J. Am. Chem. Soc. **1990**, *112*, 6854-6858

Analysis of Solvent Effects on the Kinetics of Reactions in Solution Using Kirkwood–Buff Integral Functions: Alkaline Hydrolysis of the Diazobutadiene Complex Tris(glyoxal bis(methylimine))iron(II) Complex and Spontaneous Hydrolysis of 4-Methoxyphenyl 2,2-Dichloropropionate in Water + 2-Methyl-2-propanol Mixtures at 298.2 K

Michael J. Blandamer,*,† Nicholas J. Blundell,† John Burgess,† Heather J. Cowles,† Jan B. F. N. Engberts,‡ Ian M. Horn,† and Percy Warrick, Jr.§

Contribution from the Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK, Department of Organic Chemistry, University of Groningen, Nijenborgh 16, AG 9747 Groningen, The Netherlands, and Department of Chemistry, Westminster College, New Wilmington, Pennsylvania 16172. *Received February 12, 1990*

Abstract: Rate constants and volumes of activation for the spontaneous hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate and for the alkaline hydrolysis of the low-spin iron(II) complex $[Fe(MeN{=}CHCH{=}NMe)_3]^{2+}$ in water + 2-methyl-2-propanol (*tert*-butyl alcohol) mixtures are analyzed to yield Kirkwood–Buff integral functions describing preferential solvation of solutes in this mixed aqueous solvent system. The derived integral functions characterize the affinities of initial and transition states for water and for alcohol in the mixtures. The integral functions are calculated by using kinetic data and the thermodynamic properties of the water + alcohol mixture. The dependence of rate constants on alcohol mole fraction is analyzed, yielding the change in relative affinities of the initial state for the two solvent components on proceeding to the transition state. Incorporation of data describing the dependence of volumes of activation on mixture composition offers an insight into the separate affinities of initial and transition states for the components of the solvent mixture. For the hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate, the dominant feature is preferential solvation (hydrophobic bonding) of the initial state by added alcohol. This trend is more important in determining the kinetic medium effect than solvation of the hydrophilic transition state by water. The reverse trend is established in the case of the iron(II) complex undergoing alkaline hydrolysis. With increase in mole fraction preferential solvation of the initial state by water is the dominant feature, increasing until the alcohol mole fraction reaches 0.2 before falling sharply away. As the composition of the solvent mixture becomes alcohol-rich, there is a dramatic decrease in the preferential solvation by either water or alcohol.

The kinetics of reactions involving solutes in aqueous solutions[1-3] are controlled by water–solute and by neighboring water–water interactions, where the term solute refers here to both initial and transition states in the reaction process. Confirmation of this control emerges from the marked changes in rate constants and related activation parameters when another solute or cosolvent is added. In the case of dilute aqueous solutions we have shown[4-7] that changes in kinetic parameters can be understood in terms of pairwise interaction parameters describing the effects of added solute on initial and transition states. In a further development, these pairwise interaction parameters were interpreted in terms of group interaction parameters by using procedures based on those suggested by Savage and Wood;[8,9] i.e., the SWAG model. The latter approach describes the effects on partial molar properties of solutes brought about by overlap involving solvent cospheres[10] around solutes in aqueous solutions. The treatment is limited to dilute aqueous solutions where the assumption of simple pairwise additivity for interaction energies between solutes remains valid. The analysis described below shows how the quantitative treatment developed from the model described by Kirkwood and Buff[11] can be applied to kinetics of reactions in solution across the mole fraction range, $0 < x_2 < 1.0$ where x_2 is the mole fraction of the cosolvent.

We illustrate application of this theory by reference to reactions involving an inorganic and an organic substrate in water + 2-methyl-2-propanol mixtures. We chose this mixture because the thermodynamic properties signal quite striking deviations from ideal behavior and because the kinetic parameters for reactions in this mixture as solvent show striking dependences on mixture composition.[1,2] The acyl-activated ester, 4-methoxyphenyl 2,2-dichloropropionate, undergoes hydrolysis in aqueous mixtures in a reaction that is first order in ester. In mildly acidic solutions (pH ca. 3–5), the pseudo-first-order rate constants are pH independent and the hydrolysis is a water-catalyzed process. The mechanism has been studied in some detail[12,13] and involves water-catalyzed nucleophilic attack of water on the ester carbonyl as evidenced by large solvent deuterium isotope effects [$k(H_2O)/k(D_2O) \simeq 3.2$] and large negative entropies of activation (ca. -165 J K^{-1} mol^{-1}) and the finding that the rate constant for the water reaction falls on the same Brønsted plot as the rate constants for other general-base catalysis.[14] Further support for the mechanism (Scheme I) of hydrolysis for these types of esters is provided by a proton inventory study, which showed that three protons (H_a and two H_b's; see scheme) contribute to the overall

---

† University of Leicester.
‡ University of Groningen.
§ Westminster College.

