sonably acquire them in a time compatible with their lifetime. In any case the concerted mechanism cannot compete with the one-bond scission. This alternative pathway necessitates activation energies which, even though they still appear somewhat too large in our semiquantitative scheme, are much smaller. Any improvement in our calculations (not to mention the substituent effects on the azo group) would bring these energies in a range where they could be acquired by the reacting excited states (be it the $\pi\pi^*$ sensitization experiments or the $n_-\pi^*$ singlet via direct irradiation) in a photochemically decent period of time. With the aforementioned restrictions in mind, nitrogen extrusion appears to follow a stepwise breaking mechanism of the pair of NH bonds which is initiated by the light-induced population of the lowest $n_-\pi^*$ singlet state of the azo chromophore.

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Activity Coefficients of an Electrolyte A or B in a Ternary Mixture (A + B + H₂O) and a Transition Model

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Abstract: Based on a transition model, as applied to solutions of a single electrolyte, a semiempirical expression has been proposed to predict the activity coefficients of a 1:1 electrolyte A or B in a ternary mixture (A + B + H₂O). The calculated activity coefficients compare well with their experimental values. Glueckauf and other relations of mixed electrolyte solutions follow as a consequence of cross-differentiation of the fundamental expression.

Recent years have witnessed considerable interest in the thermodynamic properties of aqueous electrolyte mixtures. Much of this interest stems from the importance of mixed electrolytes in such fields as oceanography and geochemistry and considerable attention[1-3] has been paid to predict the activity coefficients of each component of an aqueous mixed electrolyte solution. Lietzke and Stoughton[4] have recently

extended their two-structure model,[5] as applied to solutions of a single electrolyte, to predict the activity coefficients of each component in a mixed electrolyte solution with surprising accuracy. However, their fundamental equation does not explain some of the other features of these aqueous mixed electrolyte solutions (e.g., Glueckauf relations, etc.). The present work is a semiempirical extension of a transition model[6] to predict the activity coefficient data of the components A or B of a ternary (A + B + H₂O) mixture. Glueckauf and other rela-

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tions follow as a consequence of the cross-differentiation of the resultant fundamental equation.

Extension of the Transition Model of Electrolyte Solutions to Predict the Activity Coefficients of an Electrolyte in a Ternary Mixture

The transition model[6] of electrolyte solutions envisages that ions *at all concentrations* have a certain degree of mobility, it is the time average population density of these ions that corresponds to either the Debye model or the "lattice" model[7] and that ionic behavior in solution is governed by (i) interionic effects that cause the ions to be arranged on a "loose lattice" and (ii) effects due to thermal jostling. The effects due to factor (i) determine "lattice" contributions and those due to factor (ii) govern Debye's contribution. The activity coefficient of an electrolyte in water was then shown[6] to involve contributions due both to "Debye" and "lattice" ionic distributions so that

$$\log \gamma_\pm = [-A_\gamma Z_+ Z_- (\frac{1}{2}\Sigma C_i Z_i^2)^{1/2}/$$
$$(1 + ab(\frac{1}{2}\Sigma C_i Z_i^2)^{1/2})]$$
$$\times \text{ probability that an ion behaves as a Debye ion}$$
$$+ [-Ac^{1/3} + BC + \delta] \times \text{ probability that an ion behaves}$$
$$\text{as a "lattice" ion} - \log (1 + vmM_1/1000) \quad (1)$$

where the various symbols have their usual meanings.[6-8] Statistical mechanical treatment[6] of the transition model finally expresses the activity coefficients of an electrolyte in solution by

$$\log \gamma_\pm \doteq [-A_\gamma Z_+ Z_- (\frac{1}{2}\Sigma C_i Z_i^2)^{1/2}/$$
$$(1 + 1.4(\frac{1}{2}\Sigma C_i Z_i^2)^{1/2}]$$
$$\times e^{-15m} + (1 - e^{-15m})[-Ac^{1/3} + BC + \delta]$$
$$- \log (1 + vmM_1/1000) \quad (2)$$

