terpreted in terms of a mixture of di- and trisolvates; the reasons for this discrepancy are not clear to us. These latter authors have also, on the basis on rather limited data, suggested that $HFeCl_4$ forms a tetrasolvate with diisopropyl ether and perhaps a mixture of di- and trisolvates with diisoamyl ether (at least, the slope of the log E *vs.* log ether concentration plot was 2.5).[24] This suggests that the solvation number decreases as the length of the hydrocarbon chains on the ether increase, but more data should be made available before any real attempt is made to correlate these two factors.

To summarize, our work emphasizes the fact that observable solvation of strong acids by weakly basic organic substances does not necessarily involve three molecules of the base. We further suggest that, while solvation of the hydrated proton is undoubtedly important to the extraction process, the possibility of observable solvation of the anion (or, perhaps, solvation of the dipole (ion pair) as an entity) cannot be definitely rejected, at least with the very weakly basic extractants.

[24] V. V. Fomin and A. F. Morgunov, *Russ. J. Inorg. Chem.*, **5**, 112 (1960).

The Electrical Double Layer in Dimethyl Sulfoxide Solutions

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Contribution from the Air Force Cambridge Research Laboratories, L. G. Hanscom Field, Bedford, Massachusetts. *Received October 4, 1966*

Abstract: Electrocapillary curves and double-layer capacities have been measured for a number of solutions of inorganic electrolytes in dimethyl sulfoxide (DMSO) and mixtures of DMSO with water. There is a strong resemblance between the behavior of DMSO and aqueous solutions. Thus anions are specifically adsorbed from DMSO solutions in the order $I^- > Br^- > Cl^- > NO_3^- > ClO_4^- > PF_6^-$, whereas cations are not significantly adsorbed. The electrocapillary maximum (ecm) is shifted in the positive direction in DMSO as compared with water, and a large hump appears close to the limit of anodic polarization in solutions where the anion is not strongly adsorbed. The influence of the diffuse layer capacity is more marked in DMSO solutions as expected in view of the lower dielectric constant. The effect of the diffuse layer capacity at the ecm vanishes for 0.1 M KPF_6 in DMSO–water mixtures containing ~30 mole % of DMSO. The interfacial tension at the ecm is lower by ~60 dynes/cm in DMSO than in water. These results are discussed critically in terms of current theories of the double-layer structure.

The importance of dimethyl sulfoxide (DMSO) as an ionizing solvent has been recognized for some time although few results of electrochemical measurements have been reported. The study of this solvent system has recently received considerable stimulus in the United States as a result of intensive efforts to develop novel types of batteries employing couples of high specific energy density in DMSO and similar high dielectric constant aprotic solvents.[1] The need for basic thermodynamic and electrochemical data in these solvent systems is therefore firmly established. Furthermore, such data are of considerable theoretical interest. This is especially true in the area of the electrode-solution double layer. In this paper, therefore, an attempt is made to give a broad description of the electrocapillary properties of the mercury–DMSO interface. No attempt is made at a detailed analysis of the data, which indeed is not possible in the absence of thermodynamic data. Nevertheless, certain generalizations can be made which have a direct bearing on double-layer theory and the more general area of electrode reactions in DMSO solutions.

Experimental Section

The double-layer capacity at a growing mercury drop was measured with a precision of 0.1% using an ac bridge technique similar to that described previously.[2] General Radio components were used as the bridge elements. A 4-decade capacitor (Type 1423A) giving a range of 100 pf to 1.111 μf ± 0.05% was used as the capacitance standard. The resistance was measured by a 6-decade resistor (Type 1432-X) giving increments of 0.1 ohm. Variable ratio arms were constructed from two pairs of single-decade resistors (Types 510D and E) mounted in a shielding aluminum box. The oscillator (GR Type 1304B) and the detector circuits were isolated from the bridge by screened transformers (Type 578A). All connections were made with coaxial cable with the braiding connected at both ends to the component shields. The performance of the bridge at low signal levels was improved by the use of a tuned amplifier (GR Type 1232A) in the output circuit. The output was displayed on a Hewlett-Packard oscilloscope (Type 130C). Timing of the drop growth was achieved by use of a Hewlett-Packard preset decade counter (Type 5214L) giving a timed interval of up to 100 sec in 100-μsec increments with an accuracy of 0.001%. The electrode potential was measured with a precision of 0.1 mv using a Honeywell potentiometer (Type 2781), galvanometer (Type 3134), and constant current power supply (Type 2798-1). Measurements were carried out in a water thermostat controlled to 0.01°. The signal frequency in all the measurements reported was 1 kc.

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[1] This work is reviewed comprehensively by J. N. Butler, *J. Electroanal. Chem.*, in press.

[2] G. J. Hills and R. Payne, *Trans. Faraday Soc.*, **61**, 316 (1965).

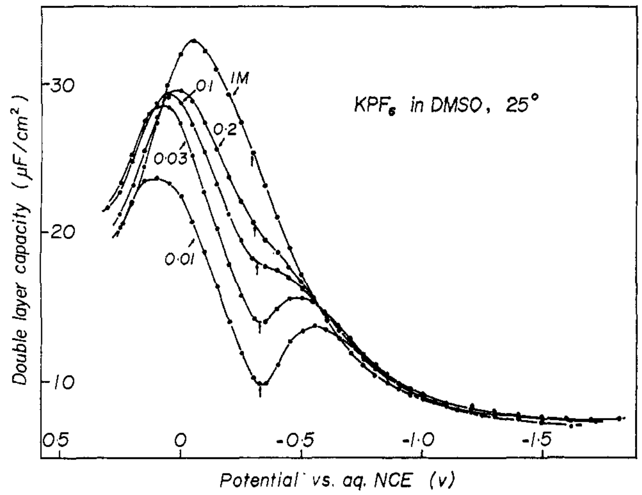

Figure 1. Differential capacity of the double layer at a mercury electrode in DMSO solutions of KPF_6 as a function of potential and concentration at 25°. Vertical arrows indicate potential of zero charge.

