and $D'_{2,M}$ values reported in Table I. The experimental values determined in this way should be compared with the ones calculated from eq 7. Some difficulties however arise when such a calculation is attempted. In the first place, various experimental methods yield different values for the number of water molecules coordinated to a given ion. This uncertainty, however, only influences the value of r_p within a factor of 1.5. Much smaller is the error introduced into eq 7 by disregarding the multiplicative constant H (see eq 5), which does not appreciably differ from unity.

As for the term in square brackets, we may only observe that the values of $(K/v)_1$ generally are of the order of 10^{-1} in g s⁻² K^{-1.37} It seems reasonable to assume that $(K/v)_p$ to be of the same order of magnitude. Accordingly, the absolute values of the term in square brackets should be between zero and 10^{-1} .

By substituting into eq 7 the experimental values of $D'_{1,2}$ obtained from the sum of $D'_{1,M}$ and $D'_{2,M}$ of Table I, one can easily check that the term $(K/v)_{\rm l} - (K/v)_{\rm p}$ ranges within the prescribed interval.

Concerning the high values experimentally found for $D'_{1,M}$ and $D'_{2,M}$, which are 1 order of magnitude higher than the corresponding ones resulting from experiments of thermal diffusion, it must be remembered that the density of the thermal energy flux in the membrane liquid-filled pores depends upon thermal conductivities of both solution and membrane matrix. Unfortunately we do not at present possess accurate measurements of thermal conductivity of the AP-20 porous septa, and, therefore, we cannot calculate the incidence of this circumstance on transport.

Another complication arises from the fact that the thermal conductivity of a liquid in close proximity to a solid surface may increase very much over its normal value. Metzik,³⁵ for instance, measured a 100-fold increase in thermal conductivity of water sandwiched between parallel silicate surfaces spaced 1 μ m apart. The close similarity

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of this situation with the one existing in the interior of the AP-20 pores suggests possible relevant discrepancies between the real value of the temperature gradient existing in membrane pores and the value calculated from the applied transmembrane temperature difference and by knowledge of the partition's thickness. In our calculations, however, we used these last values, being unable to reliably estimate the perturbing factors.

An important point which should be discussed is whether the thermal radiation forces which produce bulk flow through the membrane arise from the different value of the momentum conductivities of liquid and membrane. Just as the membrane material, if suspended in the nonisothermal liquid, would be acted upon by a thermal radiation force proportional to the difference $(K/v)_1 - (K/v)_M$, where subscript M indicates the partition matrix, so, in the presence of a fixed membrane, would the liquid be acted upon by a reaction force of opposite sign. A direct measurement of this force could be obtained by the method used by one of us to measure thermal radiation forces on macroscopic plungers.^{36,37}

Another interesting possibility is that the variation with temperature of the quantity $(K/v)_1$ produces a gradient of radiation pressure³⁰ along the pore length, driving the bulk flow through the membrane. Future work will hopefully clarify this point.

In conclusion, what can be considered satisfactorily proved is that thermodialysis is a modified form of thermal diffusion. By contrast with the more complex effect of thermoosmosis, where every dense membrane exhibits an individual behavior, nonisothermal transport through unselective porous partitions seems to obey simple, general laws. In this context the radiation-pressure theory of thermal diffusion may be a useful tool for the study of the various aspects of this kind of transport.

Moreover, the peculiar behavior of sodium chloride and potassium chloride aqueous solutions offers such interesting analogies with biological membrane transport of these salts to stimulate further research to ascertain the possible interrelationship between these two phenomena.

Use of 2,2-Diphenyl-1-picrylhydrazyl To Investigate the Chemical Behavior of Free Radicals Induced by Ultrasonic Cavitation

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The sonolysis of 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been studied in methanol-water solutions in the presence of air, oxygen, and argon. It is found that, for a specific solvent composition, 83% of the reacted DPPH is reduced to 2,2-diphenyl-1-picrylhydrazine (DPPH₂) with all the gases examined. The absolute amount of DPPH converted is greatest with oxygen and it is believed that the latter combines with the primary radicals produced in the cavitation process to give a greater concentration of stable free radicals which can readily diffuse out of the bubble to react with DPPH. The conversion of DPPH \rightarrow DPPH₂ decreases with increasing methanol concentration and it is believed to be due to the volatile alcohol inhibiting the cavitation process.

