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

The Solvation of Electrolytes in Dioxane–Water Mixtures, as Deduced from the Effect of Solvent Change on the Standard Partial Molar Free Energy[1]

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The rate of change of the standard partial molar free energy with changing mole fraction of water, dF_3^0/dZ_1, was measured in 50.00 wt. % dioxane–water for a variety of solutes. Values obtained at 25.00° were (in kcal. per formula weight): NaOH, −17.6; NaCl, −13.8; KCl, −13.8; $(CH_3)_4NCl$, −13.5; RbCl, −13.2; CsCl, −12.5; LiCl, −11.5; KBr, −11.3; $NaNO_3$, −9.8; KI, −8.5; HCl, −7.9; sodium naphthalenesulfonate (β), −4.5; $NaClO_4$, −4.0; $(C_6H_5)_4PCl$, +0.2; $HClO_4$, +0.6; $NaB(C_6H_5)_4$, +15.4; $(CH_3)_4C$, +11.8; $(C_6H_5)_4C$, +20.4; $(HOCH_2)_4C$, −0.6. In discussing the solvation of the ions, dF_3^0/dZ_1 for the electrolytes was first broken down into separate terms for individual ions, using the following extra-thermodynamic approach. Beginning with an idealized model of a large ion in which a central charge is surrounded by a sizeable insulating layer, it was argued that dF^0/dZ_1 for such an ion is equal to dF^0/dZ_1 for the identical structure without the charge, *plus* a coulombic term. Thus it was postulated that $\left(\frac{dF^0}{dZ_1}\right)_{Ph_4P^+} = \left(\frac{dF^0}{dZ_1}\right)_{Ph_4B^-} = \left(\frac{dF^0}{dZ_1}\right)_{Ph_4C} - \frac{N_{Av}e^2}{2b\epsilon}\frac{d\ln\epsilon}{dZ_1}$. The experimental value of dF_3^0/dZ_1 for the electrolyte, $Ph_4P^+Ph_4B^-$, was in good agreement with the value predicted by these equations. Single-ion values of dF^0/dZ_1 obtained in this way were slightly positive for the alkali cations and hydrogen ion and highly negative for all inorganic anions except ClO_4^-. In analyzing the values for the small cations, it was shown that a purely coulombic model of the cation–solvent interaction could not accommodate the facts, and a chemical model was developed. According to this model, the alkali cations are associated with about 2 dioxane molecules (*plus* a small but indeterminate number of water molecules), and hydrogen ion (regarded as H_3O^+) is associated with 3 dioxane molecules. On the other hand, the highly negative values of dF^0/dZ_1 for the anions are consistent with models of preferential solvation by water. The solvation of large organic ions with low density of surface charge is thought to resemble that of the analogous uncharged structures.

In discussing the solvation of ions in partly aqueous organic solvents, one of the most common assumptions is that the ions are surrounded predominantly by the water molecules, since they are more polar. This assumption has been made in interpreting thermodynamic data, not only for simple inorganic salts such as sodium chloride, but also for large organic ions such as *tetra*-isoamylammonium ion and for the transition-state complexes of organic reactions that proceed by ionic mechanisms.

The work to be described in this paper has led us to the conclusion that this assumption is not of general validity. We have measured the rate of change of the standard partial molar free energy, F_3^0, with mole fraction of water,[3] Z_1, for a wide variety of electrolytes in 50.00 wt. % dioxane–water at 25°. Our results indicate that simple inorganic cations, such as Na^+, are solvated appreciably by dioxane and that large organic ions with low density of surface charge are solvated much as if the central charge were not there.

Experimental Method

The effect of solvent change on the standard partial molar free energy of electrolytes was measured by the dynamic vapor pressure method described in recent publications from this Laboratory.[4,5] Although this method applies only to mixed solvents such as dioxane–water, it can be used for almost any electrolyte, in contrast to the e.m.f. and the solubility methods.

The vapor pressure method involves the precise measurement of the fugacities of the solvent components. A stream of nitrogen passes over the solution of the electrolyte in 50.00 wt. % dioxane–water, contained in a series of saturators. The vapor in equilibrium with the solution is entrained by the nitrogen and carried into a cold trap where it is condensed out. The nitrogen then passes over a series of saturators containing only 50.00 wt. % dioxane–water, and the vapor is again condensed out. Full details have already been given elsewhere.[6] Two experimental quantities are then determined by weighing and analyzing the vapor condensates

$$\text{The mass ratio, } \rho = \frac{(n_1)_g M_1 + (n_2)_g M_2}{(n_1^*)_g M_1 + (n_2^*)_g M_2} \cdots \quad (1)$$

where the $(n)_g$'s are the mole numbers in the vapor phase for a constant amount of nitrogen, the M's are molecular weights, subscripts 1 and 2 refer to water and dioxane, respectively, and superscript* refers to the mixed solvent in the absence of solute

$$\text{The vapor composition, } W = \frac{(n_2)_g M_2}{(n_1)_g M_1 + (n_2)_g M_2} \cdots \quad (2)$$

which represents the weight fraction of dioxane in the vapor over the solution. Experimentally we determine W–W^* by interferometry[7]; W^* is already known from independent measurements.[4]

Evaluation of $d(F_{C^+}^0 + F_{A^-}^0)/dZ_1$.—We shall assume that the standard partial molar free energy of the electrolyte is an additive function for cation and anion

$$F_3^0 = F_{C^+}^0 + F_{A^-}^0 \quad (3)$$

Throughout this paper, the standard partial molar free energy will be defined on the mole-fractional scale; that is, for the i^th component

$$F_i^0 = \lim_{N_i \to 0} (\bar{F}_i - \nu_i RT \ln N_i) \quad (4)$$

when N_i is the mole fraction, and ν_i is the number of solute particles produced per formula weight.

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(1) Work supported by the Office of Naval Research and by the National Science Foundation. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Alfred P. Sloan Fellow, 1959.

(3) We use the symbol Z_1 rather than the conventional symbol N_1 to emphasize that we are referring to the mole-fraction of water in the solvent prior to addition of the solute; that is, $Z_1 = n_1/(n_1 + n_2)$, where the n's are mole numbers.

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

(5) G. Baughman and E. Grunwald, *ibid.*, **80**, 3844 (1958).

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

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

TABLE I

VALUES OF $\ln \alpha_1/\alpha_2$ AND $\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$ IN 50 WT. % AQUEOUS DIOXANE AT 25.00°

Electrolyte	m	W[a]	1000 $\ln \alpha_1/\alpha_2$[b] (eq. 34)	$\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$[e] (kcal.)	ρ	1000 $\ln \alpha_1/\alpha_2$[b] (eqs. 37, 40)	$\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$[f] (kcal.)
LiCl	0.02404	0.83669	−10.9 ± 0.3	−11.2	1.0066	−11.5 ± 0.7	−11.7
	.04761	.83801	−20.6 ± 0.6	−11.5	1.0122	−21.1 ± .6	−11.8
KCl	.0236	.83710	−14.0 ± 1.5	−14.0	1.0089	−14.7 ± .3	−14.6
	.0500	.83876	−26.4 ± 1.1	−13.5	1.0155	−26.0 ± .3	−13.3
KBr	.02476	.83672	−11.0 ± 0.2	−11.1	1.0069	−12.0 ± .7	−11.9
	.04874	.83800	−20.4 ± .4	−11.3	1.0118	−20.7 ± .6	−11.4
KI	.02470	.83623	− 7.5 ± .3	− 8.3	1.0041	− 7.9 ± .2	− 8.6
	.04941	.83713	−14.2 ± .1	− 8.7	1.0064	−13.0 ± .7	− 8.2
$NaNO_3$	.02410	.83646	− 9.2 ± .3	− 9.8	1.0052	− 9.5 ± .4	−10.0
	.04974	.83745	−16.4 ± .4	− 9.6	1.0097	−17.6 ± .4	−10.0
$NaClO_4$	.02462	.83542	− 1.6 ± .3	− 3.5	1.0003	− 2.4 ± .6	− 4.2
	.02924	.83536	− 1.2 ± .4	− 3.2	1.0000	− 2.3 ± .2	− 4.0
	.05012	.83565	− 3.3 ± .3	− 4.3	0.9996	− 3.2 ± .3	− 4.3
	.05863	.83556	− 2.6 ± .6	− 4.1	.9994	− 3.4 ± .2	− 4.4
$HClO_4$[d]	.02980	.83446	+ 5.4[c]	+ 1.1	.9953	+ 4.4 ± .1	+ 0.5
	.04713	.83403	+ 8.5 ± .4	+ 0.6	.9920	+ 8.2 ± .6	+ .5
	.05720	.83365	+11.4 ± .4	+ 0.7	.9899	+10.6 ± .7	+ .5
	.09551	.83238	+20.8 ± .4	+ 0.4	.9820	+19.7 ± .6	+ .2
$NaBPh_4$	.02478	.83206	+22.6 ± .3	+15.8	.9833	+22.5 ± .4	+15.7
	.04932	.82900	+44.4 ± .4	+14.8	.9684	+43.0 ± .4	+14.3
CsCl	.02447	.83692	−12.7 ± .2	−12.5	1.0075	−12.8 ± .3	−12.6
$NaO_3SC_{10}H_7(\beta)$	.02505	.83550	− 2.2 ± .1	− 4.0	1.0015	− 4.2 ± .3	− 5.6
	.05026	.83572	− 3.8 ± .2	− 4.6	1.0016	− 6.1 ± .2	− 5.5
$(CH_3)_4NCl$	.02560	.83712	−14.2 ± .6	−13.3	1.0084	−14.2 ± .3	−13.3
	.05024	.83883	−27.0 ± .2	−13.7	1.0158	−26.4 ± .4	−13.5
Ph_4PCl	.02483	.83468	+ 3.8 ± 1.5	+ 0.8	0.9969	+ 2.5 ± .6	− 0.3
	.05090	.83405	+ 8.3 ± 0.3	+ 0.2	0.9936	+ 5.5 ± .2	− 0.9

[a] W* = 0.83520. [b] ± mean deviation. [c] Single determination. [d] Seven experiments were attempted, but only the four which are reported satisfied our criteria for reproducibility. [e] Results based on vapor composition. [f] Results based on mass ratio; osmotic coefficient assumed equal to that for NaCl.