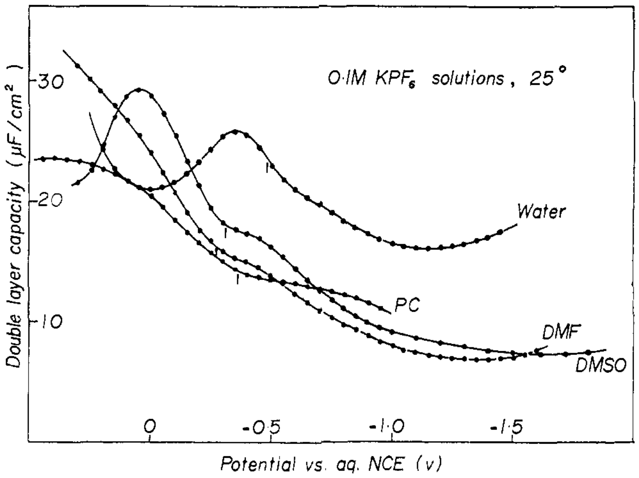

Figure 2. Differential capacity of the double layer at a mercury electrode in 0.1 M solutions of KPF_6 in water, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and propylene carbonate (PC) at 25°. The DMF and PC data are the author's unpublished measurements. Arrows indicate potential of zero charge.

The interfacial tension was measured by means of a simple form of Lippman capillary electrometer. The fine tapered capillary was inserted in the center compartment of a three-compartment cell close to the cell wall through which the meniscus was viewed with a magnification of 32 by means of a traveling microscope (Gaertner coordinate cathetometer Type M1236-46) used with a calibrated eyepiece (Type M206S). The capillary was connected directly by a flexible Teflon tube to a small reservoir clamped to a stand which could be raised or lowered by means of a laboratory jack. The height of the mercury in the reservoir was measured with a precision of 0.001 cm by means of a Gaertner universal cathetometer. The advantages of this simple arrangement over the usual method involving the use of gas pressure, which is then measured by a mercury manometer, are (1) that two cathetometer readings are eliminated and (2) that the potentially troublesome gas-pressure system is eliminated. The meniscus in the capillary could be oscillated by shaking the Teflon tube. The capillary electrode could be polarized with respect to a normal (aqueous) calomel electrode isolated from the main compartment by a ground joint and a stopcock. The potential was measured with respect to a similar reference electrode in the third compartment of the cell with a Hewlett-Packard digital voltmeter (Type 3440A). Measurements were carried out in the open laboratory in which the temperature was controlled at 25 ± 0.5°. The reproducibility of the measurements was better than 0.1%.

Solutions were usually prepared from ACS grade salts without further purification. KPF_6 solutions were prepared from Practical Grade KPF_6 supplied by Matheson Coleman and Bell, recrystallized from water, and vacuum dried before use. Dimethyl sulfoxide (Baker Analyzed Reagent) having an initial conductance of $\sim 2 \times 10^{-6}$ ohm^{-1} cm^{-1} was further purified by double vacuum distillation through a 30-cm column packed with porcelain saddles. The middle fraction boiling at 40-45° was collected. The conductance of the distillate was 3-4 $\times 10^{-8}$ ohm^{-1} cm^{-1} compared with the best previously reported value of $\sim 2 \times 10^{-8}$ ohm^{-1} cm^{-1}.[3] Rigorous exclusion of water was not attempted since small amounts of added water did not affect the measurements. Mercury was purified in the usual way by extraction with dilute nitric acid followed by multiple vacuum distillation.

Results

1. Double-Layer Capacity in KPF_6 Solutions. The double-layer capacity for five concentrations of KPF_6 in DMSO in the range 0.01 to 1 M is shown as a function of the potential in Figure 1. The curves bear a striking resemblance to typical aqueous solutions curves.[4] DMSO is the fourth solvent system in which a capacity hump has been observed.[5] The other systems are water,[4] formamide,[6-9] and N-methylformamide.[10] In the formamides, however, the hump occurs at potentials of ~0.8 v negative of the ecm, whereas in DMSO and aqueous solutions it occurs on the anodic side. This important point is discussed below.

The effect of the minimum in the diffuse layer capacity at the ecm is well illustrated in the curves of Figure 1. The position of the minimum can be compared with the ecm potentials recorded in Table I which were obtained by the method of the streaming mercury electrode.[11] The effect of the diffuse layer capacity is more pronounced in DMSO solutions than it is in aqueous solutions as can be verified by comparing 0.1 M KPF_6 solutions in the two solvents (Figure 2). This is to be expected in view of the lower dielectric constant of DMSO (46.7[1] compared with 78.3 for water) and also the fact that the capacity of the inner region of the double layer in DMSO is evidently lower than that in water in the vicinity of the ecm. The diffuse-layer capacity at the ecm for a 0.1 N solution of a nonadsorbed 1:1 electrolyte is 55.7 μf/cm² compared with 72.2 μf/cm² for a similar aqueous solution.

It is evident from Figure 2 that the hump in the DMSO solution occurs at a potential more positive of the ecm than does the hump in the aqueous solution. It also appears, within the limitations imposed by the

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[3] T. B. Reddy, Thesis, University of Minnesota, 1960.

[4] D. C. Grahame, *Chem. Rev.*, **41**, 441 (1947).

[5] It is surprising to find that the capacity is still decreasing with increasing anodic polarization at the limit where anodic current starts to flow. This behavior has not been observed in any previously studied solvent system. The capacity invariably rises sharply as the potential of the anodic reaction is approached. Although no firm conclusion can be reached without a detailed analysis of the electrode impedance, it appears that the effect of the pseudo-capacity associated with the anodic reaction is small and the rate of this reaction, therefore, by implication, slow.

[6] S. Minc, J. Jastrzebska, and M. Brzostowska, *J. Electrochem. Soc.*, **108**, 1160 (1961).

[7] R. Payne, Thesis, University of London, 1962.

[8] R. Payne, *J. Chem. Phys.*, **42**, 3371 (1965).

[9] E. Dutkiewicz and R. Parsons, *J. Electroanal. Chem.*, **11**, 196 (1966).

[10] B. B. Damaskin and Yu. M. Povarov, *Dokl. Akad. Nauk SSSR*, **140**, 394 (1961).

[11] D. C. Grahame, E. M. Coffin, J. I. Cummings, and M. A. Poth, *J. Am. Chem. Soc.*, **74**, 1207 (1952).

uncertainty of the liquid junction potentials at the DMSO-aqueous KCl liquid junction, that the ecm in the DMSO solution is ~150 mv more positive than that in the aqueous solution. The value of -0.314 v (aqueous nce) for 0.1 M KPF_6 in DMSO compares well with the value of -0.3 v (aqueous sce) estimated by Reddy[3] for 0.1 M $NaClO_4$ in DMSO from an electrocapillary curve obtained by measuring drop times.

