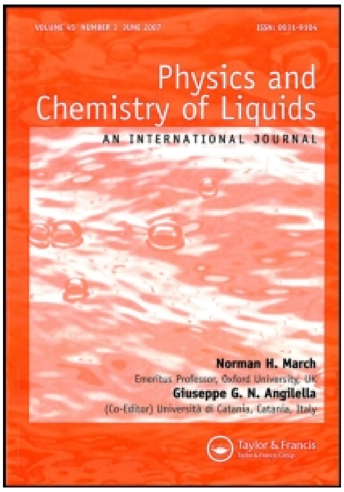

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Indicators of strong solute adsorption at container walls

M. J. Stott[a]; E. H. Voice[b]; E. H. Voice[c]
[a] Physics Department, Queen's University. Kingston, Ontario, Canada [b] Dounreay Nuclear Power Development, Establishment UKAEA (Northern Division) Thurso. Caithness, U. K. [c] School of Mathematics and Physics, University of East Anglia, Norwich, U.K.

To cite this Article Stott, M. J. , Voice, E. H. and Voice, E. H.(1982) 'Indicators of strong solute adsorption at container walls', Physics and Chemistry of Liquids, 12: 2, 135 — 140
To link to this Article: DOI: 10.1080/00319108208084547
URL: http://dx.doi.org/10.1080/00319108208084547

Phys. Chem. Liq., 1982, Vol. 12, pp. 135–140
0031-9104/82/1202-0135$06.50/0

Indicators of Strong Solute Adsorption at Container Walls

M. J. STOTT
Physics Department, Queen's University, Kingston, Ontario, Canada.

and

E. H. VOICE
Dounreay Nuclear Power Development Establishment, UKAEA (Northern Division), Thurso, Caithness, U.K.

and

W. H. YOUNG
School of Mathematics and Physics, University of East Anglia, Norwich, U.K.

(Received July 1, 1982)

Arguments are advanced to suggest the usefulness of linear response theory for indicating the occurrence of strong physisorption at container walls. On this basis, it is concluded that strong solute adsorption occurs in dilute binary systems if either (i) the fluid is nearly critical or (ii) the solute atoms are larger and more attracted to the walls than solvent atoms. The origin of the large effect observed for Cs atoms in liquid Na is tentatively explained through this size effect and a repulsion of the Na from chemisorbed surface layers.

1 INTRODUCTION

This paper is prompted by the observation[1] that there is strong adsorption at container walls of Cs impurity in liquid Na. Our intention below is to reveal at least some of the features generally responsible for behaviour of this kind and thereby to suggest the factors at work in the NaCs system in particular.

We begin by distinguishing between chemisorption and physisorption. This paper deals only with the latter, i.e. we are concerned only with those atoms which retain their fluidity even when they are near the surface. In reality, there may also, of course, be chemisorption but that is outside the scope of this work. In the following, therefore, whenever we refer to a wall (against which physisorption takes place), we mean the bare container plus any material chemisorbed thereon.

2 ONE COMPONENT FLUID

To begin with, think of a one component fluid of bulk density n in contact with a plane wall and suppose that the local density is increased by $\sim \Delta n$ over a distance $\sim l$ from the wall. Then the surface free energy per unit area may plausibly be written

$$\sigma = \frac{l}{2\kappa_T}\left(\frac{\Delta n}{n}\right)^2 - \zeta \Delta n \tag{1}$$

Here ζ measures the strength of the attraction between the fluid and the wall, which the first term arises from the elastic energy stored in the dilation, κ_T being the bulk fluid compressibility. Equation (1) can be minimized with respect to Δn and the adsorption $\Gamma = l\Delta n$ found to be

$$\Gamma = \zeta n^2 \kappa_T \tag{2}$$

For later interpretation, it is instructive to rewrite this result as

$$\Gamma = \frac{\lambda\theta}{k_B T} \tag{3}$$

where $\theta = nk_BT\kappa_T$ and $\lambda = \zeta n$. We may now formally put $\zeta = r\varepsilon$ where ε is the interaction energy between an atom and the wall and r is the distance over which the potential producing it is, in effect, operative. Then if $d = n^{-1/3}$, we have $\lambda = (r/d)\varepsilon/d^2$ which is an effective interaction energy per unit area of fluid contact with the wall.