$\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$ is evaluated by means of equation 5, which was derived previously[4]

$$\frac{1}{RT}\,\frac{\mathrm{d}(F_{C^+}{}^0 + \mathrm{F}_{A^-}{}^0)}{\mathrm{d}Z_1} = \frac{1000}{M_{12}}\left(\frac{\partial \ln \alpha_1/\alpha_2}{\partial m}\right)_{Z_1} - 2\left(\frac{\partial \ln \gamma_\pm}{\partial Z_1}\right)_m + 2mr\left(\frac{\partial \ln \gamma_\pm}{\partial m}\right)_{Z_1} \quad (5)$$

Here, Z_1 is the mole fraction of water in the mixed solvent (not counting the solute),[3] $M_{12} = Z_1M_1 + Z_2M_2$, $Z_2 = 1 - Z_1$, $r = (M_1 - M_2)/M_{12}$, m is the molality of the electrolyte, and $\gamma_\pm$ is the mean ionic activity coefficient; α_1 and α_2 are the ratios of the fugacities of the solvent components over the electrolyte solution to the fugacities over the pure mixed solvent. Note that $F_{C^+}{}^0 + F_{A^-}{}^0$ is on the mole-fractional scale, even though the right side of equation 5 involves molal quantities.

The ratio α_1/α_2 can be obtained in two independent ways: (1) from the vapor composition, W, if we ignore a negligibly small correction resulting from gas imperfections and (2) from the mass ratio, ρ, and the molality, m, if we make a reasonable and not very critical guess about the value of the osmotic coefficient (see Appendix).

Mean ionic activity coefficients can be expressed by the series

$$\ln \gamma_\pm = -Sm^{1/2} + Bm + Cm^{3/2} + \ldots$$

where S is the Debye–Hückel limiting slope, and B, C, . . . are numerical coefficients. Integration of equation 5 then yields for 50 wt. % aqueous dioxane

$$1000\,(\ln \alpha_1/\alpha_2)/M_{12} = (m/RT)\,\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1 + 27.59\,m^{3/2} + bm^2 + cm^{5/2} + \ldots \quad (6)$$

where $27.59 = (2Sr - 4\mathrm{d}S/\mathrm{d}Z_1)/3$, $b = (\mathrm{d}B/\mathrm{d}Z_1 - Br)$, . . .[8] The change of the standard chemical potential of the electrolyte with respect to solvent composition $\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$, can then be calculated provided the coefficients b, c . . . are known. The evaluation of these coefficients for a given electrolyte requires a large number of lengthy experiments. We were, however, interested in obtaining data for a wide variety of electrolytes and therefore assumed that these coefficients had the same values as for NaCl.[4] By working at low molalities (<0.06 m), terms in m^2 and higher powers of m make only a small contribution so that the errors resulting from this procedure are not large. The magnitude of this error is indicated by the fact that the use of the coefficients for HCl,[5] or the assumption that they are zero (limiting law), did not change $\mathrm{d}(F_{C^+}{}^0 + F_{A^-}{}^0)/\mathrm{d}Z_1$ by more than 0.6 kcal.

Results

Electrolytes.—Our results for electrolytes are summarized in Table I; all experiments were carried out in duplicate or triplicate and mean values of W and ρ are reported.

The values for $\ln \alpha_1/\alpha_2$ based on the vapor compositions were calculated by means of equation 34. The values for $\ln \alpha_1/\alpha_2$ based on the mass ratios were calculated *via* equations 37 and 40, assuming that

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(8) Ref. 4, equation 18.

the osmotic coefficients required in this calculation have the same values as those for NaCl at the same concentration. The latter are available from previous work[4] and have the values 1.68 at 0.025 *m*, and 1.58 at 0.05 *m*. The error due to this somewhat arbitrary assumption is serious only if the ions associate to aggregates higher than ion pairs. If the upper limit for the osmotic coefficient is taken as 2 and the lower limit as 1, the corresponding limits in 1000 ln α_1/α_2 are ± 0.4 at 0.025 *m* and ± 0.8 at 0.05 *m*. These error limits are barely larger than the mean deviations of the experimental data.

As shown in Table I, the two sets of results for ln α_1/α_2 generally agree within experimental error, except in the case of sodium β-naphthalenesulphonate. Here the discrepancies are in such a direction as to suggest the formation of micelles, but further work is required before this point can be established. For this reason, the procedure adopted in calculating $\mathrm{d}(F_{\mathrm{C}^+}{}^0 + F_{\mathrm{A}^-}{}^0)\mathrm{d}Z_1$ for this compound may be incorrect. In aqueous solution at comparable concentrations, micelle formation has been reported for sodium *d,l*-10-camphorsulfonate[9a] and for several sodium arylsulfonates.[9b]

On the other hand, the evidence is probably against micelle formation in the case of the large-ion salts, sodium tetraphenylboride and tetraphenylphosphonium chloride. This result is consistent with the fact that critical micelle concentrations are usually quite high when several large groups are attached to the center of charge.[10a] Thus tetra-*n*-butylammonium tetraphenylboride has been reported to be a "normal" electrolyte in a number of organic solvents.[10b]

The results for perchloric acid are subject to an unknown determinate error. In three out of a total of seven experiments, the vapor compositions changed gradually with time, possibly due to the formation of volatile oxidation products. These three experiments are not being reported. While there was no evidence for such drifts in the experiments reported in Table I, it is possible that they too are somewhat inaccurate.

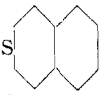
Average values of $\mathrm{d}(F_{\mathrm{C}^+}{}^0 + F_{\mathrm{A}^-}{}^0)/\mathrm{d}Z_1$ for 50 wt % dioxane–water are summarized in Table II.

Non-electrolytes.—We also measured $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ for tetraphenylmethane (Ph_4C), *neo*-pentane [$(CH_3)_4C$] and *penta*-erythritol [$(HOCH_2)_4C$]. These substances are interesting model compounds which resemble some of the ions but carry no net charge.

For *penta*-erythritol, $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ was determined by the vapor pressure method. The result was −0.6 ± 0.3 kcal. in 50 wt. % dioxane–water at 25.00°.

TABLE II

VALUES OF $\mathrm{d}(F_{\mathrm{C}}{}^{+0} + F_{\mathrm{A}}{}^{-0})/\mathrm{d}Z_1$ IN 50.00 WT. % DIOXANE–WATER AT 25.00°

Electrolyte	$\mathrm{d}(F_{\mathrm{C}^+}{}^0 + F_{\mathrm{A}^-}{}^0)/\mathrm{d}Z_1$ (kcal.)	Electrolyte	$\mathrm{d}(F_{\mathrm{C}^+}{}^0 + F_{\mathrm{A}^-}{}^0)/\mathrm{d}Z_1$ (kcal.)
NaOH	−17.6[a]	$NaNO_3$	− 9.8
NaCl	−13.8[b]	KI	− 8.5
KCl	−13.8	HCl	− 7.9[a]
$(CH_3)_4NCl$	−13.5	NaO_3S 	− 4.5
RbCl	−13.2[c]	$NaClO_4$	− 4.0
CsCl	−12.5	Ph_4PCl	+ 0.2
LiCl	−11.5	$HClO_4$	+ 0.6[d]
KBr	−11.3	$NaBPh_4$	+15.4

[a] Ref. 5. [b] Ref. 4. [c] Preliminary result obtained by Leon Gibson. [d] Value may be in error; see text.

For tetraphenylmethane, the extremely low solubility prevented the use of the vapor pressure method. Instead, the solubility of this substance was measured as a function of Z_1 and $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ deduced from the equation

$$\frac{\mathrm{d}F_3{}^0}{\mathrm{d}Z_1} = -RT\frac{\mathrm{d}\ln s_3}{\mathrm{d}Z_1} \tag{7}$$

where s_3 is the (mole-fractional) solubility. The solubility could be determined with sufficient accuracy by spectrophotometry in the wave length range, 218–230 mμ, being of the order of micromoles/liter. We measured the solubility for $Z_1 = 0.85$ (46.319 wt. % dioxane) and for $Z_1 = 0.81$ (53.422 wt. % dioxane). We then assumed that $\mathrm{d}\ln s_3/\mathrm{d}Z_1$ for $Z_1 = 0.83$ (50 wt. % dioxane) is equal to $\delta\ln s_3/\delta Z_1$ as deduced from the preceding measurements. For the aromatic hydrocarbon, naphthalene, this procedure gives excellent results.[11a]

The results for tetraphenylmethane are shown in Table III. The solubilities were measured only after extensive purification of this compound, in order to minimize errors due to traces of soluble impurities. The observed values of $\delta\ln s_3/\delta Z_1$ approached a constant limit after three recrystallizations. The final value for $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ was 20.4 ± 0.6 kcal.