(1) Engberts, J. B. F. N. In *Water A Comprehensive Treatise*; Franks, F. Ed.; Plenum Press: New York, 1973; Vol. 6, Chapter 4.

(2) Blandamer, M. J. *Adv. Phys. Org. Chem.* **1977**, *14*, 204.

(3) Blandamer, M. J.; Robertson, R. E.; Scott, J. M. W. *Prog. Phys. Org. Chem.* **1985**, *15*, 149.

(4) Blokzijl, W.; Jager, J.; Engberts, J. B. F. N.; Blandamer, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 6411.

(5) Blokzijl, W.; Engberts, J. B. F. N.; Jager, J.; Blandamer, M. J. *J. Phys. Chem.* **1987**, *91*, 6022.

(6) Blandamer, M. J.; Burgess, J.; Engberts, J. B. F. N.; Sanchez, F. *Faraday Discuss. Chem. Soc.* **1988**, *No. 85*, 309.

(7) Blandamer, M. J.; Burgess, J. *Pure Appl. Chem.* **1990**, *62*, 9.

(8) Savage, J. J.; Wood, R. H. *J. Solution Chem.* **1976**, *5*, 733.

(9) Spitzer, J. J.; Suri, S. K.; Wood, R. H. *J. Solution Chem.* **1985**, *14*, 571.

(10) Gurney, R. W. *Ionic Processes in Solution*; McGraw-Hill: New York, 1953.

(11) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 571.

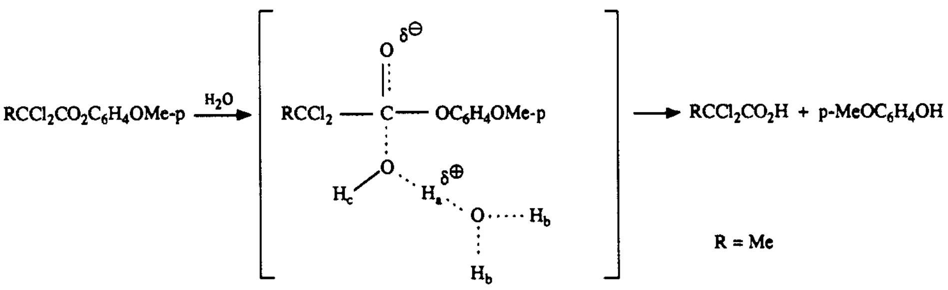
(12) Fife, T. H.; McMahon, D. M. *J. Am. Chem. Soc.* **1969**, *81*, 7481.

(13) Engbersen, J. F. J. Ph.D. Thesis, University of Groningen, 1976.

(14) Jencks, W. P.; Carriulo, J. *J. Am. Chem. Soc.* **1961**, *83*, 1743.

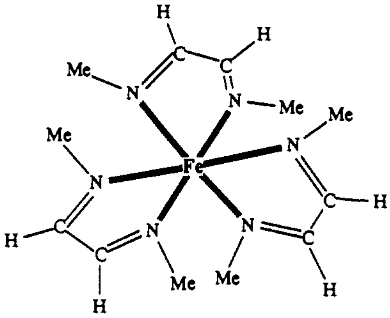
0002-7863/90/1512-6854$02.50/0

Scheme I



solvent deuterium isotope effect.[15]

In aqueous solution at 298.2 K, the low-spin iron(II) complex $[\mathrm{Fe(gmi)_3}]^{2+}$ undergoes alkaline hydrolysis, the second-order rate constant[16] being 5.2×10^{-3} $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$; gmi = glyoxal bis(methylimine), MeN=CHCH=NMe. The rate-determining step is bimolecular involving attack by $\mathrm{OH^-}$ at the complex cation.



Background to Analysis. According to the statistical thermodynamic treatment developed by Kirkwood and Buff,[11] it is possible to calculate the thermodynamic properties of a mixture from a knowledge of the dependence on intermolecular separation R of the angle-averaged orientation-averaged pair correlation function $g_{\alpha\beta}(R)$ (with $\alpha = 1, 2$ and $\beta = 1, 2$) for the mixture where 1 represents water and 2 represents the cosolvent. This correlation function is expressed in terms of integral functions $G_{\alpha\beta}$ called an affinity and defined by eq 1. As shown by Ben-Naim[17-19] and

$$G_{\alpha\beta} = \int_0^\infty [g(R) - 1.0] 4\pi R^2 \, \mathrm{d}R \qquad (1)$$

by Hall,[20] it is possible to travel in the reverse direction and calculate $G_{\alpha\beta}$ (for $\alpha = 1, 2$ and $\beta = 1, 2$) as a function of mole fraction x_2 by using the thermodynamic properties of a mixture. Unfortunately it is impossible to break from $G_{\alpha\beta}$ into the integral and hence obtain $g_{\alpha\beta}$ as a function of R. Nevertheless $g_{\alpha\beta}(R)$ is dominated by the dependence of $g_{\alpha\beta}(R)$ on R at low R. In other words, $G_{\alpha\beta}$ is an indicator of the local organization of α molecules around β molecules reflecting the "affinity" of α molecules for β molecules.

