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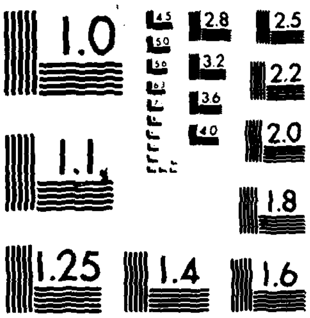

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Utility of Surface Reaction Entropies for Examining Reactant-Solvent Interactions at Electrochemical Interfaces. Ferricinium-Ferrocene Attached to Platinum Electrodes

by

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Reactant-solvent interactions are of prime importance to both the kinetics and thermodynamics of electrode processes. Since electrochemical reactions inevitably occur within the interfacial region, it is desirable to gain information on the nature of reactant solvation at the electrode surface as well as in bulk solution. We have demonstrated that useful information on the latter for simple redox couples can be obtained from the so-called reaction entropy, ΔS°_{rc}, determined from the temperature dependence of the formal potential, E^f, using a nonisothermal cell arrangement:

$$\Delta S^\circ_{rc} = F(dE^f/dT)_{ni} \qquad (1)$$

Since the temperature dependence of the thermal liquid junction potential in such a cell can be arranged to be negligibly small, ΔS°_{rc} essentially equals the difference, $(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})$, between the ionic entropies of the reduced and oxidized forms of the redox couple in the bulk solution. The reaction entropies of simple transition-metal redox couples have been found to be extremely sensitive to the chemical nature of the coordinated ligands and the surrounding solvent, illustrating the importance of specific ligand-solvent interactions to the overall redox thermodynamics.[1-5]

It would clearly be desirable additionally to determine reaction entropies for redox couples residing in the interfacial region. Such "surface reaction entropies", $\Delta S^\circ_{rc,s}$, would yield insight into the solvation changes accompanying the elementary electron-transfer step for the redox couple in a particular interfacial environment. For redox couples present at sufficiently high concentrations at the interface to enable the formal potential for the interfacial (adsorbed) redox couple, E^f_a, to be measured, values of $\Delta S^\circ_{rc,s}$ can be obtained directly from [cf Eq (1)]:

$$\Delta S^\circ_{rc,s} = F(dE^f_a/dT)_{ni} \qquad (2)$$

Whereas ΔS°_{rc} corresponds to the overall entropy driving force for transforming the <u>bulk-solution</u> reactant to product, $\Delta S^\circ_{rc,s}$ equals the thermodynamic entropy change for the heterogeneous electron-transfer step itself.[6] Thus $\Delta S^\circ_{rc,s}$ and ΔS°_{rc} are related by

$$\Delta S^\circ_{rc,s} = \Delta S^\circ_{rc} + \Delta S^\circ_p - \Delta S^\circ_s \qquad (3)$$

where ΔS°_p and ΔS°_s are the entropic work terms associated with forming the "precursor" state for electron transfer from the bulk reactant, and the "successor" state from the bulk product, respectively.[6] We report here values of $\Delta S^\circ_{rc,s}$ for a surface-attached ferricinium-ferrocene couple in several solvents in order to illustrate the virtues of such measurements for elucidating the nature of reactant-solvent interactions at electrochemical interfaces.

For surface redox couples where the redox center lies within the inner layer, ΔS_p° and ΔS_s° are expected to be both nonzero and different, so that $\Delta S_{rc,s}^\circ \neq \Delta S_{rc}^\circ$. Indeed we have recently obtained such a result for a specifically adsorbed Co(III)/(II) sepulchrate couple versus the corresponding bulk solution couple.[7] For electrode reactions where the redox center is present in the diffuse layer or at the outer Helmholtz plane, it is conventional to assume that the work terms are purely coulombic in nature[8] so that $\Delta S_p^\circ \approx \Delta S_s^\circ \approx 0$ and hence $\Delta S_{rc,s}^\circ \approx \Delta S_{rc}^\circ$. This assumption is required in order to extract true frequency factors for electron transfer from the temperature dependence of electrochemical kinetics.[6,9] However, in actuality even $\Delta S_{rc,s}^\circ$ for an outer-sphere reaction might be expected to differ significantly from ΔS_{rc}° in a given solvent medium, bearing in mind the structure sensitivity of ionic entropies[1-5] and the possibility that the solvating environment in the vicinity of the surface may differ significantly from that in the bulk solution. Indeed, one reason for pursuing the present study was to discover whether differences which we have recently observed between the energetics of structurally similar electrochemical reactions involving surface-bound and solution-phase redox couples[10] could be rationalized in terms of differences between the bulk and interfacial solvation environments.

