[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Effect of Solvent Change on the Standard Chemical Potential of Electrolytes, from Precision Measurement of the Activities of the Solvent Components. The System NaCl–Dioxane–Water[1]

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RECEIVED DECEMBER 9, 1957

Thermodynamic equations are derived for two-component mixed solvents which relate the change in ln a_1/a_2 upon addition of solute to the change of the standard chemical potential F^0 and of the molal activity coefficient γ of the solute with solvent composition. Activities of the solvent components were measured at 25.00° by a dynamic method for solutions of sodium chloride (0 to 1.2 *m*) in a solvent containing 50.00 wt. % dioxane–50.00 wt. % water. Addition of sodium chloride caused pronounced salting-out of dioxane. The mean molal activity coefficient of sodium chloride was written in the form: $\ln \gamma_{\pm} = -Sm^{1/2} + Bm + Cm^{3/2} + Dm^2 + \ldots$, where S is the Debye–Huckel limiting slope and $B, C, D, \ldots$ are parameters. Numerical values for 50 wt. % dioxane–water at 25.00° were as follows: $S = 3.866$; $B = 3.097$; $D = -0.520$; and $C, E, \ldots, = 0$. The variations of these parameters with the mole fraction Z_1 of water in the solvent were as follows: $\mathrm{d}S/\mathrm{d}Z_1 = -25.24$; $\mathrm{d}B/\mathrm{d}Z_1 = -27.95$; $\mathrm{d}D/\mathrm{d}Z_1 = 8.82$; and $\mathrm{d}C/\mathrm{d}Z_1, \mathrm{d}E/\mathrm{d}Z_1, \ldots, = 0$. The value of $\mathrm{d}F^0_{\pm}/\mathrm{d}Z_1$ was -6904 cal., which is of such a magnitude as to indicate considerable solvation of the ions. The rather small values for $B, C, \ldots$ are indicative of ionic association.

The effect of solvent change on the standard chemical potential of electrolytes has been of interest for many decades. The principal experimental methods have been the determination of solubility when the solubility is slight[2a] and of the e.m.f. of reversible cells when suitable electrodes are available.[2b] Both of these methods are subject to serious practical limitations.

In the special case of mixed solvents such as dioxane–water, another method is available which involves precision measurement of the activities of the solvent components. This method has the advantage of being applicable to any solute. In the present paper the method will be described, the thermodynamic equations will be derived and data will be presented for sodium chloride in a mixed solvent consisting of 50.00 wt.% dioxane-50.00 wt.% water at 25.00°.

In addition to illustrating the method, the system NaCl–dioxane–water is of special interest because of the very pronounced salting-out of the dioxane and salting-in of the water which has been taken to indicate the preferential hydration of the salt.[3]

Symbols.—The subscripts 1 and 2 denote the two components of the binary solvent, subscript 3 the solute if it is a non-electrolyte, and the subscript ± the *mean value* for the ions of an electrolyte.

$n_i n_j$ = mole numbers
F_i = $\partial F/\partial n_i$; partial molal free energy
Z_1 = $n_1/(n_1 + n_2)$; $Z_2 = n_2/(n_1 + n_2)$; composition of binary solvent
M_{12} = $Z_1M_1 + Z_2M_2$; molar weight of binary solvent
r = $(M_1 - M_2)/M_{12}$
x_3 = mole fraction of solute
m_3 = $1000n_3/(n_1 + n_2)M_{12}$; moles of solute per kg. of binary solvent
f_3 = mole fractional activity coefficient of the solute in a binary solvent of constant composition Z_1; $f_3 \rightarrow 1$ as $x_3 \rightarrow 0$
γ_3 = same as above, but *molal* activity coefficient
S = $4.203 \times 10^6\, d_0^{1/2}/(\epsilon T)^{3/2}$
d_0 = solvent density
N = Avogadro's number
q = $Ne^2/2\epsilon RT$ Bjerrum's distance
e = electronic charge
a_i = radius of ith ion
ζ_1, ζ_2 = fugacities in the presence of solute
ζ_1^0, ζ_2^0 = fugacities of the pure liquid solvent components
ζ_1^*, ζ_2^* = fugacities in the absence of solute at compn. Z_1
a_1, a_2 = $\zeta_1/\zeta_1^0, \zeta_2/\zeta_2^0$
α_1, α_2 = $\zeta_1/\zeta_1^*, \zeta_2/\zeta_2^*$ (note 4)
β = $(2/RT)(\mathrm{d}F_{\pm}^0/\mathrm{d}Z_1)$
δ = standard error of fit
ϵ = dielectric constant

Description of the Method.—The addition of a solute to a 2-component solvent *at constant* z_1 is attended by changes in a_1 and a_2 according to the equation

$$Z_1 \,\mathrm{d} \ln a_1 + Z_2 \,\mathrm{d} \ln a_2 = -m_3M_{12} \,\mathrm{d} \ln a_3/1000 \quad (1)$$

If the solution is ideal, a_1 and a_2 decrease by the same factor, $1 - x_3$. If the solution is not ideal, it follows from equation 1 that a_1 and a_2 may decrease by different factors. In fact, where there is strong preferential solvation of the solute by component 1, it is possible that the decrease in a_1 is so pronounced that a_2 actually increases.