TABLE III

SOLUBILITY OF TETRAPHENYLMETHANE IN THE SYSTEM DIOXANE–WATER AT 25.00°

No. recrys-talliz.	Shaking period (hr.)	s_3 (mole fraction) $Z_1 = 0.85$	s_3 (mole fraction) $Z_1 = 0.81$	$\delta\ln s_3/\delta Z_1$
4	32	8.35×10^{-8}	3.30×10^{-7}	−34.4
5	21	7.57×10^{-8}	2.88×10^{-7}	−33.4
	65	7.41×10^{-8}	3.06×10^{-7}	−35.5
			Average:	−34.4

For neopentane, $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ was deduced from measurements of the Henry's law constant of the gas as a function of Z_1, using standard experimental methods.[11b] Our results are summarized in Table IV. The final value of $\mathrm{d}F_3{}^0/\mathrm{d}Z_1$ was 11.8 ± 0.5 kcal.

Discussion

Values of $\mathrm{d}F^0/\mathrm{d}Z_1$ for Single Ions.—In order to discuss the solvation of ions, it is evidenty desirable to break down the experimental values of $\mathrm{d}(F_{\mathrm{C}^+}{}^0 +$

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(9) (a) L. Fuchs, measurements communicated to A. Jensen, F. Basolo and H. M. Neumann, THIS JOURNAL, **80**, 2354 (1958). (b) H. M. Hubbard and C. A. Reynolds, *ibid.*, **76**, 4300 (1954).

(10) (a) M. E. L. McBain and E. Hutchinson, "Solubilization," Academic Press, Inc., New York, N. Y., 1955. (b) R. M. Fuoss, J. B. Berkowitz, E. Hirsch and S. Petrucci, *Proc. Natl. Acad. Sciences* (*U. S.*), **44**, 27 (1958).

(11) (a) E. Grunwald and G. Baughman, *J. Phys. Chem.*, **64**, 933 (1960). (b) R. W. Taft, E. L. Purlee and P. Riesz, THIS JOURNAL, **77**, 899 (1955).

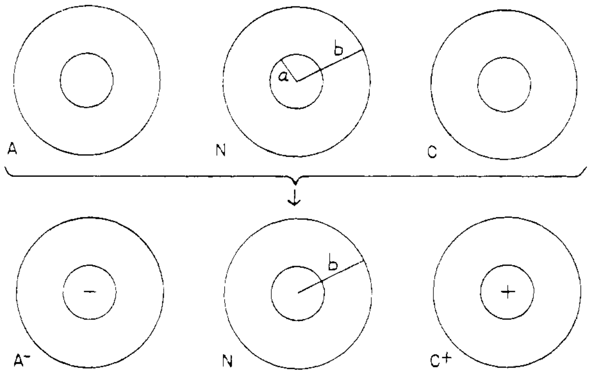


Fig. 1.—Model for obtaining values of $\mathrm{d}F^0/\mathrm{d}Z_1$ for single ions.

$F_{A^-}{}^0)/\mathrm{d}Z_1$ into separate terms for cation and anion. Since this cannot be done within the framework of classical thermodynamics, we propose the following extrathermodynamic approach.

TABLE IV

HENRY'S LAW CONSTANTS (p_3/N_3, IN ATM.) FOR NEOPENTANE AT 25° IN DIOXANE–WATER MIXTURES

Dioxane, wt. %	Z_1	Mole-fraction neopentane ($\times 10^4$)	p_3 (atm.)	p_3/N_3 (atm.)
46.319	0.8500	0.651	0.2465	3790
		1.304	.5033	3860
50.000	.8302	0.886	.2312	2610
		1.920	.4921	2560
53.422	.8100	1.218	.2069	1700

To begin, let us consider the idealized thought-experiment shown in Fig. 1. Each of the three identical systems, denoted as C, N and A, consists of a central spherical conductor with radius a, around which there is a spherical insulating layer with outer radius b and dielectric constant ϵ_i. Let us suppose that these systems are of submicroscopic dimensions and that they are immersed in a medium of dielectric constant ϵ. Now let C and A be charged reversibly at constant pressure and temperature to produce C^+ and A^-. If the radius, b, is sufficiently large, the work required per mole of "ions" so produced is given by equation 8,

$$W_{\mathrm{el}} = \frac{N_{\mathrm{Av}}e^2}{2}\left[\frac{1}{b\epsilon} + \frac{1}{\epsilon_i}\left(\frac{1}{a} - \frac{1}{b}\right)\right] \qquad (8)$$

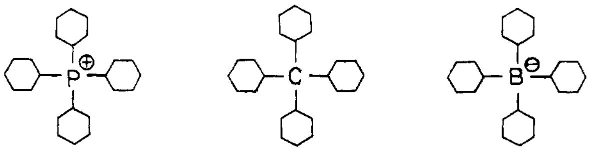
where e is the electronic charge and N_{Av} is Avogadro's number.[12] Hence we obtain equations 9 and 10 for the "standard partial molal free energy" of our idealized particles. Equation 10 suggests

$$F_{C^+}{}^0 = F_{A^-}{}^0 = F_N{}^0 + \frac{N_{\mathrm{Av}}e^2}{2}\left[\frac{1}{b\epsilon} + \frac{1}{\epsilon_i}\left(\frac{1}{a} - \frac{1}{b}\right)\right] \qquad (9)$$

$$\frac{\mathrm{d}F_{C^+}{}^0}{\mathrm{d}Z_1} = \frac{\mathrm{d}F_{A^-}{}^0}{\mathrm{d}Z_1} = \frac{\mathrm{d}F_N{}^0}{\mathrm{d}Z_1} - \frac{N_{\mathrm{Av}}e^2}{2b\epsilon}\frac{\mathrm{d}\ln\epsilon}{\mathrm{d}Z_1} \qquad (10)$$

a simple limiting law for obtaining values of $\mathrm{d}F^0/\mathrm{d}Z_1$ for single ions: as the structure of the ion is systematically changed so that the unsolvated radius becomes very large, while the charge remains "buried" at the center, $\mathrm{d}F^0/\mathrm{d}Z_1$ for the ion approaches $\mathrm{d}F^0/\mathrm{d}Z_1$ for the corresponding nonelectrolyte, *plus* a coulombic term. Physically, this means that the solvation of a large ion with very low density of surface charge closely resembles that of an uncharged molecule of equal size and structure.

In an attempt to come close to the conditions under which the limiting law might apply, we have studied the system



Tetraphenylphosphonium ion Tetraphenylmethane Tetraphenylboride ion

This system is not completely satisfactory because the phenyl groups are not perfect insulators. Particularly in the case of tetraphenylphosphonium ion one can write resonance structures in which the *plus*-charge is on the *ortho*- and *para*-positions of the benzene rings and in which the phosphorus atom swells its octet. However, the density of surface charge is not high— +0.18 unit of ionic charge for each phenyl group in the Ph_4P^+ ion, according to Pauling's method of calculation,[13] and certainly less in the Ph_4B^- ion. Moreover, the three molecules have nearly the same size and shape and the dissimilar central atoms are not in contact with solvent molecules.[14] As shown in Fig. 2, for Ph_4C the shortest distance from the center to the surface is 2.9 Å., and the longest distance (to the surface of the *para*-hydrogen atom) is 6.7 Å°. The effective average radius is taken as the harmonic mean[15] of 2.9 and 6.7 Å. or 4.05 Å. Similarly, the average radius of Ph_4P^+ and Ph_4B^- is found to be 4.2 Å.

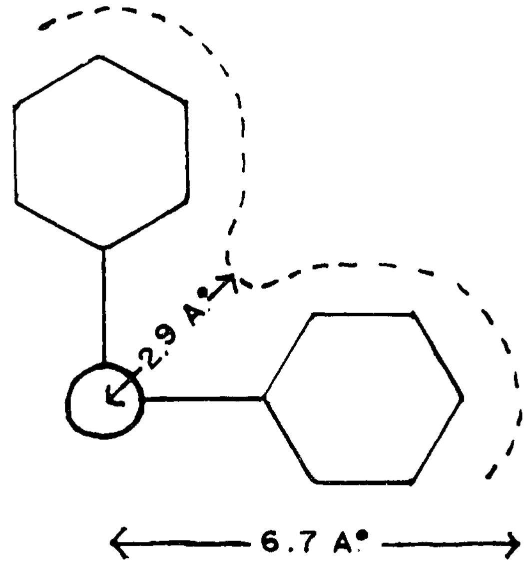


Fig. 2.—Dimensions of the Ph_4C molecule.

Another way of estimating the effective radius of these molecules is from their molar volumes. The

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[12] A careful thermodynamic analysis of the perturbing effects of high electric fields has been given by H. S. Frank, *J. Chem. Phys.*, **23**, 2023 (1955).

[13] L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

[14] M. N. Papadopoulos and E. L. Derr, THIS JOURNAL, **81**, 2285 (1959), have similarly assumed that a quaternary carbon atom does not interact appreciably with external solvent molecules.

[15] The *harmonic* mean is used because equations 8–10 require the effective average of $1/b$.

molar volume of tetraphenylmethane, as estimated from group volumes,[14] is 282 ml. at 20°. Assuming random packing of spheres,[16] the average radius per molecule is then calculated as 4.02 Å., in good agreement with the value of 4.05 Å. obtained above.

