Analysis of the Kinetics of Solvolysis of *p*-Nitrophenylsulfonylmethyl Perchlorate in Binary Alcoholic Mixtures in terms of the Thermodynamic Properties of the Solvent Mixtures

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Rate constants are reported for the solvolysis of *p*-nitrophenylsulfonylmethyl perchlorate in binary ethanolic and methanolic mixtures at 298.2 K. Co-solvents include hydrocarbons, chlorinated hydrocarbons and 1,4-dioxane. The kinetic data are examined in terms of the effect of decreasing mole fraction of reactant alcohol and in terms of deviations from the ideal of the thermodynamic properties of the solvent, a binary liquid mixture, as measured by the rational activity coefficients of the alcohols. Mixtures are identified where one of these two effects dominates and where they cancel such that the transfer chemical potentials of substrate and transition state are equal.

Rate constants for reactions in aqueous solution are often markedly sensitive to the nature and mole fraction of added co-solvent;[1] *e.g.* ethanol[2] and 2-methylpropan-2-ol.[3] At low mole fractions (molalities) of added co-solvent, the dependence of rate constant on solvent composition can be analysed using the SWAG (Savage–Wood Additivity of Group Interactions) model.[2,4,5] Across the complete mole fraction range a treatment of preferential solvation based on the Inverse Kirkwood–Buff method is informative.[6] Nevertheless, alcohol–water mixtures are complicated systems when used as solvents. In thermodynamic terms, the mixtures are far from ideal with, in some cases, a strong tendency to form microheterogeneous systems.[7,8] Moreover, in those cases where the solvent is also a reactant, as in the case of solvolytic reactions, discussion of the changes in rate constants for reaction in aqueous solution following addition of an alcohol as co-solvent raises new questions such as the change in reactivity of water as well as a concern for a simple dilution effect. Other considerations centre on the question of mixed kinetics.

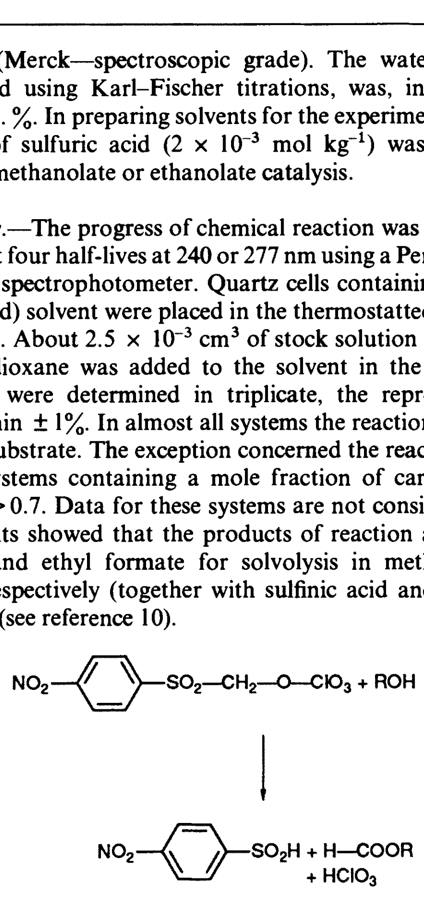
When considering medium effects in terms of hydrophobic and hydrophilic interactions between a substrate and water in an aqueous solution, the use of functionalised hydrocarbons raises new problems in view of the amphiphilic nature of the cosolvent.

In a utopian experiment, a chemically inert co-solvent such as a hydrocarbon would be added to the aqueous solution and the rates of reactions examined. However, the low solubility of hydrocarbons in water means that these otherwise interesting experiments cannot be attempted. In the study reported here we used either methanol or ethanol as solvent and solvolysing agents for the substrate, *p*-nitrophenylsulfonylmethyl perchlorate **1**. The change in rate constants when co-solvents such as hydrocarbons and chlorinated hydrocarbons were added allowed us to examine the patterns in the light of the dependences on mole fraction of alcohol of the excess molar thermodynamic properties and rational activity coefficients f_1 of both ethanol and methanol. We show that ethanolysis is more sensitive to the co-solvent than methanolysis. Comparison between kinetic and thermodynamic data identifies several interesting patterns.