Introduction

Ultrasonic cavitation gives rise to a wide variety of chemical reactions in aqueous solutions.¹⁻³ The primary

reactions are due to the thermal decomposition of the cavity contents and the formation of free radicals. For example, in aqueous solutions in the absence of any volatile solute the primary reaction in the cavitation of water gives

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Behavior of Free Radicals Induced by Ultrasonic Cavitation

TABLE I: Values of Molar Absorptivities ϵ at 320 and 520 nm for DPPH and DPPH, in Methanol-Water (60:40 by volume)

	DPPH	DPPH ₂
$\epsilon_{320}^{\ a}, {}^{a} \mathrm{M}^{-1} \mathrm{cm}^{-1}$ $\epsilon_{520}^{\ a}, \mathrm{M}^{-1} \mathrm{cm}^{-1}$	$\begin{array}{c} 1.4\times10^{4}\\ 0.8\times10^{4}\end{array}$	$1.3 imes 10^4 \ 0.05 imes 10^4$

^{*a*} The standard deviation is $\pm 5\%$.

hydrogen atoms and hydroxyl radicals. The reaction takes place entirely in the gaseous phase⁴ of a bubble during irreversible adiabatic compression.⁵ The radicals can either recombine radiatively^{3,6} or react with other gaseous components in the cavity.^{3,7,8} The products and residual free radicals can then diffuse into the condensed phase where they experience virtually continuous collision with the solute and solvent molecules leading to secondary reactions.7,9

Because of its unusual stability¹⁰ 2,2-diphenyl-1-picrylhydrazyl (DPPH) was considered a useful substrate to further probe the phenomenon of cavitation and the nature of chemical processes associated with it. We report the results of a study of the chemical conversion of DPPH to 2,2-diphenyl-1-picrylhydrazine (DPPH₂) under the influence of an intense ultrasonic field and in the presence of air, oxygen, and argon gases.

Experimental Section

Ultrasonic irradiations were carried out at 459 kHz with the apparatus and conditions described previously.^{8,11} The temperature of the insonated solutions was maintained at 25 ± 1 °C by circulating temperature-controlled water around the insonation cell.

The water used in the preparation of solvent mixtures was purified as described previously.⁸ Highest purity methanol was used as received. A fixed volume of a saturated solution of DPPH in methanol was added to the binary solvent mixtures. Aliquots (50 mL) of each solution were transferred to the insonation cell and saturated in situ by bubbling the gas through the solution for at least 15 min prior to insonation. All experiments were carried out in a large glovebag flushed with the gas used to saturate the solution. Research grade compressed gases (Liquid Carbonic Canada, Ltd.) were used without purification in all experiments.

DPPH was synthesized according to literature procedures.¹² DPPH₂ (Eastman) was purified by chromatography on alumina (540 mesh) with chloroform as eluant. DPPH is readily separated as the leading fraction. The purity of DPPH was confirmed by EPR techniques with a Bruker B-ER418S spectrometer.

Chromatographic analyses of the reaction products were carried out according to the procedures reported previously.13

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Figure 1. Change in concentration of DPPH and DPPH₂ as a function of insonation time and in the presence of various gases. DPPH: (Δ) air; (\Box) oxygen; (O) argon. DPPH₂: (\blacktriangle) air; (\blacksquare) oxygen; (\bigcirc) argon.

