N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 1084 (1959).
(26) D. Garvin and C. Schubert, *J. Phys. Chem.*, **60**, 807 (1956).
(27) J. Castonguay, M. Bertrand, J. Carles, S. Fliszar, and Y. Rousseau, *Can. J. Chem.*, **47**, 919 (1969); R. W. Murray and R. Hagen, *J. Org. Chem.*, **36**, 1103 (1971); C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **96**, 1536 (1974).
(28) The molecular parameters used in this calculation are r(C-C) = 1.514, r(C-H) = 1.08, r(C-F) = 1.38 Å, and ∠(FCH) = 120°, which bisects the plane formed by the carbon atoms.
(29) Using the structure in ref 28, bond dipole calculations give a dipole moment of 4.70 D (C-F bond dipole = 1.41 D and C-H bond dipole = 0.4 D).

Charles W. Gillies
Mallinckrodt Laboratories, Harvard University
Cambridge, Massachusetts 02138
Received November 27, 1974

Diffusion in Mixed Solvents. On the Viscosity Question[1]

Sir:

Linear plots of reaction rate constant vs. reciprocal of solvent viscosity have long been used as the classifying criteria for diffusion controlled reactions in fluid solution. These criteria in mixed hydroxylic solvents like glycerol and water have also been used to determine reaction mechanisms. Presented here are data which show that the above mentioned criteria are insufficient in many cases, where nonideal mixed solvent systems are used to increase solvent viscosity. Data correlations given below, suggest that the excess functions predominately determine the variation in reaction rate constants.

A mixed solvent study for the following irreversible reaction is reported

$$\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \xrightarrow{k_Q} \mathrm{P^{+}\cdot} + \mathrm{Fe(CN)_6}^{4-}$$

where T and $P^{+}\cdot$ are respectively the triplet state and radical monocation of zinc uroporphyrin. The reaction is charge controlled[2,3] and encounter limited in aqueous solution;[3] the distance of nonadiabatic electron transfer is 22 ± 4 Å, some 11 Å greater than the molecular radii.[3] Consequently, it is an ideal reaction with which to study nonequilibrium thermodynamics in fluid solution. The systems methanol-water and sucrose-water were chosen for reagent purity, compatibility with reactants, and the differences in the behavior of their excess functions.[4,5] For aqueous methanol,[4,6] ethanol,[4,6] and glycerol[6] systems, ΔG^E is positive, while $\Delta H^M > T\Delta S^E$ are negative; for the aqueous sucrose system,[5,7] the partial molal excess functions per mole of water are all negative, $\partial T\Delta S^E/\partial n_2 > \partial \Delta G^E/\partial n_2 > \partial \Delta H^M/\partial n_2$. Since small amounts of methanol or sucrose *increase* the observed rate constant, even though the viscosity is greater (Table I), the complete dependence on ΔG^E is negated (or k_Q would increase in one case and decrease in the other). The similar shapes[4,6] of the ΔH^M and $T\Delta S^E$ functions vs. methanol mole fraction (X_1) render determination of specific dependence on these functions impossible in this case, since there is no directly applicable theory of solutions. For sucrose, however, the partial molal excess enthalpy and entropy vs. sucrose mole fraction (X_1) functions are different in shape.[5] Figure 1 shows the dependence of the rate constants, k_Q, on the enthalpy and entropy excess functions, and viscosity for aqueous sucrose solutions. Similarly plotted data in methanol-water do not show such differences due to the similarity in the shapes of the excess functions; however, the nonagreement with the usual thoughts on reciprocal viscosity dependence is obvious (Table I).