For 50 wt.% dioxane–water at 25°, $\epsilon = 35.85$ and $d \ln \epsilon / dZ_1 = 4.35$.[17] Thus, if equation 10 were applicable, it would require that

$$\frac{d(F_{Ph_4P^+}{}^0 + F_{Ph_4B^-}{}^0)}{dZ_1} = 2\,\frac{dF_{Ph_4C}{}^0}{dZ_1} - 9.6 \text{ (kcal.)}$$

The experimental results are

$$2\,\frac{dF_{Ph_4C}{}^0}{dZ_1} - 9.6 = 31.2 \pm 1.2 \text{ kcal.} \qquad (14)$$

$$\begin{aligned} dF^0/dZ_1 \text{ for } Ph_4\,PCl &= +\ 0.2 \pm 1.0 \\ \text{for } NaBPh_4 &= +15.4 \pm 0.8 \\ -dF^0/dZ_1 \text{ for } NaCl &= \underline{-(-13.6 \pm 0.1)} \\ dF^0/dZ_1 \text{ for } Ph_4PBPh_4 &= +29.4 \pm 1.3 \text{ kcal.} \qquad (15) \end{aligned}$$

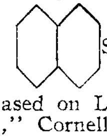
The agreement between (14) and (15) is really quite good and lends strong support to the notion that the theoretical limiting case of very large radius has been approached with sufficient accuracy. We shall therefore assume that

$$\frac{dF_{Ph_4P^+}{}^0}{dZ_1} = \frac{dF_{Ph_4B^-}{}^0}{dZ_1} = \frac{1}{2}\,\frac{d(F_{Ph_4P^+}{}^0 + F_{Ph_4B^-}{}^0)}{dZ_1} = 14.7 \text{ kcal.} \qquad (16)$$

Making use of equation 16 and the data in Table II, values of $dF°/dZ_1$ can be calculated for individual ions. The results are listed in Table V.

TABLE V

FORMAL VALUES OF dF^0/dZ_1 FOR SINGLE IONS IN 50 WT. % DIOXANE–WATER AT 25°, BASED ON EQUATION 16

Ion	$\frac{dF^0}{dZ_1}$ (kcal.)	Unsolvated radius (Å.)
Ph_4P^+	(14.7)	4.2
Li^+	3.0	0.60[a]
Na^+	0.7	0.95[a]
K^+	0.7	1.33[a]
Rb^+	1.3	1.48[a]
Cs^+	2.0	1.69[a]
$(CH_3)_4N^+$	1.0	3.0[b]
H^+	6.6	1.4[c]
Ph_4B^-	(14.7)	4.2
Cl^-	−14.5	1.81[a]
Br^-	−12.0	1.95[a]
I^-	− 9.2	2.16[a]
OH^-	−18.3	1.4
NO_3^-	−10.5	1.78[a]
ClO_4^-	− 4.7	2.00[a]
 SO_3^-	− 5.2	3.6[a]

Based on L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, Chapters 5 and 10; and J. W. Cobble, *J. Chem. Phys.*, 21, 1443 (1953). [b] Average radius, estimated from molecular models. [c] For H_3O^+.

However, before discussing these results, let us consider the possibility that the fair agreement between (14) and (15) is accidental. This leads to the question: how large does an ion have to be in order that its solvation resemble that of the corresponding non-electrolyte? In water, recent calculations of the dielectric constant as a function of the electric field[18] suggest that the (integral) dielectric coefficient is within 95% of the low-field value at a distance of 4.4 Å. from a univalent point charge. Furthermore, the lowering of the dielectric constant caused by the addition of small-ion inorganic salts can be best understood if it is attributed mainly to water molecules immediately adjacent to the ions.[19] Next-nearest water molecules, located at distances of 4–5 Å. for small ions, appear to have almost "normal" dielectric properties. Furthermore, recent applications of Stokes' law to the limiting ionic diffusion coefficients make it appear probable that tetraethylammonium ion, with an average radius of 4.00 Å., is already unhydrated.[20] While these considerations do not *prove* that the tetraphenyl compounds are sufficiently large, they nevertheless make it appear plausible.

The use of equations analogous to (9) is not original with us. For example, Zucker and Hammett,[21] writing in 1939, suggested that the change in the standard partial molar free energy with solvent composition for complex organic molecules might be an additive function for the individual groups in the molecule, *plus* a term for the electrical charge. This postulate is sufficient to explain the existence of acidity functions[21–23]; it has been used with fair success in studies of reaction mechanism[21,22]; and equation 9 is readily derived from it. However, our own method of obtaining equation 9, which regards this equation as a limiting law and insists that the ionic charge be surrounded by a sizable insulating layer, seems to us to involve fewer and less drastic assumptions.

Models of Small-ion Solvation.—In the remainder of this paper we shall accept equation 16 as being essentially correct and examine its consequences. Values of dF^0/dZ_1 for single ions calculated on this basis are listed in Table V. We shall assume that the error of these values due to the inaccuracy inherent in our extrathermodynamic approach is no greater than the discrepancy between equations 14 and 15, or 3–4 kcal. at the most.

The most striking feature of the numbers given in Table V is that the values of dF^0/dZ_1 for small cations are so much greater (in the algebraic sense) than those for small anions. For example, the average difference between values for the alkali cations and for the halide ions is 13 kcal. Within the framework of our assumptions this difference is highly significant. Even if the values for the cations were too great and those for the anions too

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[16] R. H. Stokes and R. A. Robinson, *Trans. Faraday Soc.*, **53**, 301 (1957). The actual volume of the molecules is 58% of the total volume.

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

[18] (a) D. C. Grahame, *J. Chem. Phys.*, **21**, 1054 (1953). (b) F. Booth, *ibid.*, **19**, 1327, 1615 (1951).

[19] J. B. Hasted, D. M. Ritson and C. H. Collie, *ibid.*, **16**, 1, 11 (1948).

[20] (a) E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 1381 (1959). (b) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, Inc., New York, N. Y., 1955, Chapter 6.

[21] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[22] (a) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957). (b) F. A. Long and M. A. Paul, *ibid.*, **57**, 935 (1957).

[23] E. Grunwald, *J. Phys. Colloid Chem.*, **55**, 881 (1951).

small, by 3–4 kcal., there would still be a sizable difference. We shall therefore inquire whether this difference implies a difference in the composition of the "tight" solvation shells surrounding cations and anions.

Rather than choose any particular theoretical approach, it is helpful at the outset to consider some of the models that have been used previously in discussions of small-ion solvation. We recognize two extreme types: the purely coulombic models and the chemical models.

A purely coulombic model for the solvation of small ions in media consisting of water and a less polar organic component was formulated by Debye in 1927[24] and has since been extended by others.[12,25] If the two-component solvent is treated as an ideal mixture and if the only effect of each ion is to produce an electric field (specific non-ideal ion-solvent interaction of short range being neglected), then the solvent composition varies with distance from the ion, r, approximately according to equation 17, where r is in Å. and $Z_1{}^0$ and $Z_2{}^0$ are the mole fractions at great distances from the ion.[26] Upon substituting numerical

$$\log \frac{Z_1}{Z_2} - \log \frac{Z_1{}^0}{Z_2{}^0} = \frac{467}{\epsilon r^4}\,\frac{\mathrm{d} \ln \epsilon}{\mathrm{d}Z_1} \qquad (17)$$

values for 50 wt. % dioxane–water ($Z_1{}^0$ is taken as 0.8302), equation 17 becomes

$$\log Z_1/Z_2 = \frac{56.7}{r^4} + 0.689 \qquad (18)$$

For definiteness, let us consider the sorting of solvent molecules immediately adjacent to a potassium ion. In water, the average distance from the potassium ion to adjacent water molecules is 2.9 Å.[27] Upon solving equation 18 for this distance, we obtain $Z_1 = 0.969$; that is, the nearest neighbors to potassium ion are almost exclusively water molecules. Since the region near the ion is greatly enriched in water, the region far from the ion is slightly enriched in dioxane and slightly depleted in water. This model therefore predicts that dioxane is "salted out" and water is "salted in" by potassium ion. Hence α_1/α_2 must be less than unity, and, according to equation 6, $\mathrm{d}F^0/\mathrm{d}Z_1$ for potassium ion must be negative.

This purely coulombic model is inconsistent with our data on two counts. First, it predicts that $\mathrm{d}F^0/\mathrm{d}Z_1$ for single ions is *always* negative since Z_1 in the solvent shell adjacent to an ion is always expected to be greater than $Z_1{}^0$. Second, it predicts that $\mathrm{d}F^0/\mathrm{d}Z_1$ is greater (in the algebraic sense) for the halide ions than for the alkali metal ions since $\mathrm{d}F^0/\mathrm{d}Z_1$ is expected to increase with the unsolvated ionic radius.

In view of these inconsistencies, the chemical models are of special interest. The important feature of these models is that small ions are thought to "associate" with a number of solvent molecules to form firm kinetic units of definite structure in which the solvent molecules bear a more-than-formal resemblance to, say, the phenyl groups in tetraphenylphosphonium ion. The ion-solvent bond need not be covalent but has at least *some* covalent character. The ion-solvent complex then interacts coulombically with the surrounding medium; if the complex is sufficiently large, W_{el} may be calculated from equation 8.

In a one-component solvent it is difficult to decide whether the small ion-solvent interaction is more aptly described by a purely coulombic model or by a chemical one. For example, for small cations in aqueous solution there is evidence from transport and dielectric relaxation phenomena that kinetic units consisting of the ion and a few water molecules are produced and that the water molecules in these units are "irrotationally" bound.[19,20,28] These phenomena are, however, consistent with either model, since the same macroscopic result is obtained whether the solvent molecules adjacent to the ion are bound solely by the strong electrical field or whether there is also a specific chemical interaction. On the other hand, in a two-component solvent such as dioxane–water, a distinction is possible if there is a way of finding the composition of the solvation shells. While the purely coulombic model predicts that there is always a sorting of water molecules, the chemical model can accommodate preferment of either component. For example, a given cation might have a greater affinity for dioxane than for water.