In the present method attention is focused on d ln a_1/a_2 or, what is the same thing, on the experimental quantity d ln α_1/α_2. The following derivation will show how the measurement of α_1/α_2 can lead to the value of the rate of change of the standard chemical potential with solvent composition.

Since $\partial^2F/\partial n_1\partial n_3 = \partial^2F/\partial n_3\partial n_1$, one obtains equation 2

$$\left(\frac{\partial \bar{F}_1}{\partial n_3}\right)_{n_1,n_2} = \left(\frac{\partial \bar{F}_3}{\partial n_1}\right)_{n_2,n_3} \quad (2)$$

It is convenient to express $\bar{F}_1$ and $\bar{F}_3$ as functions of the composition variables z_1 and m_3. Thus

$$\left(\frac{\partial \bar{F}_1}{\partial n_3}\right)_{n_1,n_2} = \left(\frac{\partial \bar{F}_1}{\partial Z_1}\right)_{m_3}\left(\frac{\partial Z_1}{\partial n_3}\right)_{n_1,n_2} + \left(\frac{\partial \bar{F}_1}{\partial m_3}\right)_{Z_1}\left(\frac{\partial m_3}{\partial n_3}\right)_{n_1,n_2} = \left(\frac{\partial \bar{F}_1}{\partial m_3}\right)_{Z_1} \frac{1000}{(n_1 + n_2)M_{12}} \quad (3)$$

Similarly

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(2) For example: (a) J. N. Brønsted, A. Delbanco and K. Volqvartz, *Z. physik. Chem.*, **A162**, 128 (1932); (b) H. D. Crockford, Natl. Bur. Standards (U. S.), Circ. 524, 153–64 (1953); D. Feakins and C. M. French, *J. Chem. Soc.*, 2581 (1957).

(3) M. Kortüm-Seiler and G. Kortüm, *Z. Elektrochem.*, **54**, 70 (1950)

(4) The quantities α_1 and α_2 are introduced in addition to the conventional activities a_1, a_2 because α_1 and α_2 are measured with higher precision

$$\left(\frac{\partial \bar{F}_3}{\partial n_1}\right)_{n_2,n_3} = \left(\frac{\partial \bar{F}_3}{\partial Z_1}\right)_{m_3} \frac{(1 - Z_1)}{(n_1 + n_2)} - \left(\frac{\partial \bar{F}_3}{\partial m_3}\right)_{Z_1} \frac{m_3 M_1}{M_{12}(n_1 + n_2)} \quad (4)$$

Combining equations 2, 3 and 4, one obtains equation 5

$$\frac{1000}{M_{12}} \left(\frac{\partial \bar{F}_1}{\partial m_3}\right)_{Z_1} = (1 - Z_1) \left(\frac{\partial \bar{F}_3}{\partial Z_1}\right)_{m_3} - \frac{m_3 M_1}{M_{12}} \left(\frac{\partial \bar{F}_3}{\partial m_3}\right)_{Z_1} \quad (5)$$

Analogously, equation 6 is derived from the cross-differentiation identity, $\partial^2 F/\partial n_2 \partial n_3 = \partial^2 F/\partial n_3 \partial n_2$

$$\frac{1000}{M_{12}} \left(\frac{\partial \bar{F}_2}{\partial m_3}\right)_{Z_1} = -Z_1 \left(\frac{\partial \bar{F}_3}{\partial Z_1}\right)_{m_3} - \left(\frac{\partial \bar{F}_3}{\partial m_3}\right)_{Z_1} \frac{m_3 M_2}{M_{12}} \quad (6)$$

Subtracting (6) from (5), one obtains

$$\frac{1000}{M_{12}} \left(\frac{\partial (\bar{F}_1 - \bar{F}_2)}{\partial m_3}\right)_{Z_1} = \left(\frac{\partial \bar{F}_3}{\partial Z_1}\right)_{m_3} - m_3 r \left(\frac{\partial \bar{F}_3}{\partial m_3}\right)_{Z_1} \quad (7)$$

and finally

$$\frac{1000}{M_{12}} RT \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m_3}\right)_{Z_1} = \left(\frac{\partial \bar{F}_3}{\partial Z_1}\right)_{m_3} - m_3 r \left(\frac{\partial \bar{F}_3}{\partial m_3}\right)_{Z_1} \quad (8)$$