Table I. Kinetic Parameters for Sucrose–Water and Methanol–Water Solvent Systems for the Reaction $\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \xrightarrow{k_Q} \mathrm{P\cdot^{+}} + \mathrm{Fe(CN)_6}^{4-}$

X_1	$10^{-6}k_Q^{obsd}$ (M^{-1} sec^{-1})^a	$(k_Q^{obsd}/k_Q^{H_2O})_\mu$^{b}	η(cp)	ϵ^e
		Sucrose–Water^c		
0	2.40	1	0.9^d	79
0.0080	7.38	3.05	1.3^d	75.6
0.0196	6.23	2.62	2.4^d	74.0
0.0412	9.65	2.32	8.0^d	65.5
0.0592	6.43	1.87	24.6^d	61.8
		Methanol–Water^c		
0.194	4.98	1.52	1.56^f	64.5
0.360	3.28	1.14	1.52^f	54.9
0.511	5.42	1.87	1.30^f	47.5

[a] The ionic strength, μ, varied slightly, for different k_Q values: for the methanol–water data, $1.35 \times 10^{-3}\ m < \mu < 1.91 \times 10^{-3}\ m$; for the sucrose–water data, $1.07 \times 10^{-3}\ m < \mu < 1.9 \times 10^{-3}\ m$; there was no trend with X_1. For all determinations pH ⩾7. Errors in $k_Q^{obsd} \leqslant \pm 10\%$. [b] Corrections for small differences in μ were made by dividing each k_Q by that for the same reaction in water, $k_Q^{H_2O}$, as reported in ref. 3. For sucrose mole fraction 0.059, an ionic strength variation showed that the ionic charge product of T(−8) and $\mathrm{Fe(CN)_6}^{3-}$ is the same as in water solvent[1–3] (24 within experimental error). [c] All measurements 25°, k_Q values, 25 ± 1°. [d] H. A. Sober, Ed., "Handbook of Biochemistry", Chemical Rubber Co., Cleveland, Ohio, 1968, p j-248. [e] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed, Reinhold, New York, N.Y., 1950 p 118. [f] International Critical Tables, 5:22, McGraw-Hill, New York, N.Y., 1929.

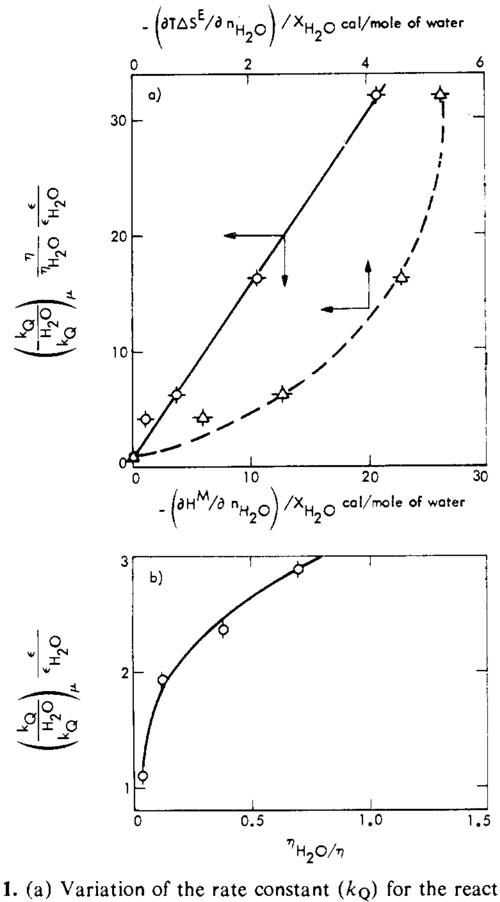

Figure 1. (a) Variation of the rate constant (k_Q) for the reaction $\mathrm{T} + \mathrm{Fe(CN)_6}^{3-} \rightarrow \mathrm{P^{+}\cdot} + \mathrm{Fe(CN)_6}^{4-}$ with the partial enthalpy of mixing and the partial excess entropy for the sucrose-water solvent system. (b) Variation of the rate constant (k_Q) with the reciprocal of the solvent viscosity for the sucrose-water solvent system. $(k_Q/k_Q^{H_2O})_\mu$ is the rate constant in a given concentration of sucrose, divided by that in water for a given ionic strength (see footnotes *a* and *b* in Table I); η and ϵ are solvent viscosity and dielectric constant, respectively.