Solvation of Small Cations.—The purely coulombic model is not at all helpful in interpreting the values of $\mathrm{d}F^0/\mathrm{d}Z_1$ for small cations in Table V. The values are generally positive, whereas the model requires that $\mathrm{d}F^0/\mathrm{d}Z_1$ be always negative. If we allow for possible error in equation 16 and subtract 3–4 kcal. from all values, some of the values do become slightly negative. But even though this arbitrary "correction" can give us the "right" sign, it still leaves us with the "wrong" magnitude. To accommodate the slightly negative values, we must postulate ionic radii that are too large to be physically reasonable.

We shall therefore interpret the values on the basis of a chemical model and, furthermore, assume that the solvated ions are large enough so that equation 10 may be used. In this context, N refers to an uncharged analog of the *solvated* ion. Although the coulombic term in equation 10 is always negative, the term, $\mathrm{d}F_{\mathrm{N}}{}^0/\mathrm{d}Z_1$, may conceivably be positive, so that positive values of $\mathrm{d}F_{\mathrm{C}^+}{}^0/\mathrm{d}Z_1$ can be accommodated, at least in principle.

When we use this approach, we find that small cations are *not* solvated preferentially by water molecules. Since this result contradicts a commonly-made assumption, we shall describe our method in detail.

For definiteness, let us consider potassium ion. In water, X-ray data indicate that potassium ion forms a substitutional solution, with most of the ions surrounded by four tetrahedrally oriented water molecules.[27] The average radius of the tetrahedral $\mathrm{K^+{\cdot}4H_2O}$ ion, as inferred from the X-ray data,[27] is about 3.5 Å. We shall therefore calculate $\mathrm{d}F^0/\mathrm{d}Z_1$ in 50 wt. % dioxane–water on the

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[24] P. Debye, *Z. physik. Chem.*, **130**, 56 (1927).

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

[26] Ref. 12, equation 42.

[27] (a) G. W. Brady and J. T. Krause, *J. Chem. Phys.*, **27**, 304 (1957); (b) G. W. Brady, *ibid.*, **28**, 464 (1958).

[28] (a) G. H. Haggis, J. B. Hasted and T. J. Buchanan, *ibid.*, **20**, 1452 (1952); (b) J. B. Hasted and G. W. Roderick, *ibid.*, **29**, 17 (1958).

assumption that the effective solute species is $K^+ \cdot 4H_2O$.

First, we note that equation 10 applies to the actual *solvated* species, whereas the values of $\mathrm{d}F^0/\mathrm{d}Z_1$ in Table V are *formal* values, computed for ions which are formally regarded as not forming solvation complexes. Using a straightforward thermodynamic approach analogous to that employed by Stokes and Robinson for aqueous salt solutions,[29] it can be shown (see Appendix) that

$$\left(\frac{\mathrm{d}F_{K^+}{}^0}{\mathrm{d}Z_1}\right)_{\text{formal value}} = \left(\frac{\mathrm{d}F^0}{\mathrm{d}Z_1}\right)_{K^+ \cdot 4H_2O} - 4RT\frac{\mathrm{d}\ln a_1}{\mathrm{d}Z_1} \quad (19)$$

where a_1 is the water activity. For 50 wt. % dioxane–water at 25°, $\mathrm{d}\ln a_1/\mathrm{d}Z_1 = 0.624$.[6] Hence, upon combining equations 19 and 10, and solving for an ion with 3.5 Å. radius in 50 wt. % dioxane–water at 25°, we obtain

$$\left(\frac{\mathrm{d}F_{K^+}{}^0}{\mathrm{d}Z_1}\right)_{\text{formal value}} = \left(\frac{\mathrm{d}F^0}{\mathrm{d}Z_1}\right)_{N \cdot 4H_2O} - 7.24\ (\text{kcal.}) \quad (20)$$

where the formal value is given in Table V as +0.7 kcal. Thus if the solvated ion were indeed $K^+ \cdot 4H_2O$, as assumed, $\mathrm{d}F^0/\mathrm{d}Z_1$ for the analogous uncharged structure $N \cdot 4H_2O$ would have to be close to +7.9 kcal. Our method of showing that the solvated ion is *not* $K^+ \cdot 4H_2O$ consists in showing that the latter prediction is absurd.

Two independent methods are used. In the first method, we approximate the uncharged tetrahydrate by the model substance, *penta*-erythritol, $(HOCH_2)_2C(CH_2OH)_2$. Admittedly this model has its flaws, but the molecules do have a tetrahedral structure with four exposed OH- groups and are of nearly the right size. On this basis, $(\mathrm{d}F^0/\mathrm{d}Z_1)_{N \cdot 4H_2O}$ is found to be -0.6 ± 0.3 kcal.

In the second method, $(\mathrm{d}F^0/\mathrm{d}Z_1)_{N \cdot 4H_2O}$ is estimated by a more theoretical approach. According to the method of Zucker and Hammett[21] and its recent refinements,[14,30] large molecules are subdivided into smaller substructures, such as CH_3-groups, OH-groups, etc., each of which is thought to interact with external solvent independently of the others. Formally, one must consider all substructures into which the molecule is divided. But according to Papadopoulos and Derr,[14] only those substructures that are actually in contact with external solvent make a significant contribution.[30a] On this basis, $\mathrm{d}F^0/\mathrm{d}Z_1$ for the uncharged analog of $K^+ \cdot 4H_2O$ is the resultant of interactions involving the exposed portions of the four water molecules of hydration. If we assume an ice-like structure, there will be twelve nearest-neighbor sites around the miniature "iceberg" which represents our tetrahydrate, as compared to four sites around a single water molecule. Thus, to this order of approximation

$$\left(\frac{\mathrm{d}F^0}{\mathrm{d}Z_1}\right)_{N \cdot 4H_2O} = \frac{12}{4}\,\frac{\mathrm{d}F_1{}^0}{\mathrm{d}Z_1} = 3RT\,\frac{\mathrm{d}\ln(a_1/Z_1)}{\mathrm{d}Z_1} \quad (21)$$

or −1.0 kcal., since $RT\,\mathrm{d}\ln(a_1/Z_1)/\mathrm{d}Z_1 = -0.344$ kcal. for 50 wt. % dioxane–water at 25°. This value is gratifyingly close to the value, −0.6 kcal., obtained from *penta*-erythritol but differs by over 8 kcal. from the value required by equation 20! Since the discrepancies are similarly large for any other reasonable hydration number, our model clearly indicates that the ions are not solvated *exclusively* by water molecules. Analogous results are obtained for the other alkali metal ions and for the hydrogen ion.

Next, we shall extend this method to obtain a rough estimate of the average number of dioxane molecules associated with these cations. If a given ionic species is solvated by n_1 water molecules and n_2 dioxane molecules, the thermodynamic equation analogous to (19) is

$$\left(\frac{\mathrm{d}F_{M^+}{}^0}{\mathrm{d}Z_1}\right)_{\text{formal value}} = \left(\frac{\mathrm{d}F^0}{\mathrm{d}Z_1}\right)_{M^+ \cdot n_1 \cdot n_2} - n_1RT\,\frac{\mathrm{d}\ln a_1}{\mathrm{d}Z_1} - n_2RT\,\frac{\mathrm{d}\ln a_2}{\mathrm{d}Z_1} \quad (22)$$

For definiteness, we shall again consider potassium ion. Using equation 10 to evaluate $(\mathrm{d}F^0/\mathrm{d}Z_1)_{K^+ \cdot n_1 \cdot n_2}$, we obtain

$$\left(\frac{\mathrm{d}F_{K^+}{}^0}{\mathrm{d}Z_1}\right)_{\text{formal value}} = \left(\frac{\mathrm{d}F^0}{\mathrm{d}Z_1}\right)_{N \cdot n_1 \cdot n_2} - n_1RT\,\frac{\mathrm{d}\ln a_1}{\mathrm{d}Z_1} - n_2RT\,\frac{\mathrm{d}\ln a_2}{\mathrm{d}Z_1} - \frac{N_{Av}e^2}{2b\epsilon}\,\frac{\mathrm{d}\ln \epsilon}{\mathrm{d}Z_1} \quad (23)$$

where b is the average radius of the solvated ions, and $N \cdot n_1 \cdot n_2$ is a non-electrolyte identical with the solvated ion except for the absence of the central charge.

A simple method of estimating b makes use of the partial molal volume, $V_{i,\text{solv.}}$, of the *solvated* ion. The latter is calculated from the *formal* partial molal volumes of the ion (V_i), water (V_1) and dioxane (V_2) by the thermodynamic equation

$$V_{i,\text{solv.}} = V_i + n_1V_1 + n_2V_2 \quad (24)$$

Comparison with molecular models indicates that the most realistic value of b is obtained by assuming random packing of spheres[16]

$$V_{i,\text{solv.}} = 4.35 \times 10^{24}b^3 \quad (25)$$

In the present case, we shall use the values: $V_{K^+} = 1.5$ ml.,[16] $V_1 = 17.8$ ml.,[31] and $V_2 = 83.6$ ml.[31] Values of b obtained in this way for several plausible values of n_1 and n_2 will be shown later.