Measurement of Surface Reaction Entropies

Although it is not feasible to evaluate $\Delta S_{rc,s}^\circ$ for outer-sphere (i.e. unadsorbed) redox couples, a suitably high interfacial concentration of normally unadsorbed, and presumably fully solvated, reactant can be achieved by attaching the redox center to the electrode surface via an inert covalent linkage. As a model system, we studied the ferricinium-ferrocene redox couple attached to a platinum electrode as shown in Fig. 1. We prepared the surface-bound ferrocene by using the chemical modification procedure described in ref. 11. This system was selected since both the bond to the platinum surface and the electroactive center itself are exceptionally stable, placing the redox center about 6-8 Å from the electrode surface.[11] In addition it was anticipated that the surface-attached couple would exhibit reversible behavior in a variety of solvents.

Efforts to prepare the same ferrocene derivative in solution were unsuccessful. Nevertheless, n-ferrocenemethylene-p-toluidine (Alfred Bader Chemicals), shown in Fig. 2, was selected as a reasonably close analog of the surface-attached complex since in the vicinity of the redox center the structures of the two substituents are closely similar. Formal potentials for either the surface-attached or bulk-solution redox couples were obtained from the average peak potentials of the cyclic voltammograms (Quasi-reversible, rather than reversible, behavior was typically observed for the surface-attached, as well as bulk-solution, couples, with anodic-cathodic peak separations up to ca 50 mV even in the presence of iR compensation; cf. ref. 11). Values of E_a^f for the reduction of the surface-bound ferricinium derivative could be measured with sufficient accuracy to enable $\Delta S^\circ_{rc,s}$ to be determined to within about 6 J. deg^{-1}. mol^{-1}. Representative E_a^f data obtained in aqueous solution are plotted against temperature in Fig. 3. Data also were obtained in methanol, acetonitrile, dimethylsulfoxide and sulfolane. Attempts were made to measure $\Delta S^\circ_{rc,s}$ in formamide, nitromethane and acetone, but were unsuccessful with the first solvent due to instability of the surface complex and with the other two because of irreproducible behavior. Either 0.1 M tetraethylammonium perchlorate or 0.2 M $LiClO_4$ was used as the supporting electrolyte. Additional experimental details are given in ref. 3.

The resulting values of $\Delta S^{\circ}_{rc,s}$ and E^{f}_{a} are summarized in Table 1, together with ΔS°_{rc} data for the ferrocene and n-ferrocenemethylene-p-toluidine couples in bulk solution. Contrary to our initial expectations, the reaction entropies for the surface couple and its solution analog were found to be in reasonable agreement in each solvent. Evidently the solvent interactions experienced by the surface-attached couple are not noticeably different from the reactant-solvent interactions occurring in bulk solution. At least for this couple, therefore, it appears that differences between solvent structure in bulk solution and in the double layer where the surface redox site is located do not greatly influence the electron-transfer energetics.

Interpretation of Surface Reaction Entropy Values

Although the two derivatized ferrocene couples (Figs. 1 and 2) yield similar reaction entropies, these tend to be less positive than the ΔS°_{rc} values for the unsubstituted ferricinium-ferrocene couple (Table 1). Furthermore, the formal potentials for the surface-attached couple in various solvents are positive of those for ferrocene itself, while the E^{f} values for the n-ferrocenemethylene-p-toluidine couple are still more positive (Table 1; note that the E^{f} values quoted are versus that for ferrocene itself in the same solvent). The differences in formal potentials between ferrocene and its derivatives are probably manifestations of the greater electron-withdrawing capabilities of carbon-nitrogen double bonds compared to hydrogen.[12] Thus such an electron-withdrawing substituent would tend to stabilize the relatively electron rich ferrocene redox center to a greater extent than for ferricinium, leaving the former more difficult to oxidize and thereby yielding a positive shift in the formal potential. The systematic differences in reaction entropies seen between ferrocene and the derivatized couples can also be rationalized on this basis. Whether the differences in formal potentials between the adsorbed couple and its solution analog result from surface attachment or from differences in substituent properties is not entirely clear. A detailed study of substituent effects on the redox thermodynamics and kinetics of several solution ferrocene derivatives is in progress in this laboratory.

