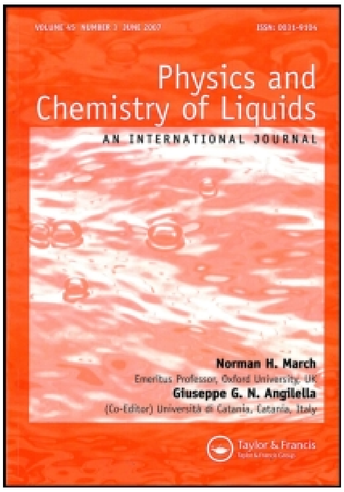

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Anion Formation in Molecular Liquids: Is it Correlated With Molecular Shape?

N. H. March[a]; G. R. Freeman[b]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] Chemistry Department, University of Alberta, Edmonton, Canada

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Anion Formation in Molecular Liquids: is it Correlated With Molecular Shape?

N. H. MARCH

Theoretical Chemistry Department, University of Oxford,
1 South Parks Rd., Oxford OX1 3TG, England.

and

G. R. FREEMAN

Chemistry Department, University of Alberta, Edmonton, T6G 2G2, Canada.

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Some facts are first presented for anion formation in three types of molecular liquids, classified according to molecular shape into (a) sphere-like, (b) flat, 2-dimensional-like, and (c) rod-like. These are then confronted with recent theoretical predictions about bound states in self-consistent potentials for neutral systems. It is concluded that the gross correlations predicted are in accord with the data: one- and two-dimensional molecules almost always lead to bound states (anions), while for sphere-like molecules the attractive potential must exceed a certain strength for bound states to form. It is recognized that for other than gross correlations, the nature of the bonding will have to be treated in detail. However, in cases (a) and (b) it is suggested that electron affinity should correlate grossly with the total number of valence electrons in the molecule. Finally, the reason why the electron affinity appears higher in the liquid than in gaseous state is attributed partly to hindered rotation, in addition to polarization effects.

1 INTRODUCTION

One of us[1] has recently studied bound state formation in a three-dimensional neutral cluster of like charges, in which a self-consistent Thomas–Fermi potential is established. The conclusion was that bound states exist when the attractive potential exceeds a certain minimum. Subsequently, work of Coutinho *et al.*[2] on two-dimensional potentials, and their bound-state properties, has enabled the study in Ref. 1 to be extended to a class of two-dimensional potentials, which includes the case of self-consistent Thomas–

Fermi potentials in a neutral system.[3] The result for two dimensions for the class of potentials discussed in Ref. 3 is that one bound state exists for all such potentials considered there, for arbitrarily weak attraction. Though the case of one-dimensional potentials was not considered in Refs. 1 and 3, the work of Coutinho *et al.*[2] when used with the methods in Refs. 1 and 3, leaves no doubt that one- and two-dimensional potentials of Thomas–Fermi self-consistent form have at least one bound state for arbitrarily weak attractive interaction. This is to be contrasted with three-dimensions, where a critical attractive strength is required before bound states occur.

These considerations have prompted us to enquire whether such a gross distinction between low dimensional potentials (one and two) and genuinely three-dimensional systems can be detected from a study of electron transport in molecular liquids. In the next section we have therefore collected together a variety of data, without attempting completeness, bearing on anion formation in the liquid state.

2 POSSIBLE ANION FORMATION IN LIQUIDS WITH DIFFERENT MOLECULAR GEOMETRIES

The division that seemed natural was to consider in turn data for:

a) almost spherical molecules
b) flat molecules
c) rod-like molecules

corresponding to 3-, 2- and 1-dimensional potentials, respectively.

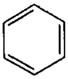
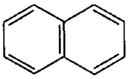
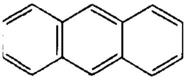
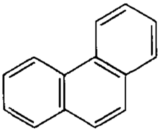
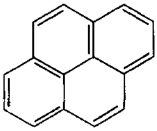
In the Table we have collected data[4–10] for a variety of molecules in classes (a), (b) and (c). Where possible we have recorded estimates of gas phase electron affinities.[8–10] In general, the solvation energy of an anion is greater than that of an extra electron in the same solvent. The charge on an anion is less dispersed than that of a solvated electron, so the charge-solvent interaction is greater for an anion than for a solvated electron. Liquid phase electron affinities are therefore greater than the gas phase values (see, for example, Table I in Ref. 11).