Liquid Mixtures. The input to the analysis comprises the dependence on x_2 of the excess molar Gibbs energy of mixing $G_m{}^E$, the densities (and hence molar volume V_m, excess molar volume $V_m{}^E$, and partial molar volumes V_1 and V_2), and the isothermal compressibility κ_T. The key step in the calculation involves the calculation of the second differential $\mathrm{d}^2G_m{}^E/\mathrm{d}x_2{}^2$ as a function of x_2. We have discussed[21,22] details of these calculations in conjunction with the calculation of G_{11}, G_{12}, and G_{22} for (i) propanone + water, (ii) DMSO + water, (iii) hydrogen peroxide + water, and (iv) acetonitrile + water mixtures.

Preferential Solvation. The analysis described above is extended to describe the properties of solute j in aqueous mixtures.[23,24] Here we use the treatment outlined by Newman[23] and applied by Covington and Newman[25] to spectroscopic properties, particularly NMR data for ions in aqueous mixtures.

The required quantities for a solute j in a mixture of water ($\equiv 1$) and cosolvent ($\equiv 2$) are the affinities G_{1j} and G_{2j}. Because G_{1j}, for example, is dominated by $[g_{1j}(R) - 1]$ at low R (cf. eq 1), G_{1j} measures the affinity of solute j for liquid 1 in the mixture. Similar comments apply to G_{2j}. Newman showed that the difference between G_{1j} and G_{2j} is related to the dependence of the standard chemical potential of solute j, $\mu_j{}^\circ$, on mixture composition as expressed by the differential $\mathrm{d}\mu_j{}^\circ/\mathrm{d}x_2$, eq 2.

$$G_{1j} - G_{2j} = (\mathrm{d}\mu_j{}^\circ/\mathrm{d}x_2) V_m / RTQ \qquad (2)$$

where

$$Q = 1 + [x_2(1 - x_2)/RT](\mathrm{d}^2G_m{}^E/\mathrm{d}x_2{}^2) \qquad (3)$$

$G_{1j} - G_{2j}$ measures the preferential solvation of solute by solvent 1 and solvent 2. V_m is the molar volume of the binary liquid mixture. Consequently, from a knowledge of the dependence on x_2 of both $G_m{}^E$ and $\mu_j{}^\circ$ we obtain the difference $G_{1j} - G_{2j}$. Newman also showed[23] that estimates of the separate terms are obtained from a knowledge of the dependence on x_2 of the limiting partial molar volume $V_j{}^\infty$, eq 4.

$$G_{1j} = x_2(V_2/V_m)[G_{1j} - G_{2j}] + \kappa_T RT - V_j{}^\infty \qquad (4)$$

Kinetics of Reactions in Binary Solvent Mixtures. Here we combine the Newman analysis[23] described above, with a description of chemical reactions in solution using transition-state theory.[26] There are two stages to the analysis.

Stage I follows on from eq 2 using kinetic data describing the dependence of rate constant on mole fraction x_2. In many cases the analysis stops at this point. Stage II develops the argument from eq 4 for those cases where the kinetic data include volumes of activation.

First-Order Reactions. According to transition-state theory,[26] but recognizing the assumptions inherent in this theory, the Gibbs energy of activation for reaction in a solvent formed by an aqueous mixture having cosolvent mole fraction x_2 $\Delta G^\ddagger(x_2)$ is related to the difference between the standard chemical potentials of initial $\mu^\circ(\mathrm{is}; x_2)$ and transition $\mu^\circ(\neq; x_2)$ states at fixed T and p, eq 5.

$$\Delta G^\ddagger(x_2) = \mu^\circ(\neq; x_2) - \mu^\circ(\mathrm{is}; x_2) \qquad (5)$$

Then the change in Gibbs energy of activation on going from an aqueous solution (aq) to a solution in a solvent mixture having mole fraction x_2 is given[27] by eq 6.

$$\begin{aligned} \Delta(\mathrm{aq} \rightarrow x_2)\Delta G^\ddagger &= \Delta(\mathrm{aq} \rightarrow x_2)\mu^\circ(\neq) - \Delta(\mathrm{aq} \rightarrow x_2)\mu^\circ(\mathrm{is}) \\ &= -RT \ln [k(x_2)/k(\mathrm{aq})] \end{aligned} \qquad (6)$$

---

(15) Karzyn, W. Ph.D. Thesis, University of Groningen, 1979.

(16) Burgess, J.; Hubbard, C. D. *J. Am. Chem. Soc.* **1984**, *106*, 1717.

(17) Ben-Naim, A. *Water and Aqueous Solutions*; Plenum Press: New York, 1974.

(18) Ben-Naim, A. *J. Chem. Phys.* **1977**, *67*, 4884.

(19) Ben-Naim, A. *Cell. Biophys.* **1988**, *12*, 255.