For $\bar{F}_3$, we shall write the alternative expressions 9 and 10

$$\bar{F}_3 = \bar{F}_3^\circ + RT \ln x_3 f_3 \quad (9)$$

$$\bar{F}_3 = \bar{F}_{3m}^\circ + RT \ln m_3 \gamma_3 \quad (10)$$

$\bar{F}_3$ is completely defined by the variables Z_1 and m_3. The activity coefficients f_3 and γ_3 will be defined by the following choice of reference state. For any given value of m_3 and Z_1, the reference state (*i.e.*, $f_3 = \gamma_3 = 1$) will be chosen as the extremely dilute state ($m_3 = 0$) of the given solute in a binary solvent of the same composition Z_1. By this definition, the reference state varies with Z_1, and hence $\bar{F}_3^\circ$ and $\bar{F}_{3m}^\circ$ are functions of Z_1.

It is convenient to solve equation 8 using $\bar{F}_3$ as given by equation 10. Then

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m_3}\right)_{Z_1} = \frac{1}{RT} \frac{\mathrm{d}\bar{F}_{3m}^\circ}{\mathrm{d}Z_1} + \left(\frac{\partial \ln \gamma_3}{\partial Z_1}\right)_{m_3} - r - r m_3 \left(\frac{\partial \ln \gamma_3}{\partial m_3}\right)_{Z_1} \quad (11)$$

Equation 11 can be simplified slightly. $\bar{F}_3^0$ and $\bar{F}_{3m}^\circ$ in equations 9 and 10 are related by the equation

$$\bar{F}_{3m}^\circ = \bar{F}_3^\circ + RT \ln (M_{12}/1000) \quad (12)$$

Hence one obtains

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m_3}\right)_{Z_1} = \frac{1}{RT} \frac{\mathrm{d}\bar{F}_3^\circ}{\mathrm{d}Z_1} + \left(\frac{\partial \ln \gamma_3}{\partial Z_1}\right)_{m_3} - r m_3 \left(\frac{\partial \ln \gamma_3}{\partial m_3}\right)_{Z_1} \quad (13)$$

It is obvious from equation 13 that the measurement of α_1/α_2 can lead to the value of the rate of change of the standard chemical potential with solvent composition. Integration of values obtained at different Z_1 leads to a knowledge of $\bar{F}_3^\circ$ as a function of Z_1.

A suitable experimental method is the dynamic method of vapor pressure measurement as developed by Washburn and Heuse,[5] which recently has been adapted for use with binary solvents.[6] The method is applicable to any solute but would normally be used mainly for non-volatile solutes, for which it is also more accurate than for volatile ones. By suitable modification equation 13 can be made to apply to ionic solutes and hence there is a method for the evaluation of $F_\pm^\circ$ as a function of solvent composition for the large class of electrolytes which are inaccessible to measurement by the solubility or e.m.f. techniques.

Application to 1-1 Electrolytes.—Equations analogous to (1) and (13) are obtained readily for 1-1 electrolytes. The particular equations which we shall find useful are

$$\frac{1000}{M_{12}} \left(\frac{\partial \ln a_1/a_2}{\partial m}\right)_{Z_1} = \frac{2}{RT} \frac{\mathrm{d}F_\pm^\circ}{\mathrm{d}Z_1} + 2\left(\frac{\partial \ln \gamma_\pm}{\partial Z_1}\right)_m - 2mr \left(\frac{\partial \ln \gamma_\pm}{\partial m}\right)_{Z_1} \quad (14)$$

$$\frac{1000}{M_{12}} [Z_1 \,\mathrm{d} \ln a_1 + Z_2 \,\mathrm{d} \ln a_2] = -2\mathrm{d}m - 2m \,\mathrm{d} \ln \gamma_\pm \quad (15)$$

Here m is expressed in formula weights of electrolyte per kg. of binary solvent, and $F_\pm^\circ$ is the mean value of F° for cation and anion. It is useful to expand $\ln \gamma_\pm$ in power series in $m^{1/2}$ according to Scatchard and Prentiss[7]

$$\ln \gamma_\pm = -Sm^{1/2} + Bm + Cm^{3/2} + Dm^2 + Em^{5/2} + \ldots \quad (16)$$

In equation 16, S is the Debye–Hückel limiting slope and $B, C, D, E, \ldots$ are adjustable constants. The latter are evaluated from the experimental data as follows. Substitution of (16) in (15) and integration leads to

$$-\frac{1000}{M_{12}} (Z_1 \ln \alpha_1 + Z_2 \ln \alpha_2) = 2m - \frac{2}{3} Sm^{3/2} + Bm^2 + \frac{6}{5} Cm^{5/2} + \frac{4}{3} Dm^3 + \frac{10}{7} Em^{7/2} + \ldots \quad (17)$$

The terms on the left and the first two terms on the right involve only experimental data and known solvent properties. The adjustable constants in the remainder are evaluated by standard least-squares methods.[8]