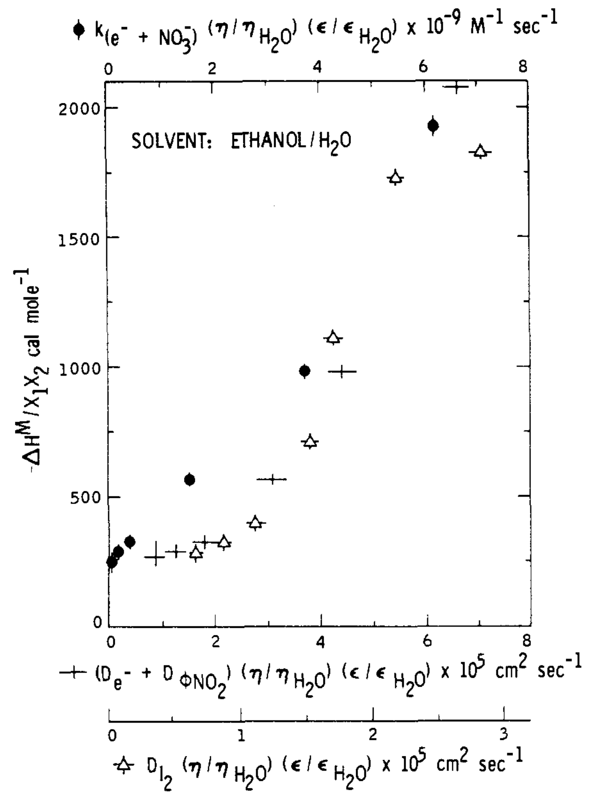

Figure 2. Variation of diffusion coefficients and reaction rate constants with $-\Delta H^M/X_1X_2$: diffusion coefficients of iodine, ref 8; diffusion coefficients of solvated electron and nitrobenzene, and reaction rate constant of solvated electron and nitrate ion, ref 10; heat of mixing data for ethanol-water system, ref 4.

This phenomena is observed in other diffusion controlled systems as well. Both molecular iodine diffusion coefficient[8,9] data and solvated electron reaction rate constant data[10] are available in alcohol-water systems. For both of these, anomalies using reciprocal viscosity dependencies are noted.[8-11] Since diffusing species demix the solvent as they move forward, causing it to remix in their wake, it is only logical that the heats involved in the mixing process be important to diffusion.[12] Graphs of $-\Delta H^M/X_1X_2$ vs. diffusion coefficient or rate constant corrected for viscosity and dielectric constant changes yield slight S-shaped curves about the same linear line (Figure 2).[13] Contrary to the original interpretation for the solvated electron rate constants,[10] all the data points correlate with the $-\Delta H^M/X_1X_2$ plot. Further, the maxima in the entropy and enthalpy of activation for the fluorescence quenching of indole at $X_1 < 0.04$[14] coincides with the maxima in the $-T\Delta S^E/X_1X_2$ and $-\Delta H^M/X_1X_2$ curves for the solvent mixture. Similar extrema are also found for entropies and enthalpies of activation for equilibrium type reactions.[15] Ultrasound measurements[16] in mixed solvents have also detected maxima at low concentrations of a second component. *This phenomenon is most certainly a property of the solvent.* It appears that in the systems discussed, the key to understanding lies in the field of thermal diffusion.[17]

The sucrose-water system results are more defined partly because the reactants are soluble in *only* the water, not the sucrose, hence the partial molal excess functions are important. In the alcohol-water mixtures, both components are individually solvents for the reactants; consequently, activities of the reactants in the various components of the solvent at different mole fraction ratios must be taken into consideration. The same argument can be applied to the solvated electron reaction rate constant data[10] and the diffusion coefficient data for iodine in alcoholic (Figure 2) and nonalcoholic organic mixed solvents.[8,9,18] An exothermic $(-)\Delta H^M$ will lead to an increase and an endothermic $(+)\Delta H^M$ will lead to a decrease in diffusion coefficients in solvent mixtures.[19]