The DMSO solution curves also differ from the aqueous solution curves in the shape of the cathodic branch. The DMSO capacity is uniformly lower than that of the aqueous solution, decreasing monotonically to a value of ~7.2 μf/cm^2 close to the limit of polarization.[12] The ratio of the integral capacities for the two solvent systems measured at $q = -15$ μcoulombs/cm^2 is 1.71, which is remarkably close to the ratio of the dielectric constants (1.68). This must, however, be regarded as fortuitous since the thickness of the inner layer condenser, which presumably depends on the size of the solvent molecule[13] and the nature of the cation solvation sheath, will be at least as important as the effective dielectric constant of the inner layer. Furthermore, studies of other solvent systems show no definite correlation of the inner layer capacity with the bulk dielectric constant,[14] as would be expected since association of the solvent molecules in the bulk which contributes in large part to the high dielectric constant is presumably absent in the adsorbed state. On the other hand, the high dielectric constant does seem to be essential for the occurrence of the capacity hump, which has until now been observed for no solvent of dielectric constant lower than that of water.[14a]

2. Specific Adsorption of Anions. Electrocapillary curves for several 0.1 M solutions of alkali metal salts in DMSO are shown in Figure 3. Again there is a striking similarity to the corresponding aqueous solution curves.[15] As in aqueous solutions, anions are evidently specifically adsorbed in the order $I^- > Br^- > Cl^- > ClO_4^- > PF_6^-$, and the interfacial tension of the cathodic branch of the curve is almost independent of the identity of the cation.[16] The interfacial tension at the ecm for the $LiClO_4$ solution (for which the anion specific adsorption appears to be slight at the ecm) is 370.1 dynes/cm at 25° which compares with 425.4 dynes/cm for a nonadsorbed electrolyte (0.1 M NaF) in water. It follows, therefore, that dimethyl sulfoxide in common with all other previously studied organic solvents is considerably more strongly adsorbed on mercury than water, at least in the vicinity of the ecm. This is confirmed by the measurements of the double-layer capacity in mixed water–DMSO solutions which are described below.

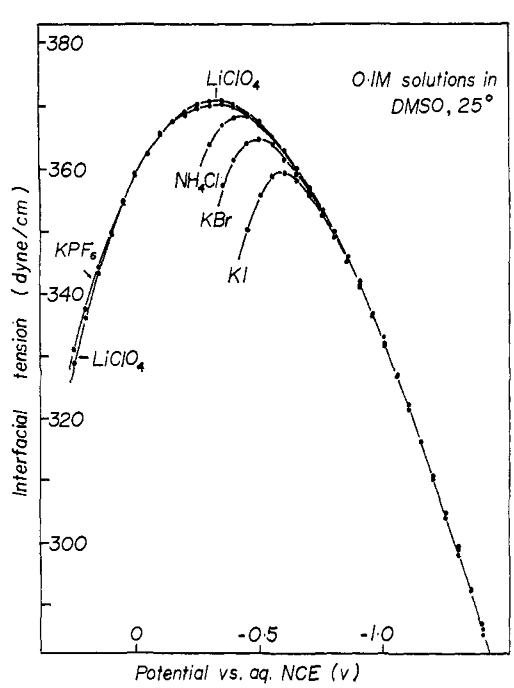

Figure 3. Electrocapillary curves for 0.1 M solutions of the salts named in DMSO at 25°.

Capacity–potential curves for several 0.1 M salt solutions in DMSO are shown in Figure 4. These confirm the strong specific adsorption of the halide anions. The diffuse layer minimum at the ecm appears in the KNO_3 and $LiClO_4$ solutions confirming the inference drawn from the electrocapillary measurements that specific adsorption of these anions at the ecm is less than that found in the corresponding aqueous solutions,[17–19] although the sharp rise in the capacity at more positive potentials suggests the occurrence of specific adsorption in this region. It is interesting to note that the capacity hump appears also in the $LiClO_4$ solution. In the KNO_3 solution the hump is no more than an inflection, and in the NH_4Cl and KBr solutions it is completely masked by the rapidly increasing capacity due to specific adsorption of anions. These conclusions are broadly confirmed by the potentials and interfacial tensions at the electrocapillary maximum which are compared with similar aqueous solution data in Table I. Thus the order of specific adsorption of anions in the two solvents is essentially

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(12) The measured capacity actually passes through a shallow minimum close to the limit of polarization. It is not clear, however, that this is a genuine minimum in the double-layer capacity. It is probably due to the effect of the pseudo-capacity associated with cation deposition but may also be due to adsorption of small amounts of water. It should also be mentioned that the inflection in the electrocapillary curve noted by Reddy[3] cannot be correct since it implies a negative capacity.

(13) Molecular models and crystallographic data for solid DMSO suggest that the thickness of a monomolecular layer could not be less than ~4.8 A compared with the value of 3 A usually assumed for the water layer; see, for example, J. R. Macdonald and C. A. Barlow, *J. Chem. Phys.*, **36**, 3062 (1962). The thickness effect therefore should be at least as important as the dielectric constant effect and should enhance it.

(14) A. N. Frumkin, *Z. Physik. Chem.*, **103**, 43 (1923).

(14a) Note Added in Proof. It now appears that these capacity humps are more widespread in nonaqueous solutions than has been supposed. Recent work in this laboratory has demonstrated the occurrence of pronounced humps similar to the DMSO hump in the 5-membered cyclic esters 4-butyrolactone and 4-valerolactone and a flat extended hump in the related cyclic carbonates propylene carbonate and ethylene carbonate. The lowest dielectric constant in this series is that of 4-butyrolactone (39.1).

(15) The strong correlation between specific adsorption of anions in solvent systems of such widely differing properties tends to support the opinion of Grahame[4] that the specific metal–ion interaction rather than the solvation energy as stated by Bockris, Devanathan, and co-workers is the more important contribution to the adsorption energy; see, for example, J. O'M. Bockris, M. A. V. Devanathan, and K. Müller, *Proc. Roy. Soc.* (London), **A274**, 55 (1963).

(16) Comparison of the electrocapillary curves with the doubly integrated capacities revealed systematic discrepancies on the cathodic side. This was traced to a trivial error resulting from the use of the digital voltmeter in a high resistance (~100 Kohms) circuit which was effectively loaded by the finite impedance (11 Mohms) of the instrument. This error of up to 20 mv in the potential does not affect the arguments.