Experimental

Materials.—The substrate **1** was synthesised using the method previously described.[9] All solvents were used as supplied (Merck—spectroscopic grade). The water content, determined using Karl-Fischer titrations, was, in all cases, ≤ 0.03 vol. %. In preparing solvents for the experiments a small amount of sulfuric acid (2×10^{-3} mol kg^{-1}) was added to suppress methanolate or ethanolate catalysis.

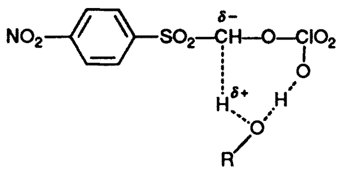
Kinetics.—The progress of chemical reaction was monitored for at least four half-lives at 240 or 277 nm using a Perkin-Elmer lambda-2 spectrophotometer. Quartz cells containing 2.5 cm^3 of a (mixed) solvent were placed in the thermostatted cell compartments. About 2.5×10^{-3} cm^3 of stock solution containing **1** in 1,4-dioxane was added to the solvent in the cell. Rate constants were determined in triplicate, the reproducibility being within ± 1%. In almost all systems the reaction was first-order in substrate. The exception concerned the reaction in the solvent systems containing a mole fraction of carbon tetrachloride > 0.7. Data for these systems are not considered. GC experiments showed that the products of reaction are methyl formate and ethyl formate for solvolysis in methanol and ethanol respectively (together with sulfinic acid and $HClO_3$); Scheme 1 (see reference 10).



Scheme 1

Analysis.—Kinetics. Based on a previously established[10,11] mechanism for hydrolysis in aqueous solutions, the reaction in Scheme 1 is represented as proceeding through a cyclic transition state involving rate-determining proton transfer to the alcohol and stabilisation of the transition state by hydrogen bonding; Scheme 2. In these terms the substrate, *p*-nitrophenylsulfonylmethyl perchlorate, and alcohol ROH are reactants in a range of systems which contain different mole fractions of alcohol. In terms of transition state theory, the pseudo-chemical equilibrium has the form shown in eqn. (1) where Z represents

$$\text{Z(soln.)} + \text{ROH(mix.)} \longleftrightarrow \text{Z*(soln.)} \qquad (1)$$



Scheme 2

the perchlorate **1** and ROH (= substance 1) is the alcohol, both reactant and solvent component. We assume that the system is sufficiently dilute in both Z(soln.) and transition state Z*(soln.) that the ratio of (Henry's Law) activity coefficients γ_z and γ^* is unity in all systems. However, the (Raoult's Law) activity coefficient f_1 of the alcohol is not unity in all except, it is assumed, the solution in pure alcohol. Then the equilibrium in eqn. (1) can be described using an equilibrium constant $K^*(x_1)$ which is a function of the mole fraction composition of the solvent; eqn. (2). Hence using transition state theory the first-order rate constant $k(x_1)$ for reaction in a particular solvent mixture is given by eqn. (3).

$$K^*(x_1) = c_\ddagger / c_z x_1 f_1 \qquad (2)$$

$$k(x_1) = (k_B T/h) K^*(x_1) x_1 f_1 \qquad (3)$$

Here,

$$\Delta^\ddagger G^0(x_1) = -RT \ln K^*(x_1) = \mu_\ddagger^0(\text{soln. } x_1) - \mu_z^0(\text{soln. } x_1) - \mu_1^*(\text{l}) \qquad (4)$$

Consequently, $K^*(x_1)$ through the Gibbs energy of activation measures the difference in standard chemical potentials of transition state and initial state (substrate) in a given solvent mixture in conjunction with the chemical potential of pure alcohol at the same temperature and pressure. For solvolysis in the pure alcohol, the product $(x_1 f_1)$ is effectively unity (see above). Therefore

$$k(x_1 = 1) = (k_B T/h) K^*(x_1 = 1) \qquad (5)$$

hence

$$k(x_1)/k(x_1 = 1) x_1 f_1 = K^*(x_1)/K^*(x_1 = 1) \qquad (6)$$

For reaction where pure alcohol is the solvent the analogue of eqn. (4) is given by eqn. (7). Then the change in the Gibbs energy of activation on going from the pure alcohol as solvent to a mixture mole fraction x_1 is given by eqn. (8) where