Equation 16 is also useful in connection with equation 14. Since $S, B, C, \ldots$ are functions of Z_1, integration leads to equation 18

$$\frac{1000}{M_{12}} \ln (\alpha_1/\alpha_2) = \beta m - m^{3/2} \left[\frac{4}{3} \frac{\mathrm{d}S}{\mathrm{d}Z_1} - \frac{2}{3} Sr\right] + m^2 \left[\frac{\mathrm{d}B}{\mathrm{d}Z_1} - Br\right] + m^{5/2} \left[\frac{4}{5} \frac{\mathrm{d}C}{\mathrm{d}Z_1} - \frac{6}{5} Cr\right] + m^3 \left[\frac{2}{3} \frac{\mathrm{d}D}{\mathrm{d}Z_1} - \frac{4}{3} Dr\right] + m^{7/2} \left[\frac{4}{7} \frac{\mathrm{d}E}{\mathrm{d}Z_1} - \frac{10}{7} Er\right] \ldots \quad (18)$$

where $\beta = (2/RT)(\mathrm{d}F_\pm^0/\mathrm{d}Z_1)$.

Except for the coefficient of $m^{3/2}$ which is given by the Debye–Hückel theory, the other coefficients on the right in equation 18 are obtained by

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(5) E. W. Washburn and E. O. Heuse, THIS JOURNAL, **37**, 309 (1915).

(6) A. L. Bacarella, A. Finch and E. Grunwald, *J. Phys. Chem.*, **60**, 573 (1956).

(7) G. Scatchard and S. S. Prentiss, THIS JOURNAL, **56**, 1486 (1934).

(8) Equation 17 is written in a form which might be misleading. Normally, in fitting the data, one would use only a limited number of the terms in the power series. For best fit, these need not be adjacent lowest terms in the series. An objective method for selecting the best set of terms has been reported by L. Marcus, *General Motors Eng. J.*, **4**, No. 2, 1 (1957).

fitting the data. Note that one obtains in this way not only $dF_0^{\pm}/dZ_1$, but also the derivatives with respect to Z_1 of B, C, D, . . ., and hence the effect of medium change on $\ln \gamma_{\pm}$. Indeed, measurement of α_1 and α_2 provides a powerful tool for learning about medium effects on the thermodynamic properties of the solute.

Experimental Part

Solutions of purified[9] sodium chloride in a mixed solvent consisting of 50.00 wt. % dioxane–50.00 wt. % water were freshly prepared for each experiment by standard gravimetric techniques from pure[6] dioxane and water. Relative fugacities α_1 and α_2 were measured at 25.00° using a dynamic vapor pressure apparatus built in this Laboratory which has been fully described elsewhere.[6] In a typical experiment, the carrier gas, pure nitrogen, passed first over a train of saturators contained 50% dioxane–water followed by a cold trap at −80°, then over a train of saturators containing the sodium chloride solution and through a second cold trap. The mass ratio of the two vapor condensates was determined, as well as the difference in their compositions. From these data, α_1 and α_2 were computed as described previously,[6] using the slightly imperfect real gas model and second virial coefficients as obtained previously.[6] The experiments were done over an extended period of time during which the accuracy gradually improved. The standard error of the mass ratios ranged from 0.08% for the early experiments (series II, Table I) to 0.03%. The difference in the compositions of the vapor condensates was measured at first with a Bausch and Lomb dipping refractometer with a standard error of 0.02% (series II), later with a Hilger-Rayleigh interferometer, using a special cell for volatile liquids,[10] with a standard error of 0.007%. The vapor in equilibrium with 50.00 wt. % dioxane–water was found to contain 83.520 wt. % dioxane (previous value,[6] 83.524%) at 25.00° in the presence of nitrogen at a total pressure of 1 atm. The activities of water and dioxane in 50.00 wt. % dioxane, referred to the pure liquids, are 0.8614 and 0.5862, respectively, at 25.00° and 1 atm. total pressure.[6]

TABLE I

VALUES OF α_1 AND α_2 FOR SOLUTIONS OF SODIUM CHLORIDE IN 50.00 WT. % DIOXANE–50.00 WT. % WATER AT 25.00°

Series I[a]			Series II[a]		
m	α_1	α_2	m	α_1	α_2
0	1.00000	1.00000	0.0226	0.9955	1.0097
0.01136	0.9982_9	1.0050_5	.0482	.9905	1.0191
.02560	$.9958_0$	1.0118_6	.1263	.9846	1.0439
.03933	$.9963_6$	1.0155	.1418	.9826	1.0483
.1174	.98547	1.0409	.1503	.9831	1.0513
.2547	.9720	1.0831	.2544	.9724	1.0833
.3368	.9638	1.1066	.2656	.9705	1.0847
.3928	.9557	1.1211	.3946	.9565	1.1229
.8824	.9035	1.2495	.4120	.9534	1.1266
			.5650	.9359	1.1680
			.8345	.9081	1.2372
			1.0041	.8908	1.2802
			1.2076	.8683	1.3298

[a] Series I—vapor composition determined with an interferometer to ±0.007%; series II—vapor composition determined with a dipping refractometer to ±0.02%. Total pressure 1 atm. in both series.

