Complementary Lewis Acid–Base Description of Solvent Effects. I. Ion–Ion and Ion–Dipole Interactions

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Abstract: An empirical model describing the effect of solvent on physicochemical properties measured in solution is described. It is proposed that the solvent effect depends directly on the Lewis acidity and Lewis basicity of the solvent, the relative contributions of these interactions being estimated for a given solvent using the Dimroth–Reichardt acidity parameter and the Gutmann donor number, respectively. The empirical equation has been tested with more than 30 sets of experimental data describing solvent effects on parameters related to ion–solvent and ion–ion interactions. A successful correlation was obtained in 90% of the cases considered.

As is well known,[1-6] a general theory describing solvent effects on physicochemical properties measured in solution has not been developed to date. However, in many cases, reliable predictions of solvent effects can be obtained from empirical relationships. Thus, the effect of the solvent on the quantity being measured, Q can often be described by a linear relationship of the form

$$Q = aP + b \tag{1}$$

where P is an empirical parameter which is postulated to describe the main contribution of the solvent's influence on Q, and a and b are constants obtained by linear regression. In some other cases, multiparameter regressions have been used.[1] Many different suggestions for the parameter P have been made in the literature. Those usually chosen are the rate constants[7,8] or the spectral properties[9,10] associated with the following types of processes:[5]

$$AB \longrightarrow A^+ B^- \tag{2a}$$

or

$$A^+ B^- \longrightarrow AB \tag{2b}$$

where AB is assumed to be a species which interacts very weakly with solvent molecules, whereas the dipolar entity $A^+ B^-$ interacts strongly.[5] The solvent effect in reaction 2 is chiefly to stabilize the separation of charge so that the associated parameter P is often called the ionizing power of the solvent.[3]

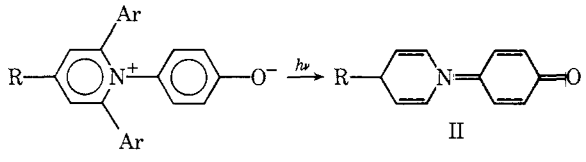
The main purpose of the present paper is to describe solvent effects in such a way that all solute–solvent interactions influencing the various physical and chemical properties can be defined in terms of the general concept of the Lewis acidity and basicity of the solvent.

The Model. It is postulated that the solvent effect on a physicochemical quantity Q can be represented as a linear function of two independent but complementary parameters describing the Lewis acidity, A, and Lewis basicity, B, of the given solvent:

$$Q = Q_0 + \alpha A + \beta B \tag{3}$$

α and β are constants describing the sensitivity of the property Q to acidic and basic solvent properties.

The Dimroth–Reichardt parameter E_T[3,10] is chosen as a measure of Lewis acidity A, E_T being the energy associated with the $\pi \rightarrow \pi^*$ transition of a model compound (I) (see eq 4), Ar being a phenyl or p-methylphenyl group. On excitation, the strongly dipolar molecule (I) is transformed into the weakly dipolar excited state (II). The ground state is strongly influenced by the acidic properties of the solvent, because the positive charge on the nitrogen atom is partly delocalized on the ring and also shielded by the aryl substituents, whereas the negative oxygen atom can interact freely with the solvent. Since the excited state is much less polar, it is assumed that the energy associated with the transition is a quantitative measure of the Lewis acidity of the solvent. Similar conclusions have been reached by Koppel and Palm in their investigations.[1]



I

II

(4)

The Gutmann donor number,[11,12] DN, is chosen as a measure of solvent basicity B where DN is the negative of the enthalpy of formation of adducts between the uncharged Lewis acid $SbCl_5$ and a given solvent molecule as Lewis base in dilute 1,2-dichloroethane solutions:

$$SbCl_5 + \text{solvent} \overset{\Delta H_f}{\rightleftharpoons} SbCl_5 \cdot \text{solvent} \tag{5}$$

The above interpretation of DN as a parameter measuring solvent basicity is supported by Erlich and Popov's measurements[13,14] of the NMR chemical shifts of $^{23}Na^+$ nuclei carried out in various solvents.

Thus, it is assumed that the solvent effect on property Q can be described in terms of the regression plane

$$Q = Q_0 + \alpha E_T + \beta \text{DN} \tag{6}$$

Values of E_T and DN in units of kcal mol^{-1} are summarized for a large collection of solvents in Table I.

