to pure A as the reference state. In (11), h_A (mm mol^{-1} l.) is the measured Henry's law constant, $P_A{}^0$ is the vapor pressure of pure solvent A at 25°, d_B is the density of solvent B, and M_B is the molecular weight of solvent B. Equation 11 follows from the relationship

$$f_A = \frac{P_A}{P_A{}^0 X_A} = \frac{h_A}{P_A{}^0}\frac{d_B 1000}{M_B}$$

since

$$h_A = \frac{P_A}{C_A} = \frac{P_A}{X_A}\frac{M_B}{d_B 1000}$$

where P_A is the vapor pressure of A at concentration C_A mol l.$^{-1}$ in B and X_A is the corresponding mole fraction of A in B.

Conclusions

(1) It has been shown that contributions to the liquid junction potentials from the free energy changes associated with the transport of solvent molecules across the junction ($E_{j,s}$) may be as high as 100 mV in cell A. For cells A in which solvent S2 is water, formamide, or methanol and the bridge solvent S3 is any one of a variety of solvents, an excellent linear correlation has been found between the observed emf and the mutual heats of solution of the various solvents in the cell.

(2) The contribution to the liquid junction potential from the free energy changes associated with the passage of ions across the boundary ($E_{j.ion}$) depends upon $\int_1{}^2 t_i \mathrm{d}\mu_i$, where t_i is the transport number of ion i in a given region, across which there is a free energy change of $\mathrm{d}\mu_i$. $E_{j.ion}$ will be zero if $\int_1{}^2 t_i \mathrm{d}\mu_i$ is equal for all ions crossing the junction. It is suggested that because of a general tendency of an ion to have a low mobility in a solvent where it is heavily solvated, $\int_1{}^2 t_i \mathrm{d}\mu_i$ may remain fairly constant (and hence $E_{j,ion}$ small) even for ions involving quite large changes in free energy on crossing the boundary.

(3) It is possible to reduce the liquid junction potentials in cells between different solvents by careful selection of bridge solvents and electrolytes. In order to minimize the liquid junction potential between two different solvents (as in cell A), it is necessary for the bridge solvent to be such that it does not strongly interact with either of the other solvents and the bridge electrolyte should be such that the transport numbers of the cation and anion and their free energy changes on crossing the junction should be equal. The choice of either tetraethylammonium picrate or tetrabutylammonium tetraphenylboride as bridge electrolytes seems reasonable.

On the Relation between Surface Tension and Dielectric Constant

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Received February 19, 1972

Abstract: Recently an empirical relation between surface tension and dielectric constant has appeared in the literature [H. A. Papazian, *J. Amer. Chem. Soc.*, **93,** 5634 (1971)]. Theoretical reasons behind this correlation are examined in this paper. It is found that the Lifshitz theory of macroscopic forces can be used to treat a previously proposed model for calculation of surface tension. Theoretical expressions are demonstrated which imply a correlation between surface tension and dielectric constant, and these expressions are compared with experimental data.

In a recent article Papazian[1] has noted a correlation between the surface tension (γ) and the function $(\epsilon_0 - 1)/(2\epsilon_0 + 1)$, where ϵ_0 is the static dielectric constant, for nonpolar liquids. For polar liquids he finds that γ correlates with $(n^2 - 1)/(2n^2 + 1)$, where n is the index of refraction. It is the purpose of this paper to discuss theoretical relationships between γ and ϵ_0 (or n^2) and to offer some comments on the relationship of dispersion forces to the surface tension. A more detailed analysis of the experimental correlation between γ and functions of ϵ_0 for nonpolar liquids will also be offered.