Absence of Systematic Errors.—To evaluate the activities of all three components, the measurement of two independent quantities, such as mass ratio and vapor composition, is sufficient since a third relation exists in the form of equation 15. When the activity of one component is already known, only one additional measurement will suffice to evaluate the activities of the other two. This situation is very nearly realized at low solute concentrations ($m < 0.05$) where terms of the order of m and higher in equation 16 (which would be inaccurate in case of systematic error) make only a small contribution to $\ln \gamma_{\pm}$. Hence one may obtain α_1/α_2 from either the mass ratio or the vapor composition, and the measurement of the one is virtually independent of possible error in the measurement of the other. Agreement between them is good evidence in favor of the accuracy of both sets of measurements since it is improbable that systematic errors would be such as to give equal results. Two sets of values of β (equation 18) were obtained in this way, using only data at $m<0.05$: from the mass ratios, $\beta = -23.0 \pm 0.7$; from the vapor compositions, $\beta = -23.5 \pm 1.5$. The standard errors are fairly large due to the low concentrations, but the agreement is very satisfactory. For comparison, the least-squares adjusted value of β based on *all* the data in Table I (up to 1.2 m) is −23.304.

Results

Experimental values of α_1 and α_2 for solutions of sodium chloride in 50.00 wt. % dioxane–50.00 wt. % water at 25.00° are shown in Table I. In this and all subsequent connections, the subscript 1 denotes water and 2 denotes dioxane. The dielectric constant of the solvent was taken as 35.85 at 25°.[11] It is worth noting the marked decrease in α_1 and the even greater increase in α_2 with increasing salt concentration. Although not shown in the table, the orthobaric vapor pressure over the solution *increases* when salt is added. The results suggest considerable preferential hydration of the solute, as pointed out by previous workers.[3,12]

The data were treated according to equation 17, where B, C, . . . are the empirical constants of equation 16 for $\ln \gamma_{\pm}$. The results of the least-squares calculation are shown in the first two lines of Table II. The data are fitted well by a two-parameter equation in which B and D are finite and the other coefficients are zero. A four-parameter treatment in which B, C, D and E are finite and the other coefficients zero offers no further improvement; C and E are small and of the same sign as D.

TABLE II

CONSTANTS IN EQUATIONS FOR ACTIVITY COEFFICIENT OF SODIUM CHLORIDE IN 50.00 WT. % DIOXANE–WATER AT 25.00°

å, Å.	S	B	C	D	E	s^a	$\gamma_{\pm}(1\ m)$
				Equation 16			
	3.866	3.097	0	−0.520	0	0.00084	0.275
	3.866	3.126	−0.144	− .320	−0.085	.00086	.275
				Equation 19			
4	3.866	−0.036	.....	0.218	.....	0.00129	0.328
2	3.866	.811	.....	− .086	.....	.00102	.296
0	3.866	3.097	.....	− .520	.....	.00084	.275
−1	3.866	4.977	.....	1.359	.....	.00087	.268

[a] Standard error of fit of $(Z_1 \ln \alpha_1 + Z_2 \ln \alpha_2)$.

In order to study the effect of the neglected higher-order terms in (16), the data also were treated according to equation 19, based on the Debye–Hückel theory, for $\epsilon = 35.85$ at 25°, which contains the parameters B_1, D_1 and the "finite distance of approach of the ions," å.[13] Equation 16 might conceivably be an expansion of (19).

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[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 568.

[10] E. Grunwald and B. J. Berkowitz, *Anal. Chem.*, **29**, 124 (1957).

[11] F. E. Critchfield, J. A. Gibson and J. L. Hall, THIS JOURNAL, **75**, 1991 (1953).

[12] G. R. Lucas and L. P. Hammett, *ibid.*, **64**, 1928 (1942), have given an analogous interpretation to their freezing point data.

[13] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, equations 12-5-3 and 3-7-13; pp. 380–381

Equations of the form (19) are successful in fitting data for aqueous electrolytes.[13] When (19) was

$$\ln \gamma_{\pm} = \frac{-3.866\ m^{1/2}}{1 + 0.495\ \mathring{a} m^{1/2}} + B_1 m + D_1 m^2 \qquad (19)$$

substituted in (15) and the resulting expression was integrated, the integral was not of a convenient form for the evaluation of all three parameters $\mathring{a}$, B_1 and D_1 in a single least-squares treatment. The following method was used. A set of values was chosen for $\mathring{a}$, and for each value, B_1 and D_1 were calculated by least-squares. The appropriateness of the chosen value of $\mathring{a}$ was judged in each case by the standard error of fit, δ. The results are shown in Table II. It is seen that δ is at a minimum for $\mathring{a} = 0$. This result is somewhat surprising since in water $\mathring{a} = 4.2$ Å. for sodium chloride. It will be shown however that at least part of the difference can be ascribed to the more extensive ion association in 50% dioxane.