However, in a ternary mixture (A + B + H$_2$O) the ionic behavior of say A (although being determined by the factors (i) and (ii) stated above) is influenced by the presence of ions due to B. At the same time the ionic behavior of B is also being perturbed by their interactions with ions due to A. The activity coefficients of A in the ternary mixture is then determined by the following:

(a) The extent to which the ionic behavior of A in water is governed by the presence of ions due to B. This may be expressed by the normal ionic behavior of A in water times the probability that an ion due to B behaves as a Debye ion and so influences the ion behavior of the ions due to A. This probability was shown[6] to be given by $C'e^{-15m}$ and so the contribution to the activity coefficient of A in the ternary mixture due to this factor may then be expressed by

$$[C'e^{-15m_B}] \log \gamma_\pm(A)_0 \quad (3)$$

where C' is a constant, $\gamma_\pm(A)_0$ is the activity coefficient of A in a solution containing only this electrolyte in water at a molality m_A and m_B is the molality of the solution due to B.

(b) The ionic behavior of B as perturbed by their interactions with the ions due to A. This may further be assumed to be determined by (1) the unperturbed behavior of B in water and (2) a perturbation term. The contribution due to this factor would depend on an interaction parameter, α_{AB}, and on the ionic strength[9] ($\mu = \frac{1}{2}\Sigma m_B Z_B^2$) of the solution due to B.

The contribution to the activity coefficients of A in the ternary mixture due to this factor may then be expressed by

$$\log \gamma_\pm(B)_0 + \alpha_{AB}\mu_B \quad (4)$$

If the contributions due to factors "(a)" and "(b)" mentioned above operate independently, the activity coefficient of an electrolyte A in the ternary mixture may then be expressed by a semiempirical equation

$$\log \gamma_\pm(A)_B = C'e^{-15m_B} \log \gamma_\pm(A)_0$$
$$+ \log \gamma_\pm(B)_0 + \alpha_{AB}\mu_B \quad (5)$$

where $\gamma_\pm(A)_0$ represents the activity coefficients of A in a solution containing only this electrolyte at a molality m_A and $\gamma_\pm(B)_0$ represents the corresponding quantity for B at a molality m_B.

Results of the Calculations

Evaluation of $\gamma_\pm(A)_B$ from eq 5 requires the knowledge of C' and α_{AB}. However, there is no direct method to evaluate both of these and for the present one could evaluate α_{AB} by fitting the experimental $\gamma_\pm(A)_B$ value for a 1 M solution of B in water to expression 5. This value of α_{AB} could next be used to calculate C' by fitting $\gamma_\pm(A)_B$ at $m_B = 0.01$ to eq 5. This procedure when applied to the activity coefficient data[10] of aqueous hydrochloric acid (A) ($m_A = 0.01$) in sodium chloride solution yielded $C' = 0.324$. Since C' does not depend on the particular nature of an electrolyte, we take $C' = 0.324$ in expression 5 and express $\log \gamma_\pm(A)_B$ by

$$\log \gamma_\pm(A)_B = 0.324e^{-15m_B} \log \gamma_\pm(A)_0$$
$$+ \log \gamma_\pm(B)_0 + \alpha_{AB}\mu_B \quad (6)$$

We shall use this equation to calculate $\gamma_\pm(A)_B$ in a ternary mixture. The only unknown quantity α_{AB} would be evaluated by fitting the experimental $\gamma_\pm(A)_B$ at 1 M concentration of B to eq 6.

Activity coefficients of hydrochloric acid (A) ($m_A = 0.01$) in aqueous sodium chloride, potassium chloride, and lithium chloride solutions and of hydrobromic acid (A) ($m_A = 0.01$) in aqueous sodium bromide and potassium bromide solutions (in which m_B is being continuously varied and $m_A + m_B$ is further not constant) calculated in this way are recorded in Table I and they compare well with their corresponding experimental values.[10] The $\gamma_\pm(B)_0$ values for different concentrations of B and $\gamma_\pm(A)_0$ for $m_A = 0.01$ were calculated[6] from eq 2. The necessary data for this purpose were taken from our earlier work.[6]