ΤА	BL	E	I
_			_

	consumption of DPPH		formation of DPPH ₂		<u> </u>
as	initial rate, M min ⁻¹ × 10 ⁶	net in 10 min, $M \times 10^4$	initial rate, M min ⁻¹ × 10 ⁶	net in 10 min, M × 10 ⁴	DPPH to DPPH ₂ convrn, %
air	12	1.9	10	1.6	84
J ₂	11	1.8	9.9	1.5	83
Ar	1.6	0.6	1.3	0.5	83

Results and Discussion

Both DPPH and DPPH₂ have electronic absorption maxima at 320 and 520 nm, with the absorption for DPPH₂ at 520 nm being relatively weak. Using the Beer-Lambert law, we obtained values of the extinction coefficient ϵ for both compounds at 320 and 520 nm in methanol-water (60:40 by volume) by measuring the absorbances of standard solutions. The value of ϵ , in units of M^{-1} cm⁻¹, obtained are given in Table I. The standard deviation in any of these values is $\pm 5\%$. Knowing ϵ and measuring the solution absorbance, we can determine the concentrations of DPPH and DPPH₂ by solving eq 1 and 2 simultaneously, where l is the spectral pathlength in cm.

$$A_{520}^{\text{total}} = (\epsilon_{520}Cl)^{\text{DPPH}_2} + (\epsilon_{520}Cl)^{\text{DPPH}}$$
(1)

$$A_{320}^{\text{total}} = (\epsilon_{320}Cl)^{\text{DPPH}_2} + (\epsilon_{320}Cl)^{\text{DPPH}}$$
(2)

The results of the studies of the conversion of DPPH \rightarrow DPPH₂ under the influence of an ultrasonic field and in the presence of various gases are shown in Figure 1 and Table II. The converse changes in DPPH and DPPH₂ concentrations occur rapidly (Figure 1) over the first few minutes of insonation and then the rates of change diminish considerably, approaching a value of zero for insonation periods longer than 10 min. A mass balance of DPPH consumed and DPPH₂ produced over the above time span was determined by measuring areas under the various curves in Figure 1. The results (Table II) show that the amount of DPPH consumed is greatly influenced by the nature of the dissolved gas, the order being air \simeq $O_2 > Ar$. As well, in all cases it was found that approximately 83% of the reacted DPPH is converted into DPPH₂. Estimates of the rate of disappearance of DPPH (Table II) were obtained from initial slopes of curves in Figure 1.

Ultrasonic Chemical Activity vs. the Nature of the Dissolved Gas. The chemical system as described above has a volatile (methanol) and relatively nonvolatile (DP- PH) component dissolved in water. The exact composition of a bubble during the cavitation process is extremely difficult to determine; however, to a first approximation, it may be assumed to be proportional to the equilibrium vapor pressures of the components within the bubble. Therefore, it would be expected that the order of abundance inside the bubble is permanent gas > methanol >H₂O. The bubbles may contain a small amount of DPPH (see discussion below). The sequence of chemical reactions that occur within and outside a cavity will be greatly influenced by the reactivity of the dissolved gas. In the presence of Ar the primary radicals produced from water can undergo radical recombination and in the presence of the alcohol the OH radicals can abstract a labile α hydrogen to produce α -hydroxyalkyl radicals which can subsequently become involved in further reactions such as decomposition and disproportionation. At the relatively high temperatures attained in the cavity it is also possible that thermal decomposition of the alcohol could occur and a wide variety of products can emerge with molecular hydrogen and formaldehyde being the major ones. Analytical studies of the sonolysis of isopropyl alcohol¹⁴ are consistent with this qualitative description. Any free radicals that survive the reactive pathways in the gas phase could diffuse out of the bubble to react with the nonvolatile solute, viz, DPPH. The results obtained in this work suggest that, in the presence of argon gas, a majority of the radicals, including H atoms, are not migrating into the solution phase but are being removed through processes in the gaseous cavity. This may also explain why there is a relatively stronger sonoluminescence, which has been shown to be due to radical recombination inside the cavities.¹⁵ from argon-saturated solution.