The estimation of $\mathrm{d}F^0/\mathrm{d}Z_1$ for $N \cdot n_1 \cdot n_2$ is more difficult than for the corresponding tetrahydrate. The dioxane molecule is probably too large to be treated as a single interacting group in the same way as the water molecule. Moreover, since one, or —possibly—both of the oxygen atoms are coordinated with the potassium ion, the portion of the dioxane molecule which is actually in contact with external solvent is probably less polar than the entire molecule. On account of these uncertainties, it did not seem practical to attempt a calculation for a model which assumes the interaction of exposed groups.

On the other hand, if we resort to the next *lower* approximation, which is represented by the unmodified postulate of Zucker and Hammett,[21]

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[29] R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).

[30] See, for example: (a) J. A. Barker, I. Brown and F. Smith, *Discussions Faraday Soc.*, **15**, 141 (1953); (b) O. Redlich, E. L. Derr and G. J. Pierotti, THIS JOURNAL, **81**, 2283 (1959).

[30a] This represents an improvement over the original postulate of Zucker and Hammett,[21] according to which the interaction of a group is independent of how large a fraction of the surface of the group is actually exposed.

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

calculation of dF^0/dZ_1 for $N{\cdot}n_1{\cdot}n_2$ becomes easy and direct. According to this approximation, dF^0/dZ_1 is simply an additive function for all substructures. Thus

$$\left(\frac{dF^0}{dZ_1}\right)_{N\cdot n_1\cdot n_2} = n_1\frac{dF_1{}^0}{dZ_1} + n_2\frac{dF_2{}^0}{dZ_1} + \left(\frac{dF^0}{dZ_1}\right)_{\text{central atom}} \quad (26)$$

Solubility data for inert gases suggest that dF^0/dZ_1 for a neutral atom of the size and polarizability of potassium ion would be in the range of from 0 to 2 kcal.[32]; we shall adopt a value of 1.0 kcal. Since, from thermodynamics

$$dF_1{}^0/dZ_1 = RT(d \ln a_1/dZ_1 - 1/Z_1)$$

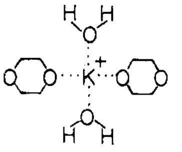
$$dF_2{}^0/dZ_1 = RT\,(d \ln a_2/dZ_1 + 1/Z_2)$$

we obtain upon substitution of (26) in (23)

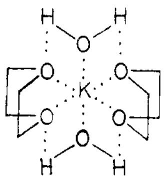
$$\left(\frac{dF_{K^+}{}^0}{dZ_1}\right)_{\text{formal value}} = -\frac{n_1RT}{Z_1} + \frac{n_2RT}{Z_2} - \frac{N_{Av}e^2}{2b\epsilon}\,\frac{d \ln \epsilon}{dZ_1} + 1.0\ (\text{kcal.}) \quad (27)$$

Since equation 27 contains two unknown parameters, n_1 and n_2, unique solution is evidently not possible. However, dF^0/dZ_1 is not very sensitive to the assumed value of n_1, since changes in the term n_1RT/Z_1 tend to be compensated by changes in the Born charging term on account of its dependence on b. As long as n_1 remains within a reasonable range, the value of n_2 required to obtain agreement with +0.7 kcal. is close to 2. We therefore suggest that the average dioxanation number of potassium ion is near 2.

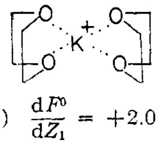
A most satisfying aspect of this result is that one can postulate some very reasonable structures in which potassium ion is complexed to two dioxane molecules. Some of these are shown in (28) to (30), together with calculated values of dF^0/dZ_1 and b for each. Of course, the actual state of dissolved potassium ion is an equilibrium state consisting of a number of species such as these. However, as shown in the Appendix, species for which dF^0/dZ_1 differs greatly from the average value for the all-inclusive formal solute species are not present in appreciable amounts.



(28) $\dfrac{dF^0}{dZ_1} = +1.0$ kcal.
$b = 3.61$ Å.



(29) $\dfrac{dF^0}{dZ_1} = +1.0$ kcal.
$b = 3.61$ Å.



(30) $\dfrac{dF^0}{dZ_1} = +2.0$ kcal.
$b = 3.39$ Å.

Analogous calculations lead to dioxanation numbers in the neighborhood of two also for the other alkali metal ions and to a dioxanation number of three for the solvated hydrogen ion. If water is a stronger base than dioxane,[33] the solvated hydrogen ion might be depicted as consisting of a central H_3O^+ ion, with each proton "hydrogen-bonded" to a dioxane molecule.

In this connection, it may be significant that many electrolytes crystallize from dioxane or dioxane–water mixtures with dioxane of crystallization. Thus, solid dioxanates have been reported of LiCl, LiBr, LiI, NaI, KI, $NaClO_4$, NH_4I, $AgClO_4$, $SbCl_3$ $HgCl_2$ and $TiBr_4$.[34–37]

Solvation of Small Anions.—There is evidence for aqueous solutions that the water molecules around simple inorganic anions, such as Cl^-, have considerably more rotational freedom than those around simple cations, such as K^+. This is partly because of the larger size of anions and partly because of a difference in the orientation of water molecules adjacent to cations and anions.[19,28,38] ($M^+ \ldots OH_2$ vs. $X^- \ldots HOH$). Thus Hasted and coworkers[19,28] have interpreted their data on the dielectric properties of aqueous salt solutions on the assumption that most of the "irrotational" binding of water molecules takes place around cations rather than anions. If the rotational mobility of water molecules in the solvation shell of anions were indeed high, the chemical model might not be a good one. However, be that as it may, the highly negative values obtained for dF^0/dZ_1 of small anions (Table V) indicate that these ions are surrounded primarily by water molecules, regardless of which reasonable model is used to interpret the results. Thus we suggest that Cl^-, Br^-, I^-, OH^- and NO_3^- are predominantly hydrated in 50 wt. % dioxane–water. On the other hand, the value of dF^0/dZ_1 for ClO_4^- is appreciably greater, suggesting possibly that solvation by dioxane is not negligible. Although it is difficult to write a plausible structure for a perchlorate–dioxane complex, the possibility of complex formation between perchlorate ion and organic non-electrolytes in aqueous solution has been suggested before.[39]

Large Organic Ions.—The good agreement between equations 14 and 15 suggests that the solvation of large organic ions with low density of surface charge is very much like that of the corresponding structures without a net charge. Thus there is no necessity in most cases to expect a large excess of the more polar solvent component in the vicinity of the ion; indeed, the mole fractions may be rather like those in the bulk of the solvent. In support of this view, there are a number of examples where a carbonium ion intermediate has reacted with the less polar, more "organic" component of a mixed solvent.[40]

Furthermore, the postulate that large organic ions interact with adjacent solvent molecules in much the same way as the corresponding uncharged

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[32] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Chapter XV.

[33] H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).

[34] C. C. Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

[35] H. Rheinboldt, A. Luyken and H. Schmittman, *J. prakt. Chem.*, **148**, 81 (1937).

[36] L. W. Daasch, *Spectrochim. Acta*, 726 (1959); R. F. Rolsten and H. H. Sisler, THIS JOURNAL, **79**, 1819 (1957).

[37] E. F. J. Duynstee and E. Grunwald, unpublished work.

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structure enables us to explain a number of facts that otherwise seem to defy explanation. We shall discuss only one of these: Miller and Fuoss[41] have reported the following ion-pair dissociation constants for tetra-*n*-butylammonium bromide at 25°

$$\text{In MeOH, } \epsilon = 32.5,\ K_{\text{dissoc}} = 0.055 \quad (31)$$

$$\text{In 98.32 mole \% MeOH–1.68 mole \% benzene, } \epsilon = 31.3 \quad K_{\text{dissoc.}} = 0.31 \quad (32)$$

The puzzling fact here is that addition of a small amount of benzene to methanol greatly favors dissociation. The explanation which has been given,[41] namely that benzene promotes the de-polymerization of methanol and hence the solvation of the free ions by methanol, seems to us to make use of a fact that is irrelevant. The thermodynamically significant quantity is the *activity* of methanol, rather than the monomer fraction, and this quantity decreases slightly as benzene is added. The enhanced dissociation is readily explained, however, if it is assumed that the solvation of tetra-*n*-butylammonium ion resembles that of the hydrocarbon, tetra-*n*-butylmethane.

Deviations from Equation 10. Tetramethylammonium Ion.—Equation 10, which is basic to our method of obtaining dF^0/dZ_1 for single ions, is really a limiting law which becomes the more accurate the greater the ionic radius. Although several kinds of evidence have suggested that equation 10 is a good approximation for Ph_4P^+ and Ph_4B^- (b = 4.2 Å.), it would certainly help to check this hypothesis by means of ions with still larger radius. Unfortunately, practical difficulties have so far prevented us from doing this. However, by availing ourselves of the data for $(CH_3)_4N^+$ and its uncharged analog, $(CH_3)_4C$, we can at least find out how quickly the deviations from equation 10 mount as the ionic radius is reduced. It will be noted that the structure of $(CH_3)_4N^+$ is consistent with the theoretical requirement that the charge be "buried" at the center. The average radius of this ion is 3.0 Å.

The relevant data for $(CH_3)_4N^+$ and for the larger cation, Ph_4P^+, are given in Table VI. For dF_N^0/dZ_1, we have used the experimental value for the analogous hydrocarbon. The discrepancy between dF_C^0/dZ_1 as calculated from equation 10 and the value as listed in Table V (which we have been using throughout this paper) is +4.1 kcal. for $(CH_3)_4N^+$ and +0.9 kcal. for Ph_4P^+. It is encouraging that the discrepancy for $(CH_3)_4N^+$ exceeds that for Ph_4P^+ only by about 3 kcal., in spite of the critical difference in ionic radius. The comparison tends to support our hypothesis that values of dF^0/dZ_1 for single ions as listed in Table V are substantially correct.