Equation (2) (or (3)) is the result suggested by linear response theory. However, the *form* of Eq. (2) should have more generality than this would suggest. For suppose, instead of the behaviour postulated in the previous paragraph, the excess fluid density varies fairly uniformly from Δn to zero over an effective distance L out from the wall. Then, in the Cahn-Hilliard theory,[3,4] Eq. (1) is replaced by

$$\sigma = \frac{L}{C\kappa_T}\left(\frac{\Delta n}{n}\right)^2 + B\left(\frac{\Delta n}{L}\right)^2 - \zeta \Delta n \tag{4}$$

where B and C are constants (the latter being of order unity) which are determined by the bulk fluid. Minimization of this expression with respect to L gives the same form for σ as in Eq. (1). Hence, now the adsorption is $\frac{1}{2}L\Delta n = (2/C)\mu n^2\kappa_T$, which is the same result as before apart from a pure numerical factor of order unity.

Equation (4) lies beyond linear response theory and indeed Bhatia and March[5,6] have used a variant of it to describe free liquid surfaces. Also, incidentally, it shows that $L = 4n(\kappa_T B/C)^{1/2}$ so that, for suitable B, the distance over which the fluid density differs significantly from the bulk value can be larger than the range of the wall-fluid interaction. This conclusion would not appear to be reasonable on the basis of Eq. (1) above.

In an Appendix, we present a more realistic and detailed, though somewhat more mathematically involved, version of the above discussion. It provides a link between the Cahn–Hilliard and density functional theories and leads once more to the basic Eq. (2).

Equation (2) would appear to have qualitative applicability to high physisorption when such occurs (in class I systems in the terminology of Dash[7]). It predicts a divergence at the critical point and this is indicated by Saam and Ebner's machine calculations.[8] It also indicates, in agreement with observation,[7] that the adsorption of a gas will rise as the saturated vapour pressure is approached.

3 BINARY FLUID

The above discussion encourages us to consider binary systems similarly and we begin by generalizing Eq. (1). Suppose we have a system with number density n, enhanced by $\Delta n = \Delta n_1 + \Delta n_2$ in a surface layer of thickness l. If we take c to be the concentration of species 1, then the concentration fluctuation Δc can be defined by $n\Delta c = (1 - c)\Delta n_1 - c\Delta n_2$ and the generalized form of Eq. (1) expressed as[6,9]

$$\sigma = \frac{l}{2\kappa_T}\left\{\left(\frac{\Delta n}{n} + \delta\Delta c\right)^2 + \frac{\theta}{S_{cc}}(\Delta c)^2\right\} - \zeta_1\Delta n_1 - \zeta_2\Delta n_2 \tag{5}$$

Here $\theta = nk_BT\kappa_T$ where κ_T is the compressibility,

$$\delta = \frac{(v_1 - v_2)}{\{cv_1 + (1 - c)v_2\}}$$

where v_1 and v_2 are the partial molar volumes, and

$$S_{cc} = \frac{nk_BT}{(\partial^2 G/\partial c^2)_{T,P,N}}$$

where G is the Gibbs free energy density. In the above description, each of n, κ_T, δ and S_{cc} refers to the bulk binary fluid. Minimization of (5) with respect to Δn_1 and Δn_2 now leads to an adsorption $\Gamma_1 = l\Delta n_1$ of species 1 of

$$\Gamma_1 = \{\zeta_1[\theta c^2 + S_{cc}(1 - c\delta)^2] + \zeta_2[\theta c(1 - c) - S_{cc}(1 - c\delta)(1 + \delta - c\delta)]\}\, n/k_BT \tag{6}$$

When c is small, $S_{cc} \sim c$, so that, to first order, Eq. (6) becomes

$$\Gamma_1 = \frac{\{\zeta_1 + \zeta_2[\theta - (v_1/v_2)]\}nc}{k_BT} \tag{7}$$

where n, θ, v_2 and ζ_2 are now pure solvent parameters and v_1 and ζ_1 refer to the solute at infinite dilution. We will now use this result for a qualitative discussion of solute adsorption, even though it is merely the linear response result. For, as was seen in the previous section, the linear response result appears to retain its validity even within a non-linear context.