There is an ongoing discussion about whether the solvated electron structure includes a solvent molecular anion, or is simply an electron localized in an interstitial–network potential well.[12] For the present discussion we use the model that includes a solvent anion. Stable anions are formed in the liquids of the larger flat molecules and the rod-like molecules; an electron conductance signal was not separable from the cation signal in these liquids.[5,7]

Anion formation is negligible in class (a) liquids, but it occurs readily in liquids of classes (b) and (c) (Table I). Mobilities of the cations in the liquids

TABLE I

Correlation of anion formation with molecular shape

Molecules	Gas phase EA(eV)[a]	Liquid phase $\mu_e(10^{-4}\ \mathrm{m^2/Vs})$[b]	Comment re liquid phase
(*a*) *Sphere-like*			
methane	neg.	400[4]	negligible anion
neopentane	neg.	68[4]	negligible anion
Chain			
ethane	neg.	0.56[4]	solvated electron or highly transient anion
n-pentane	neg.	0.19[4]	
(*b*) *Flat*			
ethene	−1.6[9]	0.003[4]	transient anion
cyclopropane	neg.	0.006[4]	transient anion
 benzene	−1.5[10]	1.1[5,6]	highly transient anion
 napthalene	−0.3[10] to +0.2[8]	—	anion[5]
 anthracene	+0.5[10] to 0.6[8]	—	anion[5]
 phenanthrene	+0.1[10] to 0.3[8]	—	anion
 pyrene	+0.5[10] to 0.6[8]	—	anion
(*c*) *Rod-like*			
acetylene	—	—	anion[7]
propyne	—	—	anion[7]
butyne-2	—	—	anion[7]

[a] Electron affinity. Neg. = negative.

[b] Electron mobility at the normal boiling point of the liquid, refs. indicated. The corresponding mobilities of the cations in methane to benzene are all $1 - 2 \times 10^{-7}\ \mathrm{m^2/Vs}$, Refs. 12–14.

methane to benzene in Table I, at their normal boiling points, are all 1–2 $\times 10^{-7}$ m^2/Vs.[13–15] Anion mobilities are often about double the cation values, so they should be roughly 2–4 $\times 10^{-7}$ m^2/Vs. Delocalized electrons in these systems have mobilities $\sim 10^{-2}$ m^2/Vs.[4] Mobilities in the range $10^{-6} \lesssim \mu_e \lesssim 10^{-3}$ m^2/Vs therefore involve the participation of transient localized states. In this discussion we take the localized state to be an anion.

A full interpretation would require a quantitative description of the participation of the π-bonding, but that is not our purpose here. Rather, we stress that the evidence supports the relative ease with which anion formation occurs in this series, which has been stressed in the studies of Pucci and March[16] to have properties strongly related to the two-dimensional character. This is the first theoretical interpretation of the well known molecular shape effect on electron transport in fluids.[4]

There are fewer data for class (c) than (b), but the entries in the Table support the ease with which anion formation occurs for rod-like molecules in the liquid phase.

With regard to electron transport in these fluids, long-range interactions dominate in the gases, whereas short-range interactions are dominant in the liquid phase.[4] Our present considerations are about the short-range interactions, though we recognize that molecular polarizability is a factor that will have to be accounted for in any quantitative treatment.

3 DISCUSSION AND SUMMARY

In addition to the point just made, we expect anion formation to be more readily observable in molecular liquids in which there is hindered rotation, than in the gaseous phase. Rotation is progressively more hindered in flat and rod-like molecules, respectively.

We feel that there is evidence supporting a gross division of anion formation between low dimensional molecules in classes (b) and (c) on the one hand, and almost spherical molecules in class (a) on the other.

In conclusion, we hope that the present note will stimulate more experiments on anion formation in all three classes, to see if such a clear distinction as set out in Refs. 1 and 3 for model potentials emerges. It might be asked whether Refs. 1 and 3, though making only gross distinctions between 2- and 3-dimensions, nevertheless point to any factors relating to the magnitude of electron affinities. The answer is that while the rather mathematical arguments there focus on the question whether or not bound states form, in the criteria used the number of electrons N consistently enters. This is for 2- and 3-dimensions; such a simple N dependence of the criteria for bound states is not found in 1-dimension. In the present context, N should be interpreted as the number of valence electrons. It is perhaps worth remarking from Table I that: the electron affinity increases with N on going from benzene to naphthalene to anthracene; EA is greater for the more linear anthracene than for the nonlinear phenanthrene with the same N; to obtain the same EA a larger N is required for a disk-like structure (pyrene) than for the more linear anthracene.

It might turn out that for anion formation in a series like the linear polyacenes, the electron affinities correlate with the number of conjugated π-bonds (particle in a box). That is a further theoretical question, beyond the scope of techniques in Refs. 1–3, to tell what is the law. However, for ionization potentials, which often correlate inversely with electron affinities in a series, the law for linear polyacenes has been exposed by Pucci and March.[16]

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