The situation may be different in the presence of O_2 and air, since more DPPH is consumed than in the presence of Ar. This implies that a mechanism involving O_2 is operative, leading to the production of more stable free radicals that diffuse out of a bubble to react with DPPH. There is considerable evidence¹⁶ that pulsed ionizing radiation of oxygenated aqueous solutions of alcohol produce α -hydroxyalkylperoxyl radicals which subsequently undergo spontaneous and base-catalyzed HO₂· elimination. The strong similarities shown to exist between the effect of high-energy ultrasound and ionizing radiation^{7,15,17} allows, by analogy with pulse radiolysis, the prediction of the following reaction scheme:

$$H_2O \longrightarrow H_{\cdot}, \cdot OH$$
 (3)

$$H \cdot + O_2 \to HO_2 \cdot \tag{4}$$

$$\mathrm{HO}_{2^{\star}} \rightleftharpoons \mathrm{H}^{+} + \mathrm{O}_{2}^{-} \cdot \tag{5}$$

$$OH + CH_3OH \rightarrow H_2\dot{C}OH + H_2O$$
(6)

$$H_2\dot{C}OH + O_2 \rightarrow H_2C(OH)O_2$$
 (7)

$$H_2C(OH)O_2 \rightarrow H_2C = O + H^+ + O_2 \overline{} \qquad (8)$$

$$DPPH + HO_2 \rightarrow DPPH_2 + O_2 \tag{9}$$

$$DPPH + H_2C(OH)O_2 \rightarrow DPPH_2 + H_2C = O + O_2 \quad (10)$$

Reaction 8 proceeds via a rate-determining step of HO₂. elimination followed by dissociation according to eq 5. The rate constant of the spontaneous HO2. elimination increases with methyl substitution in the α position. A value of $k_8 < 10 \text{ s}^{-116}$ has been reported for the α -hydroxyalkylperoxyl radicals formed from methanol. Since even the base-catalyzed reaction is somewhat below diffusioncontrolled conditions,¹⁶ it is logical to assume that the radicals produced by reaction with O₂ have longer lifetimes and can react directly with DPPH in solution.

Quantitative support of this argument can be presented in two ways. Consider first the case of scavenging of H atoms by oxygen molecules. Using estimates of cavity parameters we found it possible to estimate the ratio of the number of hydrogen atoms scavenged by O_2 to the number recombining to give H_2 . If we assume the mean radius of the bubble during the collapse to be $\sim 2 \times 10^{-7}$ m^{18,19} and the number of radicals in a bubble prior to transport to be 2.2×10^{4} ,^{18,19} the estimated radical concentration inside the bubble will be 1.1×10^{-3} M. If we take the concentration of O_2 gas in the bubble during the collapse to be greater than 1 M,20 the ratio of the number of H atoms scavenged by O_2 to the number forming H_2 is given by

$$\frac{\frac{R(H+O_2)}{R(H+H)}}{\frac{k_{HO_2}[O_2][H]}{k_{H_2}[H][H]}} \simeq \frac{1.9 \times 10^{10} \times 1}{1.3 \times 10^{10} \times 1.1 \times 10^{-3}} \simeq 1.3 \times 10^{3}$$

where the values of the bimolecular rate constants have been taken from Spinks and Woods.²¹ This result shows that, under the prescribed conditions, the oxygen present in the cavities would be more than sufficient to scavenge the H atoms produced. Since the depletion of HO₂ radicals via recombination is a relatively slow process (k = 8.60 $\times 10^5$ M⁻¹ s⁻¹)²² much of HO₂ could diffuse out of the bubble to react further. As well, the combination of reactions shown by eq 6-10 may provide even better pathways through which interaction of DPPH with stable radicals can occur in the bulk medium.