(20) Hall, D. G. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 25.

(21) Blandamer, M. J.; Blundell, N. N.; Burgess, J.; Cowles, H. J.; Horn, I. M. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 277.

(22) Blandamer, M. J.; Blundell, N. J.; Burgess, J.; Cowles, H. J.; Horn, I. M. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 283.

(23) Newman, K. E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1387.

(24) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3019.

(25) Covington, A. K.; Newman, K. E. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1393.

(26) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw Hill: New York, 1941.

Stage I. The dependence of rate constant on cosolvent mole fraction is described in terms of the differential, $d\Delta(aq \rightarrow x_2)\Delta G^{\ddagger}/dx_2$. Combination of eqs 2 and 6 yields eqs 7, which we use

$$[G_{1\neq} - G_{2\neq}] - [G_{1is} - G_{2is}] \equiv [G_{1\neq} - G_{1is}] - [G_{2\neq s} - G_{2is}] = V_m[d\Delta(aq \rightarrow x_2)\Delta G^{\ddagger}/dx_2]/RTQ = g_k \text{ (by definition)} \quad (7)$$

to define a quantity g_k. Hence g_k is the change in the relative affinities for water (liqud 1) and cosolvent (liquid 2) of the substrate on going from initial to transition state. As shown by eq 3, the excess molar Gibbs energy of the mixture is contained within the quantity Q.

Stage II. According to eq 4, the affinity for the initial state is given by eq 8.

$$G_{1is} = x_2(V_2/V_m)[G_{1is} - G_{2is}] + \kappa_T RT - V_{is}^{\infty}(x_2) \quad (8)$$

Similarly for the transition state

$$G_{1\neq} = x_2(V_2/V_m)[G_{1\neq} - G_{2\neq}\neq] + \kappa_T RT - V_{\neq}^{\infty}(x_2) \quad (9)$$

Incorporating eq 7 we define quantity g_{k1}.

$$[G_{1\neq} - G_{1is}] = V_m[d\Delta(aq \rightarrow x_2)\Delta G^{\ddagger}/dx_2]/RTQ = g_{k1} \text{ (by definition)} \quad (10)$$

Here $G_{1\neq} - G_{1is}$ is the change in affinity for water (liquid 1) of the substrate on activation. Having calculated this difference, g_{k1}, we obtain, using g_k, the corresponding change in affinity for the cosolvent (liquid 2) measured by $G_{2\neq} - G_{2is}$, defined as g_{k2}.

Second-Order Reactions. For this class of reactions there are two initial states isA and isB, which form a single transition state, symbol $\neq$. Here we rewrite eq 6.

$$\Delta(aq \rightarrow x_2)\Delta G^{\ddagger} = \Delta(aq \rightarrow x_2)\mu^{\circ}(\neq) - \Delta(aq \rightarrow x_2)\mu^{\circ}(isA) - \Delta(aq \rightarrow x_2)\mu^{\circ}(isB) = -RT \ln [k(x_2)/k(aq)] \quad (11)$$

Here $\ln [k(x_2)/k(aq)]$ is the ratio of second-order rate constants.

Stage I. The analogue of eq 7 incorporates terms describing the affinities for the two reactants, isA and isB, eq 12. The

$$[G_{1\neq} - G_{2\neq}] - [G_{1isA} - G_{2isA}] - [G_{1isB} - G_{1isB}] = V_m[d\Delta(aq \rightarrow x_2)\Delta G^{\ddagger}/dx_2]/RTQ = g_k \text{ (by definition)} \quad (12)$$

left-hand side of eq 12 again measures the change in relative affinities, in this case for three solutes.

Stage II. If the activation volumes are available we use the analogue of eq 10 to obtain $[G_{1\neq} - G_{1isA} - G_{1isB}]$ and hence $[G_{2\neq} - G_{2isA} - G_{2isB}]$.

Water + 2-Methyl-2-propanol Mixtures. Excess Gibbs energies of mixing were taken from the compilation given by Kenttamaa and co-workers.[28,29] The dependence of G_m^E on mole fraction x_2 (Figure 1) was fitted to the orthogonal polynomial[30] in eq 13.