The contribution involving θ is $\zeta_2\theta nc/k_BT$ and so, by Eqs. (2) and (3), is interpreted as the impurity component carried to the wall in the solvent as a result of the direct wall-solvent interaction. To understand the remaining terms, it is useful to write down the analogue of Eq. (3), which is

$$\Gamma_1 = \frac{\{\lambda_2\theta + (v_1/v_2)(\lambda_1 - \lambda_2)\}c}{k_BT} \tag{8}$$

where now $\lambda_i = \zeta_i N/v_i$. The second contribution arises from a competition of the two species, through their atom-wall interactions, for proximity to the wall. It is clear from Eqs. (7) and (8) that Γ_1 is large if the wall-solvent interaction is strongly attractive and the fluid is nearly critical or the solute is more attracted to the wall than the solvent and the solute/solvent size ratio is large.

The latter remark offers a clue to the explanation of the observed behaviour, mentioned at the beginning of this account, of Cs impurity in liquid Na near its triple point (where $\theta \approx 0.025$). Of all atoms (with the likely exception of Fr), Cs gives the largest size ratio (~ 3) under these conditions. Thus the second term of Eq. (8) offers the possibility of exceptionally large physisorption provided that $\zeta_2 < 0$, i.e. that the Na atoms are repelled from the wall. The latter requirement is, as yet, unproved.

4 SUMMARY

In this paper we have been concerned with finding the conditions under which exceptionally large physisorption occurs. In Section 2 we considered a one component fluid and argued in detail that the result of linear response theory had, in fact, a more general validity.

With its credibility thus established, linear response theory was applied in Section 3 to binary systems. In the limit of small concentrations, the solute/solvent atom size factor was found to play an important role and it was suggested that this is the key to the large adsorption observed in NaCs.

Acknowledgement

We are grateful to SERC for its support and to helpful comments from Professor C. C. Addison, Dr. A. A. Cottey, Dr. R. Evans and Dr. M. Silbert.

References

1. M. H. Cooper and G. R. Taylor, *Nuclear Technology*, **12**, 83 (1971).
2. See, e.g., N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids* (London: Macmillan) (1976).
3. J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.*, **28**, 258 (1958).
4. B. Widom, *J. Chem. Phys.*, **43**, 3892 (1965).
5. A. B. Bhatia and N. H. March, *J. Chem. Phys.*, **68**, 1999 (1978).
6. A. B. Bhatia and N. H. March, *J. Chem. Phys.*, **68**, 4651 (1978).
7. J. G. Dash, *Phys. Rev. B*, **15**, 3136 (1977).
8. W. F. Saam and C. Ebner, *Phys. Rev. A*, **17**, 1768 (1978). These results have been criticised by J. E. Lane, T. H. Spurling, B. C. Freasier, J. W. Perram, and E. R. Smith, *Phys. Rev. A*, **20**, 2147 (1979), but not at the level at which they are used here. Indeed a similar divergence seems to be indicated by Lane *et. al.*'s work.
9. A. B. Bhatia and D. E. Thornton, *Phys. Rev. B*, **2**, 3004 (1970).
10. See, for example, the recent review by R. Evans, *Adv. Phys.*, **28**, 143 (1979).

Appendix

This Appendix shows how the result given by Eq. (2) can be derived by density functional theory.

Consider a surface at $z = 0$ in contact with a fluid of density $n(z) = n + \Delta n(z)$. Then a clear generalization of Eqs. (2) and (4) is

$$\sigma = \frac{1}{2\kappa_T n^2} \int_0^\infty dz\,[\Delta n(z)]^2 + \tfrac{1}{2}A \int_0^\infty dz \left[\frac{d}{dz}\Delta n(z)\right]^2 + \int_0^\infty dz n(z)V(z) \quad \text{(A1)}$$

where A is a constant and $V(z)$ describes the interaction between the wall and the fluid atoms. Minimization with respect to $\Delta n(z)$ is now achieved if

$$A\frac{d^2}{dz^2}\Delta n(z) = \frac{1}{\kappa_T n^2}\Delta n(z) + V(z) \quad \text{(A2)}$$

The solution of this differential equation in the half space $z > 0$ is

$$\Delta n(z) = -\frac{\lambda}{2A}\int_0^\infty dz' V(z')(e^{-|z-z'|/\lambda} + e^{-|z+z'|/\lambda}) \tag{A3}$$

where $\lambda^2 = An^2\kappa_T$. Thus the adsorption is

$$\Gamma = \int_0^\infty dz\, \Delta n(z) = -n^2\kappa_T \int_0^\infty dz'\, V(z') \tag{A4}$$

in agreement with Eq. (2).

The formalism of this Appendix arises from conventional density functional theory [10] by linearization, on assuming $\Delta n(z)/n$ is small.