A further quantitative argument can be developed to show that the ratio of the number of radicals (primary or secondary) that diffuse from the bubbles to those that undergo recombination depends upon the nature of the gaseous contents. Consider a small spherical²³ collapsing bubble containing primary free radicals at an average concentration C. The bubble is surrounded by an interphase of thickness ca. λ , the mean free path, which separates the radical-rich zone from the bulk medium containing DPPH. During a bubble collapse there is a simultaneous flow of heat, mechanical (shockwaves), and chemical (free radicals and molecular products) energy from the bubble into the surrounding medium. This gives rise to complex interactions between the various fluxes under highly irreversible conditions. As well, due to the presence of shockwaves, heat and radical propagation in the vicinity of the collapsing bubble will be turbulent. Although the second-order effects due to thermodynamic irreversibility and hydrodynamic nonlinearity could be

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(20) Division the production of the collement of the collemen

⁽²³⁾ This is an approximation. During the collapse, the combination of surface waves at the interphase, the intense inward force, and the resistance of cavity contents to compression deforms the bubble configuration. Therefore, the exact shape of a bubble at the collapse is not completely understood.

Behavior of Free Radicals Induced by Ultrasonic Cavitation

important, it is not yet possible to determine precisely their influence on the transport of individual free radicals. If we assume that their effect on radicals of different chemical stability are more or less the same, then Fick's law can be used to a first approximation to obtain information on the number of radicals that diffuse. Accordingly, the number of moles, n_D , of free radicals R that diffuse through the interphase of thickness λ in the time interval Δt is given by the expression

$$n_{\rm D} \simeq 4D\pi r^2 \Delta t (\Delta C/\lambda) \tag{11}$$

where D is the diffusion coefficient of the substance and ΔC the concentration difference between the two surfaces of the interphase of thickness λ .

In the time interval Δt , the number of moles of radicals, $n_{\rm R}$, that combine in the radical-rich zone is given by the relation

$$n_{\rm R} = (4\pi r^3/3) k_{\rm R_2} (\Delta C)^2 \Delta t \tag{12}$$

Taking the ratio of eq 12 to 11 results in the expression

$$n_{\rm R}/n_{\rm D} = (k_{\rm R} r \Delta C \lambda)/3D \tag{13}$$

Assuming, that the primary free radicals, e.g., H, react almost instantaneously with DPPH, their concentration at the outer boundary of the interphase will approach zero, i.e., $\Delta C \simeq C$ and eq 13 becomes

$$n_{\rm R}/n_{\rm D} = (k_{\rm R_2} r C \lambda)/3D \tag{14}$$

On the other hand, secondary free radicals that are less reactive (HO₂·) may not be used up, instantaneously, as they approach the surface of the interphase. If C_0 is the concentration of HO₂· at the outer face of the interphase, then $\Delta C = C - C_0$ and eq 13 takes the form

$$n_{\rm R}/n_{\rm D} = \frac{k_{\rm (HO_2)_2} r \lambda (C - C_0)}{3D}$$
(15)

or

$$n_{\rm R}/n_{\rm D} \le k_{({\rm HO}_{\rm g})_2} r \lambda C/3D$$

If we take representative values of $\lambda = 1 \times 10^{-9}$ m, $C = 1.1 \times 10^{-3}$ M, $r = 2 \times 10^{-7}$ m, $D = 10^{-9}$ m² s⁻¹,²⁴ $k_{\text{H}_2} = 1.3 \times 10^{10}$ M⁻¹ s⁻¹,²¹ and $k_{(\text{HO}_2)_2} = 8.6 \times 10^5$ M⁻¹ s⁻¹,²² eq 14 and 15 give the value of $n_{\text{R}}/n_{\text{D}}$ to be 0.95²⁵ and less than 6.3 $\times 10^{-525}$ for H and HO₂*, respectively. This means that in the absence of O₂ almost equal numbers of H radicals undergo diffusion and recombination, whereas in the presence of O₂ comparatively larger numbers (i.e., $\geq 1.7 \times 10^4$) of hydrogen radicals diffuse from the bubbles as HO₂ radicals as compared to the number of H radicals that undergo recombination. Therefore, it appears that O₂ may act as a "carrier" of H· into the bulk phase where the HO₂· radicals react with DPPH to produce greater amounts of DPPH₂, as observed experimentally.