(17) R. Payne, *J. Phys. Chem.*, **69**, 4113 (1965).

(18) R. Payne, *ibid.*, 70, 204 (1966).

(19) R. Payne, *J. Electrochem. Soc.*, **113**, 999 (1966).

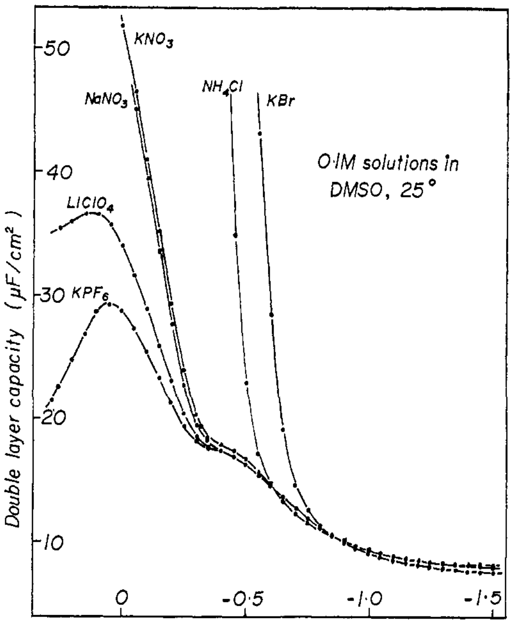

Figure 4. Differential capacity of the double layer at a mercury electrode in 0.1 *M* solutions of the salts named in DMSO at 25°.

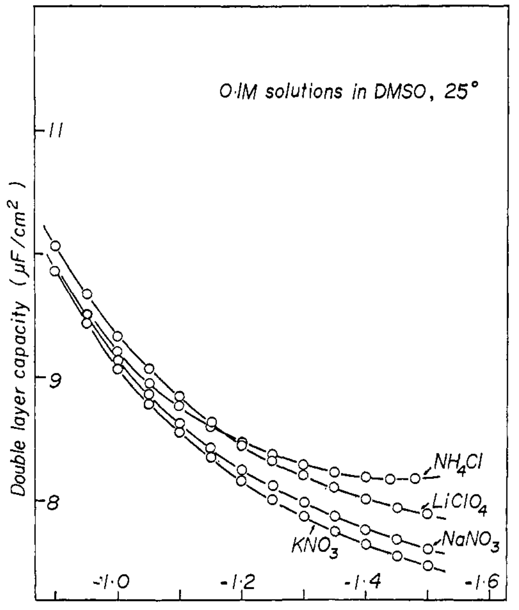

Figure 5. Cathodic branch of four of the curves of Figure 4 showing the effect of the cation on the capacity.

the same, while the maximum interfacial tension is reduced by 50–60 ergs/cm², and the potential of the ecm is shifted in the positive direction by 0.1–0.2 v in the DMSO system.

The absence of specific adsorption of cations, which is suggested by the electrocapillary curves, is also confirmed by the capacity curves which show only a small dependence of the capacity on the identity of the cation. It appears from Figure 5 that the cathodic capacity decreases in the order $Li^+ > Na^+ > K^+$ which is the reverse of the order found in aqueous solutions.[20]

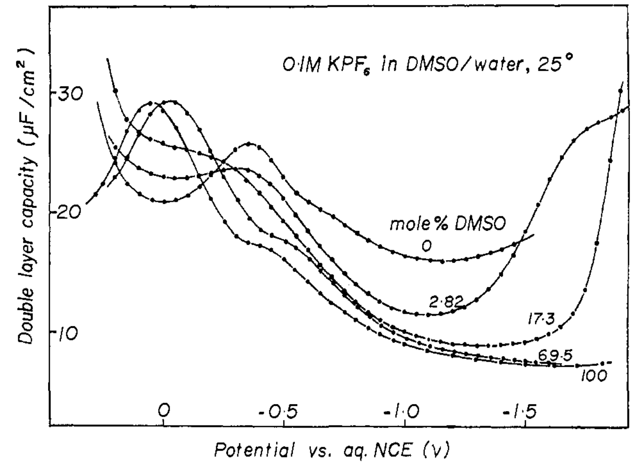

Figure 6. Differential capacity of the double layer at a mercury electrode in 0.1 *M* solutions of KPF_6 in mixtures of DMSO with water.

3. Double-Layer Capacity in Mixed DMSO–Water Solutions. The capacity is shown as a function of potential in Figure 6 for five solutions of 0.1 *M* KPF_6 in mixtures of DMSO and water covering the complete range from pure DMSO to pure water. A number of interesting observations can be made. It is clear as previously inferred from the electrocapillary measurements that DMSO is fairly strongly adsorbed on mercury especially on the cathodic branch of the curve where the desorption peak usually found for organic adsorbates is not observed within the experimental range of polarization. This is probably attributable to the large dipole moment (3.96 D.)[21] of the DMSO molecule. The situation on the anodic side is more complex. The well-known hump occurring in the pure aqueous solution at ∼−0.35 v disappears with the addition of DMSO and is eventually replaced by the DMSO hump close to $E = 0$ for concentrations of DMSO $\gtrsim$ 50 mole %. The two humps do not appear to coexist for any composition of the solvent. A further interesting point is the behavior of the diffuse layer which can be inferred qualitatively from the effect of solvent composition on the minimum in the diffuse-layer capacity close to the ecm. This minimum

Table I. Coordinates of the Electrocapillary Maximum for 0.1 *M* Solutions in Dimethyl Sulfoxide at 25° Compared with Corresponding Aqueous Solutions

	$-E_{ecm}$, v *vs.* aq nce			γ_{ecm}, dynes/cm	
Salt	Streaming electrode	Electrocapillary curve	Corresponding aq soln	DMSO soln	Aq soln
KPF_6	0.314	0.334	0.484[a]	370.2	425.6[a]
$LiClO_4$	0.319	0.320	0.509[b,c]	370.5	424.8[a,d]
KNO_3	0.311	...	0.517[b]	...	424.1[e]
$NaNO_3$	0.303	...	0.516[b]	...	...
NH_4Cl	0.417	0.423	0.503[b]	368.3	425.1[e,f]
KBr	0.493	0.494	0.574[b]	364.5	422.4[e,g]
KI	...	0.588	0.732[b]	359.2	413.3[e]

[a] This work. [b] Data of D. C. Grahame and co-workers tabulated in "Electrochemical Data," B. E. Conway, Ed., Elsevier Publishing Co., Amsterdam, 1952. [c] $KClO_4$. [d] $HClO_4$. [e] Data of G. Gouy, *Ann. Chim. Phys.*, **29**, 145 (1903). [f] NaCl. [g] HBr.