In general, the independent variables E_T and DN do not vary by the same amounts in a given data set. Thus, it is not possible to obtain a quantitative measure of the relative importance of solvent acidity and basicity for a given physicochemical quantity just by examining the regression coefficients α and β. In order to determine the relative importance of the solvent parameters, the partial regression coefficients α' and β' or "beta coefficients" defined in the statistics of multiple linear regression[15] were calculated. These coefficients are given by the relationships in eq 7a and 7b,

$$\alpha' = |\alpha| \left(\frac{\sum_{i=1}^{n} (E_{T_i} - \bar{E}_T)^2}{\sum_{i=1}^{n} (Q_i - \bar{Q})^2} \right)^{1/2} \tag{7a}$$

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Table I. Acidity Parameter E_T (Dimroth and Reichardt) and Basicity Parameter DN (Gutmann) for Various Solvents

Solvent	Abbreviation	DN[a]	E_T[b]
Acetic anhydride	AA	10.5	43.9
Acetone	A	17.0	42.2
Acetonitrile	AN	14.1	46.0
Benzene	B	0.4	34.5
Benzonitrile	BN	11.9	42.0
1,2-Dichloroethane		0.0	41.9
Diethyl ether	DEE	20.0	34.6
N,N-Dimethylacetamide	DMA	27.6	43.7
N,N-Dimethylformamide	DMF	26.6	43.8
Dimethyl sulfoxide	DMSO	29.8	45.0
Ethanol	EtOH	(31.5)	51.9
Ethyl acetate	EA	17.1	38.1
Formamide	F	(24.7)	56.6
Hexamethylphosphoramide	HMPA	38.8	40.9
Methanol	MeOH	(25.7)	55.5
1-Methyl-2-pyrrolidone		27.3	42.2
Nitrobenzene	NB	4.4	42.0
Nitromethane	NM	2.7	46.3
Propionitrile	PN	16.1	43.7
Propylene carbonate	PC	15.1	46.6
Pyridine	Py	33.1	40.2
Sulfolane	TMS	14.8	44.0
Tetrahydrofuran	THF	20.0	37.4
Water	W	(33.0)	63.1

[a] Taken from ref 12; values shown in parentheses (protic solvents) are from ref 18. [b] Taken from ref 3 and 1.

and

$$\beta' = |\beta| \left(\frac{\sum_{i=1}^{n} (\mathrm{DN}_i - \overline{\mathrm{DN}})^2}{\sum_{i=1}^{n} (Q_i - \bar{Q})^2} \right)^{1/2} \qquad (7b)$$

where E_{Ti}, $\mathrm{DN_i}$, and Q_i are the values of E_T, DN, and Q in a given solvent, and $\bar{E}_T$, $\overline{\mathrm{DN}}$, and $\bar{Q}$ are the average values of these quantities for the given data set containing n points. Since α' and β' are on the same scale, comparison of these parameters gives one directly an estimate of the relative importance of solvent acidity and basicity for the solvent effect being considered. For convenience, α' and β' are normalized in the way shown in eq 8a and 8b. Thus, $\bar{\alpha}$ and $\bar{\beta}$

$$\bar{\alpha} = 100\alpha'/(\alpha' + \beta') \qquad (8a)$$

and

$$\bar{\beta} = 100\beta'/(\alpha' + \beta') \qquad (8b)$$

may be regarded as estimates of the percentage contributions from solvent acidity and basicity, respectively, to the observed solvent effect.

Finally, it should be noted that the sign associated with α or β indicates either direct (+) or reverse (−) proportionality between the solvent effect and E_T or DN, respectively. The errors in α and β and the multiple correlation coefficient R reported below were estimated using standard statistical methods.[15] In the usual way, R^2 may be interpreted as the fraction of the observed variation in Q which is accounted for by the proposed relationship (eq 6).

The results of applying eq 6–8 to some popular solvent parameters used previously are summarized in Table II. A more detailed analysis of these data will be presented later, but the following salient points should be noted. Winstein and Grunwald's parameters Y[7] and log k_{ion},[8] Kosower's Z,[9] Berson's Ω,[16] and Dubois' F[17] chiefly describe the acidic properties of the solvent, whereas the Koppel and Palm parameter B[1] correlates very well with the basicity parameter DN. Thus, these parameters can be described satisfactorily using the model presented here. It then follows that solvent effects previously discussed in terms of these parameters can also be discussed in terms of the present model. Finally, it should be noted that there is no correlation between the acidity parameter E_T and the basicity parameter DN.

Applications

A. Description of the Solvent Effect for $^{23}\mathrm{Na}^+$ NMR Chemical Shifts. Recently Erlich, Popov, and their colleagues[13,14,18] have published data for the NMR chemical shifts of $^{23}\mathrm{Na}^+$ nuclei as a function of the nature of the salt, salt concentration, and the nature of the solvent. They observed a linear relationship between the chemical shifts and Gutmann's DN values[13,14] which was especially apparent in the case of $\mathrm{NaClO_4}$ solutions. They also found that the chemical shifts were independent of salt concentration in the cases of $\mathrm{NaClO_4}$ and $\mathrm{NaBPh_4}$ solutions. The latter observation indicates that ion pairing is weakest in these systems.