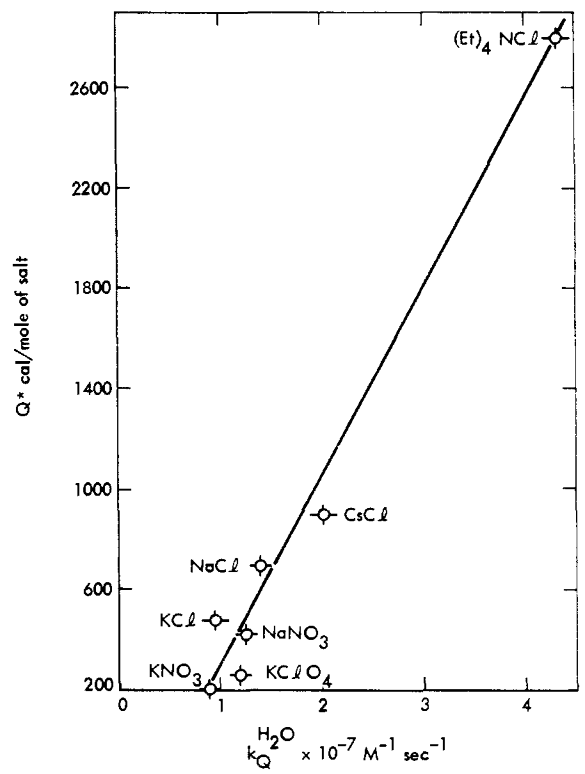

Figure 3. Variation of the rate constant with heats of transport:[28] salt concentrations 0.01 *m*; for k_Q determinations, pH 7; solvent, water.

Nonequilibrium thermodynamic theories for nonideal solutions have been presented;[17,20-26] however, they have limited applicability. Heats of transport (a measure of thermal diffusion) for mixed solvent systems have long been recognized as being of greater magnitude than those for ions in solution.[25,27] A semiempirical approach to the measurement of heats of transport[28] of aqueous salt solutions employs a similar model to that used in this communication (used here as a rationale for correlating normalized diffusion parameters with $-\Delta H^M/X_1X_2$). It seems, then, that both Q^*, the heat of transport of the salt solutions,[28] and $-\Delta H^M/X_1X_2$ should be proportional to the same diffusion parameters of a given reaction. For the 0.01 *m* salt solutions, corrections for viscosity and dielectric constant need not be made to the rate constants. Measurement of k_Q in several aqueous salt solutions revealed a definite dependence on the heats of transport, Q^*,[28] for those salts (Figure 3). Further, the k_Q values cannot be correlated with the usual electrochemical parameters. Thus, it appears that $\Delta H^M/X_1X_2$ is an important parameter in diffusion, and, if an inert substance such as sucrose be added as a viscosity agent, the function $(\partial H^M/\partial n_2)/X_2$ can be a diffusion control indicator.

These findings have importance in chemical kinetics, thermodynamics, reaction methanisms, and in biologically related areas such as energetics and kinetics of transport across membranes and biological reactions.

Acknowledgment. The author wishes to thank Dr. Stanley Manatt for his constant encouragement, Dr. Gerald Voecks for several helpful discussions, and a referee for valuable comments. This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by NASA.