TABLE VI

EQUATION 10 AS A LIMITING LAW

Ion	$(CH_3)_4N^+$	Ph_4P^+
b (Å.)	3.0	4.2
dF_N^0/dZ_1 (kcal.)[a]	11.8	20.4
$\dfrac{-N_{Av}e^2}{2b\epsilon}\dfrac{d\ln\epsilon}{dZ_1}$ (kcal.)	−6.7	−4.8
$dF_{C^+}^0/dZ_1$ (predicted, eq. 10)	5.1	15.6
$dF_{C^+}^0/dZ_1$ (Table V)	1.0	14.7
Discrepancy (kcal.)	4.1	0.9

[a] The value of dF_3^0/dZ_1 for the analogous hydrocarbon is used here.

Experimental

Materials.—Reagent grade **potassium bromide** and **sodium nitrate** were recrystallized twice from doubly distilled water and dried thoroughly *in vacuo*. Reagent grade **potassium iodide** was similarly recrystallized in an atmosphere of nitrogen, washed with ethanol and dried *in vacuo*. C.P. **sodium perchlorate** was recrystallized from aqueous dioxane; the crystals contained dioxane of crystallization which was removed by drying for 8 hr. in a vacuum oven at 85°. **Perchloric acid** was J. T. Baker Analyzed Reagent, containing 60 wt. % $HClO_4$. Purified **cesium chloride** was recrystallized from acetone–water and dried to constant weight at 78° *in vacuo*. Equivalent weight: 169.4 by Volhard titration for chloride; calcd., 168.4. Reagent grade **lithium chloride** was dried *in vacuo* to constant weight. Equivalent weight: 42.51; calcd., 42.40. Eimer and Amend tested **potassium chloride** was further purified by Walton's method[42] and was dried at 120° before use.

Tetraphenylphosphonium chloride was prepared by Dr. E. F. J. Duynstee by the method of Willard, Perkins and Blicke.[43] The salt is hygroscopic and was dried in a vacuum oven at 80° just before use. Equivalent weight: 374.2 by Volhard titration for chloride; calculated for $Ph_4P^+Cl^-$, 374.8.

Sodium tetraphenylboride was the best grade available from F. Heyl, Berlin. The commercial product was dried to constant weight *in vacuo* before use.

Eastman white label **tetramethylammonium chloride** was dried to constant weight at 130° before use. The dry salt was neutral and had an equivalent weight of 109.5 (by chloride titration); calcd., 109.6.

Sodium beta-naphthalenesulfonate was prepared by dissolving 12.3 g. of sodium acetate trihydrate and 20.6 g. of beta-naphthalenesulfonic acid in a minimum amount of hot water. Ethanol was added to the hot solution and the salt crystallized out by cooling in ice. The product was twice decolorized with charcoal, recrystallized from ethanol–water, washed with ethanol and dried *in vacuo* over anhydrous magnesium perchlorate.

Anal. C, 52.05; H, 3.25; (calcd.: C, 52.17; H, 3.07).

Pentaerythritol.—A commercial sample was carefully purified by fractional sublimation *in vacuo* at 200°; m.p., 260.5°.

Tetraphenylmethane was prepared by Fred Impastato according to the method of Seibert and Bergstrom.[44] The product was recrystallized once from benzene, then repeatedly from glacial acetic acid; m.p. (number of times recrystallized): 283–284 (1); 284–285 (2); 282.5–284.5 (3); 283.5–285.0 (4); 285.0–285.7 (5).

Dioxane and water were purified by the methods previously described.[4,5]

Procedure.—The apparatus and method of vapor pressure measurement were the same as previously described.[4,5] Solutions were prepared following standard gravimetric practice. When perchloric acid was the solute, dioxane was added to compensate for the water in the 60% reagent; when potassium iodide was the solute, a small amount of sodium thiosulphate (equivalent to 0.5% of the iodide) was added in equal concentrations to both the reference solvent and the salt solution in order to repress the formation of traces of iodine.

Solubility of Tetraphenylmethane.—Pure solid and solvent were placed in ampoules which had previously been flushed with pure nitrogen. The amount of solid was adjusted so that approximately one-half of it would dissolve. The sealed ampoules, and an equal number of "controls" containing only the solvent, were attached to a vertical disk which was immersed in a thermostat at 25.00° and rotated at 20 r.p.m. At intervals, three "controls" and three ampoules were withdrawn from the thermostat and opened

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[41] R. C. Miller and R. M. Fuoss, THIS JOURNAL, **75**, 3076 (1953).

[42] H. F. Walton, "Inorganic Preparations," Prentice-Hall, New York, N. Y., 1948, p. 71.

[43] H. H. Willard, L. R. Perkins and F. F. Blicke, THIS JOURNAL, **70**, 737 (1948).

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quickly. The contents were then poured onto fritted glass filters which were thermostatted at 25.00°. The liquids were forced through these filters by a gentle pressure of purified nitrogen, collected directly in 1 cm. cuvettes and analyzed spectrophotometrically. The optical density was taken as the difference between the mean value for the saturated solutions and that for the "controls." Since analyses were performed at 218–230 mμ, scrupulous care was employed in cleaning the cuvettes. Extinction coefficients were determined for each solvent composition and wave length under the same instrumental conditions as for the unknowns and were reproducible to better than 2%.

Appendix

The Relation Between W and α_1/α_2. (i) Ideal Behavior in the Gas Phase.—If the gas over the solution and over the pure solvent behaves ideally

$$\alpha_1 = (x_1)_g/(x_1^*)_g,\ \alpha_2 = (x_2)_g/(x_2^*)_g \qquad (33)$$

where the $(x)_g$'s are mole fractions in the gas phase.

From the definition of W (equation 2), we then have

$$\alpha_1/\alpha_2 = W^*(1 - W)/W(1 - W^*) \qquad (34)$$

i.e., W is a function of the variable α_1/α_2 only, since W^* is constant.

(ii) **Non-ideal Behavior in the Gas Phase.**—It will be shown that the correction term which must be introduced into equation 34 because of gas imperfections is negligibly small. If we represent this term by $(1 + \delta)$

$$\alpha_1/\alpha_2 = (1 + \delta)W^*(1 - W)/W(1 - W^*) \qquad (35)$$

then it can be shown, using the slightly-imperfect-gas model and the earlier expressions for the fugacity of the solvent components,[6] that

$$\delta RT/P = 2B_{11}[(x_1)_g - (x_1^*)_g] + 2B_{12}[(x_2)_g - (x_2^*)_g - (x_1)_g + (x_1^*)_g] + 2(B_{13} - B_{23})[(x_3)_g - (x_3^*)_g] - 2B_{22}[(x_2)_g - (x_2^*)_g] \qquad (36)$$

where Bij is the second virial coefficient for interactions between molecules of the ith and jth species.[45] Equation 35 is identical with 34 if δ is negligibly small.

An estimate of the magnitude of δ was obtained by assuming ideal behavior of gases $[(x_i)_g/(x_i^*)_g = \alpha_i]$ and a dilute solution $[\ln \alpha_1/\alpha_2 = (2m\mathrm{M}_{12}/1000RT)\mathrm{d}F_3^0/\mathrm{d}Z_1]$. For dilute solutions ($m<0.1$), α_1 and α_2 and the exponential term in equation 40 do not differ greatly from unity, and we can make the approximations

$$\alpha_1 - 1 = \ln \alpha_1 = Z_2 \ln (\alpha_1/\alpha_2);$$
$$\alpha_2 - 1 = \ln \alpha_2 = -Z_1 \ln(\alpha_1/\alpha_2)$$

Applying these considerations to equation 36 and substituting the values of the virial coefficients,[6] we have for 50 wt. % aqueous dioxane

$$\delta = 0.67 \times 10^{-3}\, m\, \mathrm{d}F_3^0/\mathrm{d}Z_1$$

when $\mathrm{d}F_3^0/\mathrm{d}Z_1$ is expressed in kcal.

For 0.05 m NaOH, δ is thus -6×10^{-4}, and $1 + \delta$ can be equated with unity in view of the experimental accuracy of α_1/α_2. The term $1 + \delta$ is even closer to unity for the other electrolytes now studied.

The Relation Between ρ, α_1/α_2 and the Osmotic Coefficient, g.—Substitution from equation 33 in equation 1 yields

$$\rho = \frac{(x_1^*)_g M_1\alpha_1 + (x_2^*)_g M_2\alpha_2}{(x_1^*)_g M_1 + (x_2^*)_g M_2} \cdot \frac{n_g}{n_g^*} \qquad (37)$$

where $n_g = (n_1 + n_2 + n_3)_g$, and the subscript 3 refers to nitrogen. Since the same amount of nitrogen passes over the solution and the solvent, $(n_3)_g = (n_3^*)_g$. An expression for the magnitude of n_g/n_g^* was obtained on the same basis as was that for δ in the preceding section

$$n_g/n_g^* = 1 - 0.0202 \ln (\alpha_1/\alpha_2)$$
$$= 1 - 1.02 \times 10^{-3}\, m\, \mathrm{d}F_3^0/\mathrm{d}Z_1 \qquad (38)$$

where $\mathrm{d}F_3^0/\mathrm{d}Z_1$ is expressed in kcal. From the definition of the osmotic coefficient

$$Z_1 \ln \alpha_1 + Z_2 \ln \alpha_2 = -g\, mM_{12}/1000 \qquad (39)$$

it follows that

$$\alpha_1 = (\alpha_1/\alpha_2)^{Z_2} \exp(-g\, mM_{12}/1000)$$
$$\alpha_2 = (\alpha_1/\alpha_2)^{-Z_1} \exp(-g\, mM_{12}/1000) \qquad (40)$$

Hence α_1/α_2 can be evaluated when ρ and g are known. Fortunately the calculation is rather insensitive to changes in the value of g. Hence g could be estimated with sufficient accuracy by using the known value for NaCl at the same molality.[4]

$\mathrm{d}F_3^0/\mathrm{d}Z_1$ for a Solvated Solute.—The experimental value of $\mathrm{d}F_3^0/\mathrm{d}Z_1$ is a *formal* quantity which is computed without regard to the solvation of the electrolyte in solution. This formal quantity will now be related to the average value per mole of $\mathrm{d}F^0/\mathrm{d}Z_1$ for the various solvates which actually exist in solution.