The results of applying eq 6–8 to these data are summarized in Table III. It is immediately apparent that regular trends in $\bar{\alpha}$ and $\bar{\beta}$ are obtained in the case of $\mathrm{NaClO_4}$. As the concentration of the salt increases, $\bar{\alpha}$ changes from 3 to 15, whereas $\bar{\beta}$ changes from 97 to 85. This result can be attributed to the formation of agglomerates or ion pairs at higher concentrations so that the chemical shift for $^{23}\mathrm{Na}^+$ is influenced by solvent acidity as well as solvent basicity. The acidic interaction occurs at the negative part of the $\mathrm{Na^+\ ClO_4^-}$ agglomerate. At low concentration, ion pairs are not present to any significant extent, and the solvent as a base interacts chiefly with the isolated $^{23}\mathrm{Na}^+$ ion. The same effect is not observed in the case of $\mathrm{NaBPh_4}$. Since the $\mathrm{BPh_4^-}$ is weakly solvated and thus does not interact strongly with any solvent, the acidic properties of the solvent are not important for $^{23}\mathrm{Na}^+$ chemical shifts in $\mathrm{NaBPh_4}$ solutions whether or not ion pairs are formed. In both cases, $\bar{\beta}$ is large and negative in agreement with established ideas regarding cation solvation. The greater is the basicity of the solvent (DN), the greater cation solvation, and the more negative the chemical shift.

In the cases of NaSCN and NaI, no significant correlation was obtained, the correlation coefficients being in the range 0.6–0.7. Since ion pairing is strong in these systems, ion–ion interactions will vary greatly from one solvent to another. The present result agrees with the observations of Erlich and Popov[13,14,18] who found that the chemical shifts depend markedly on salt concentration.

It should also be noted that the value of Q_0, the predicted chemical shift in the absence of solvent interactions (E_T = DN = 0), is high (17.5–20.1), whereas the largest experimental values are for $\mathrm{NaClO_4}$ in EA (9.7) and TMS (9.25). This comparison gives one some feeling for the magnitude of the solvent effect on this particular quantity.

B. Description of Solvent Activity Coefficients. Parker[19] has published an extensive list of so-called solvent activity coefficients, ${}^{\circ}\gamma_i^{s}$; which are defined by the equation

$$\bar{\mu}_i^{s} = \bar{\mu}_i^{\circ} + RT \ln {}^{\circ}\gamma_i^{s} \qquad (9)$$

$\bar{\mu}_i^{s}$ and $\bar{\mu}_i^{\circ}$ are the standard chemical potentials of solute "i" (hypothetically ideal with respect to Henry's law in unimolar solution) in solvent "s" and in a reference solvent "o" (MeOH), respectively. The extrathermodynamic assumptions used to obtain $\bar{\mu}_i^{s}$ in the case of ionic solutes have been discussed in detail by Parker.[19] Negative values of log ${}^{\circ}\gamma_i^{s}$ indicate that solute i is more stable in solvent "s" than in the reference solvent. The results of applying eq 6–8 to these data are summarized in Tables IV and V.

1. Cations. As a rule, α is positive and β negative for cations. Thus, with increasing solvent acidity log ${}^{\circ}\gamma_i^{s}$ decreases, and the solute is destabilized; with increase in solvent basicity, log ${}^{\circ}\gamma_i^{s}$ decreases, and the solute is stabilized. The latter observation is expected since cations as Lewis

Table II. Application of the Complementary Lewis Acid–Base Description of Solvent Effects to Some Popular Solvent Parameters

Parameter	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	n^a	R	Point of maximum deviation^b
Winstein–Grunwald Y parameter[7]	0.36 ± 0.16	−0.11 ± 0.19	−17.0	80	20	5	0.909	MeOH
Winstein–Fainberg log k_{ion}[8]	0.22 ± 0.035	0 ± 0.03	−14.4	99	1	13	0.908	F
Berson Ω[16]	0.015 ± 0.002	−0.001 ± 0.001	−0.009	91	9	7	0.961	EtOH
Kosower Z[9]	1.3 ± 0.1	−0.02 ± 0.07	10.1	98	2	16	0.970	TMS
Dubois F[17]	0.013 ± 0.003	0.002 ± 0.002	−0.487	84	16	7	0.956	DMF
Palm–Koppel B[1]	−2.38 ± 0.75	4.79 ± 0.44	136.2	22	78	15	0.954	EA

^{a}Number of data points. ^{b}Solvents are designated using the abbreviations listed in Table I.