$$\Delta^* G^0(x_1 = 1) = \mu_\ddagger^0(\text{soln. } x_1 = 1) - \mu_z^0(\text{soln. } x_1 = 1) - \mu_1^*(\text{l}) \qquad (7)$$

$$\Delta(l_1 \longrightarrow x_1)\Delta^* G^0 = -RT \ln [K^*(x_1)/K^*(x_1 = 1)] = \Delta(l_1 \longrightarrow x_1)\mu_\ddagger^0(\text{soln.}) - \Delta(l_1 \longrightarrow x_1)\mu_z^0(\text{soln.}) \qquad (8)$$

$\Delta(l_1 \longrightarrow x_1)\mu_\ddagger^0(\text{soln.})$ and $\Delta(l_1 \longrightarrow x_1)\mu_z^0(\text{soln.})$ are the transfer chemical potentials of the transition state and substrate respectively. In other words the ratio, $k(x_1)/k(x_1 = 1)x_1 f_1$ [eqn. (6)] signals the extent to which the dependence of rate constant on mixture composition emerges from the related dependence of transfer parameters for transition state and substrate. The product $x_1 f_1$ signals the reactivity of the alcohol as a function of mixture composition. For example, if the ratio $k(x_1)/k(x_1 = 1)x_1 f_1$ is unity then $\Delta(l_1 \longrightarrow x_1)\mu_\ddagger^0(\text{soln.})$ equals $\Delta(l_1 \longrightarrow x_1)(\mu_z^0(\text{soln.})$. In addition therefore to measuring the dependence of $k(x_1)/k(x_1 = 1)$ on mixture mole fraction x_1 and on the nature of the co-solvent, we wanted to probe the related dependence of $k(x_1)/k(x_1 = 1)x_1 f_1$ which required calculating the rational activity coefficient f_1 from thermodynamic data.

Thermodynamic Properties of Liquid Mixtures.—Published thermodynamic data yield the excess molar Gibbs energy of mixing G_m^E for a given binary liquid mixture at fixed T and ambient pressure;

$$G_m^E/RT = x_1 \ln f_1 + x_2 \ln f_2 \qquad (9)$$

Then, from the Gibbs–Duhem equation, and eqn. (9),

$$\ln f_1 = (1/RT)[G_m^E + (1 - x_1) dG_m^E/dx_1] \qquad (10)$$

Using a published dependence of G_m^E on x_1, the calculated G_m^E and differential dG_m^E/dx_1 at the required mole fraction and 298.2 K were obtained using a FORTRAN program in conjunction with the Redlich–Kister relationship [eqn. (11)].

$$G_m^E = x_1(1 - x_1) \sum_{i=1}^{i=j} a_i(1 - 2x_1)^{i-1} \qquad (11)$$

The series in eqn. (11) was terminated using conventional criteria associated with a linear least-squares analysis.

In some cases published estimates of G_m^E were at temperatures other than 298.2 K. Combination of the G_m^E estimates and excess molar enthalpies (*i.e.* H_m^E) with, in some cases, excess molar isobaric heat capacities C_{pm}^E yielded the required G_m^E at 298.2 K using the Gibbs–Helmholtz equation.

In this study, five classes of mixtures were used as solvent media; (i) ethanol–hydrocarbons, (ii) ethanol–chlorinated hydrocarbons, (iii) ethanol–1,4-dioxane, (iv) methanol–chlorinated hydrocarbons and (v) methanol–1,4-dioxane.

At 298.2 K, G_m^E for ethanol–cyclohexane,[12] ethanol–hexane[13] and ethanol–iso-octane[14] is positive, as is the excess molar enthalpy of mixing H_m^E. The excess molar entropies of mixing are negative.[12–15] The general pattern conforms to the idea of a disruption of the associated ethanol molecules by added hydrocarbon.[16] G_m^E data at 313.2, 323.2 and 333.2 K for ethanol–1,2-dichloroethane[17,18] were used to calculate G_m^E at 298.2 K. G_m^E for ethanol–trichloromethane at 298.2 K was calculated using[19] G_m^E at 308.2 K and excess molar enthalpies.[20] G_m^E at 298.2 K for ethanol–carbon tetrachloride mixtures were calculated using the Gibbs–Helmholtz equation in conjunction with G_m^E data[21] at 318.2 and 338.2 K.