TABLE III

CONSTANTS IN EQUATION 20 FOR 1000 ln $(\alpha_1/\alpha_2)/M_{12}$; SODIUM CHLORIDE IN 50.00 WT. % DIOXANE–WATER AT 25.00°

β	$\left[\frac{4}{3}\frac{\mathrm{d}S}{\mathrm{d}Z_1} - \frac{2}{3}Sr\right]$	b	c	d	e	δ^a
23.304	−27.59	−20.689	0	4.254	0	0.00182
(−23.304)^b	−27.59	−21.21	0.90	4.15	−0.26	0.00178

^{a} Standard error of fit of ln α_1/α_2. ^{b} Value obtained in line 1.

Values of ln α_1/α_2 were fitted to equation 18 which, using numerical constants for 50% dioxane, is written as

$$33.428 \ln (\alpha_1/\alpha_2) = \beta m + 27.59 m^{3/2} + bm^2 + cm^{5/2} + dm^3 + em^{7/2} + \ldots \qquad (20)$$

Numerical values of the parameters are listed in Table III. The data are fitted satisfactorily with a three-parameter equation in which β, b, d are finite and c, e, . . . are zero, in close analogy to our experience with equation 17. When c and e are introduced as additional parameters, their values are small and the fit is not improved noticeably. From the data in Tables II and III, the rates of change with solvent composition of a number of quantities of thermodynamic interest have been computed and are listed in Table IV.

TABLE IV

RATES OF CHANGE WITH SOLVENT COMPOSITION FOR VARIOUS THERMODYNAMIC FUNCTIONS OF SODIUM CHLORIDE IN 50.00 WT. % DIOXANE–WATER AT 25.00°

$\mathrm{d}F_{\pm}^0/\mathrm{d}Z_1$	− 6,904 cal.	
$\mathrm{d}S/\mathrm{d}Z_1$	−25.24	
$\mathrm{d}B/\mathrm{d}Z_1$	−27.95^a	(−28.53)^b
$\mathrm{d}C/\mathrm{d}Z_1$	0^a	(1.63)^b
$\mathrm{d}D/\mathrm{d}Z_1$	8.82^a	(7.72)^b
$\mathrm{d}E/\mathrm{d}Z_1$	0^a	(0.05)^b
$\mathrm{d} \ln \epsilon/\mathrm{d}Z_1$	4.35	
$\mathrm{d} \ln \mathrm{S}/\mathrm{d} \ln \epsilon$	− 1.500	
$\mathrm{d} \ln B/\mathrm{d} \ln \epsilon$	− 2.075^a	
$\mathrm{d} \ln D/\mathrm{d} \ln \epsilon$	− 3.897^a	

^{a} Based on data in line 1 of Tables II and III. ^{b} Based on data in line 2 of Tables II and III.

Previous Work on the System NaCl–Dioxane–Water.—Scatchard and Benedict[14] have reported precise thermodynamic data for sodium chloride in aqueous solution containing up to 2m dioxane at 0°. Their results complement rather than overlap ours (50% dioxane–water contains 11.35 moles of dioxane per kg. of water) and allow a number of comparisons to be made in the next section. Mögling[15] has obtained data at a single NaCl concentration, usually 0.7–0.8m, over a wide range of dioxane concentrations, up to 81 wt. % dioxane. Although no valid quantitative comparisons can be made, qualitatively his results agree with ours in that they illustrate the very considerable salting-out of dioxane over the entire composition range.

Discussion

Effect of Solvent Change on Standard Chemical Potential for Sodium Chloride.—The value of $\mathrm{d}F_{\pm}^0/\mathrm{d}Z_1$ obtained for 50 wt.% dioxane–water at 25.00° is − 6,904 cal. (Table IV). For this solvent mixture, $\mathrm{d} \ln \epsilon/\mathrm{d}Z_1 = 4.35$; hence $\mathrm{d}F_{\pm}^0/\mathrm{d} \ln \epsilon = -1587$ cal. At least a part of this derivative is attributable to the decrease in the Born charging energy of the ions. Another part may be due to preferential solvation of the ions by water since the water activity increases with increasing ϵ. Regarding the former, the electrical work required to charge the two ions of sodium chloride in a continuous dielectric is given by

$$W_{\mathrm{el}} = \frac{e^2}{2\epsilon}\left(\frac{1}{a_{\mathrm{Na}}} + \frac{1}{a_{\mathrm{Cl}}}\right) = \frac{e^2}{\epsilon a_{\pm}} \qquad (21)$$

where $a_{\pm}$ is the harmonic mean of the two ionic radii. Hence the electrical contribution to $\mathrm{d}F_{\pm}^0/\mathrm{d} \ln \epsilon$ is equal to

$$\frac{N}{2}\frac{\mathrm{d}W_{\mathrm{el}}}{\mathrm{d} \ln \epsilon} = -\frac{Ne^2}{2\epsilon a_{\pm}} = -\frac{RTq}{a_{\pm}} \qquad (22)$$