A curious aspect of the results is the marked solvent dependence of both the $\Delta S^{\circ}_{rc,s}$ and ΔS°_{rc} values. The magnitude of these quantities expected from purely continuum electrostatic considerations is given by eqn (4):[3]

$$\Delta S^{\circ}_{rc,s}(=\Delta S^{\circ}_{rc}) = -(e^{2}N/2r\varepsilon T)(d\ln\varepsilon/d\ln T) \qquad (4)$$

where e is the electronic charge, N is Avogadro's number, ε is the dielectric constant of the solvent, and r is the radius of the ferricinium cation. The $\Delta S^{\circ}_{rc,s}$ values listed in the last column of Table 1 are obtained from Eq (4) using literature values of ε and assuming that $r = 3.8$Å.[13]. There is clearly no general pattern of agreement between the experimental and these calculated quantities, the Born treatment predicting a much milder solvent dependence of $\Delta S^{\circ}_{rc,s}$ than is observed. Similar breakdowns of the dielectric continuum model in predicting reaction entropies have been found for several bulk solution couples in a number of solvents.[1-5]

A probable reason for the failure of eqn. (4) is that the major property determining the entropy of charge-induced solvent reorientation is the degree of "internal order" of the solvent (i.e., self-association and long range structuring induced by hydrogen bonding), rather than the macroscopic dielectric properties.[14,15] Thus, a solvent having a high degree of internal order would be relatively unperturbed by a charged molecule, whereas considerable solvent ordering around the ion would occur in a medium having little intermolecular structure. Since such charge-dipole interactions will be absent for neutral ferrocene, a positive contribution to the reaction entropy $(\bar{S}^\circ_{red} - \bar{S}^\circ_{ox})$ would be anticipated for the present redox couples, especially in relatively nonassociated solvents. Criss and co-workers[14,15] have suggested estimating the degree of internal order of a solvent from the difference in boiling point, ΔT_{bp}, compared to that for a structurally analogous hydrocarbon. These values of ΔT_{bp} are also listed in Table I. Indeed, the $\Delta S^\circ_{rc,s}$ values for the surface-attached ferrocene couple do for the most part vary as expected with the corresponding values of ΔT_{bp}.

An unusual result which merits comment is the large negative value of $\Delta S^\circ_{rc,s}$ (-50 J deg^{-1} mol^{-1}) found in water (Table 1). A small negative value of ΔS°_{rc} has previously been observed for the bulk-solution ferrocene couple, also in water.[3] This indicates that the net solvent ordering in the vicinity of the surface-attached redox center is <u>less</u> extensive in the cationic than in the neutral state, in qualitative disagreement with the expectations from an electrostatic treatment. These negative reaction entropy values probably result from donor-acceptor interactions between the cyclopentadienyl rings and the acidic water hydrogens.[3] Since the electron density on the cyclopentadienyl rings will be greater in the reduced state, such specific solvent interactions should be enhanced leading to increased solvent ordering and a decrease in entropy compared with that for the oxidized state. If such an explanation were correct a correlation between $\Delta S^{\circ}_{rc,s}$ and the acidity of the solvent might be expected. Figure 4 shows a plot of the reaction entropies for the adsorbed couple and its solution analog as well as for unsubstituted ferrocene versus the solvent "acceptor number" which is an empirical measure of the electron-accepting capabilities of the solvent.[16] A reasonable correlation is indeed observed. Evidently, then, both non-Bornian ion-dipole interactions and specific donor-acceptor interactions are important in determining the redox properties of the surface-attached as well as solution ferrocene couples.