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(20) D. C. Grahame, *J. Electrochem. Soc.*, **98**, 343 (1951).

(21) H. Dreizler and G. Dendl, *Z. Naturforsch.*, **19a**, 512 (1964).

is well developed in the pure aqueous solution as mentioned previously but disappears on addition of DMSO to the solution. The effect of the diffuse layer reappears in the preponderantly DMSO solutions. These unexpected results are discussed below.

Discussion

1. Specific Adsorption of the PF_6^- Ion. Although specific adsorption of PF_6^- ion is evidently less than that of the other anions studied in this work, there is little doubt that some specific adsorption occurs as in the corresponding aqueous solutions.[22] This can be demonstrated by calculating the capacity of the inner region (C^i) from diffuse-layer theory assuming the absence of specific adsorption and using the simple series condenser model of Grahame.[4] The resultant values of C^i for 0.01, 0.1, and 1 *M* solutions are plotted against the electrode charge in Figure 7. In contrast to the concentration-independent inner-layer capacity found by Grahame for aqueous NaF solutions,[4,23,24] the inner-layer capacity calculated in this way for the KPF_6–DMSO system is strongly dependent on the concentration, suggesting that anions are specifically adsorbed even on a negatively charged electrode. According to Table II, the ecm potential apparently shifts in the positive direction with increasing salt concentration. This, however, is due to the liquid-junction potential deliberately introduced between the 0.1 *M* KPF_6 solution and the solution in which the measurements are being made, which is done in order to avoid disturbing the aqueous–nonaqueous liquid junction at the reference electrode. Crude calculations of the liquid-junction potential between the two KPF_6 solutions have been made using the equation

Table II. Potential of the Electrocapillary Maximum for KPF_6 Solutions in Dimethyl Sulfoxide at 25°

C, *M*	$-E_{\mathrm{meas}}$,[a] v	$-E_{\mathrm{cor}}$,[b] v
0.01	0.332	0.320
0.03	0.323	0.317
0.1	0.314	0.314
0.2	(0.308[c]) 0.328[d]	0.312
1.0	0.295	0.306

[a] E_{meas} is the emf of the cell

$$\mathrm{Hg}|\mathrm{Hg_2Cl_2}|1\ M\ \text{aq KCl}\overset{\mathrm{LJP1}}{|}\underset{\text{in DMSO}}{0.1\ M\ \mathrm{KPF_6}}\overset{\mathrm{LJP2}}{|}\underset{\text{in DMSO}}{x\ M\ \mathrm{KPF_6}}|\mathrm{Hg}$$

[b] E_{cor} is value corrected for LJP2 using the data in ref 25 and 26. [c] Interpolated value. [d] Solution in direct contact with aqueous calomel electrode.

$$E_{\mathrm{LJP}} = (2t^+ - 1)(RT/F)\ln\frac{a_\pm}{a_\pm^{0.1M}} \qquad (1)$$

where $a_\pm$ is the mean ionic activity. The cation transference number t^+ was estimated at 0.37 from the conductance data of Sears, Lester, and Dawson[25] using the limiting conductance of the ClO_4^- anion as a substitute for the PF_6^- anion for which no data are available. The mean ionic activities in eq 1 were estimated from the activity coefficients for LiCl solutions reported by Dunnett and Gasser.[26] The corrected ecm potentials shown in Table II still vary in the positive sense with increasing concentration of KPF_6. This, however, almost certainly reflects the crudeness of the assumptions necessarily made in the calculation of the liquid-junction potential (LJP), and it is not possible to reach any firm conclusion. The variation of E_{ecm} with concentration in this system, however, is probably small. The unexpectedly large difference of 20 mv between the interpolated value (−0.308 v) and the directly measured value (−0.328 v) for the 0.2 *M* solution is probably connected with differences in the DMSO–aqueous solution LJP under the two different experimental conditions. The same factor also probably accounts for the difference of 8 mv in the ecm potential for KNO_3 and $NaNO_3$ (Table I).

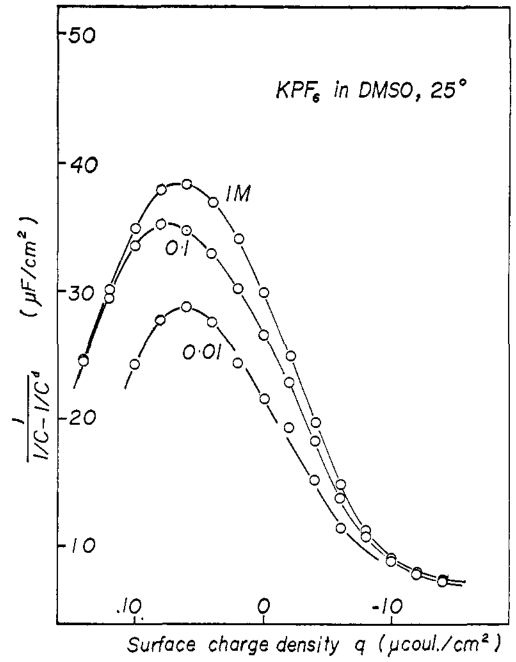

Figure 7. Capacity of the inner region of the double layer for KPF_6 solutions in DMSO at 25° calculated from diffuse layer theory assuming the absence of specific adsorption. Values of the surface charge density *q* were obtained by computer (IBM 7044) integration of the capacity.

2. Nature of the Capacity Hump. The capacity hump in DMSO solutions of KPF_6 occurs at a positive charge on the electrode of ~8 μcoulombs/cm² almost independent of the concentration. This compares with the corresponding hump in aqueous NaF solutions which occurs at $q \approx 4$ μcoulombs/cm².[24] It is tempting, therefore, to argue, following Macdonald,[27] that the hump in both cases is the result of a maximum in the effective dielectric constant of the inner region and that the dimethyl sulfoxide dipole is positively oriented toward the electrode more strongly than the similarly oriented water dipole. This simple picture, however, is unsatisfactory for several reasons, not least of which is the considerable accumulated evidence

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(22) Although no detailed studies of specific adsorption of the PF_6^- ion from aqueous solution have been reported, the occurrence of specific adsorption can be inferred from the ecm potential (−0.484 v *vs.* nce) which is significantly more negative than the value (−0.472 *vs.* nce) found for a nonadsorbed electrolyte.[4]

(23) D. C. Grahame, *J. Am. Chem. Soc.*, **76**, 4819 (1954).