$$G_m^E/RT = \sum_{i=2}^{N} a_{i-1}P_i(x_1, x_2) \quad (13)$$

where

$$P_2 = x_1x_2 \quad (14)$$

$$P_3 = x_1x_2(1 - 2x_2) \quad (15)$$

$$P_4 = x_1x_2[1 - (14x_2/3) + (14x_2^2/3)] \quad (16)$$

$$P_5 = x_1x_2[1 - 8x_2 + 18x_2^2 - 12x_2^3] \quad (17)$$

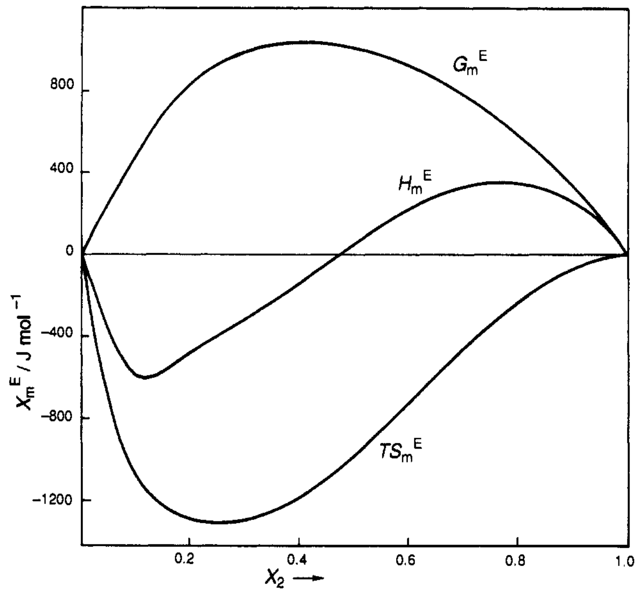


Figure 1. Excess thermodynamic properties of water + 2-methyl-2-propanol mixtures at 298 K. The curves describe the dependence on mole fraction of alcohol of excess molar Gibbs energy G_m^E and enthalpy H_m^E together with the product TS_m^E where S_m^E is the excess molar entropy of mixing.

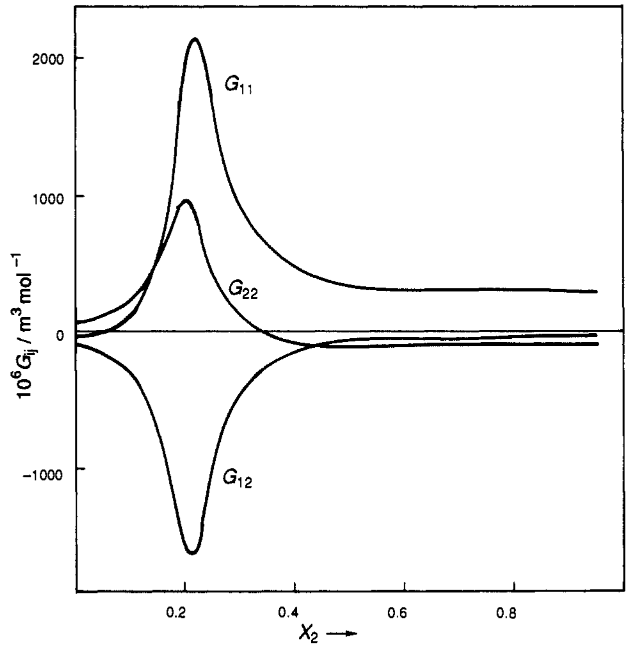


Figure 2. Dependence on mole fraction of alcohol of Kirkwood–Buff affinities, G_{11}, G_{22}, and G_{12} where 1 = water and 2 = 2-methyl-2-propanol.

This orthogonal polynomial is particularly well suited[16,17] for analysis where G_m^E is large and positive. The dependence of G_m^E on mole fraction x_2 is compared in Figure 1 with the dependence of the excess molar enthalpy of mixing[28,31] H_m^E. The latter shows that the mixing is exothermic at low x_2 and endothermic at high x_2. Nevertheless, across the whole mole fraction range $|TS_m^E| > |H_m^E|$, placing this mixture in the typically aqueous class.[2,32]

Volumetric parameters including partial molar volumes of water and alcohol were calculated by using the density data reported by Sakurai.[33] Isothermal compressibilities were calculated by using the compressions reported by Moriyoshi and co-workers.[34] Kirkwood–Buff integral functions were calculated by the proce-

---

(27) Blandamer, M. J.; Burgess, J.; Clark, B.; Duce, P. P.; Hakin, A. W.; Gosal, N.; Radulovic, S.; Guardado, P.; Sanchez, F.; Hubbard, C. D.; Abu-Gharib, E.-E. A. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1471.

(28) Kenttamaa, J.; Tommila, E.; Marti, M. *Ann. Acad. Sci. Fenn.* **1959**, *AII*, 932.

(29) The data refer to the properties of the mixture at 298.2 K. We assume that the patterns in the second differentials $d^2G_m^E/dx_2^2$ are the same at 298.2 and 299.2 K.

(30) Swinton, F. L.; Rowlinson, J. S. *Liquids and Liquid Mixtures*, 3rd ed.; Butterworths: London, 1982.

(31) Koga, Y. *Can. J. Chem.* **1986**, *64*, 206; **1988**, *66*, 1187.

(32) Franks, F.; Reid, D. In ref 1; Vol. 2, p 323.

(33) Sakurai, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1.

(34) Moriyoshi, T.; Morishita, Y.; Inubushi, H. *J. Chem. Thermodyn.* **1977**, *9*, 571.