Table III. Application of the Complementary Lewis Acid–Base Description of Solvent Effects to NMR Chemical Shifts for $^{23}Na^+$

Salt	Concn, M	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	n	R
$NaClO_4$	0.01	−0.01 ± 0.02	−0.58 ± 0.03	19.5	3	97	6	0.997
	0.05	−0.03 ± 0.04	−0.54 ± 0.05	19.7	7	93	8	0.984
	0.1	−0.04 ± 0.04	−0.52 ± 0.04	19.7	9	91	8	0.985
	0.2	−0.05 ± 0.04	−0.50 ± 0.04	19.7	11	89	8	0.985
	0.3	−0.06 ± 0.04	−0.48 ± 0.04	20.0	13	87	8	0.983
	0.4	−0.06 ± 0.04	−0.49 ± 0.05	19.9	13	87	8	0.982
	0.5	−0.07 ± 0.04	−0.48 ± 0.05	20.1	15	85	8	0.983
$NaBPh_4$	0.01	0.01 ± 0.05	−0.56 ± 0.08	17.5	4	96	7	0.967
	0.05	0.0 ± 0.05	−0.54 ± 0.06	17.5	1	99	8	0.976
	0.1	0.0 ± 0.05	−0.54 ± 0.06	17.5	0	100	8	0.974
	0.2	0.0 ± 0.05	−0.54 ± 0.06	17.7	0	100	8	0.975
	0.3	0.01 ± 0.05	−0.55 ± 0.06	17.4	2	98	8	0.974
	0.4	0.0 ± 0.07	−0.54 ± 0.07	17.7	0	100	7	0.973
	0.5	0.0 ± 0.07	−0.54 ± 0.07	18.0	0	100	7	0.973

Table IV. Application of the Complementary Lewis Acid–Base Description to Solvent Activity Coefficients for Several Cations[19]

Cation	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	n	R	Point of maximum deviation
Ag^+	0.31 ± 0.10	−0.25 ± 0.07	−13.7	45	55	9	0.880	AN
K^+	0.11 ± 0.05	−0.13 ± 0.04	−4.8	43	57	7	0.891	F
Cs^+	0.16 ± 0.04	−0.15 ± 0.05	−7.0	58	42	6	0.942	F
$AsPh_4^+$	0.29 ± 0.04	0.04 ± 0.04	−16.4	88	12	8	0.960	F

Table V. Application of the Complementary Lewis Acid–Base Description to Solvent Activity Coefficients for Several Anions[19]

Anion	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	n	R	Point of maximum deviation
Br^-	−0.40 ± 0.04	0.03 ± 0.04	21.7	93	7	7	0.983	DMSO
Cl^-	−0.51 ± 0.06	0.01 ± 0.04	29.0	98	2	10	0.960	PC
N_3^-	−0.39 ± 0.04	0.0 ± 0.02	22.4	100	0	9	0.973	DMSO
BPh_4^-	0.29 ± 0.04	0.02 ± 0.03	−15.5	93	7	9	0.953	AN
SCN^-	−0.21 ± 0.03	−0.02 ± 0.02	12.5	88	12	10	0.936	DMSO
I^-	−0.20 ± 0.03	−0.04 ± 0.02	11.9	80	20	9	0.955	DMSO

acids will be more stable in solvents which are strong Lewis bases. The former observation requires a more detailed explanation. The acidity-basicity parameters chosen here measure the enthalpy change associated with solute-solvent interactions but do not account for order-disorder changes accompanying these interactions. If the entropic change accompanying solution is correlated with E_T, then the values of α obtained reflect not only acidic interactions of the solvent but also disruption of solvent structure. Such a correlation is expected to a first approximation since the highly structured H-bonded solvents have the highest values of E_T, whereas the nonstructured aprotic solvents have the lowest. Obviously an improved model of solvent effects should deal with entropic effects separately. This matter will be dealt with in more detail later. In conclusion, the positive values of α obtained here are interpreted as indicating the amount of disruption to solvent structure accompanying solvation.

2. Anions. For anions, α is usually large and negative, whereas β is positive and small. The observed values of α are easily interpreted as indicating that the acidic properties of the solvent are important in stabilizing an anion. In the case of BPh_4^-, the negative charge is well shielded by the large phenyl groups so that the acidic properties of the solvent are not important. Thus, this bulky anion acts only to disrupt solvent structure, and α is greater than zero.

C. Description of the Enthalpies of Ionic Solvation. Recently Parker and colleagues[20] published an extensive list of enthalpies, entropies, and free energies of transfer of ions from a reference solvent (in this case AN) to another solvent, the extrathermodynamic assumption being that the BPh_4^- and $AsPh_4^+$ ions are equally solvated. It was found that the method described here successfully describes solvent effects on the enthalpy of transfer; however, in the cases of entropies and free energies of transfer, the correlation coefficients were less than 0.8. The latter observation indicates that there is no correlation between the structural changes in the solvent and the acidity parameter E_T in the present case.