In general, G_m^E is positive for ethanol–chlorinated hydrocarbon mixtures although there is good evidence for inter-component interaction. For example, in the case of ethanol–trichloromethane mixtures, the plots of H_m^E and S_m^E against mole fraction are S-shaped. G_m^E data at 298.2 K for ethanol–1,4-dioxane mixture were calculated from G_m^E at 323.2 K[22] and H_m^E at 298.2 K.[23]

Activity coefficients[24] for both components in methanol–dichloromethane and methanol–trichloromethane mixtures at 298.2 K were used to calculate G_m^E and hence *via* eqns. (11) and (12) G_m^E at 298.2 K was obtained at the mole fractions of the mixtures used in the kinetic experiments. Activity coefficients[25] for the methanol–tetrachloromethane mixtures at several temperatures were used to obtain *via* G_m^E the required information at 298.2 K. G_m^E data[26] for methanol–1,2-dichloroethane at 298.2 K were analysed using eqns. (10) and (11). G_m^E data[27] for mixtures at 303.2 K together with H_m^E data[28] at 303.15 and 308.15 K were used to calculate G_m^E at 298.2 K for methanol–1,4-dioxane mixtures.

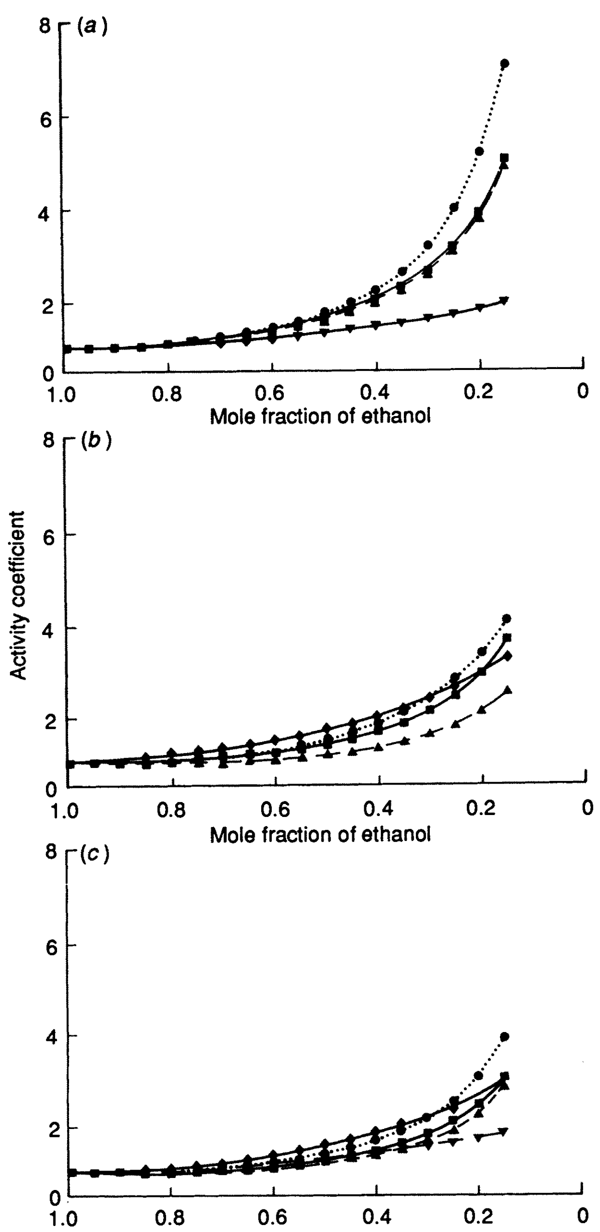


Fig. 1 Dependence of rational activity coefficient at 298.2 K in binary mixtures for: (*a*) ethanol in mixtures with (i) hexane (■), (ii) cyclohexane (▲), (iii) octane (●) and (iv) 1,4-dioxane (▼); (*b*) ethanol in mixtures with; (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆) and (iv) 1,2-dichloroethane (●); (*c*) methanol in mixtures with; (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆), (iv) 1,2-dichloroethane (●) and (v) 1,4-dioxane (▼)