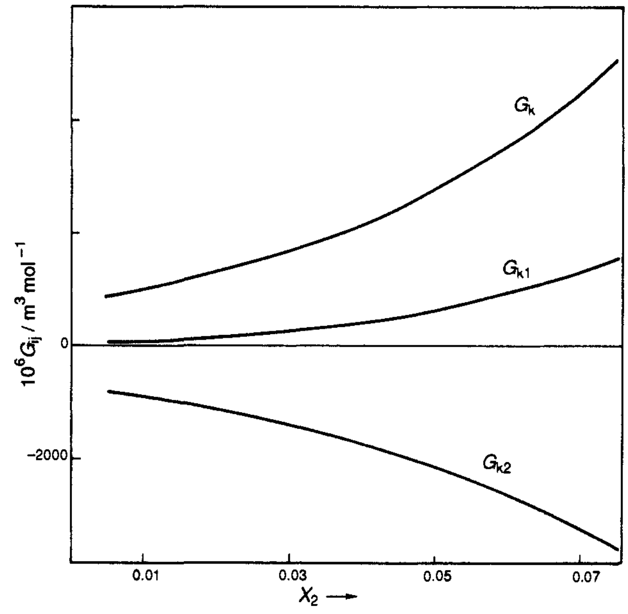


Figure 3. Spontaneous hydrolysis of 4-methoxyphenyl 2,2-dichloropropionate in water + 2-methyl-2-propanol mixtures. Dependence on mole fraction x_2 of preferential solvation parameters, g_k, g_{k1}, and g_{k2}.

dures previously described.[21,22] The results are summarized in Figure 2. The overall pattern is very similar to that reported by Matteoli and Lepori.[35] The dominant features are the intense maxima in G_{11} and G_{22} together with a sharp minimum in G_{12} near mole fraction $x_2 = 0.2$. This pattern can be understood in terms of microheterogeneities[2,36] comprising short-lived water-rich and alcohol-rich domains for mixtures having mole fractions $0.05 \leq x_2 \leq 0.25$.

Kinetics of Hydrolysis of 4-Methoxyphenyl 2,2-Dichloropropionate. At 298.2 K the first-order rate constant for this reaction is 1.15×10^{-5} s^{-1}, decreasing dramatically with increase in mole fraction of added 2-methyl-2-propanol. The volume of activation for hydrolysis equals -32.0 cm^3 mol^{-1}, decreasing when alcohol is added.[37,38] The dependences of Gibbs energies $\Delta G^{*}(x_2)$ and volumes of activation $\Delta V^{*}(x_2)$ were fitted to polynomials in mole fraction x_2. The polynomial for $\Delta G^{*}(x_2)$ was used to calculate $d\Delta(aq \rightarrow x_2)\Delta G^{*}(x_2)/dx_2$ as a function of x_2. The polynomial for $\Delta V^{*}(x_2)$ was used to calculate $\Delta V^{*}(x_2)$ at selected mole fractions. These data were combined with the properties of the solvent mixture (cf. Figures 1 and 2) to yield g_k as defined in stage I by eq 7; Figure 3. By incorporating information from volumes of activation together with eq 10 we obtain the dependence on mole fraction x_2 of both g_{k1} and g_{k2} as defined as eq 8–10.

Alkaline Hydrolysis of an Iron(II) Complex. For this reaction, the second-order rate constant increases with increase in mole fraction of added alcohol at 298.2 K. The volume of activation, 16.7 cm^3 mol^{-1}, decreases[16] with increase in mole fraction x_2. The analysis was repeated to yield the results summarized in Figure 4. By use of the trends in second-order rate constants and the properties of the solvent mixture (stage I), the derived quantity g_k shows a sharp minimum near $x_2 = 0.2$. Introducing information about the volumes of activation, we obtain (stage II) the dependence of the two quantities g_{k1} and g_{k2}.

Discussion

The kinetics of reactions involving substrates in binary aqueous mixtures show quite diverse patterns,[2,6,7] both in terms of the dependence of rate constant on mixture composition and, particularly, in terms of the dependences of derived parameters such as enthalpies and isobaric heat capacities[39] of activation. These patterns are understood in terms of preferential solvation of both initial and transition states by one or other of the components of the solvent mixture. The term "preferential solvation" means that the composition of the cosphere around a solute (initial or transition state in the present context) differs from that of the bulk solvent. Here the argument is based on the supposition that Kirkwood–Buff affinities for solute j, G_{1j} and G_{2j} are, as discussed above, dominated by the composition of the solvent in close proximity to solute j. Therefore the quantities g_k (eq 7 and 12), g_{k1}, and g_{k2} (eq 10) offer information about the change in local composition around solutes during the activation process. We chose the two reactions described above as examples of systems where the hydrophobic/hydrophilic characters change in the activation process.[6]