The parameters obtained from the correlations for the enthalpy of solvation are summarized in Table VI. The results obtained here are quite similar to those given in Tables IV and V. In the case of cations, α is positive and increases with cation size. This is interpreted as evidence of the disruption of solvent structure which increases as the solute size increases. On the other hand, β is negative and decreases in magnitude with increase in solvent size. Thus, the

Table VI. Application of the Complementary Lewis Acid–Base Description to Enthalpies of Ionic Solvation[20]

Ion	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	n	R	Point of maximum deviation
Li^+	0.19 ± 0.18	−0.55 ± 0.20	−0.18	28	72	5	0.902	MeOH
Na^+	0.23 ± 0.08	−0.35 ± 0.09	−8.5	36	64	8	0.927	DMSO
K^+	0.38 ± 0.04	−0.24 ± 0.04	−19.2	58	42	8	0.977	DMSO
Rb^+	0.35 ± 0.04	−0.16 ± 0.03	−19.5	64	36	7	0.976	DMF
Cs^+	0.35 ± 0.07	−0.13 ± 0.07	−19.9	71	29	6	0.945	DMF
$AsPh_4^+$	0.28 ± 0.06	−0.03 ± 0.05	−15.2	89	11	8	0.914	PC
Cl^-	−0.33 ± 0.04	−0.14 ± 0.04	23.3	70	30	7	0.974	PC
BPh_4^-	0.28 ± 0.06	−0.03 ± 0.05	−15.2	89	11	8	0.914	PC

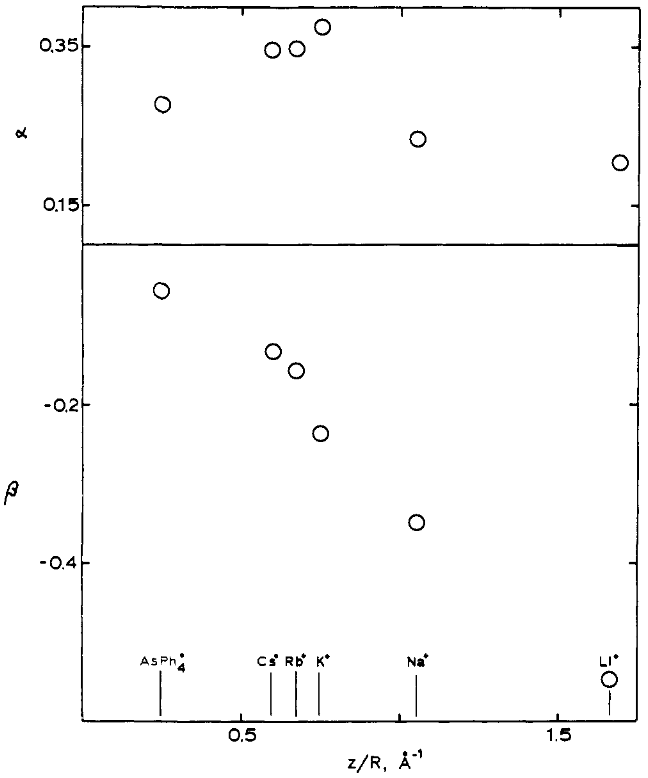
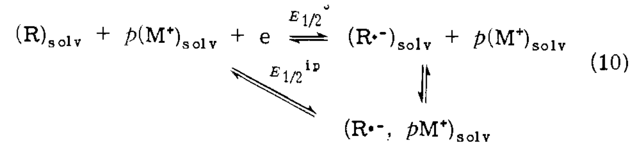


Figure 1. α and β determined from fits of eq 3 to data for the enthalpies of solvation of various cations[20] plotted against the Cartledge[21] ionic potential, z/R where z is the charge on the cation and R its crystallographic radius.

larger the cation, the less it interacts with the solvent as a Lewis base. These results are illustrated in Figure 1, where α and β are plotted against the so-called ionic potential according to Cartledge.[21] The latter quantity is defined as $\Phi = z/R$ where z is the charge on the ion and R its crystallographic radius and is given in units of $Å^{-1}$. As is apparent from the figure, there is an approximate correlation between α and β on the one hand and Φ on the other. The fact that the correlation of β with Φ is much better than that of α can be rationalized if β only describes changes in the enthalpy of ion-solvent interactions, whereas α also contains contributions from reorganization of solvent structure caused by the cation. Finally, the results for anions are similar to those obtained for solvent activity coefficients, and the interpretation offered is the same.