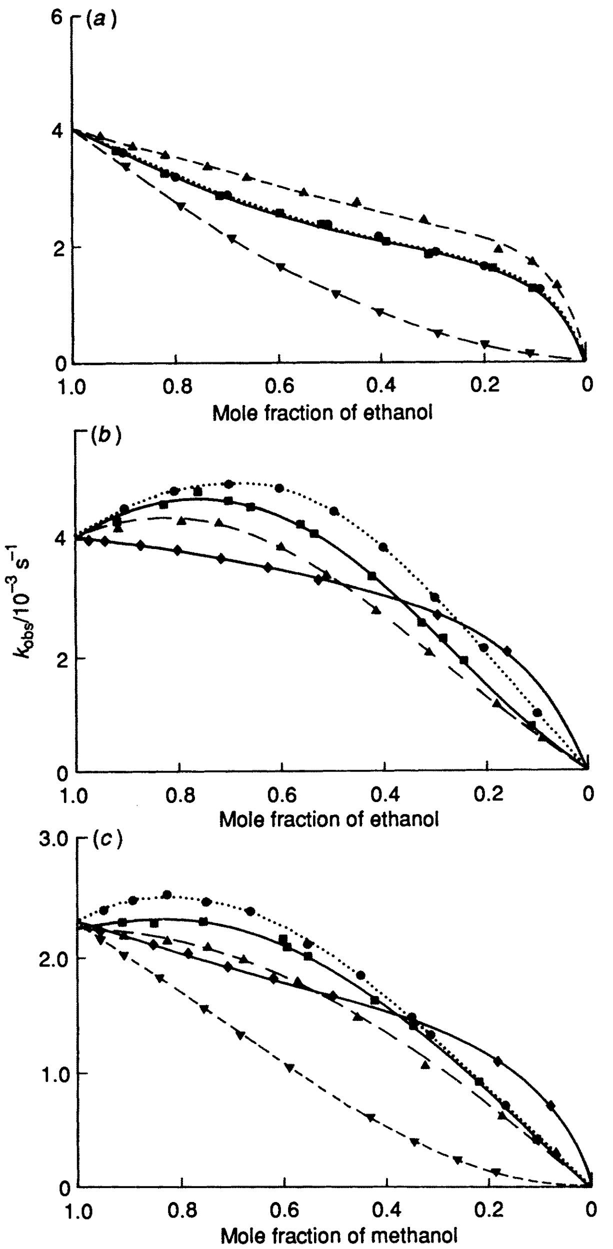


Fig. 2 First-order rate constants for the solvolysis of *p*-nitrophenylsulfonylmethyl perchlorate at 298.2 K in binary mixtures formed by: (*a*) ethanol and (i) hexane (■), (ii) cyclohexane (▲), (iii) iso-octane (●) and (iv) 1,4-dioxane (▼); (*b*) ethanol and (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆) and (iv) 1,2-dichloroethane (●); (*c*) methanol and (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆), (iv) 1,2-dichloroethane (●) and (v) 1,4-dioxane (▼)

Results

In this section we review activity coefficient data for several ethanol- and methanol-based binary liquid mixtures and kinetic data for the solvolysis of substrate **1**. For all studied mixtures, the rational activity coefficients (Fig. 1) increase with decrease in alcohol mole fractions. Added hexane and cyclohexane change the rational activity coefficients of ethanol in an almost identical fashion. The impact of adding iso-octane is greater than that for either hexane or cyclohexane. The effects of adding chlorinated hydrocarbons fall into a group, the increase in f_1 when $CHCl_3$ is added being less dramatic. Although the interactions of $CHCl_3$ and 1,4-dioxane with alcohols are quite different ($CHCl_3$ donating a hydrogen atom in the formation of a hydrogen bond and 1,4-dioxane accepting a hydrogen atom in the formation of a hydrogen bond), the pattern of the composition dependence of rational activity coefficients f_1 are very similar.