The present work demonstrates the feasibility of determining surface reaction entropies and illustrates the utility of these measurements for elucidating the various elements of interfacial reactant-solvent interactions. Given the sensitivity of $\Delta S^{\circ}_{rc,s}$ measurements to the solvent structure we suggest that this approach might also usefully be employed to gain insight into reactant solvation in polymer film electrodes for which the question of solvent penetration within the film is of current interest.

Acknowledgements

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Figure Captions

Figure 1. Mode of attachment of ferrocene to platinum surface.

Figure 2. Ferrocene derivative (n-ferrocenemethylene-p-toluidene) used as solution analog of surface-attached ferrocene in Fig. 1.

Figure 3. Representative plot of formal potential for surface-attached ferricinium-ferrocene couple, E_a^f, versus temperature in aqueous 0.1 M TEAP. Potentials versus saturated calomel electrode at 24°C, using nonisothermal cell arrangement.[1]

Figure 4. Plot of reaction entropies for surface-attached and solution-phase ferricinium-ferrocene couples in various solvents versus solvent Acceptor Number, taken from ref. 16. Filled triangles: surface-attached ferrocene (Fig 1); *open triangles: bulk-solution derivatized ferrocene* (Fig 2); open circles: bulk-solution ferrocene. Key to solvents: 1, acetone; 2, dimethylformamide; 3, propylene carbonate; 4, acetonitrile; 5, dimethylsulfoxide; 6, nitromethane; 7, N-methylformamide; 8, formamide; 9, methanol; 10, water.

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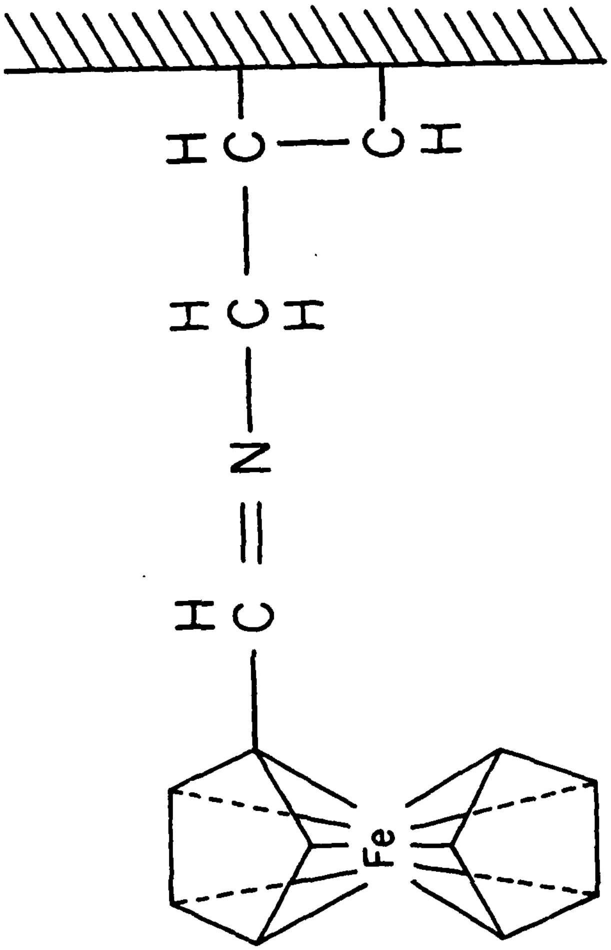

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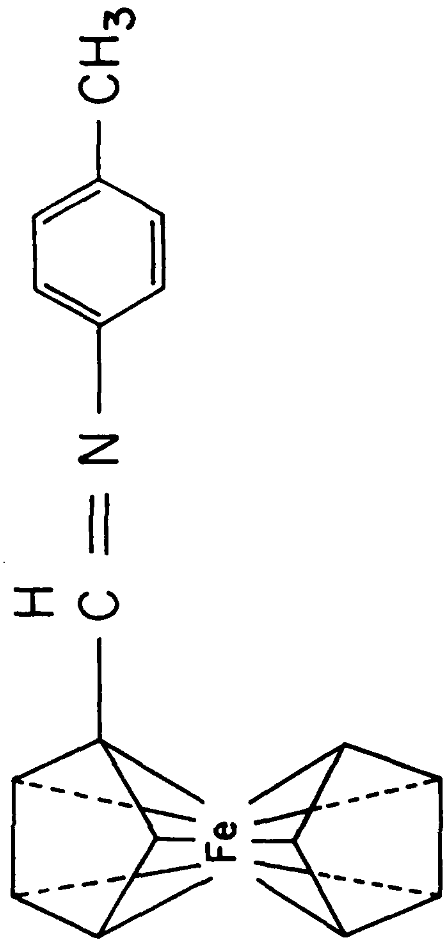