It is instructive to compute a lower limit for $a_{\pm}$ by assuming that $\mathrm{d}F_{\pm}^0/\mathrm{d} \ln \epsilon$ is entirely due to the Born charging term, equation 22. Using numerical values for 50 wt.% dioxane, the Bjerrum distance $q = 7.81_4$ Å. at 25°, and $a_{\pm} = 2.92$ Å. For comparison, the harmonic mean of the crystal radii of sodium ion and chloride ion is 1.25 Å.[16] The large discrepancy indicates that the ions are solvated. If, as is likely, the solvation is preferentially by water,[17] it will contribute a negative term to $\mathrm{d}F_{\pm}^0/\mathrm{d} \ln \epsilon$, and $a_{\pm}$ of the solvated ions is actually greater than 2.92 Å.

In their studies of the water-rich portion of the system dioxane–water–NaCl, Scatchard and Benedict[14,18] obtained at 0° and $Z_1 = 1$: $\mathrm{d}F_{\pm}^0/\mathrm{d}Z_1 = -3874$ cal.; $\mathrm{d}^2F_{\pm}^0/\mathrm{d}Z_1^2 = 19{,}430$ cal. Assuming the second derivative to be constant, one obtains for 50 wt.% dioxane ($Z_1 = 0.8302$): $\mathrm{d}F_{\pm}^0/\mathrm{d}Z_1 = -7173$ cal. at 0°. In spite of the long extrapolation, this value differs only by a few per cent. from our measured value at 25°.

Activity Coefficients.—The salient feature of the

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[14] G. Scatchard and M. A. Benedict, THIS JOURNAL, **58**, 837 (1936).

[15] D. Mögling, results reported in ref. 3.

[16] L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1944, Chapter 10.

[17] G. Scatchard, *J. Chem. Phys.*, **9**, 34 (1941).

[18] (a) Data of ref. 14 were recalculated to our concentration units: $m = M_1/2(1 + 0.088M_2)$; $RT \ln \gamma_1 = RT \ln \gamma_{\pm} - RT \ln(1 + 0.088M_2) - F_{\pm}^0$. M_1, M_2, γ_1 as defined in ref. 14. (b) To calculate B, C, D, . . . for $Z_1 = 0.8302$, data of ref. 14 were expanded in Taylor series about $Z_1 = 1$ and terms of higher order than quadratic were neglected.

empirical constants, B, C, D, E, . . . in equation 16 for sodium chloride in 50 wt.% dioxane–water is their small magnitude. This is brought out most clearly by comparison of the actual values in Table II with the following values, obtained by extrapolation of the data of Scatchard and Benedict[14,18] to 50 wt.% dioxane: $B = 6.4$; $C = -6.4$; $D = 3.9$; $E = -1.4$. The effect may be attributed to short-range ionic interactions whose relative importance increases rapidly with decreasing dielectric constant. If to a first approximation attention is paid only to the formation of short-range ion pairs, then $\gamma = \gamma'\alpha$, where α is the free-ion fraction and γ' the molal activity coefficient of the free ions.[19] Upon introducing the ion-pair dissociation constant $K = \alpha^2(\gamma')^2m/(1 - \alpha)$, and writing $\ln \gamma'$ in a form analogous to (16): $\ln \gamma' = -S\cdot(\alpha m)^{1/2} + B' \alpha m + C'(\alpha m)^{3/2} + \ldots$, the following power series was obtained for $\ln \gamma$

$$\ln \gamma = -Sm^{1/2} + (B' - K^{-1})m + (C' + 5S/2K)m^{3/2} + (D' - 3S^2/K + 3B'/K + 3/2K^2)m^2 + \ldots \quad (23)$$

Equation 23 shows that the limiting-law term, $Sm^{1/2}$, is unaffected by the short-range interactions, but each of the higher terms is multiplied by a coefficient reflecting the ionic association. Equation 23 allows only for ion-pair formation; to a better approximation ionic interactions of higher order than pairwise also need be included. Such refinement will cause addition of further terms to the coefficients of m^2, $m^{5/2}$, . . . , but the coefficients of m and $m^{3/2}$ will remain unchanged. Thus the empirical value of B equals $B' - K^{-1}$.