Differentiation between the co-solvents is more striking (Fig. 2) in the context of kinetic data. Addition of hydrocarbons to the solution in ethanol leads to a decrease in rate constant. However, at all mole fractions the measured rate constant k was larger than the product $[k(x_1 = 1)x_1]$. Interestingly, addition of hexane and iso-octane leads to a nearly identical pattern for the kinetic data. Addition of chlorinated solvents (except CCl_4) produced an initial increase in rate constant. The effectiveness of these cosolvents, in terms of maximum rate acceleration was in the order $CHCl_3 < CH_2Cl_2 < CH_2Cl{-}CH_2Cl$. The pattern in the case of CCl_4 as cosolvent deviates from the other chlorinated hydrocarbons but resembles that of the hydrocarbons. Added 1,4-dioxane produced a dramatic decrease in

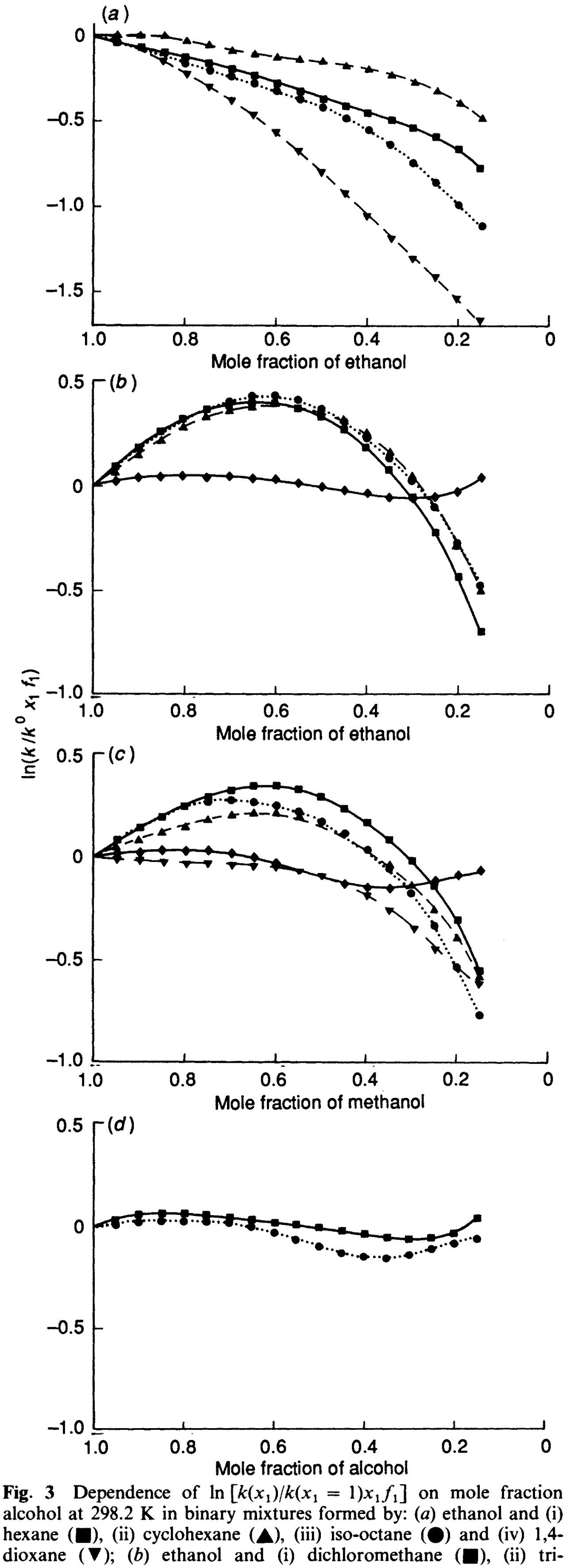


Fig. 3 Dependence of $\ln [k(x_1)/k(x_1 = 1)x_1 f_1]$ on mole fraction alcohol at 298.2 K in binary mixtures formed by: (*a*) ethanol and (i) hexane (■), (ii) cyclohexane (▲), (iii) iso-octane (●) and (iv) 1,4-dioxane (▼); (*b*) ethanol and (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆) and (iv) 1,2-dichloroethane (●); (*c*) methanol and (i) dichloromethane (■), (ii) trichloromethane (▲), (iii) tetrachloromethane (◆), (iv) 1,2-dichloroethane (●) and (v) 1,4-dioxane (▼); (*d*) methanol–tetrachloromethane (●) and ethanol–tetrachloromethane (■)

rate constant and, contrary to the ethanol–hydrocarbon mixtures, the rate constants are all smaller than the product, $[k(x_1 = 1)x_1]$.