Minor Products. The data in Table I show that for all experimental conditions of added gas only 83% of the



Figure 2. Percent degradation of DPPH as a function of mole fraction content of methanol, X_{MeOH} (O); correlation between percent degradation of DPPH and free energy of cavitation $\Delta \tilde{A}$ (--).

reacted DPPH is converted to DPPH₂. Two factors that contribute to this imbalance are the direct decomposition of DPPH₂ by ultrasound and the possible formation of products other than $DPPH_2$. The insonation of $DPPH_2$ under the conditions used with DPPH produced no detectable change in the absorption spectra, indicating that DPPH₂ does not degrade during the insonation process. Paper chromatography of the final insonation products of DPPH in MeOH- H_2O , using benzene as solvent and a 1:1 by volume mixture of petroleum ether and carbon disulfide as eluant, gave two spots with $R_{\rm f}$ values of 0.85 and ~ 0 . Analysis under conditions identical with authentic samples of DPPH and DPPH₂ gave $R_{\rm f}$ values of 0.86 for both compounds. Some unreported results from this laboratory have shown similarities exist between the products derived from photochemical and sonolytic decomposition of certain substrates. Although studies¹³ of the photochemical decomposition of DPPH showed that mononitrated DPPH₂ is produced ($R_{\rm f} = 0.26$ under the chromatography conditions described previously), it was not detected as a product in this ultrasonic study. However, chromatographic analysis of a sample of dinitrated DPPH₂, provided by Dr. J. A. Weil, University of Saskatchewan, gave an $R_{\rm f}$ $\simeq 0$ for conditions similar to those used in the analysis of the sonolysis products. It is too early to conclude that one of the minor products is a dinitrated form of DPPH₂. The low concentrations of minor products have not allowed for a positive identification by means of regular analytical methods. Any further studies to elucidate the nature of these minor products will require a comprehensive experiment based on more sensitive analytical procedures.

Effect of the Composition of the Solvent Mixture. The composition of the solvent mixture has considerable effect on the yields of chemical reactions induced by cavitation. The solvent constituents can penetrate into the cavities and participate in intracavity chemical reactions and/or influence one or all of the three stages of cavitation (i.e., inception, growth, and collapse). Previous studies^{7,26} have shown that alcohols, when present in low concentrations (0–20 mM), participate in the intracavity reactions and do not affect the cavitation phenomenon appreciably. However, it was suggested that at higher concentrations the physical effect of alcohol on cavitation could predominate over its chemical involvement.⁷ In order to examine this claim we studied the conversion of DPPH to DPPH₂ under

⁽²⁴⁾ The values of D for e⁻ and OH· are $4.9 \times 10^{-5} 2^{-1}$ and $2.3 \times 10^{-5} \text{ cm}^2$ s^{-1,19} respectively. Because D is inversely proportional to the molecular diameter, the value of D for H· should be between 2.3×10^{-5} and $4.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and that for HO₂ should be $<2.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. That is, the value of D for H· should not be more than 5 times that of HO₂. In the present situation, as the concern is the relative magnitudes, it is reasonable to assume D for the two cases to be $\sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ or $\sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

⁽²⁵⁾ These values are based on the choice of λ as 1/50 of the bubble radius. It must be pointed out that any other suitable λ value could have been used without changing the argument. Although a change in λ would change the numerical values of $n_{\rm R}/n_{\rm D}$ for H and HO₂, it should not change the magnitude of their ratio. Therefore, the conclusion that many more H radicals appear to leave the bubble in the presence of O₂ than in the presence of an inert gas still remains valid.