D. Description of Solvent Effects on the Standard Potentials for Reduction of Organic Molecules. From voltammetric studies, the reaction scheme for electroreduction of π-electron systems in aprotic solvents can usually be written as shown in eq 10.[22] The organic molecule R is reversibly reduced to its corresponding anion radical, but the observed half-wave potential $E_{1/2}{}^{ip}$ is influenced by ion pairing between the anion radical and the cation M^+. This effect can be described quantitatively using a modification of the Nernst equation due to Peover and Davies.[23] Since the half-wave potential in the absence of ion pairing $E_{1/2}{}^{\circ}$ is simply related to the standard potential for a reversible reaction, one may easily show that



$$(R)_{solv} + p(M^+)_{solv} + e \overset{E_{1/2}{}^{\circ}}{\rightleftharpoons} (R\cdot^-)_{solv} + p(M^+)_{solv} \qquad (10)$$
$$\searrow^{E_{1/2}{}^{ip}} \qquad \updownarrow$$
$$(R\cdot^-,\ pM^+)_{solv}$$

$$\Delta E_{1/2} = E_{1/2}{}^{ip} - E_{1/2}{}^{\circ} = \frac{RT}{F} \ln \{1 + K_{as}[M^+]^p\} \qquad (11)$$

where K_{as} is the association constant for ion-pair formation (eq 10) and p, the coordination number (usually 1 but sometimes 2). Normally ion pairing is strong ($K_{as}[M^+]^p \gg 1$) and $p = 1$ so that eq 11 simplifies to eq 12. This may be

$$\Delta E_{1/2} = \frac{RT}{F} \ln \{K_{as}[M^+]\} \qquad (12)$$

rewritten in terms of the standard free energy of association (eq 13). Thus, when $\Delta E_{1/2}$ is measured at constant support-

$$F\Delta E_{1/2} = -\Delta G^{\circ}{}_{as} = G^{\circ}(R)_{solv} + G^{\circ}(M^+)_{solv} - G^{\circ}(R\cdot^-, M^+)_{solv} \qquad (13)$$

ing electrolyte concentration in a series of solvents, one may estimate the related change in the standard free energy of association, that is

$$F\Delta\Delta E_{1/2} = -\Delta\Delta G^{\circ}{}_{as} \qquad (14)$$

where $\Delta\Delta E_{1/2}$ is the change in the shift in half-wave potential due to ion pairing with change in solvent, and $\Delta\Delta G^{\circ}{}_{as}$, the corresponding change in the standard free energy of association.

Fujinaga et al.[24] have measured half-wave potentials for the polarographic reduction of 1,2-naphthoquinone in five different solvents (DMF, DMSO, PC, AN, and A) and in the presence of various cations (TEA^+, Li^+, Na^+, and K^+). These data were analyzed using the present model, the results being summarized in Table VII. When Li^+ and Na^+ are the supporting electrolyte cations, β is negative and large in magnitude, whereas for K^+ and TEA^+, it is positive. This implies that the reduction potential becomes more negative for increase in solvent basicity when cations of small radii are involved. Thus, as interaction between the cation and the solvent is enhanced, ion pairing, a competing process, is reduced. However, for cations of larger radius, solvation is not as important, and interaction between the radical anion and the cation is preferred. This in turn results in values of β greater than zero.

Interpretation of the positive values of α is somewhat more difficult. If the basicity of the reactant, 1,2-naphthoquinone, and thus the value of $G^{\circ}(R)_{solv}$, were the only important considerations, α would be constant. The dependence of α on the nature of the cation suggests that the term $G^{\circ}(R\cdot^-,M^+)$ is important in shifting $\Delta E_{1/2}$ to more positive values when solvent acidity increases. The solvation of the ion pair depends on its properties as a dipole. The positive pole of the ion pair is solvated by the basic properties of the solvent. This contribution decreases with increase in cation-

Table VII. Application of the Complementary Lewis Acid–Base Description to Polarographic Data for the Reduction of 1,2- and 1,4-Naphthoquinones in Various Solvents[24]

Depolarizer	Counter ion	α	β	Q_0	$\bar{\alpha}$	$\bar{\beta}$	R	n
1,2-Naphthoquinone	Li^+	0.019 ± 0.005	−0.012 ± 0.001	−1.333	27	73	0.993	5
1,2-Naphthoquinone	Na^+	0.015 ± 0.007	−0.004 ± 0.002	−1.476	49	51	0.928	5
1,2-Naphthoquinone	K^+	0.018 ± 0.005	0.002 ± 0.001	−1.806	67	33	0.927	5
1,2-Naphthoquinone	TEA^+	0.024 ± 0.005	0.004 ± 0.001	−2.111	61	39	0.967	5
1,4-Naphthoquinone	TEA^+	0.026 ± 0.006	0.005 ± 0.001	−2.352	55	45	0.966	5

Table VIII. Application of Equation 15 to $E_{1/2}$ Values for the Electroreduction of 1,2-Naphthoquinone in Various Solvents

Medium	$E_{1/2}^{\circ}$, V	μ, V Å	R
Interactionless solvent (E_T = DN = 0)	−2.237	0.589	0.959
AN	−1.103	0.266	0.963
PC	−1.026	0.205	0.958
A	−1.126	0.218	0.978
DMF	−1.014	0.086	0.943
DMSO	−0.950	0.056	0.955

ic size. Thus, the fraction of solvent interactions which are acidic must decrease with increase in the cation's radius.