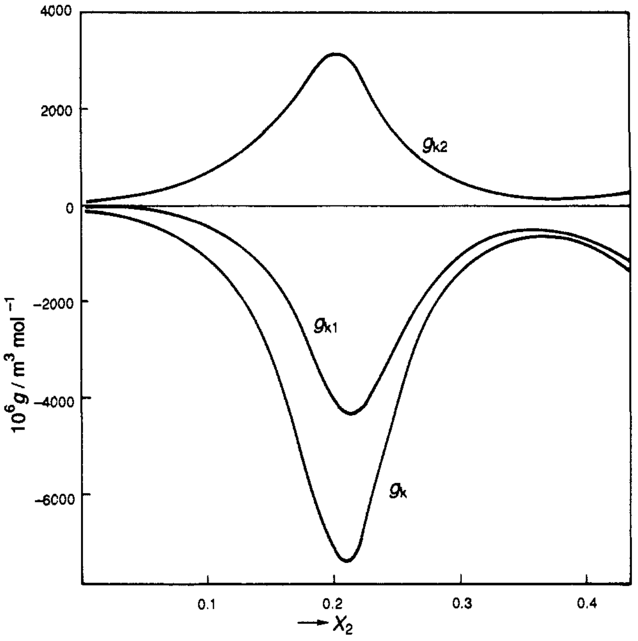


Figure 4. Alkaline hydrolysis of iron(II) complex, $[Fe(gmi)_3]^{2+}$, in water + 2-methyl-2-propanol mixtures. Dependence on mole fraction x_2 of the preferential solvation parameters, g_k, g_{k1}, and g_{k2}.

In the spontaneous hydrolysis of 4-methoxyphenyl 2,2-dichoropropionate the hydrophobic character of the initial state decrease during activation with attendant increase in hydrophilic character. The dramatic increase in g_k with increase in x_2 points to a marked difference between the composition of cospheres and bulk solvent. Recalling that g_k is given by $[G_{1\neq} - G_{1is}] - [G_{2\neq} - G_{2is}]$, this increase cannot be identified immediately with any one of the four terms. Perhaps the traditional approach would set $[G_{2\neq} - G_{2is}] \simeq 0$, and $G_{1\neq} > G_{1is}$ so that the trend in g_k is dominated by preferential solvation of the polar transition state by water. Another approach discussed by Robertson[39] might argue that $G_{1\neq} \simeq G_{2\neq}$, and that $|G_{2is}| > |G_{2\neq}|$. In which case, hydrophobic bonding between initial state and added alcohol is the dominant feature. Further insight into the factors affecting the solvent dependence of the rate constant are revealed by the separate dependences of g_{k1} and g_{k2}. In fact, both models advanced above accounting for the trends in g_k have merit. However, the magnitude of g_{k2} is at least twice that of g_{k1}, indicating that the trend in g_k and hence the dependence of rate constant on x_2 is dominated by hydrophobic association between substrate and added alcohol. This supports the conclusion reached previously.[1]

The patterns revealed for the organic substrate are limited by the small amount of data for the volumes of activation. Kinetic data for the alkaline hydrolysis of $[Fe(gmi)_3]^{2+}$ cover a broader range of mole fractions. In this reaction, there is a dramatic decrease in the hydrophilic character arising from the incorporation of OH$^-$ ions into the complex cation (the hydroxide ions being effectively buried) and extension of Fe–N bonds pushing the

---

(35) Matteoli, E.; Lepori, L. *J. Chem. Phys.* **1984**, *80*, 2856.

(36) Haak, J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1986**, *108*, 1705.

(37) Holterman, H. A. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1982**, *104*, 6382.

(38) Holterman, H. A. J. Ph.D. Thesis, University of Groningen, 1982.

(39) Robertson, R. E.; Sugamori, S. E. *J. Am. Chem. Soc.* **1969**, *91*, 7254.

hydrophobic ligands further into the solvent. For this system the dependence of rate constants and mixture properties on composition shows a rapid decrease in g_k when alcohol is added to the aqueous solution containing the iron(II) complex and hydroxide ions. In terms of the initial state (= complex + OH^-), we anticipate that preferential hydration of OH^- by water is the dominant influence leading to $G_{1\neq} \simeq 0$ with $G_{1is} > 0$, and hence $g_k < 0$, becoming more negative with increase in x_2. In terms of the transition state we anticipate that the hydrophobic interactions with added alcohol results in $G_{2\neq} > 0$ and hence $g_k < 0$. By incorporating the activation volume data, we see that $|g_{k1}| > |g_{k2}|$ which we associate with the preferential solvation of OH^- in the mixture by water. These trends continue until around $x_2 = 0.2$. In fact, Figure 4 highlights the way in which the structure of the binary solvent mixture and the properties of solutes in the mixture are closely linked. The properties of the mixture lead to a subdivision in terms of mole fraction ranges. At low mole fraction x_2 the added alcohol enhances water–water interactions. As more alcohol is added, water–water cooperative hydrogen bonding attempts to maintain local water-rich domains with incipient tendencies to partial miscibility. As still more alcohol is added, the system takes on the character of a mixture of a polar and a nonpolar liquid in which the alcohol disrupts water–water hydrogen bonding. The situation is akin to that indicated by the thermodynamic properties when liquid CCl_4 is added to liquid methanol. Indeed as revealed by the Kirkwood–Buff integral functions in Figures 3 and 4, in a liquid mixture where $x_2 > 0.3$, there is little preferential solvation, the composition of the cospheres being not very different from that of the bulk mixture.

