solvent composition (Table IV), great care was exercised to mini-

mize changes in composition due to volatilization during preparation and handling of the solutions. (The vapor contains about 83% dioxane.) We believe, on the basis of the good precision of a large number of "controls," that we have succeeded in repressing this source of error. The over-all accuracy of  $S_2^0/S_1$  is believed to be better than 0.5%.

**Density Measurements.**—Density measurements were made by William B. Brogden, Jr., using a set of bicapillary pycnometers made to specification by the Daylight Vacuum Products Co., Chicago, Ill. The pycnometers were made in the form of flat-bottomed bulbs with a pair of precision capillaries about 10 cm. long attached to the upper surface of the bulb. These capillary tubes were graduated along the middle 6 cm. of their length, and terminated at the top with a pair of standard taper joints. The pycnometers were filled by gravity flow from an auxiliary reservoir designed in such a way that the solutions could be out-gassed prior to filling. Out-gassing was done in the usual way by repeated freezing, evacuation and thawing under vacuum. The volume per unit length of each capillary was obtained by measuring the length of a weighed drop of mercury, and the bulb volume of each pycnometer was then determined by filling with water and weighing. In each series of measurements, the density of 50.00 wt. % dioxane-water was measured as a "control" along with that of several salt solutions. From the reproducibility of a number of "controls" we estimate the precision of our results as 0.003%.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY, TALLAHASSEE, FLA.]

## Salt-induced Medium Effects. II. Kinetic Salt Effects in the Solvolysis of Neophyl *p*-Toluenesulfonate and in the Racemization of L-(+)-*threo*-3-Phenyl-2-butyl *p*-Toluenesulfonate in 50 Wt. % Dioxane-Water<sup>1a</sup>

BY E. F. J. DUYNSTEE, ERNEST GRUNWALD<sup>1b</sup> AND MARTIN L. KAPLAN

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In order to resolve the problem whether kinetic salt-effects in the ionization step of SN1 reactions are colligative, rate constants,  $k_1$ , were measured for the solvolysis of neophyl *p*-toluenesulfonate and for the racemization of L-(+)-*threo*-3-phenyl-2-butyl *p*-toluenesulfonate in 50 wt. % dioxane-water in the presence of the following salts: NaOH, NaCl, LiCl, NaBr, NaNO<sub>3</sub>, NaI, NaClO<sub>4</sub>, 2-C<sub>10</sub>H<sub>7</sub>SO<sub>3</sub>Na, (CH<sub>3</sub>)<sub>4</sub>NCl, (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>PCl. The salt effects were highly specific; values of the parameter,  $S$ , in the empirical equation:  $\log(k_1/k_1^0) = Sm_1$  (where  $m_1$  is the salt molality) ranged from ca. +0.5 for NaClO<sub>4</sub> to ca. -0.6 for NaOH. Comparison of  $k_1$  with rate constants for direct second-order reactions with anions indicated that such reactions could not account for the observed specificity of salt-effects on  $k_1$ . For the solvolysis of neophyl *p*-toluenesulfonate, such parallel reactions should be insignificant; for *threo*-3-phenyl-2-butyl *p*-toluenesulfonate, newly measured rate constants for the substitution reaction of this compound and of ethyl *p*-toluenesulfonate with lithium bromide in anhydrous acetone indicated that direct reaction with the anion might possibly make a small contribution to the observed salt effect on the racemization rate when the salt is NaOH, NaBr and NaI. According to Grunwald and Butler's semi-empirical treatment of salt-effects on the activity coefficients of non-electrolytes,<sup>2</sup> if the variation of  $S$  for different salts were due to long-range electrostatic and salt-induced medium effects, one would expect eq. 12, where  $Z_1$  is the mole-fraction of water in the solvent,  $F_{sm}^0$  is the standard partial molal free energy of the salt, and  $A$  and  $B$  are adjustable constants, to apply. This equation was found to fit the effect of all simple inorganic salts on the solvolysis of neophyl *p*-toluenesulfonate, and of all inorganic salts except NaBr and NaI on the racemization of *threo*-3-phenyl-2-butyl *p*-toluenesulfonate. Significant deviations from this equation were observed for all organic salts, suggesting that short-range interaction between organic ions and organic non-electrolytes is significant.

In the preceding study of salt effects on the activity coefficients of non-electrolytes,<sup>2</sup> we found that electrostatic models alone could not accommodate the facts, but that a combination of electrostatic effects and "salt-induced medium effects" could account for the observations involving simple inorganic salts. We now use the equations developed in that connection to resolve one of the classical problems in the kinetics of SN1 substitution of organic compounds (RX): whether or not the effect of salts at low concentrations on the rate

constant,  $k_1$ , for the initial ionization of RX is a colligative function of the ionic strength.

According to the transition-state theory, the effect of salts on  $k_1$  is formally given by eq. 1

$$k_1 = k_1^0 \gamma_{RX} / \gamma_{\ddagger} \quad (1)$$

where  $k_1^0$  denotes the rate constant at infinite dilution, and  $\gamma_{RX}$  and  $\gamma_{\ddagger}$  denote the molal activity coefficients of RX and of the transition state complex with respect to their infinitely dilute reference states. In a highly influential paper published in 1940, Bateman, Church, Hughes, Ingold and Taher<sup>3</sup> developed a theory according to which most of the

(1) (a) Work supported by Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States government. (b) Alfred P. Sloan fellow, 1959.

(2) E. Grunwald and A. F. Butler, THIS JOURNAL, **83**, 5647 (1960).

(3) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, J. Chem. Soc., 979 (1940).