Our analysis is based on a model proposed in 1968 by Padday and Uffindell.[2] Their approximate theory for calculation of surface tensions of hydrocarbons calculated the interaction energy due to van der Waals forces at the surface of a liquid. For nonpolar liquids this energy consists solely of a dispersion term. Consider the formation of two unit areas of surface from bulk liquid. Thermodynamically the increase in energy per unit area of surface formed is

$$E = W/2 + Q/2 = \gamma + TS \tag{1}$$

where W is the work done on the system, Q is the heat required to obtain equilibrium, T is the temperature, and S is the entropy of surface formation. Padday and Uffindell obtain W by calculating the decrease in potential energy occurring when two semiinfinite surfaces of a liquid are brought together from an infinite distance to a distance at which the surface region is indistinguishable from the bulk liquid. They then make the assumption, justified *a posteriori*, that TS

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(1) H. A. Papazian, *J. Amer. Chem. Soc.*, 93, 5634 (1971).

(2) J. F. Padday and N. D. Uffindell, *J. Phys. Chem.*, 72, 1407 (1968).

$= Q/2$. This yields

$$\gamma = {}^1/_2 W \tag{2}$$

The quantity W is calculated by integrating the Slater–Kirkwood formula[3] for the interaction energy between two particles across the semiinfinite surfaces. They obtain for ${}^1/_2 W$ the following

$${}^1/_2 W = N^2 he(sZ)^{1/2}\alpha_0{}^{3/2}/64(m)^{1/2}r^2 \tag{3}$$

Here N is the number density, h is Planck's constant, e and m are the charge and mass of the electron, s is the number of valence electrons, Z is the number of outer-shell electrons, α_0 is the static polarizability, and r is the distance of closest approach between the two plane surfaces. The authors use eq 2 and 3 to calculate γ for a series of hydrocarbons and find good agreement with experiment. From the Clausius–Mosotti equation

$$4\pi\alpha_0/3 = \frac{1}{\rho}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right) \tag{4}$$

where ρ is density, it is seen that the theory of Padday and Uffindell predicts a correlation between γ and $[(\epsilon_0 - 1)/(\epsilon_0 + 2)]^{3/2}$. There are several difficulties inherent in the use of eq 3 to calculate macroscopic dispersion forces across a distance r. First, it assumes a particular model for intermolecular forces (here the Slater–Kirkwood equation proposed in 1931). Second, it assumes pairwise additivity, and nonadditive effects can be quite important in calculating forces between macroscopic bodies.[4,5] It also assumes a homogeneous concentration of particles up to and on the surface.

A more desirable method for treating forces of attraction between two condensed phases is the macroscopic approach of Lifshitz.[4–7] The Lifshitz theory has recently been used quite successfully by Ninham and Parsegian to calculate dispersion forces across triple-layer films.[5,7] In 1967 Krupp suggested its use in estimating attractive pressure leading to surface tension.[8] We will use the Lifshitz theory to calculate that part of the interaction energy leading to surface tension which is dependent on the dielectric constant. The theory predicts that the interaction energy per unit area between two surfaces a distance r apart is given by eq 5. Here $\epsilon(i\omega)$ is the frequency dependent

$$U(r) = -W = \frac{-\hbar}{32\pi^2 r^2}\int_0^\infty \mathrm{d}\omega \times \int_0^\infty x^2\left[\left(\frac{\epsilon(i\omega) + 1}{\epsilon(i\omega) - 1}\right)^2 e^x - 1\right]^{-1} \mathrm{d}x \tag{5}$$

dielectric susceptibility evaluated along the imaginary axis.

Two assumptions are inherent in the use of eq 5 to estimate W. First, the Lifshitz theory assumes that r is larger than intermolecular distances. It is thus assumed that eq 5 adequately estimates the ϵ_0 dependence of the attractive energy contributing to W at interplaner distances such that the Lifshitz approach is valid. Krupp applies the Lifshitz equations at distances approaching 4 Å and asserts that satisfactory approximations to W are obtained provided chemical bonding is not involved.[8] In the case of two nonpolar media the assumption appears well justified. Ninham and Parsegian also discuss the Lifshitz theory at distances as short as 5 Å. Second, eq 5 actually represents a low temperature limit. However, Lifshitz shows that for distances and temperatures such that $rkT/\hbar c < 1$, where k is the Boltzmann constant and c is the speed of light, eq 5 is valid.[9,10] This approximation does not imply that W is temperature independent, only that the temperature dependence of W is contained in that of $\epsilon(i\omega)$. Under these two conditions we now show that the Lifshitz theory predicts a dependence of W (and hence γ) which is followed by experimental data.