Finally we considered the effectiveness of eq 6 to predict γ(hydrochloric acid) in hydrochloric acid (A) + sodium chloride (B) + water mixture in which both m_A and m_B are varied subject to the condition that $m_A + m_B = 0.5$. For this purpose we used the α_{AB} value as obtained in the analysis of activity coefficient data[10] of HCl(A) in HCl(A) + NaCl(B) mixture at 25 °C (when $m_A = 0.01$ and m_B was varied continuously) in terms of eq 6 in the manner described earlier in this paper. The activity coefficient data at 25 °C of HCl(A) in HCl(A) + NaCl(B) mixture calculated in this manner are recorded in Table II and it compares reasonably well with the corresponding experimental data.[11] We now consider another aspect of eq 6.

The activity coefficient of B in the ternary mixture is expressed by

$$\log \gamma_\pm(B)_A = (\frac{1}{3})(e^{-15m_A}) \log \gamma_\pm(B)_0$$
$$+ \log \gamma_\pm(A)_0 + \alpha_{BA}\mu_A \quad (7)$$

while that of A is expressed by eq 6. Then following McKay,[12] we express the total ionic strength as

$$\mu_A + \mu_B = \mu$$

so that

$$\mu_A = \mu - \mu_B = jm_A$$

and

$$\mu_B = \mu - \mu_A = km_B$$

where j and k are constants, each of which is characteristic of the valence type of the electrolyte. Consequently the cross-

Table I. Comparison of the Mean Activity Coefficient of Hydrochloric Acid and of Hydrobromic Acid in Various Halide Solutions[a] with Their Corresponding Experimental Values at 25 °C

m		$\gamma_{HCl(A)}$ in			$\gamma_{HBr(A)}$ in	
		NaCl	KCl	LiCl	NaBr	KBr
	α_{AB}	0.0474	0,0770	0.0149	0.0676	0.0754
0.01	Calcd	0.874	0.878	0.877	0.882	0.879
	Exptl[10]	0.874	0.874	0.881	0.878	0.874
0.02	Calcd	0.853	0.850	0.857	0.856	0.853
	Exptl[10]	0.854	0.852	0.861	0.859	0.853
0.05	Calcd	0.819	0.811	0.823	0.816	0.816
	Exptl[10]	0.818	0.816	0.827	0.821	0.818
0.10	Calcd	0.784	0.776	0.789	0.791	0.781
	Exptl[10]	0.784	0.782	0.796	0.791	0.783
0.20	Calcd	0.757	0.745	0.761	0.762	0.751
	Exptl[10]	0.752	0.747	0.766	0.761	0.750
0.5	Calcd	0.731	0.709	0,753	0.756	0.717
	Exptl[10]	0.730	0.707	0.757	0.756	0.717

[a] Acid concentration = 0.01 M; salt concentration = m.

Table II. Comparison of the Mean Activity Coefficient of Hydrochloric Acid in HCl + NaCl Mixture at a Total Molality of 0.5 M with Their Corresponding Experimental Values at 25 °C

m_{HCl}	m_{NaCl}	γ_{HCl} Calcd	γ_{HCl} Exptl[11]
0.25	0.25	0.746	0.741
0.10	0.40	0.724	0.732
0.05	0.45	0.720	0.729
0.01	0.49	0.719	0.726
0.001	0.499	0.718	0.726

differentiation equation

$$\nu_A \left[\frac{\partial\{\log \gamma_\pm(A)_B\}}{\partial m_B} \right]_{m_A} = \nu_B \left[\frac{\partial}{\partial m_A}\{\log \gamma_\pm(B)_A\} \right]_{m_B}$$

yields

$$\nu_A k \left[\frac{\partial}{\partial\mu} \log \gamma_\pm(B)_0 + \alpha_{AB} + (\mu - \mu_A) \frac{\partial}{\partial\mu} \alpha_{AB} \right.$$

$$\left. + (-5)(e^{-15\mu_B}) \log \gamma_\pm(A)_0 \right] = \nu_B j \left[\frac{\partial}{\partial\mu} \log \gamma_\pm(A)_0 + \alpha_{BA} \right.$$

$$\left. + \mu_A \frac{\partial}{\partial\mu} \alpha_{BA} - 5(e^{-15\mu_A}) \log \gamma_\pm(B)_0 \right] \quad (8)$$