The results for the methanol-based mixtures are similar to those for the ethanol systems. However, the impact on the rate constant for solvolysis in methanol of added cosolvent was less dramatic. The rate accelerations induced by the chlorinated hydrocarbons were less than those observed for the ethanol-based systems; the decrease in rate constant following addition of 1,4-dioxane was less marked.

Discussion

The different kinetic effects induced by all inert cosolvents is surprising. However, a few distinct classes of cosolvents can be recognised. Clearly the hydrocarbons fall into one category, reducing the observed rate constants in a similar way. Interestingly, the kinetic results do not match the thermodynamic data. The rational activity coefficients of hexane and cyclohexane are identical, whereas only the linear hydrocarbons exert the same influence on the kinetics.

Addition of chlorinated hydrocarbons (except CCl_4) to either ethanol or methanol produces an initial increase in rate constant, more cosolvent eventually leading to a decrease of the rate constant. This suggests that two opposing effects are in operation: the chlorinated hydrocarbons increase the kinetic basicity of alcohol, but the cosolvents also dilute the reactive component of the medium and the reduced concentration of ethanol eventually leads to the observed deceleration. The influence of CCl_4 as a cosolvent is quite different from the three other chlorinated cosolvents. No acceleration is observed and the overall effect of CCl_4 as a cosolvent is similar to the influence exerted by hydrocarbons.

As previously outlined the quantity $\ln [k(x_1)/k(x_1 = 1)x_1 f_1]$ describes the influence of the cosolvent on the transfer parameters of the substrate and the activated complex (Fig. 3). The data show examples where all the possibilities are observed. The transition state can be stabilised relative to the substrate $\{\ln [k(x_1)/k(x_1 = 1)x_1 f_1] > 0$, *e.g.* the EtOH-$CHCl_3$ system in the ethanol-rich region$\}$. The transition state can be destabilised relative to the substrate $\{\ln [k(x_1)/k(x_1 = 1)x_1 f_1] < 0$, *e.g.* the EtOH–hexane system at all concentrations$\}$. The transfer parameters are hardly affected by the cosolvent $\{\ln [k(x_1)/k(x_1 = 1)x_1 f_1] \approx 0$, *e.g.* the EtOH–$CCl_4$ system at all concentrations$\}$. Of course, in all these cases, the transfer parameters of the substrate and transition state may individually depend on mole fraction x_1.

Close inspection of the kinetic and the thermodynamic data reveals that the non-ideal properties of the mixtures cannot account solely for the observed rate constants or the change in transfer parameters. This is surprising since the rational activity coefficients reflect the chemical reactivity of the alcohol. Several examples illustrate this conclusion. Although the rational activity coefficients of ethanol in EtOH–$CHCl_3$ and EtOH–1,4-dioxane are similar, the effect of these cosolvents on the kinetic results differ markedly. The kinetic effect induced by hexane and iso-octane are very similar, in contrast to their rational activity coefficients. These examples show that there is no clear relationship between the rational activity coefficients of the alcohol component of the medium and the observed rate constants. In addition, we also note that the rational activity coefficients of the alcoholic component of the mixtures do not account for the different sensitivities of the methanolysis and ethanolysis toward the cosolvents.

Three interesting points have emerged from this study. First, we have clearly shown that, although the transfer parameters of the reactants and the transition state depend on the non-ideal properties of the mixture, the rational activity coefficients of the solvolysing agent do not account for the observed rate constants of the solvolysis of the perchlorate. This implies that the sensitivity of the substrate and the transition state toward the medium governs the kinetics of the solvolysis. Second, the ethanolysis of the perchlorate is more sensitive to the cosolvent than the methanolysis. The impact of the cosolvents on the rate constants is similar for both alcohols, the influence on the ethanolysis being more pronounced. Third, we have shown that the dependence of rate constant on solvent composition for these alcoholic systems is quite small when set against the dependence in aqueous systems.

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