In both examples discussed above, the structural models that emerge from the Kirkwood–Buff integral functions offer an interesting insight into solvent effects on kinetics of reactions in binary aqueous mixtures and the basis of a quantitative approach for probing the role of preferential solvation in kinetics. This type of approach is clearly superior to analyses of medium effects which require that rate constants are plotted as a function of parameters measuring macrosopic solvent properties. We contend that kinetic medium effects treated by using SWAG[4] or, as here, Kirkwood–Buff models offer possibilities for quantitative insights into the interactions that govern the solvent effects on rate constants and offer possibilities for using medium effects as effective probes for mechanistic studies in physical organic chemistry.

Acknowledgment. We thank Professor Y. Yoga and Professor M. Sakurai for sending us complete sets of data and preprints of papers concerning enthalpies and volumes of mixing respectively of 2-methyl-2-propanol + water mixtures. We thank SERC for a grant to H.J.C., the University of Leicester for a travel grant to M.J.B., and the Hickinbotham Charitable Trust for their support.

Small PbS Clusters Prepared via ROMP Block Copolymer Technology

V. Sankaran,[†] C. C. Cummins,[‡] R. R. Schrock,*[,‡] R. E. Cohen,[†] and R. J. Silbey[‡]

Contribution from the Department of Chemistry and Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
Received March 5, 1990

Abstract: Small particles of lead sulfide have been prepared by H_2S treatment of block copolymer films wherein aggregates of poly[$(C_7H_9CH_2C_5H_4)_2Pb$] reside as microdomains distributed throughout a polynorbornene matrix. The block copolymers were prepared by sequential addition of 200 equiv of norbornene and 5, 10, and 20 equiv of $(C_7H_9CH_2C_5H_4)_2Pb$ (**1**) to Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2), followed by quenching with benzaldehyde. The interdomain spacings (320–480 Å) before and after H_2S treatment were revealed by small-angle X-ray scattering (SAXS). Average cluster diameters (20–40 Å) were determined by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The clusters were identified as PbS by X-ray fluorescence analysis performed on the STEM and by wide-angle X-ray powder diffraction.

In the past 5 years, several groups have shown that the electronic structure of a semiconductor varies with particle size[1] and that semiconductor clusters with diameters in the range 20–100 Å exhibit nonlinear optical properties.[2] In order to exploit the potential of these materials fully, it is necessary that the clusters be as close to a single size as possible.[1b] Workers have achieved varying degrees of success at controlling cluster growth in zeolites,[3] borosilicate glass,[4] colloids,[5] hydrophobic/hydrophilic random copolymers,[1c,d] and reverse micelles,[6] among other methods.[7] In this paper, we disclose a new approach that takes advantage of microdomain formation,[8] a phenomenon that has been shown to result in spherical, cylindrical, or sheet morphologies, most notably for polystyrene/polybutadiene block copolymers.[9] We employ Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2),[10] an especially mild ROMP (ring-opening metathesis polymerization) catalyst[11] that is relatively tolerant of functionalities.

[†] Department of Chemical Engineering.

[‡] Department of Chemistry.

(1) (a) Steigerwald, M. L.; Brus, L. E. *Annu. Rev. Mater. Sci.* **1989**, *19*, 471. (b) Brus, L. *New J. Chem.* **1987**, *11*, 123. (c) Wang, Y.; Suna, A.; Mahler, W.; Kasowski, R. *J. Chem. Phys.* **1987**, *87*, 7315. (d) Mahler, W. *Inorg. Chem.* **1988**, *27*, 435. (e) Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Micic, O. I.; Rajh, T. *J. Phys. Chem.* **1985**, *89*, 397. (f) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1985**, *82*, 552.

(2) (a) Loung, J. C. *Superlattices Microstruct.* **1988**, *4*, 385. (b) Stegeman, G. I.; Seaton, C. T. *J. Appl. Phys.* **1985**, *58*, R57.

(3) (a) Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D. E.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530. (b) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257.

(4) Kuczynski, J.; Thomas, J. K. *J. Phys. Chem.* **1985**, *89*, 2720.

(5) Watzke, H. J.; Fendler, J. H. *J. Phys. Chem.* **1987**, *91*, 854.

(6) (a) Alivisatos, A. P.; Harris, T. D.; Carroll, P. J.; Steigerwald, M. L.; Brus, L. E. *J. Chem. Phys.* **1989**, *90*, 3463. (b) Lianos, P.; Thomas, J. K. *Chem. Phys. Lett.* **1986**, *125*, 299.

0002-7863/90/1512-6858$02.50/0