Since $\gamma_\pm(A)_0$, $\gamma_\pm(B)_0$, α_{AB}, and α_{BA} are functions of μ only, we can replace the partial differentials with the total differentials so that eq 8 yields

$$\nu_A k \left[\frac{d}{d\mu} \log \gamma_\pm(B)_0 + \alpha_{AB} + (\mu - \mu_A) \frac{d}{d\mu} \alpha_{BA} \right.$$

$$\left. - 5e^{-15\mu_B} \log \gamma_\pm(A)_0 \right] = \nu_B j \left[\frac{d}{d\mu} \log \gamma_\pm(A)_0 + \alpha_{BA} \right.$$

$$\left. + \mu_A \frac{d}{d\mu} \alpha_{BA} - 5e^{-15\mu_A} \log \gamma_\pm(B)_0 \right] \quad (9)$$

Expression 9 now requires that for all values of μ and μ_A, the coefficients of μ_A must vanish. Thus

$$\frac{d}{d\mu} [-\nu_A k \alpha_{AB} - \nu_B j \alpha_{BA}] = 0$$

or

$$\nu_A k \alpha_{AB} + \nu_B j \alpha_{BA} = \text{constant} \quad (10)$$

This result first established by Glueckauf[13] is the same as Harned and Owen[14] derived following the method of McKay[12] on the assumption that the activity coefficient of A in the ternary mixture is given by an empirical equation

$$\log \gamma_\pm(A)_B = \log \gamma_\pm(A)_0 - \alpha_{AB}\mu_B \quad (11)$$

We now consider the relationship between α_{AB} and α_{BA}. From eq 9 we have

$$\nu_B j \frac{d}{d\mu} [\alpha_{BA}\mu]_{\mu_B} = \nu_A k \left[\frac{d}{d\mu} \log \gamma_\pm(B)_0 \right.$$

$$\left. + \mu_B \frac{d}{d\mu} \alpha_{AB} + \alpha_{AB} - 5e^{-15\mu_B} \log \gamma_\pm(A)_0 \right]$$

$$- \nu_B j \left[\frac{d}{d\mu} \log \gamma_\pm(A)_0 - 5e^{-15\mu_A} \log \gamma_\pm(B)_0 \right] \quad (12)$$

Integration of eq 12 at constant μ_B between the limits $\mu = \mu_B$ and $\mu = \mu$ yields

$$\nu_B j [\alpha_{BA}\mu] = \nu_A k [\log \gamma_\pm(B)_0]_{\mu_B}^\mu + \nu_A k \mu_B \alpha_{AB}$$

$$+ \nu_A k \int_{\mu_B}^\mu \alpha_{AB} \, d\mu - 5\nu_A k e^{-15\mu_B} \int_{\mu_B}^\mu \log \gamma_\pm(A)_0$$

$$- \nu_B j [\log \gamma_\pm(A)_0]_{\mu_B}^\mu + 5\nu_B j \log \gamma_\pm(B)_0 \int_{\mu_B}^\mu e^{-15\mu_A} \, d\mu$$

$$(13)$$

Expression 13 thus provides a method to evaluate α_{BA}.

The limiting value of α_{BA} at $\mu_A = \mu$ as $\mu_B \rightarrow 0$ follows from eq 13 and is given by

$$\mu\nu_B j \alpha_{BA(\mu)} = \nu_A k \log \gamma_\pm(B)_0 + \nu_A k \int_0^\mu \alpha_{AB} \, d\mu$$

$$- 5\nu_A k \int_0^\mu \log \gamma_\pm(A)_0 \, d\mu - \nu_B j \log \gamma_\pm(A)_0 \quad (14)$$

which for a ternary solution containing two 1:1 electrolytes reduces to

$$\mu\alpha_{BA} = \log \gamma_\pm(B)_0 - \log \gamma_\pm(A)_0$$

$$+ \int_0^\mu \alpha_{AB} \, d\mu - 5 \int_0^\mu \log \gamma_\pm(A)_0 \, d\mu \quad (15)$$

If we assume that α_{AB} does not vary with μ and that log $(\gamma_\pm(B)_0/\gamma_\pm(A)_0) = B\mu$ (Akerlof and Thomas' relation[15]) holds, then eq 15 is equivalent to Harned and Owen's eq[16] (14-5-7).