Evaluating the integral over x yields

$$W = \frac{\hbar}{16\pi^2 r^2}\int_0^\infty \mathrm{d}\omega \sum_{K=1}^{\infty}\frac{1}{K^3}\left(\frac{\epsilon(i\omega) - 1}{\epsilon(i\omega) + 1}\right)^{2K} \tag{6}$$

The behavior of $\epsilon(i\omega)$ along the imaginary axis is well understood. It is a real, monotone decreasing function with maximum ϵ_0 at $\omega = 0$ and minimum 1 at $\omega = \infty$. Thus the sum in eq 6 is absolutely convergent and in fact converges rather rapidly for nonpolar liquids with $\epsilon_0 \leq 3.0$.[11]

Ninham and Parsegian have developed a semiempirical expression for the dielectric dispersion along the imaginary axis.[7] For hydrocarbons they use a low frequency approximation for $0 \leq \omega \leq 2 \times 10^{16}$, a high frequency approximation for $\omega \gg 3 \times 10^{16}$, and a monotone decreasing linear interpolation connecting the two. Their expressions are shown in eq 7

$$\epsilon(i\omega) = \begin{cases} 1 + (\epsilon_0 - 1)/(1 + \omega^2/C_1{}^2), & 0 \leq \omega \leq 2 \times 10^{16} \\ C_2\omega + C_3, & 2 \times 10^{16} \leq \omega \leq 10^{17} \\ 1 + C_4/\omega^2 & \omega > 10^{17} \end{cases} \tag{7}$$

where the values of C_1, C_2, C_3, and C_4 are determined from experimental data and limiting laws. For a typical hydrocarbon Ninham and Parsegian find $C_1 = 1.76 \times 10^{16}$. Substitution of eq 7 back into eq 6 shows the explicit dependence of W on ϵ_0. We note that the integral from 0 to ∞ can be broken into three parts from the three expressions in eq 8, and only the

$$W = \frac{\hbar}{16\pi^2 r^2}\sum_{K=1}^{\infty}\frac{1}{K^3}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1}\right)^{2K} \times \int_0^{\omega_1}\left[1 + \frac{2\omega^2}{C_1{}^2(\epsilon_0 + 1)}\right]^{-2K} \mathrm{d}\omega + \epsilon_0 \text{ independent term} \tag{8}$$

first part, *i.e.*, the integral from $\omega = 0$ to $\omega = \omega_1 \equiv 2 \times 10^{16}$, will contain ϵ_0. For brevity we show only the ϵ_0-dependent term in eq 8. Here we have switched orders of integration and summation. The integral over ω can be written down for any K, but the general

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(3) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, 37, 682 (1931).

(4) J. E. Dzyloshinskii, E. M. Lifshitz, and L. P. Pitaevski, *Advan. Phys.*, 10, 165 (1961).

(5) B. W. Ninham and V. A. Parsegian, *J. Chem. Phys.*, 52, 4578 (1970).

(6) N. G. van Kampen, B. R. A. Nijboer, and K. Schram, *Phys. Lett. A*, 26, 307 (1968).

(7) B. W. Ninham and V. A. Parsegian, *Biophys. J.*, 10, 646 (1970).

(8) H. Krupp, *Advan. Colloid Interface Sci.*, 1, 111 (1967).

(9) E. M. Lifshitz, *Sov. Phys. JETP*, 2, 73 (1956).