Finally, it is noted that the values of the half-wave potential in the absence of solvent interactions (Q_0) vary considerably with cation size. This in turn indicates that the association constant, K_{as}, varies with cation size, being the most negative for the largest cation considered. This effect can be described empirically using an equation derived by Kalinowski[25] which relates the half-wave potential in the presence of ion pairing $E_{1/2}^{\text{ip}}$ to the ionic potential Φ:

$$E_{1/2}^{\text{ip}} = E_{1/2}^{\circ} + \mu\phi \qquad (15)$$

where μ is the sensitivity of $E_{1/2}^{\text{ip}}$ to change of cation size, and $E_{1/2}^{\circ}$ is the half-wave potential in the absence of ion-pair formation. Values of μ, $E_{1/2}^{\circ}$, and the correlation coefficient R obtained from analysis of the data of Fujinaga et al.[24] are summarized in Table VIII. It is immediately apparent that the sensitivity parameter μ depends considerably on the nature of the solvent and has its largest value in the hypothetical interactionless solvent. Thus, in the absence of solvent interactions ion pairing depends only on the properties of the two ions. As the solvating power of the medium increases, the individual ions interact much less with one another since they strongly interact with the solvent itself.

Conclusions

Application of the model described in this paper resulted in good fits in 55% of the cases interpreted; that is, the correlation coefficients obtained were greater than 0.95. Acceptable fits with correlation coefficients in the range $0.90 \leq R < 0.95$ were obtained for 35% of the fits. For only 10% was the value of R less than 0.9. Thus it is concluded that the present model offers an acceptable empirical method of analyzing solvent effects. Furthermore it is readily apparent from examination of the data in Tables II–VII that both solvent parameters are needed to describe the observed solvent effects. Thus, use of one parameter (eq 1), as has been most common in the past, would result in much poorer correlation between the observed quantity and the chosen parameter for approximately 50% of the cases considered.

It should be noted that the electrophilicity parameter E defined by Koppel and Palm[1] was considered here as a scale of solvent acidity. This parameter is related to E_T by eq 16,

$$E = E_T - 25.57 - 14.39[(\epsilon - 1)/(\epsilon + 2)] - 9.08[(n^2 - 1)/(n^2 + 2)] \qquad (16)$$

where ϵ is the dielectric constant of the solvent and n, its refractive index. The last two terms account for nonspecific solvation.[1] Applications of the present model with E replacing E_T did not result in any improvement in the fit to experimental data. The parameter E_T was chosen over E since the former is obtained directly from experiment, whereas the latter involves two additional empirical parameters. Finally, use of $1/\epsilon$ as a second parameter replacing E_T results in much worse correlations.

When the property affected by the solvent is directly related to an entropy change, the model proposed here is not as useful as when the solvent effect involves only enthalpy changes. It seems probable that a useful extension would involve the addition of a parameter to account for the entropic change so that eq 6 is then replaced by eq 17, where S is

$$Q = Q_0 + \alpha E_T + \beta \text{DN} + \gamma S \qquad (17)$$

a parameter describing the degree of order in the solvent and its resistance to changes in structure. Such an extension of the above model for solvent effects is presently under consideration.

Finally it should be pointed out that concepts which are similar in principle have been developed by Pearson[26] and Drago[27] to describe the hardness and softness of acids and bases. However, these approaches have been applied to make more quantitative the general concept of hardness and softness[28] rather than to discuss solvent effects in the form proposed in this paper.

Very recently, Chapman, Shorter, and colleagues[29] applied Palm and Koppel's multiparameter regression[1] to analyze data for the kinetics and mechanism of the reaction between carbocyclic acids and diazophenylmethane in donor aprotic solvents. When the above model is applied to the same data, the fit obtained is statistically as good as that obtained using the Palm–Koppel analysis. It must be emphasized that the latter model involves a four-parameter fit with the parameters ϵ, n, E, and B, whereas the present model only involves two. It seems that when data involving solvents with a wide range of properties are tested, a model introducing the dielectric parameters ϵ and n does not result in a better fit to the data.