Conclusions

The present work thus suggests that eq 6 may be very useful for obtaining quick and reasonable estimate of activity coefficient values for components A or B of a ternary (A + B +

H$_2$O) electrolyte mixture. An additional advantage of the present treatment is that it not only predicts the activity coefficient data of the components of a ternary electrolyte mixture but Glueckauf's relation and Harned and Owen's eq (14-5-7) also follow as a direct consequence of the cross-differentiation of the fundamental eq 6. Further only one adjustable parameter is needed unlike models which retain the Debye–Hückel term at all values of the ionic strength and for which more parameters are required to represent equally well the activity coefficient data. In view of the lack of any satisfactory theory of mixed electrolytes solution, the semiempirical eq 6 is a good representation of the activity coefficient data of the components A or B of a (A + B + H$_2$O) mixture over an appreciable concentration range.

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Topological Orbitals, Graph Theory, and Ionization Potentials of Saturated Hydrocarbons[1]

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Abstract: Graph theory is used to obtain a complete set of degenerate orthonormal eigenvectors on a bond orbital basis for saturated hydrocarbons. After symmetry and topological analyses, the eigenvector coefficients are written by inspection. The obtained wave functions are used as zero-order functions to parametrize a bond orbital theory of molecular ionization potentials. The parametrization method uses experimental data and a novel reverse similarity transformation to generate all parameters in a single step. The final parameters, obtained after iteration, give calculated ionization potentials that compare favorably with experimental values (correlation coefficient 0.9995).

I. Introduction

At the simplest levels, the π electrons of unsaturated molecules are customarily treated by three different theoretical techniques. These are the Hückel[2] and perturbational molecular orbital[3] methods (HMO and PMO), which give numerical results that can be compared with experimental values, and the use of orbital-symmetry principles[4,5] (Woodward–Hoffmann rules), which lead to significant qualitative predictions concerning reactivity in pericyclic reactions. The quantitative results obtained by the PMO method[3] are particularly noteworthy since their correlations with structure–reactivity data are as good as those obtained using more complex LCAO-MO–SCF calculations. An additional feature is that PMO calculations are very simple to carry out by hand making use of the mathematical properties of nonbonding molecular orbitals.

In saturated systems, several different levels of quantum-mechanical empirical approximations have been tested, with numerous published applications.[6] Orbital symmetry principles have also been applied in discussions of reactivity problems involving σ electrons.[5] However, a parallel development of a perturbational MO theory for σ systems has not materialized. This may be due to the fact that it is not generally realized that a complete set of orthonormal bond orbital coefficients can be obtained for σ systems simply from a knowledge of the system topology. The situation is actually more advantageous than in the case of π systems, where usually only a single nonbonding orbital will have predetermined coefficients.

Some characteristics of these localized topological orbitals were first described by Platt in 1959 and 1961,[7,8] and Herndon has outlined a single example of their use in predicting molecular ionization potentials.[9] A similar treatment by Thompson has been used to predict MO symmetries from localized pair models.[10] None of these works sufficiently illustrates the utility of this approach. Therefore, the objective of this article is first to show how topological wave functions are quickly and efficiently obtained for saturated systems. The exposition will make use of elementary concepts of group theory and graph theory where appropriate. In order to avoid an abstract presentation of necessary concepts, the procedures will be demonstrated by application to the simplest organic compounds, i.e., the saturated alkanes.

In a following section, the obtained orbitals will be used as starting points for parametrization of a highly correlative empirical MO theory of ionization potentials. The development will employ first-order perturbation theory and a novel averaging algorithm that is very effective for operations of this type. A large number of MO theories have been used to correlate ionization potentials.[6,11–17] The present method gives quan-