(10) L. D. Landau and E. M. Lifshitz, "Electrodynamics of Continuous Media," Pergamon Press, New York, N. Y., 1960, p 256ff.

(11) The sum is related to the Riemann ζ function; *cf.* E. T. Whittaker and G. M. Watson, "Modern Analysis," Cambridge University Press, London, 1965, p 280, problem 7.

term is rather complicated.[12] The contribution of the $K = 2$ term is less than 10^{-3} for $\epsilon_0 \sim 2$, and each succeeding term in the sum is smaller. Thus to a very good approximation we can deduce the dependence of W on ϵ_0 by examining the $K = 1$ term. On performing the integral and simplifying, we obtain eq 9.

$$W = \frac{\hbar}{16\pi^2 r^2}\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1}\right)^2 \omega_1 \left\{\left[1 + \frac{2\omega_1^2}{C_1^2(\epsilon_0 + 1)}\right]^{-1} + \frac{C_1}{\omega_1}\left(\frac{\epsilon_0 + 1}{2}\right)^{1/2} \tan^{-1}\left(\frac{2\omega_1^2}{C_1^2(\epsilon_0 + 1)}\right)^{1/2}\right\} + (\epsilon_0 \text{ independent terms}) + (\text{higher order terms}) \quad (9)$$

This equation and eq 1 show explicitly how γ is related to ϵ_0 as predicted by the Lifshitz theory.

We have performed a regression analysis of the linear relation between γ and various functions of ϵ_0 for 18 nonpolar liquids, ranging from liquid helium to *n*-undecane. Table I shows the results of analysis of the relationship

$$\gamma = aF(\epsilon_0) + b \quad (10)$$

Table I shows that γ correlates remarkably well with *all* of the functions considered. This is understandable, since all of the functions in Table I behave very much like ϵ_0 itself for the liquids considered (*i.e.*, $1.04 \leq \epsilon_0 \leq 3.09$). The correlation coefficient between ϵ_0 and the other functions in Table I is greater than 0.96 in all cases. If each of the other functions is expanded in a Taylor's series about the point $\epsilon_0 = 2$, the first two terms (*i.e.*, the constant term and the term proportional to $\epsilon_0 - 2$) predominate in all cases. Therefore if γ correlates well with any one of the functions in Table I, it will correlate well with all of them.

Table I. Correlation between γ and Functions of ϵ_0

$F(\epsilon_0)$	Correlation coefficient	Standard error of estimate	a	b
ϵ_0	0.97	2.6	20.9	−20.5
$\frac{\epsilon_0 - 1}{2\epsilon_0 + 1}$	0.96	3.0	149.2	−7.0
$\frac{\epsilon_0 - 1}{\epsilon_0 + 2}$	0.97	2.4	105.9	−4.1
$\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2}\right)^{3/2}$	0.97	2.5	157.3	1.7
$\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1}\right)^2$	0.97	2.8	154.0	3.9
Eq 9	0.96	3.1	92.8	4.9

The results in Table I illustrate that both the microscopic approach of Padday and Uffindell and the macroscopic theory of Lifshitz lead to results which imply a correlation between the surface tension and the dielectric constant. These results also indicate the difficulty in choosing a "best" function of ϵ_0 to correlate with γ. Also of some interest is the fact that the wide range of temperatures represented in the regression analysis indicates that the temperature dependence of γ parallels that of ϵ_0. This was pointed out in Papazian's paper where he showed that γ correlates with $(n^2 - 1)/(2n^2 + 1)$ for CS_2 and C_2H_5OH over a wide temperature range.[1]

Acknowledgment. The author would like to thank Professors J. H. Wharton, N. R. Kestner, D. A. McQuarrie, and the referees for helpful comments.

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[12] I. S. Gradshteyn and I. M. Ryzhik, "Tables of Integrals, Series, and Products," Academic Press, New York, N. Y., 1965, p 66, formula 2.148.4.