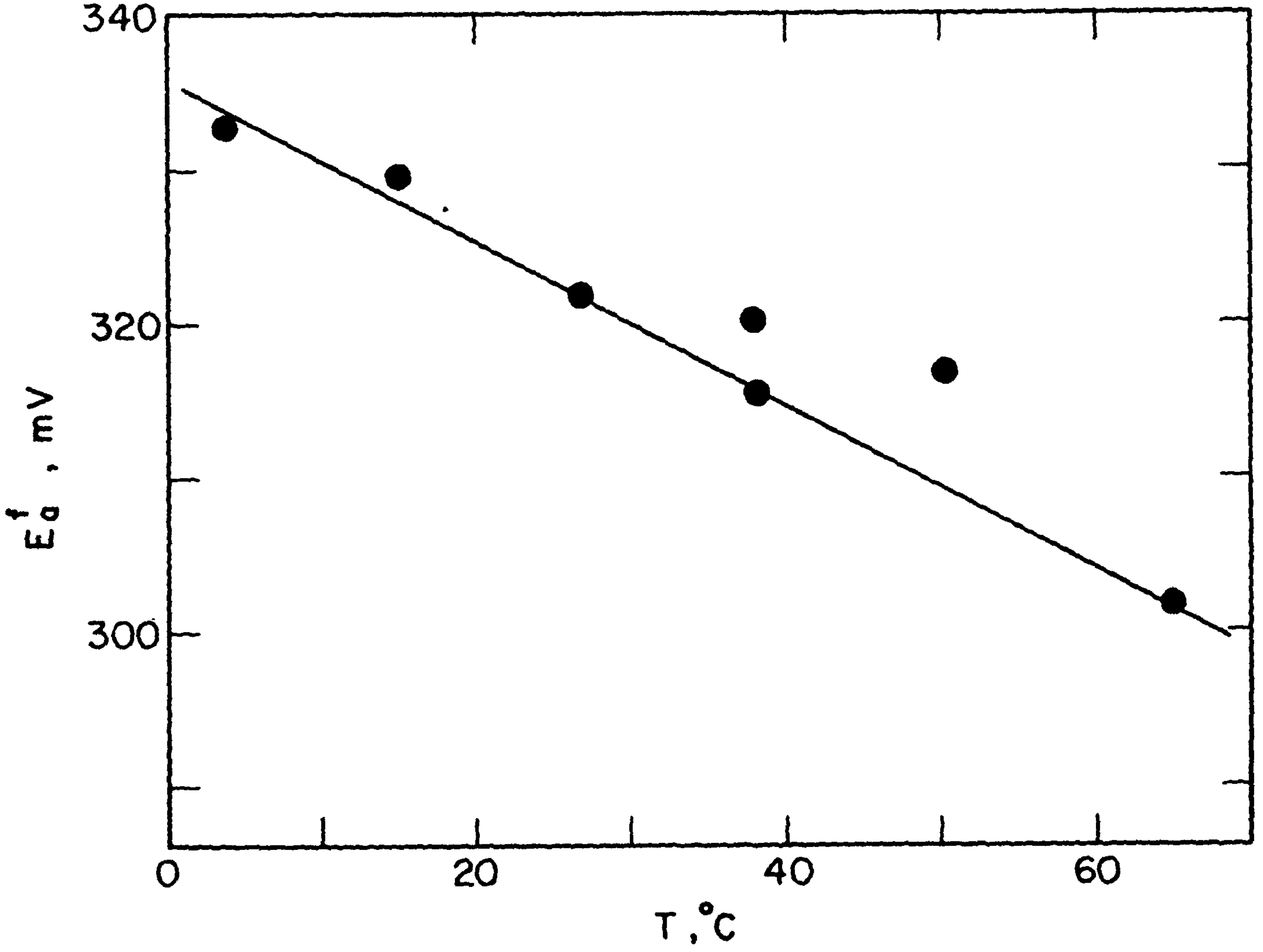

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