References and Notes

(1) Presented at the 5th International Congress of Radiation Research, Seattle, Wash., July 14–20, 1974.
(2) P. A. Carapellucci and D. Mauzerall, Abstracts, 162nd National Meeting of the American Chemical Society, 1971; P. A. Carapellucci and D. Mauzerall, IVth IUPAC Symposium on Organic Photochemistry, Baden-Baden, 1972.
(3) P. A. Carapellucci and D. Mauzerall, *Ann. N.Y. Acad. Sci.*, **244**, 214–238 (1975).
(4) R. F. Lama and B. C.-Y. Lu, *J. Chem. Eng. Data*, **10**(3), 216 (1965).
(5) J. B. Taylor and J. S. Rowlinson, *Trans. Faraday Soc.*, **51**, 1183 (1955).
(6) J. S. Rowlinson, "Liquids and Liquid Mixtures", Butterworths, London, 1959, p 185.
(7) Reference 6, p 186.
(8) K. Nakanishi and T. Ozasa, *J. Phys. Chem.*, **74**, 2956 (1970).
(9) K. Nakanishi and S. Kitajima, *J. Phys. Chem.*, **76**, 2470 (1972).
(10) F. Barat, L. Gilles, B. Hickel, and B. Lesigne, *J. Phys. Chem.*, **77**, 1711 (1973).
(11) R. W. Gurney, "Ionic Processes in Solution," Dover, New York, N.Y., 1953, p 228–229. Here it is shown that plots linear with $1/\epsilon$ may be illusory.
(12) P. A. Carapellucci, part II in this series, submitted for publication.
(13) Data from ref 8 and 10.
(14) R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).
(15) J. F. J. Engbersen and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, **96**, 1231 (1974).
(16) S. Nishikawa, T. Yasunaga, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **46**, 2992 (1973).
(17) H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids," Butterworths, London, 1961.
(18) K. Nakanishi, T. Ozasa, and K. Ashitani, *J. Phys. Chem.*, **75**, 963 (1971).
(19) Compare with data in ref 18.
(20) T. L. Hill, "An Introduction to Statistical Thermodynamics", Addison-Wesley, Reading, Mass., 1960, Chapter 20.
(21) W. B. Brown, *Proc. R. Soc. London, Ser. A*, **240**, 561 (1957).
(22) G. Still, *J. Chem. Phys.*, **59**, 3926 (1973).
(23) G. R. Dowling and H. T. Davis, *J. Chem. Phys.*, **59**, 3235 (1973).
(24) R. J. Bearman and J. G. Kirkwood, *J. Chem. Phys.*, **28**, 136 (1958).
(25) R. J. Bearman, J. G. Kirkwood, and M. Fixman, *Adv. Chem. Phys.*, **6**, 1 (1958).
(26) E. Grunwald and A. Effio, *J. Am. Chem. Soc.*, **96**, 423 (1974).
(27) E. Helfand and J. G. Kirkwood, *J. Chem. Phys.*, **32**, 857 (1960).
(28) J. N. Agar, *Adv. Electrochem. Electrochem. Eng.*, **3**, 31 (1963).
(29) NAS-NRC Senior Resident Research Associate, 1973–1975 at Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

P. A. Carapellucci[29]
California Institute of Technology, Jet Propulsion Laboratory
Pasadena, California 91103

Received June 12, 1974

New Lanthanide Alkyl and Aryl Derivatives of the Type $(\eta^5\text{-}C_5H_5)_2LnR$

Sir:

Recently, there has been a resurgence of interest in the organometallic chemistry of the actinides, with a great deal of the focus being on σ-bonded complexes.[1] However, σ-bonded organolanthanide compounds have avoided close scrutiny. The work done with organolanthanide complexes has been centered about the ionic π-bonded cyclopentadienyl[2] and cyclooctatetraenyl[3] ligands. The only well-characterized σ-bonded organolanthanide complexes are the lithium salts of the Lu and Yb tetrakis(2,6-dimethylphenyl) compounds[4] and a series of phenylacetylide complexes which we have synthesized: $(\eta^5\text{-}C_5H_5)_2LnC{\equiv}CPh$ (Ln = Gd, Er, Yb; Ph = phenyl).[5] We have now extended this series and would like to present our preliminary results in synthesizing alkyl and aryl derivatives of the type $(\eta^5\text{-}C_5H_5)_2LnR$ (Ln = Gd, Er, Yb; R = Ph, CH_3). The methyl derivatives are the only well characterized, stable lanthanide alkyls,[6,7] and the phenyl compounds are the first aryl derivatives known for Gd and Er. These are the only σ-bonded organolanthanide complexes known for these elements aside from the aforementioned Yb–aryl compound[4] and the phenylacetylide derivatives.[5]