Consider a homogeneous solution consisting of n_1 formula weights of water, n_2 formula weights of dioxane, and n_3 formula weights of a solute, S, which may but need not be an electrolyte. For simplicity, n_3 is kept sufficiently small so that the solute may be regarded as dilute. The *formal* expression for the free energy of this system is given by equation 41, where the quantities F denote the formal partial molar free energies.

$$F = n_1\bar{F}_1 + n_2\bar{F}_2 + n_3\bar{F}_3 \qquad (41)$$

For the sake of generality, the actual solute will be assumed to be an equilibrium mixture of unsolvated S and various solvates, a typical equilibrium being shown in equation 42.

$$\mathrm{S} + i\ \mathrm{H_2O} + j\ \mathrm{Dioxane} = \mathrm{S}\cdot i\ \mathrm{H_2O}\cdot j\ \mathrm{Dioxane} \qquad (42)$$

Since equilibrium exists, equations 43 and 44 apply

$$\bar{F}_{00}' + i\,\bar{F}_1' + j\,\bar{F}_2' = \bar{F}_{ij}' \qquad (43)$$

$$\mathrm{d}\bar{F}_{00}' + i\,\mathrm{d}\bar{F}_1' + j\,\mathrm{d}\bar{F}_2' - d\bar{F}_{ij}' = 0 \qquad (44)$$

It will be noted that primed symbols are used when referring to actual molecular species and unprimed symbols when referring to the formal species.

If the *fractions* of the formal solute which exist in the molecular forms S(unsolvated) and S·i H$_2$O·j Dioxane be denoted, respectively, by ϕ_{00} and ϕ_{ij}, then the average hydration number, h, of the solute is given by equation 45, and the average dioxanation number, d, by equation 46.

$$h = \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} i\phi_{ij} \qquad (45)$$

$$d = \sum_{i=0}^{n_1} \sum_{j=0}^{n_2} j\phi_{ij} \qquad (46)$$

Next, equations 47 and 48 are obtained by multiplying equations 43 and 44 by ϕ_{ij} and then summing over all possible values of i and j. Note that $\sum_i \sum_j \phi_{ij} = 1$.

$$\bar{F}_{00}' + h\bar{F}_1' + \mathrm{d}\bar{F}_2' = \sum_i \sum_j \phi_{ij}\bar{F}_{ij}' \qquad (47)$$

$$\mathrm{d}\bar{F}_{00}' + h\mathrm{d}\bar{F}_1' + d\mathrm{d}\bar{F}_2' - \sum_i \sum_j \phi_{ij}\mathrm{d}\bar{F}_{ij}' = 0 \qquad (48)$$

We are now ready to write the expression for the free energy of the system in terms of actual molecular species

$$F = (n_1 - hn_3)\bar{F}_1' + (n_2 - dn_3)\bar{F}_2' + n_3 \sum_i \sum_j \phi_{ij}\bar{F}_{ij}' \qquad (49)$$

In this expression, hn_3 and dn_3 are equal, respectively, to the formula weights of water and of dioxane that are removed from the solvent as a result of the solvation of the solute. Upon utilizing equation 47, equation 49 reduces to

$$F = n_1\bar{F}_1' + n_2\bar{F}_2' + n_3\bar{F}_{00}' \qquad (50)$$

Equation 50 and the formal equation, 41, represent two alternative ways of writing the free energy of the solution as a function of the formal composition. Since n_1, n_2 and n_3 may be varied at will, the two equations are consistent with one another only if, for each formal composition

$$\bar{F}_1 = \bar{F}_1' \qquad (51a)$$

$$\bar{F}_2 = \bar{F}_2' \qquad (51b)$$

$$\bar{F}_3 = \bar{F}'_{00} \qquad (51c)$$

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(45) In ref. 6, the symbol z was employed for mole fractions in the gas phase, now denoted by $(x)_g$.

In other words, the partial molar free energy of the solvent components is the same, whether the solute be treated as a formal species or as a solvated species; and the formal partial molar free energy of the solute is equal to that of the unsolvated portion of the solute.

Using equations 45–51, expressions relating the formal *standard* partial molar free energy of the solute to that of actual molecular species can be obtained. Two alternative expressions are shown in equations 52 and 53, where $\phi_{ij}{}^0$ denotes the limiting value of ϕ_{ij} as n_3 approaches zero at constant n_1, n_2.

$$F_3{}^0 = F_{00}{}^{0\prime} + RT \ln \phi_{00}{}^0 \tag{52}$$

$$F_3{}^0 = \sum_i \sum_j \phi_{ij}{}^0 F_{ij}{}^{0\prime} + RT \sum_i \sum_j \phi_{ij}{}^0 \ln \phi_{ij}{}^0 - h^0 \bar{F}_1 - d^0 \bar{F}_2 \tag{53}$$

It is seen that the formal *standard* chemical potential, $F_3{}^0$, is *not* simply equal to that of the unsolvated monomer, in contrast to F_3; nor is $F_3{}^0$ simply the average of the standard chemical potentials of the various solvates, as has so often been assumed in the previous literature.

Differentiation of equation 53 and simplification of the result (subtract equation 48 from the differential of 47) finally leads to

$$\sum_i \sum_j \phi_{ij}{}^0 \frac{dF_{ij}{}^{0\prime}}{dZ_1} = \frac{dF_3{}^0}{dZ_1} + h^0RT \frac{d \ln a_1}{dZ_1} + d^0RT \frac{d \ln a_2}{dZ_1} \tag{54}$$

In other words, the average value of $dF^{0\prime}/dZ_1$ for *all* solvates (weighted in proportion to $\phi_{ij}{}^0$) is equal to the experimental, formal quantity, $dF_3{}^0/dZ_1$, plus two terms—one proportional to h^0 and one to d^0—which allow for the changing activities of the solvent components and are evaluated for $m_3 = 0$. All terms involving $d\phi_{ij}{}^0/dZ_1$, dh^0/dZ_1, or dd^0/dZ_1 have cancelled out.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Chronopotentiometric Studies on the Oxidation of Ferrocene, Ruthenocene, Osmocene and Some of their Derivatives[1]

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Oxidation–reduction potentials obtained by chronopotentiometric methods at a platinum electrode in an acetonitrile solution indicate electron withdrawing substituents decrease the ease of oxidation, while electron donating substituents increase the ease of oxidation with respect to the parent metallocenes. This is in accord with the results normally expected from inductive effects. The $E_{1/4}$ values of ferrocene and its derivatives have been correlated with the substituent constants of the Ingold–Taft equation. Ruthenocene has been observed to undergo a one step, two-electron oxidation while osmocene undergoes a two step, one electron each, oxidation. Ferrocene shows only a one electron transfer. The reversibilities of the electrode reactions are evaluated.

Introduction

It has been observed[3] that the reactivity of the metal cyclopentadienyl compounds toward electrophilic substitution decreases with corresponding decrease of the apparent electron density of the molecules. Thus, the compounds containing a metal atom which withdraws electrons from the ring more in comparison to the iron compounds should be less reactive toward electrophilic substitution than ferrocene. These effects are exhibited also in a similar manner by ring substituents. Thus, carboxyl or acyl substituents decrease the reactivity of the substituted rings towards electrophilic substitution, while alkyl substituents enhance the reactivity. Moreover, these effects are, in part, transmitted through the metal atom to the second ring.

The oxidation–reduction chemistry of the metallocenes should closely parallel the above observed effects for electrophilic substitutions. That is, the more easily oxidized compounds should be those which are more reactive toward electrophilic substitutions and consequently, appear to have a greater electron density around the metal atom and rings. Metallocenes of the group VIII elements, iron, ruthenium and osmium, show trends in electrophilic substitution reactions, which indicate a lower electron density around the rings for the lower elements of this group.[4] Thus osmocene and ruthenocene are expected to have a greater stability toward oxidation than ferrocene.

Page and Wilkinson[5] have reported the polarography of ferrocene, ruthenocene and cobaltocene at the dropping mercury electrode (DME) in 90% ethanol solution containing $NaClO_4$ and $HClO_4$ as supporting electrolytes. The polarographic half-wave potentials, $E_{1/2}$, for ferrocene and ruthenocene were reported as + 0.31 and + 0.26 v. *vs.* saturated calomel electrode (SCE), respectively. Reynolds and Wilkinson[6] have published recently the $E_{1/2}$ value for the more easily air oxidized 1,1′-dimethylferrocene as + 0.38 v. *vs.* SCE.

The theoretical and experimental considerations of chronopotentiometry have been well developed by Delahay and Berzins,[7] Delahay,[8] Gierst and Juliard[9] and Reilley, *et al.*[10]

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