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Deamination of Aliphatic Amines in Ethanol

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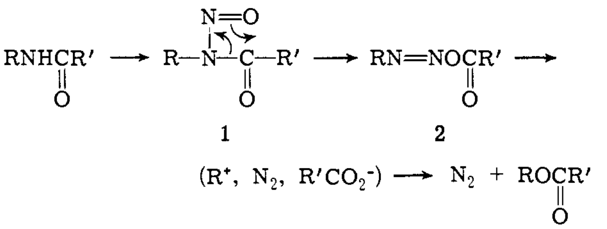
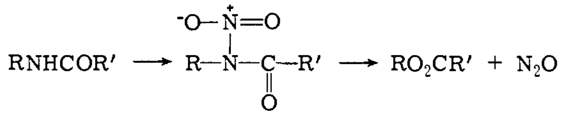
Abstract: The methyl and ethyl *N*-butyl-*N*-nitrocarbamates based on *n*-butylamine, *sec*-butylamine, and *tert*-butylamine were decomposed in ethanol and in other solvents, and the product distributions were measured. These results and those from related nitrocarbamates are discussed in terms of inert gas-separated ion-pair intermediates that appear to be characteristic of deamination reactions. The product distributions indicate a gradual change in mechanism with carbonium ion stability; discontinuities as a function of the substituent were not seen.

Deamination reactions, in which carbonium ions are formed by the loss of nitrogen or nitrous oxide from diazonium ion-like intermediates, are profoundly different from their solvolysis counterparts.[1,2] The present study involving the decomposition of a series of nitrocarbamates in ethanol was undertaken to elucidate these differences and also to clarify results reported for the deamination of primary and secondary alkylamines in acetic acid.

We chose the general "nitrosoamide" approach to deamination[1,3] rather than the triazene[1,4] or nitrous acid[1,2] methods because of the clean, unimolecular nature of the reaction. In the nitrosoamide approach, the reactant (**1**) is "primed" in that it bears a nitroso group, which together with the nitrogen of the amine (or amide) forms the nitrogen gas that is produced (eq 1); thus, no other reagent need be present in the reaction mixture. *N*-Nitroamides (**3**) are also "primed"; these derivatives yield nitrous oxide and the corresponding esters (eq 2).[5] Specifically, we used *N*-nitrocarbamates (**3**, R′ = O-alkyl) as the primed molecules[5b,6,7,8] in this study, because all members of the series R = primary, secondary, and tertiary are stable enough to be isolated and purified; in no other "primed" series investigated is this true.



$$\underset{\displaystyle O}{\underset{\|}{RNHCR'}} \longrightarrow \underset{\mathbf{1}}{R{-}\overset{\displaystyle N{=}O}{\overset{|}{N}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R'} \longrightarrow \underset{\mathbf{2}}{RN{=}NO\underset{\displaystyle O}{\underset{\|}{C}}R'} \longrightarrow (R^+,\ N_2,\ R'CO_2^-) \longrightarrow N_2 + RO\underset{\displaystyle O}{\underset{\|}{C}}R' \quad (1)$$



$$RNHCOR' \longrightarrow R{-}\overset{\displaystyle {}^-O{-}\overset{+}{N}{=}O}{\overset{|}{N}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}R' \longrightarrow RO_2CR' + N_2O \quad (2)$$

3, R′ = alkyl or O-alkyl

A reactive solvent was used to act as a scavenger for carbonium ion intermediates. Solvent-derived products were expected from carbonium ions that had escaped domination by the counterion, whereas the carbonate ester product (eq 2) was expected from noninterceptible carboxylate ion pairs (Chart I).[1,7] Although acetic acid has been used as a scavenger in the past,[1] we used ethanol in this study because of a serious side reaction of acetic acid. Acidic solvents, in general, exchange with the counterion of reaction intermediates (e.g., **7**) in proportion to their acidities (frontside exchange).[1,3d] Thus, the decomposition of a nitrosobenzamide (eq 1, R′ = C_6H_5) in acetic acid yields a benzoate ester (the intramolecular product) and also an acetate ester; the latter stems in part from frontside exchange and in part from a scavenging of the carbonium ions, e.g., from **8**, by the solvent.[1,3d] Ethanol as the solvent functions only, or largely, in the latter capacity because of its relatively low acidity.

In the present study, the methyl *N*-nitrocarbamates[6b] of *n*-butylamine (**4a**), *sec*-butylamine (**4b**), and *tert*-butylamine (**4c**) (Chart I) and also the corresponding ethyl esters (**5a–c**) were decomposed in ethanol and in other solvents (Table I).

Discussion

Products. The decomposition of methyl *N*-nitrocarbamates **4a–c** in inert solvents yields the corresponding carbonate esters, olefins, nitrous oxide, carbon dioxide, and methanol (Chart I, Table I).[5a,6b] In a reactive solvent such as ethanol, in addition to the above products (which constitute the intramolecular portion of the reaction), solvent-derived products are formed, namely the butyl ethyl ethers. Prolonged reaction times are required for the decomposition of the *n*-butyl derivatives (**4a** and **5a**) and, in these cases, ester