The new complexes are prepared as shown in eq 1 by the reaction in THF of the appropriate $(\eta^5\text{-}C_5H_5)_2LnR$[8] with either methyl- or phenyllithium at −78°. The complexes are precipitated from the reaction solution by concentrating the solvent in vacuo and the addition first of toluene and then of hexane. The compounds are purified by continuous extraction with benzene.[9,10]

$$(\eta^5\text{-}C_5H_5)_2LnCl + RLi \xrightarrow[-78^\circ]{THF} (\eta^5\text{-}C_5H_5)_2Ln\text{–}R + LiCl \tag{1}$$

All of the compounds are very sensitive to oxygen and moisture, decomposing rapidly upon exposure. However, all of them are fairly thermally stable, as none either decompose or melt below 130° in argon filled capillaries. Indeed, it would seem that high thermal stabilities are the rule for $(\eta^5\text{-}C_5H_5)_2LnR$ compounds[5] as well as for $(\eta^5\text{-}C_5H_5)_3UR$ complexes.[1]

Infrared spectra of these compounds support the presence of methyl and phenyl moieties which are σ-bonded to the various lanthanides. For the phenyl complexes, the band at 3048 cm^{-1} is assigned as the C–H stretching vibration. The characteristic C–H out-of-plane bending vibrations appear at 718 and 701 cm^{-1} and are indicative of a monosubstituted phenyl ring. Bands at 1412, 1468, and 1483 cm^{-1} are assigned as C–C stretching vibrations while the series of absorptions between 1300 and 1000 cm^{-1} arises from the C–H in-plane bending modes.

For the methyl derivatives, the C–H stretching vibration is seen as a weak, broad absorption centered at 2890 cm^{-1}. All of the methyl complexes have a strong band at ~1190 cm^{-1}. Nakamoto ascribes this band to the symmetric deformation of the methyl group, and it is characteristic of complexes containing a methyl moiety bound to a metal.[11] Also present are bands at 1360 and 1328 cm^{-1} which are assigned as C–H bending vibrations of the methyl ligand.

In addition, all of the complexes have bands at ~3100, 1440, 1010, and 775 cm^{-1}, characteristic of η^5-cyclopentadienyl moieties.[12]

Visible spectra were obtained for both the methyl and phenyl derivatives of erbium. However, unlike the phenylacetylide complex,[5] there is no evidence of any hypersensitivity in the f–f transitions which were observed.[13-15] In this respect, the spectra resemble that of the starting chloride complex. These spectra did, however, show the presence of a charge transfer band which originates in the uv and extends into the visible region. Visible spectra of the gadolinium complexes were devoid of f–f transitions, but contained the tail end of a charge transfer band as in the erbium complexes. These are assigned as ligand to metal charge transfer bands,[3b,5,16] and indicate that there is at least some interaction, other than purely electrostatic, between the metal and the R group. The visible spectra of the ytterbium complexes are uninformative as they are dominated by a large charge transfer band which is present in the spectrum of the starting chloride complex.[17]

One of the reasons behind preparing these complexes was the desire to study f electron participation and covalency (if any) in the bonding. Studies of organolanthanide complexes which contain only π-bonded ligands have shown that the bonding is essentially ionic.[18] However, in compounds containing lanthanide-carbon σ bonds, the electron density of the σ-bonded ligand should be more available for localized interaction with the metal than for π-bonded systems. This could possibly lead to a greater enhancement of f orbital participation in the bonding than in, for instance, the π-cyclopentadienyl moiety. In this context, magnetic susceptibility studies of these alkyl and aryl complexes[19] have revealed some unusual results which may be attributed to this. The room temperature magnetic susceptibilities of these complexes (some of which are given in Table I) are all in agree-