Upon using for B' the value 6.4, extrapolated from the data of Scatchard and Benedict,[14] K is estimated as *ca.* 0.3. In spite of the crudeness of this estimate, the value is at least of the right order of magnitude: In 70 wt.% dioxane–water K for sodium chloride was found to be[20] 5.35×10^{-3} at 25°. Using the equation $K = 1000/[32\ \pi N\cdot q^3Q(b)]$ to describe the solvent dependence,[13] K is estimated as 0.10 for 50 wt.% dioxane.

Possibly a better estimate of B' may be made on the basis of the equation $\ln \gamma' = -S(\alpha m)^{1/2}/[1 + S(\alpha m)^{1/2}]^{2/3}$, which was derived and tested in previous papers[19b,20] for systems where $q >> \mathring{a}$. Upon expansion in power series, it turns out that $B' = 2S^2/3$, or 10.0 for 50% dioxane. Correspondingly, $K = (B' - B)^{-1}$ is estimated at 0.145, in better agreement with the value 0.10 obtained above.

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[19] (a) N. Bjerrum, *Kgl. Danske Videnskab Selskab, Math-fys. Medd.*, **7**, No. 9 (1926); (b) H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953).

[20] E. L. Purlee and E. Grunwald, THIS JOURNAL, **79**, 1366 (1957).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Effect of Solvent Change on the Standard Chemical Potential of Electrolytes. Comparison of Vapor Pressure and E.M.F. Data for HCl, NaOH and K_W in the System Dioxane–Water[1]

BY GEORGE BAUGHMAN AND ERNEST GRUNWALD

RECEIVED DECEMBER 9, 1957

The rate of change of the standard chemical potential with changing mole fraction of water, $\mathrm{d}F^0/\mathrm{d}Z_1$, was obtained in 50.00 wt. % dioxane–water for HCl and NaOH from vapor pressure data. Values at 25.00° were: for HCl, $\mathrm{d}(F^0{}_{\mathrm{H}^+} + F^0{}_{\mathrm{Cl}^-})/\mathrm{d}Z_1 = -7.9$ kcal.; for NaOH, $\mathrm{d}(F^0{}_{\mathrm{Na}^+} + F^0{}_{\mathrm{OH}^-})/\mathrm{d}Z_1 = -17.6$ kcal. The value for HCl may be compared with the value, −8.0 kcal., deduced from potentiometric data for the cell H_2/HCl, dioxane–water/AgCl–Ag. The values for HCl and NaOH, when combined with a previous value[2] for NaCl, lead to -19.8 ± 1.0 for $\mathrm{d}\ln K_w/\mathrm{d}Z_1$, where K_w is the autoprotolysis constant. This differs significantly from the potentiometric value of −22.3. The discrepancy may be due to lack of reversibility of the Ag–AgCl electrode at high *p*H in the dioxane-rich solvent compositions.

Precision measurements of the activities of the solvent components may be used to obtain thermodynamic data for electrolytes in mixed solvents. A suitable method was reported in the preceding paper.[2] Results of this method will now be compared with results based on the e.m.f. of reversible cells in order to have a cross-check on the validity of both methods. Two systems were selected: (i) Hydrogen chloride in dioxane–water, because potentiometric data for the cell (1) were already

$$\mathrm{Pt}\text{–}\mathrm{H_2}(g,\ 1\ \mathrm{atm})/\mathrm{HCl}(m),\ \mathrm{dioxane}(Z_2),\ \mathrm{water}(Z_1)/\mathrm{AgCl}\text{–}\mathrm{Ag} \quad (1)$$

available for a number of solvent compositions[3–6]; (ii) Sodium hydroxide in dioxane–water, because these data, taken in conjunction with the data for HCl and NaCl[2], may be compared with potentiometric values[7] of the autoprotolysis constant K_W.

The mathematical symbols that will be used have been defined in the preceding paper.[2]

Experimental Part

Reagents and Solutions.—Constant boiling aqueous hydrochloric acid was prepared from reagent grade acid[8] and

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[1] Work supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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

[3] H. S. Harned and J. O. Morrison, *ibid.*, **58**, 1908 (1936); H. S. Harned, *ibid.*, **60**, 336 (1938); H. S. Harned and C. Calmon, *ibid.*, **60**, 2130 (1938); 20, 45, 70 wt. % dioxane.

[4] E. L. Purlee and E. Grunwald, *ibid.*, **79**, 1366 (1957); 70 wt. % dioxane.

[5] H. P. Marshall and E. Grunwald, *J. Chem. Phys.*, **21**, 2143 (1953), extrapolations.

[6] A. F. Butler, Ph.D. Thesis, Florida State University, Tallahassee, Fla., August, 1956; 50 wt. % dioxane; experimental methods similar to those of ref. 4.

[7] H. S. Harned and L. D. Fallon, THIS JOURNAL, **61**, 2374 (1939); 20, 45, 70 wt. % dioxane.

[8] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).