A condition on the derivative of the potential in the primitive model of an electric double layer

Lesser Blum, Joel L. Lebowitz, and Douglas Henderson

Articles you may be interested in

Revisiting density functionals for the primitive model of electric double layers
J. Chem. Phys. **140**, 044714 (2014); 10.1063/1.4862990

Density-functional theory of spherical electric double layers and ζ potentials of colloidal particles in restricted-primitive-model electrolyte solutions
J. Chem. Phys. **120**, 7223 (2004); 10.1063/1.1676121

Interactions between primitive electrical double layers
J. Chem. Phys. **97**, 9258 (1992); 10.1063/1.463301

The primitive model of the electric double layer: Nonsymmetric electrolytes
J. Chem. Phys. **90**, 5738 (1989); 10.1063/1.456381

Pair correlation functions and density profiles in the primitive model of the electric double layer
J. Chem. Phys. **88**, 2712 (1988); 10.1063/1.454001

---

163 (1974).

[3]K. S. Kim and N. Winograd, Chem. Phys. Lett. **30**, 91 (1975).

[4]V. Y. Young, R. A. Gibbs, N. Winograd, and K. S. Kim, Chem. Phys. Lett. **41**, 188 (1978).

[5]V. Y. Young, R. A. Gibbs, and N. Winograd, J. Chem. Phys. **70**, 5714 (1979).

[6]P. Aascarelli, M. Cini, G. Missoni, and N. Nistico. J. Phys. **38**, C2–125 (1977).

[7]L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B **8**, 2392 (1973).

[8]R. E. Watson, J. F. Herbst, and J. W. Wilkins, Phys. Rev. B **14**, 18 (1976).

[9]F. P. Larkins, J. Phys. C **10**, 2461 (1977).

[10]C. E. Moore, "Atomic Energy Levels," Natl. Bur. Stand. Circ. 467, Vol. II and Vol. III (1952, 1958).

[11]N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1978).

[12]A. R. Williams and N. D. Lang, Phys. Rev. Lett. **40**, 954 (1978).

[13]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), p. 154.

NOTES

A condition on the derivative of the potential in the primitive model of an electric double layer

Lesser Blum[a)]

Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

Joel L. Lebowitz[b)]

Department of Mathematics, Rutgers University, New Brunswick, New Jersey 08913

Douglas Henderson

IBM Research Laboratory, San Jose, California 95193

Recently,[1] it has been demonstrated that integral equations, which are useful in the theory of bulk fluids, can be used to describe fluids near a wall. This has led to an interest in the application of these integral equations to the electric double layer.

One unexpected and interesting result of such studies of the double layer is the fact that, in the mean spherical approximation (MSA) at high concentrations[2] and in the hypernetted chain approximation (HNCA) at high electrode charge density,[3,4] the diffuse part of the potential difference across the double layer, ϕ, can decrease as the charge density on the electrode is increased.

This decrease of ϕ with increasing charge density is related to the physically plausible oscillations in the change profiles predicted by these approximations. The purpose of this note is to show rigorously that the total potential difference, V, is a monotonically increasing function of the charge density. Although we do not show that ϕ can decrease as the charge density on the electrode is increased, as long as V is a monotonically increasing function of the charge density, a decrease in ϕ is not prohibited by our result.

Consider an electric double layer consisting of the charged hard ions in a medium of uniform dielectric constant, ϵ, and in the presence of a hard charged wall. In order to keep the overall system electrically neutral, a hard wall with an opposite charge is placed at infinity.

If A_E is the surface free energy per unit area when the wall has a surface charge density of $\epsilon E/4\pi$, then

$$\beta A_E = -\ln \int \exp\{-\beta(H_0 + U_E)\} \, d\Omega \, , \tag{1}$$

where H_0 is the Hamiltonian when the wall is uncharged,

$$U_E = -E \sum_i z_i x_i \, , \tag{2}$$

z_i and x_i are the charge and distance from the wall of the the center the ith hard sphere.

Differentiating

$$\left(\frac{\partial A_E}{\partial E}\right)_T = \langle \psi \rangle = -\sum_{\alpha=1}^{m} z_\alpha \rho_\alpha \int x \, h_\alpha(x) dx \tag{3}$$

and

$$\left(\frac{\partial^2 A_E}{\partial E^2}\right)_T = -\beta[\langle \psi^2 \rangle - \langle \psi \rangle^2] \leq 0 \, , \tag{4}$$

where $\psi = U_E/E$. Apart from a multiplicative coefficient, the sum in (3) is the total potential drop across the double layer. Thus,

$$\left(\frac{\partial V}{\partial E}\right)_T \geq 0 \, . \tag{5}$$

Equation (5) is a rigorous bound as long as all the field dependent interactions are given by (2).