(24) D. C. Grahame, *ibid.*, **79**, 2093 (1957).

(25) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

(26) J. S. Dunnett and R. P. H. Gasser, *Trans. Faraday Soc.*, **61**, 922 (1965).

(27) J. R. Macdonald, *J. Chem. Phys.*, **22**, 1857 (1954).

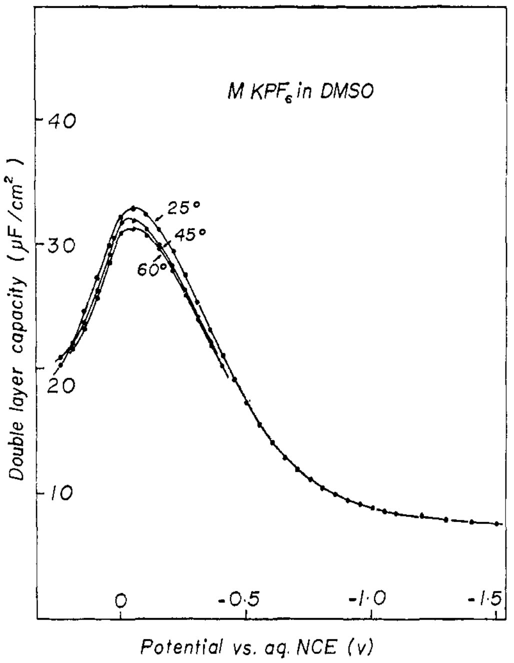

Figure 8. Effect of temperature on the capacity for a 1 *M* solution of KPF$_6$ in DMSO.

that the preferred orientation of the water dipole is that with the negative end toward the metal;[28] the hump should, therefore, occur on the negative side of the ecm. Furthermore, the variation of the potential of zero charge with solvent composition in mixed solvent systems cannot easily be explained in terms of this simple model, especially in the case of the formamides where the hump occurs on the negative side of the ecm at $q \approx -8$ μcoulombs/cm^2. The problem must therefore be examined in more detail.

The temperature dependence of the capacity hump for 1 *M* KPF$_6$ solution in the range 25–60° is shown in Figure 8. The capacity decreases with temperature in this region as previously found for aqueous solutions, and also for formamide[7] and N-methylformamide[10] solutions. The temperature dependence of the capacity at the hump amounts to ~0.02 μf/cm^2 deg, which is considerably lower than the value previously found for aqueous solutions (typically 0.10 μf/cm^2 deg for 0.1 *M* NaNO$_3$ at 25°).[29] It is interesting to note that the temperature coefficient of the dielectric constant of DMSO (0.075/deg)[30] is likewise smaller than that of water (0.36/deg)[31] also by a factor of ~5. It should be stressed, however, that correlations of this kind are of doubtful significance since the effective thickness of the layer must also be temperature dependent. Furthermore, such arguments should be applied to the *integral* capacity rather than the differential capacity and can only be meaningful when the temperature coefficient is calculated at constant charge on the electrode (or at constant potential[32]) since both the effective dielectric constant and the thickness of the inner layer are presumably dependent on the electrical variable.[33]

There seems little doubt in view of the behavior normally found with simple aliphatic molecules that the preferred orientation of the DMSO molecule on the mercury electrode will be that with the two methyl groups, *i.e.*, the positive end of the dipole facing the metal.[36] Furthermore, in view of the large dipole moment (3.96 D.) attributable mainly to the sulfoxide group, a large positive (toward the metal) surface potential would be expected to be generated by a layer of adsorbed DMSO molecules. Molecular models together with the crystallographic data of Thomas, Shoemaker, and Eriks[37] for solid DMSO at 5° suggest that the thickness of such an oriented layer would be ~4.8 A and that the dipole might be directed away from the normal to the interface by as much as 60°. It is not possible to predict with any certainty the effect on the DMSO generated surface potential of deviations from a normal orientation of the dipole or of the screening effect of diffuse layer ions, but it seems likely that the net effect should be a substantial positive surface potential resulting in a shift of the potential of zero charge in the positive direction (as compared with aqueous solutions) as found. It should also be mentioned that the same positive shift in the potential of zero charge is usually found for aliphatic organic solvents, *e.g.*, dimethylformamide (DMF) (Figure 2). In view of the large permanent dipole moment of the DMSO molecule and the probability that there is no strong attachment of the methyl groups to the metal, it also seems reasonable to suppose that the dipole undergoes some form of reorientation at sufficiently positive potentials resulting in the capacity hump observed.

A similar argument can be developed to explain the behavior of formamide and its N-substituted methyl derivatives. The capacity–potential curves for 0.1 *M* KPF$_6$ in DMF is shown in Figure 2. The potential of zero charge in this system occurs at −0.280 v (*vs.* nce) which (within the usual limitations of the unknown LJP) is ~30 mv more positive than in the corresponding DMSO solution and ~200 mv more positive than the corresponding aqueous solution. It seems reasonable to conclude, therefore, that the

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(28) See, for example, R. Parsons and F. G. R. Zobel, *J. Electroanal. Chem.*, **9**, 333 (1965).

(29) G. J. Hills and R. Payne, *Trans. Faraday Soc.*, **61**, 326 (1965).

(30) Y. Doucet, F. Calmes-Perrault, and M. Durand, *Compt. Rend.*, **260**, 1878 (1965).

(31) "Handbook of Electrochemical Constants," R. Parsons, Ed., Butterworth & Co., Ltd., London, 1959.

(32) The concept of constant metal–solution potential differences is especially difficult when the temperature (or pressure) is varied and is best avoided by choice of the charge as the electrical variable.