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an ultrasonic field in methanol-water mixtures of varying composition. The results (Figure 2), shown as a plot of logarithm of percentage degradation of DPPH vs. concentration, reveal that the degradation decreases almost exponentially as the mole fraction of methanol is increased from 0.3 to 0.7. Similar curves are obtained for ethanolwater, acetone-water, and 2,4-dioxane-water binary mixtures. If alcohol (or other volatile components of the mixture) were to influence only the chemical yields by participating in the intracavity reactions, one would expect DDPH degradation to increase with an increase in alcohol concentration. Thus the results appear to confirm the earlier supposition about the role of alcohol under these experimental conditions.

The effect of high alcohol concentrations on the cavitation phenomenon arises primarily through modification of the growth and collapse of bubbles rather than their inception. Since the latter is largely associated with submicroscopic inhomogeneities, an addition of readily miscible component, like alcohol, to the insonated medium will not affect the nucleation process significantly. However, it can decrease the energy required to promote bubble growth during the negative pressure phase of the ultrasonic wave because the vaporization of the alcohol into the bubble will enhance expansion of the bubble. As a consequence the expanding bubbles gain less energy from the ultrasonic field and release less upon collapse. As well, the volatile component provides a cushioning effect thereby dampening the rapid collapse process and accompanying energy release.

Due to the complex nature of bubble implosion it is not yet possible to accurately correlate energy release with cavity composition. However, it has been shown²⁷ that when the hydrostatic pressure and the pressure amplitude of the sound wave are of the order of 1 and 10 atm, respectively, the free energy of cavity formation $(\Delta \tilde{A})$ is related to vapor pressure (P_v) of the cavity contents by the simple relation

$$\Delta \tilde{A} = RT \ln \left(P_{\rm v} / P_{\rm T} \right) \tag{16}$$

where R is the molar gas constant and T and $P_{\rm T}$ are the ambient temperature and pressure, respectively, of the cavity contents at the beginning of bubble growth. Because the chemical energy released during bubble collapse should be related to the energy gained by the bubble during its growth, to a first approximation one might expect a correlation between degradation of DPPH and ΔA . The results²⁸ in Figure 2 support this argument.

In conclusion, the results of this study show that chemical reaction of relatively nonvolatile solutes occurs primarily outside the collapsing bubble in the bulk liquid phase and is due to diffusion of long-lived radicals out of the bubbles to the bulk liquid. Also, the DPPH to DPPH₂ conversion is diminished as the methanol content is increased because the latter inhibits the physical process of cavitation.

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"Effective" Dipolar Forces in Electrolytic Solutions of Structure-Breaking Salts[†]

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A new parametrization of the infinite dilution limit of the mean force ion-ion potential relevant to strong electrolytic solutions is analyzed. It does physically correspond to assuming that solvated ions behave as rigid polarizable charged spheres. The polarizability is due to possible reorientations of water molecules inside the solvation cosphere of one of the two ions under the effect of the electric field of the remaining ion. After having argued that polarizability effects can be approximately accounted for by substituting induced dipoles with effective permanent ones, we evaluate the corresponding excess free energy by summing up the contributions of all ring diagrams and of two-point protographs. Moreover, the resulting approximation takes on, to a fair accuracy, an algebraic form. The subsequent best fit of the most typical alkaline halides and nitrates turns out to be quite satisfactory up to 1 M, practically with only one free parameter for each salt. The results show that the effective dipole moments and hence the polarizability of solvated ions are present only for structure-breaking salts, in qualitative agreement with other results.

1. Introduction

The determination of the behavior of electrolytic solutions from first principles is to a large extent an open problem.¹ However, useful information can be obtained by using McMillan-Mayer (MM) theory and a kind of "trial-and-error" procedure. With this purpose, one first chooses a well-defined functional form for the MM ion-ion interaction (i.e., the infinite dilution limit of the ion-ion mean force potential, obtained by averaging over solvent molecule configurations). Then one uses MM theory for

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[†]A brief summary of this paper has been presented at the 31st Meeting of the International Society of Electrochemistry, held in Venice in September 1980. S. Ciccariello, C. Dejak, and D. Gazzillo, "Proceedings of the 31st Meeting of ISE", Vol. II, E. Vecchi, Ed., 487.

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