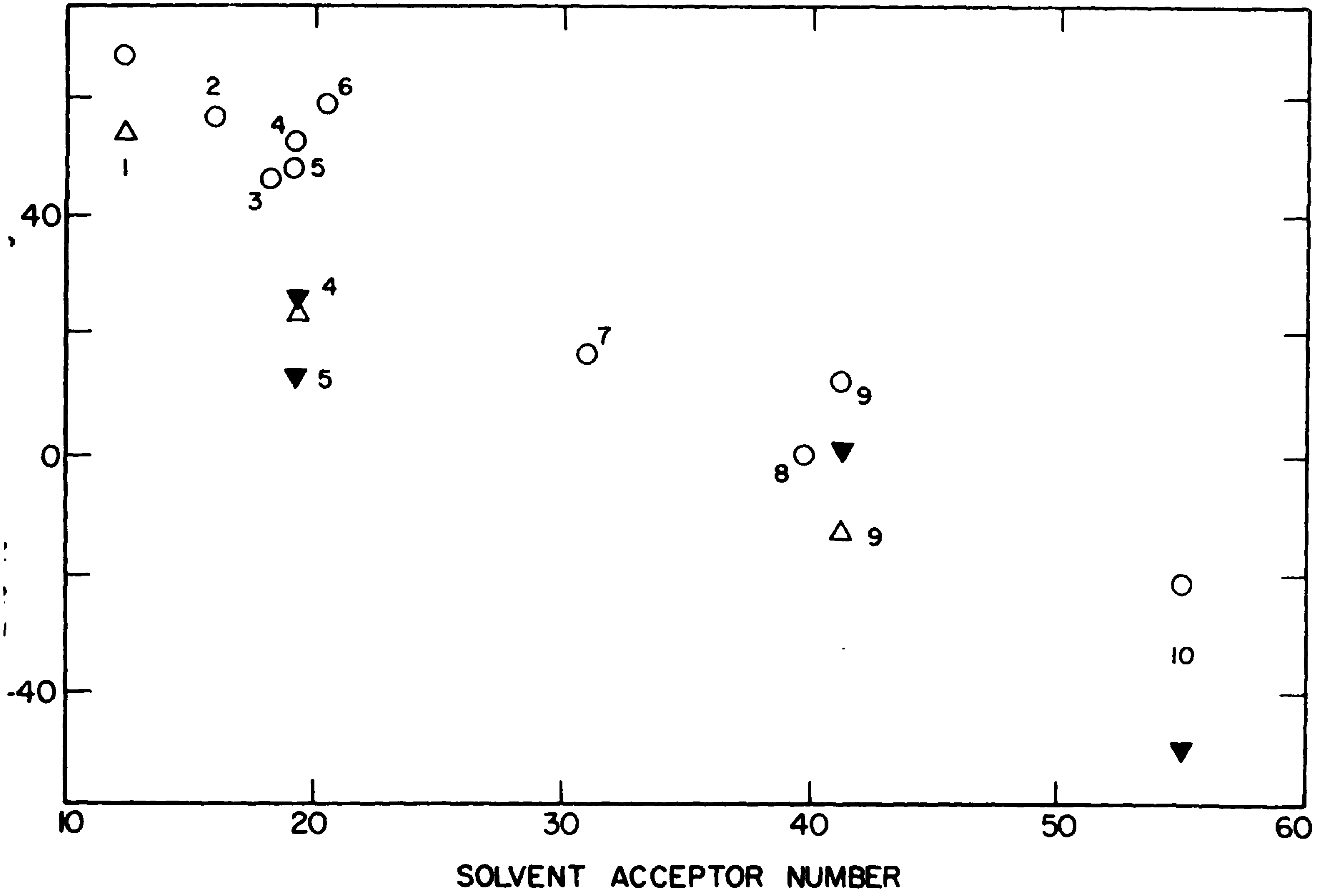
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