(33) The views recently expressed by M. A. V. Devanathan and B. Tilak, *Proc. Roy. Soc.* (London), **A290**, 527 (1966), on the origin of the capacity hump in aqueous solutions are in the opinion of the author incorrect. Although the inflection in the plot of specifically absorbed charge (q^1) against electrode charge (q) found in certain systems may be casually connected with solvent adsorption, it is certainly not true as originally suggested by Bockris, *et al.*,[15] that this is the principal source of the hump in the case of halide anions, although it is admittedly an important factor in the case of more complicated ions like nitrate and perchlorate[17–19] and especially benzenedisulfonate.[34] On the other hand, it is clear from Grahame's work on iodide ion adsorption[35a] that the hump is retained after the effect of the adsorption on the capacity has been substracted. This result has since been confirmed for the chloride ion[35b] and also the nitrate, perchlorate, and benzenedisulfonate ions. Furthermore the inflection in the q^1 *vs.* q plots occurs also in the adsorption of iodide ions from formamide solutions where there is certainly no capacity hump on the anodic side of the ecm (see also ref 8).

(34) J. M. Parry and R. Parsons, *Trans. Faraday Soc.*, **59**, 241 (1963).

(35) (a) D. C. Grahame, *J. Am. Chem. Soc.*, **80**, 4201 (1958); (b) D. C. Grahame and R. Parsons, *ibid.*, **83**, 1291 (1961).

(36) A. N. Frumkin and B. B. Damaskin in "Modern Aspects of Electrochemistry," Vol. 3, J. O'M. Bockris and B. E. Conway, Ed., Butterworth Inc., Washington, D. C., 1964, p 149.

(37) R. Thomas, C. R. Shoemaker, and K. Eriks, *Acta Cryst.*, **21**, 12 (1966).

DMF dipole is also oriented with the two N-methyl groups (*i.e.*, the positive end of the dipole) facing the metal and that the orientation is somewhat stronger than in the case of DMSO so that no reorientation, and therefore no capacity hump, occurs within the experimental range of anodic polarization.[38] In the case of formamide and N-methylformamide (NMF), on the other hand, a capacity hump appears at potentials of ~0.5 v *negative* of the ecm, suggesting a strong preferred negative orientation of the solvent dipole toward the metal. Such a reversal of the preferred orientation would be understandable, especially in the case of the formamide molecule, because of the availability of the N-hydrogen atoms for hydrogen bonding with bulk solvent molecules (or interaction with diffuse layer ions) which is also the factor responsible for the large dielectric constants of these solvents. However, adsorption of a strongly negatively oriented dipole should cause a correspondingly large negative shift in the ecm (as found when thiourea, for example, is adsorbed[39]) which is not observed. This is illustrated in Figure 9 where the shift of the ecm with composition is shown for mixtures of DMSO, DMF, NMF, and formamide with water. The DMSO-water solutions contain KPF_6 at a concentration of 0.1 *M;* the other systems are 0.1 *M* with respect to NaF. These results show that addition of DMSO and DMF to aqueous solutions shifts the ecm in the positive direction as expected and also, since the dipole moments and molecular dimensions of DMSO and DMF are similar, suggest that DMF is more strongly adsorbed than DMSO. (This may be due to differences in the interaction energy of DMSO and DMF with water but is also to be expected from the measurements in the pure solvents mentioned earlier.) The formamide and NMF adsorption from aqueous solutions, however, does not produce the expected large negative shift of the ecm. Formamide has little effect on the ecm,[40] while NMF actually produces a *positive* shift comparable in magnitude with the shift produced by DMSO adsorption.[41] Thus, although the behavior of DMF and DMSO, in which there is little doubt concerning the preferred orientation of the dipole, can be explained reasonably in simple terms, the model breaks down in the case of formamide and NMF where the preferred orientation of the molecule is uncertain. Since the dipole moments of the formamides are closely similar (3.8 ± 0.1 D.),[42] the apparent differences in the surface potential generated by the adsorption of these molecules are undoubtedly connected with dipole orientation, although other effects, notably the contribution of the replaced water dipoles to the surface potential, must also be considered. These problems will be further discussed elsewhere.

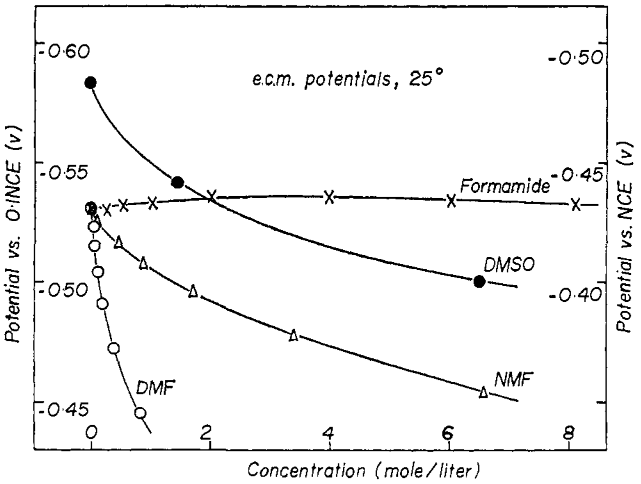

Figure 9. Effect on the zero charge potential of the adsorption from aqueous solutions of formamide, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and N-methylformamide (NMF). The DMSO results were obtained with 0.1 *M* KPF_6 solutions and a normal calomel electrode (right-hand potential scale). Other data are unpublished results of the author obtained with 0.1 *M* NaF solutions and a 0.1 *N* calomel electrode (left-hand potential scale).

3. Mixed DMSO-Water Solutions. The disappearance of the diffuse layer minimum in the capacity curve for mixed DMSO-water solutions in the intermediate range of composition raises an interesting question. The possibility that ion association in DMSO solutions might reduce the diffuse layer capacity (by reducing the ionic strength) has been mentioned previously so that it could be argued that addition of water to DMSO solutions simply increases the ionic strength. In that case the diffuse layer capacity might become sufficiently large so that no observable effect would be exerted on the total capacity. This, however, cannot be true since the diffuse layer minimum is also observable in the pure aqueous solution where the salt is presumably completely dissociated.

A more plausible explanation is that the effective dielectric constant in the diffuse layer goes through a maximum in the intermediate range of DMSO-water compositions. Recent measurements of the dielectric constant in DMSO-water mixtures[30] actually do show positive deviations from ideal linear behavior, with a maximum deviation of ~3.5 occurring at ~25 mole % DMSO. Nevertheless, the effect is too small since the dielectric constant still decreases monotonically (although not linearly) with composition. Furthermore, the diffuse layer capacity is proportional to the square root of the dielectric constant[4] and is therefore relatively insensitive to its value.