Since there is no screening of the field between the wall and the distance of the closest approach, V is related to ϕ by

$$V = E\,\sigma/2 + \phi \ . \tag{6}$$

Hence,

$$\left(\frac{\partial \phi}{\partial E}\right)_T \geq -\sigma/2 \ . \tag{7}$$

The MSA always satisfied Eq. (7). However, at low concentrations and high fields, the HNCA fails to satisfy Eq. (7). The MSA and HNC are improvements over the Poisson–Boltzmann (PB) theory of Debye and Hückel for bulk ionic fluids and, except for the extreme conditions where Eq. (7) is not satisfied by the HNCA, are expected to be improvements over the PB theory of Gouy and Chapman.

[1] D. Henderson, F. F. Abraham, and J. A. Barker, Mol. Phys. 31, 1291 (1976).
[2] L. Blum, J. Phys. Chem. 81, 136 (1977).
[3] D. Henderson, L. Blum and W. R. Smith, Chem. Phys. Lett. 63, 381 (1979).
[4] S. L. Carnie, D. Y. C. Chan, D. J. Mitchell, and B. W. Ninham, J. Chem. Phys. (in press).

The barrier to planarity in aminopyrazine

R. A. Kydd and A. R. C. Dunham

Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada T2N 1N4
(Received 10 July 1979; accepted 6 December 1979)

The far-infrared vapor-phase spectra of aromatic amines can provide useful information about the structure of the amino group in the isolated molecule, unperturbed by intermolecular interactions. Such spectra are dominated by transitions involving the double minimum inversion (umbrella) vibration of the amino group. From the observed transitions the inversion barrier opposing planarity, which is difficult to obtain in any other way, readily can be determined. Because of partial conjugation between the amino nitrogen and the aromatic ring, this barrier is very sensitive to changes in the electronic structure of the molecule; in particular, for certain of these molecules a correlation has been found with the calculated electron density on the nitrogen atom.[1,2]

In this note is reported the assignment of the far-infrared vapor phase spectrum (50–650 cm^{-1}) of aminopyrazine, which has two nitrogen atoms *para* to each other in the ring and one amino group attached to a ring carbon. The spectrum was obtained at a resolution of 1 cm^{-1} at 42 °C on a Digilab FTS-16 interferometer equipped with a Wilks variable path gas cell set at 20.25 m. The identification of lines due to transitions in the inversion vibration is straightforward (*cf.* earlier assignments[1–3]) and appears in Fig. 1.

A quadratic/quartic potential function of the form $V = V_2 x^2 + V_4 x^4$ has been successful in calculating the inversion barriers for similar molecules[1,2] and will be used here. A computer program, described elsewhere,[4] which gives a least-squares fit to the observed energy levels by refinement of the parameters V_2 and V_4 was used. To estimate the positions of the minima in the potential function, and hence get an approximate out of plane angle for the amino group, the results are reported in terms of the dimensioned coordinate x. It is therefore necessary to have a value for the reduced mass, m, for the vibration. Because of the uncertainties inherent in calculating m from some assumed form for the motion it was decided simply to use the same reduced mass (i. e., $m = 4.0\ u$) which for aniline caused the minima in the potential function to occur at ± 0.3 Å, the observed out of plane distance of the amino hydrogens.[5] A value of $m = 4.0\ u$ has also been found to work well for 2-aminopyrimidine.[1] In any event, the barrier height equals $V_2^2/4V_4$ and is independent of the reduced mass.

The best-fitting parameters, $V_2 = -657.4 \times 10^{-3}$ cm^{-1} pm^{-2} and $V_4 = 0.529 \times 10^{-3}$ cm^{-1} pm^{-4}, give a barrier of 204 ± 25 cm^{-1}. The calculated energy levels, 101.7,
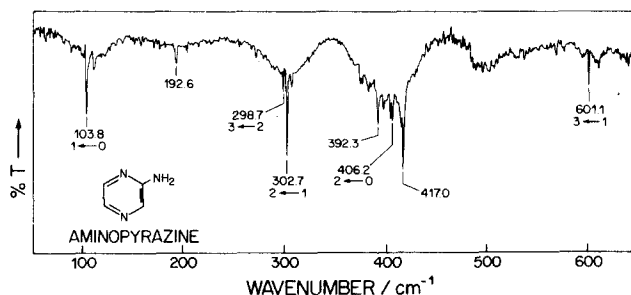

FIG. 1. Vapor phase spectrum of aminopyrazine from 50 to 650 cm^{-1}. Path length 20.25 m, temperature at 42 °C.

0021-9606/80/074250-02$01.00