The capacity curves measured for the 2.82 and 17.3 mole % DMSO solutions (Figure 6) are reminiscent of curves obtained for aqueous solutions in the presence of moderate specific adsorption of anions which suggests the most probable explanation of the observed effect. The disappearance of the diffuse layer minimum in moderately dilute (0.1 *M*) aqueous solutions in the presence of specifically adsorbed anions[4] is due not to any effect of the adsorption on the inner layer capacity (C^i) but to the way in which C^i and the diffuse layer capacity (C^d) are combined in producing the observed total capacity (C)[43]

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(38) It is possible that a hump would be found in DMF solutions of fluoride ions which are presumably less specifically adsorbed than PF_6^- ions.

(39) F. W. Schapink, M. Oudeman, K. W. Leu, and J. N. Helle, *Trans. Faraday Soc.*, **56**, 415 (1960).

(40) The ecm for 0.1 *M* NH_4F in pure formamide occurs at −0.504 v (*vs.* 0.1 nce) compared with the value of −0.531 v found for 0.1 *M* NaF in water: R. Payne, unpublished data.

(41) Specific adsorption of PF_6^- at the ecm would of course reduce the positive shift.

(42) I. P. Gol'dshtein, Yu. M. Kessler, Yu. M. Povarov, and A. I. Gorbanev, *Zh. Strukt. Khim.*, **4**, 445 (1963).

(43) M. A. V. Devanathan, *Trans. Faraday Soc.*, **50**, 373 (1954).

$$1/C = 1C^{i} + 1/C^{d}(1 + dq^{1}/dq) \qquad (2)$$

where q^1 is the charge due to specifically adsorbed anions and q is the excess charge on the metal. Since q^1 is negative for anions, the effect of the diffuse layer on the measured capacity is eliminated when $dq^1/dq \approx -1$ and the second term in (2) disappears.[44] The results, therefore, can be tentatively explained in terms of enhanced specific adsorption of anions in mixed solvents containing a preponderance of water. This is an interesting result which should have some correlation with the thermodynamic properties of the mixed solvent system.

The nonideality of the variation of the dielectric constant with composition reported by Doucet, *et al.*,[30] is paralleled by similar positive deviations of the viscosity, density, and heat of mixing, which have been reported by Cowie and Toporowski.[45] The maximum deviations occur at 30–40 mole % DMSO and suggest the probable existence of a stable DMSO hydrate with a 2:1 DMSO to water ratio or at least strong hydrogen-bonded association between the two molecules. It is probable, therefore, that the solvation energy of the PF_6^- ion would pass through a minimum at this solvent composition, resulting in enhanced specific adsorption. Studies of the effect of solvent composition on specific adsorption of anions in this system would therefore provide an interesting tool for investigation of the contribution of the solvation energy to the adsorption energy if this interpretation is correct.

Conclusions

1. Electrocapillary and double-layer capacity measurements have been reported for the DMSO solvent system. The results show a strong resemblance to the corresponding aqueous solutions.
2. The interfacial tension at the Hg–DMSO interface in the absence of specific adsorption is 370.5 ± 0.2 dynes/cm at 25° compared with 425.4 dynes/cm for the Hg–water interface.
3. A large capacity hump occurs in KPF_6 solutions at $q \approx 8$ μcoulombs/cm². The positive shift in the ecm in DMSO solutions in consistent with Macdonald's theory that such humps are due to reorientation of positively (toward the metal) oriented solvent dipoles. Similar results for formamide and N-methylformamide, however, are not consistent with this theory. The minimum capacity on the cathodic side is ~7μf/cm².
4. As found in aqueous solutions, anions are specifically adsorbed in the order $I^- > Br^- > Cl^- > NO_3^- > ClO_4^- > PF_6^-$, and cations are not appreciably adsorbed.
5. Specific adsorption of anions from mixed DMSO–water solutions is enhanced by strong interaction between DMSO and water in the range 20–30 mole % DMSO.

[44] Precisely this situation occurs in the case of nitrate ion adsorption from KNO_3 solutions where dq^1/dq is very close to -1 when $q \gtrsim 2$ μcoulombs/cm².[19] Under these conditions the measured capacity is a close approximation to the inner layer capacity.

[45] J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2240 (1961); see also J. Kenttämaa and J. J. Lindberg, *Suomen Kemistilehti*, B33, 98 (1960).

An Infrared Study of Hydrogen Bonding between Adenine and Uracil Derivatives in Chloroform Solution

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Abstract: The association constants K for hydrogen-bonded dimer formation in chloroform solution by 9-ethyladenine and by 1-cyclohexyluracil, as well as for the formation of the 1:1 hydrogen-bonded complex of the two bases, have been measured by infrared spectroscopy over the temperature range 4–58°. At 25°, K_{AU} for the mixed dimer is 30 times larger than K_{AA} for the 9-ethyladenine dimer and 15 times larger than K_{UU} for the 1-cyclohexyluracil dimer. From the temperature dependence of association constants, $\Delta H°$ for association is found to be -4.3 ± 0.4 kcal/mole of dimer for cyclohexyluracil, -4.0 ± 0.8 kcal for ethyladenine, and -6.2 ± 0.6 kcal for the mixed dimer. The entropy differences $\Delta S°$ are -11.0 ± 1, -11.4 ± 2, and -11.8 ± 1.2 eu, respectively. The structures of the dimers in solution are discussed on the basis of their infrared spectra.

In the double-stranded structures of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), adenine specifically forms hydrogen bonds with thymine (or uracil) and guanine with cytosine. These specific bondings are believed to be the molecular basis of information transfer by nucleic acids. Much work has been done to find the basis of this specificity. Crystallographic studies have shown that specific hydrogen bonds are formed even between the constituent purines and pyrimidines.[1-4] Recently Hamlin, Lord, and Rich[5] have found by infrared spectroscopic methods that 1-cyclohexyluracil and 9-ethyl-

[1] K. Hoogsteen, *Acta Cryst.*, 12, 822 (1959); **16**, 907 (1963).

[2] F. S. Mathews and A. Rich, *J. Mol. Biol.*, **8**, 89 (1964).

[3] L. Katz, K. Tomita, and A. Rich, *ibid.*, 13, 340 (1965).

[4] A. E. V. Haschemeyer and H. M. Sobell, *Proc. Natl. Acad. Sci. U. S.*, **50**, 872 (1963).

[5] R. M. Hamlin, Jr., R. C. Lord, and A. Rich, *Science*, **148**, 1734 (1965).